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Review

Beliefs and facts in permanganate chemistry – An overview on the synthesis and the reactivity of simple and complex permanganates

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ABSTRACT

Potassium permanganate is one of the most widely used chemicals in chemistry and chemical industry, however, the available information about the chemistry of other permanganate compounds has not been reviewed. In this paper synthetic methods and reactivity of simple and complex permanganates other than the potassium salt are critically reviewed. Generalized synthetic methods are proposed for various types of high purity permanganates. Properties and the reactivities of these compounds are discussed.

KEYWORDS: permanganates, permanganic acid, manganese heptaoxide, organic permanganates, complexes

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1. INTRODUCTION

Permanganates are the salts of permanganic acid ($HMnO_4$) containing the manganese in +7 oxidation state (d^0). The only commercially available permanganate salt is the potassium permanganate, however, numerous other salts such as inorganic complexes or salts with organic cations have been prepared [1-5]. Tetraalkylammonium- or phosphonium type salts like the purple benzene (Bu_4NMnO_4) are soluble in organic solvents and can be used in homogeneous organic oxidation reactions [6]. Heterogeneous organic oxidation reactions of transition metal permanganates such as zinc permanganate, hydrated copper permanganate or pyridine and bipyridine complexes of silver and copper have been studied intensively [7-26]. Permanganates of ion-exchange resins [27-36], MnO_4-intercalated sodalite [37] or permanganate bound in a two-dimensional infinite lattice such as $[Cu(OH)_3MnO_4]$ [38] are also known.

Properties of permanganates strongly depend on the nature of the cation. All of the permanganate compounds are purple solids which have general oxidation ability. Their oxidation potential strongly depends on the counter-ion as well as the form of state and the reaction conditions such as temperature, solvent, or in case of aqueous solutions, the pH. The permanganates are sensitive to light and heat. Their thermal decomposition generally leads to MnO_2 or Mn_3O_4. This provides a special feature of permanganate chemistry, namely the autocatalysis of the primary decomposition products on the parent process. There are some other interesting features of permanganate chemistry, e.g. the presence or absence of auto-oxidation processes between the cation and the anion. For example, existence of $Ag^{II}Mn^{VI}O_4$ and $Ag^{I}Mn^{VII}O_4$ [39-40] compound pair, the Guyard reaction when a Mn(II) compounds reacts with a permanganate ion with

the formation of MnO_2 and O_2 instead of $Mn(MnO_4)_2$ formation [41-42]. At the same time, the analogous $Mn(ReO_4)_2$ is a stable and well-characterized compound [43]. Depending on the conditions, some compounds which are stable at room temperature can be decomposed by self-oxidation, e.g. the ignition of [tetraammine-copper(II)] permanganate [44] or the auto-oxidation phenomenon of cetyltrimethyl-ammonium permanganate [45].

2. A general overview of the general synthetic methods of permanganate chemistry

The first permanganate compound was prepared by J. R. Glauber, an alchemist, in 1659 when a mixture of potash (K_2CO_3) and pyrolusite (MnO_2) was heated and the formed mass was leached with water [46]. Solid potassium permanganate was prepared by Chevillot and Edwards [47-48] from a mixture called "mineral chameleon" by Scheele [49-52] and formed during heating MnO_2, KOH and KNO_3. Starting from potassium permanganate, in a direct exchange reaction or via intermediates such as permanganic acid, silver-, aluminium- or barium permanganate, manganese heptaoxide or barium manganate numerous simple and complex permanganate salts can be prepared [1-2].

Since permanganates contain heptavalent manganese, there are two basic methods for their preparations. One of them is the oxidation of metallic manganese or lower valence manganese compounds with chemicals (PbO_2, bismuthates, persulphates etc.) or by an electrochemical route. This is the most widely used preparation method of potassium permanganate. Unfortunately, only permanganic acid and alkaline or alkaline earth permanganates can be directly prepared this way. The other one is the transformation of a heptavalent manganese compound, e.g permanganic acid, manganese heptoxide or other permanganate compounds into the required permanganate salt [1-2]. These compounds are the precursors of other derivatives; therefore our efforts have been focused on these types of processes.

Several permanganate compounds can directly be synthesized in a metathesis reaction of potassium permanganate. Sometimes the $KMnO_4$ has to be previously transformed into another precursor, e.g. to barium permanganate. Barium permanganate is a thermally stable compound (T_{dec}= 170 ^oC) [53] and it has excellent solubility in water (75 g/100 g water at 18 ^oC) [54]. Its reaction with metal sulfates gives insoluble barium sulphate, therefore the barium permanganate is an ideal starting material to produce many types of permanganate compounds [55]:

$$Ba(MnO_4)_2 + M_xSO_4 = 2M_{x/2}MnO_4 + BaSO_4 \quad (1)$$

In other words, the key step in the synthesis of permanganate salts is synthesizing barium permanganate from potassium permanganate.

2.1. Preparation and properties of manganese heptaoxide and permanganic acid

Permanganic acid (as a strong acid) and its anhydride the manganese heptaoxide directly reacts with basic metal compounds. The acid can be prepared by anodic dissolution of silicomanganese in phosphoric acid solution [56], or combining this method with the diaphragma technique originally developed to prepare potassium permanganate [57, 58]. Permanganic acid is stable in pure state and in dilute solutions. Presence of contaminants or increasing acid concentration leads to its rapid decomposition with the formation of oxygen and manganese dioxide. It is not stable in solutions more concentrated than 20%, but its dilute solutions (<0.5%) is stable even on heating [59, 60]. Low temperature vacuum evaporation – depending on the conditions – leads to the formation of solid $HMnO_4$, $HMnO_4.2H_2O$ or so-called pseudo-permanganic acid, $(H_3O)_2[Mn(MnO_4)_6].11H_2O$ [61-63]. Permanganic acid is well soluble in water, it is slightly soluble in fluorinated hydrocarbons and does not dissolve in $CHCl_3$ or CCl_4 [61]. Depending on the type of method and the electrolyte solution used, pK values were found to be between -4.5 and -2.25 in sulphuric and perchloric acid medium, respectively [64-67]. A pure 0.1 M solution of permanganic acid was prepared by the reaction of barium permanganate with sulphuric acid, and the pH measurement gave a pK value of -2.09 [68]. It indicates that the permanganic acid almost completely dissociated in this solution. Hence basic oxides, hydroxides, carbonates, hydrogen carbonates and other non-oxidisable salts of metals can be used to prepare

permanganate salts [69, 70] by reacting them with permanganic acid.

$$M(OH)_n + nHMnO_4 = M(MnO_4)_n + nH_2O \quad (2)$$

As an oxidising agent and strong acid, permanganic acid can dissolve most of the metals. However, this type of synthesis is not recommended. Since most of the metals are oxidised by the permanganic acid, the lower valence manganese compounds formed as bye-product, cause contamination. Further, the librated hydrogen can also react with the permanganic acid and the permanganate salt formed [71-72].

Reaction of potassium permanganate with sulphuric acid seems to be the simplest way to prepare permanganic acid, followed by its extraction with tributyl phosphate or tert-butanol [73-74]. The distribution of potassium permanganate between the water and the organic phase depends on the sulphuric acid concentration. The method, however, does not have high preparative value because of solubility of the potassium permanganate in tributyl phosphate [75].

If the sulphuric acid concentration is increased (depending on the $KMnO_4$:H_2SO_4:H_2O molar ratio), a different kind of reactions can be observed. Concentrated sulphuric acid (98%) gave almost pure permanganyl sulphate solution:

$$KMnO_4 + 3H_2SO_4 \rightarrow KHSO_4 + O_3MnOSO_3H + [H_3O]HSO_4 \quad (3)$$

The reaction was confirmed by conductivity, cryoscopic and UV spectrophotometric studies [67, 76-77]. The amount of water and the ratio of the reactants are key parameters in the product distribution. With 96% H_2SO_4, manganese heptaoxide is the main product, but permanganyl sulphate is also formed. The formed manganese heptaoxide is not miscible with the sulphuric acid and settles as a dark liquid (Mp = 5.9 °C, d = 2.396 g/mL) [78]. Dimanganese heptaoxide is thermodynamically unstable (P_{diss} = 50 MPa at 25 °C) and its decomposition temperature is low (T_{dec} = 55 °C) [79]. The reaction due to its strongly exothermic nature has to be performed under intensive cooling. Adding concentrated sulphuric acid to solid $KMnO_4$ results in the formation of vapours, which can be condensed to ice and permanganic acid [42, 43]. But this is a very hazardous process. Zhang *et al.* developed a non-hazardous method to prepare manganese heptaoxide, in which concentrated sulphuric acid and solid $KMnO_4$ are reacted in the presence of CCl_4. The Mn_2O_7 formed is extracted immediately into the organic phase. This organic phase is stable for hours, non-explosive and can be treated with $Cd(OH)_2$ and rare-earth metal oxides to obtain the appropriate permanganate salts [69, 70]. An improved Zhang's method avoids contamination due to permanganyl sulphate [80]. The organic phase containing Mn_2O_7 and the permanganyl sulphate is reacted with barium carbonate wetted with a catalytic amount of water:

$$Mn_2O_7[CCl_4] + H_2O_{(l)} = 2HMnO_{4(aq)} + CCl_4 \quad (4a)$$

$$2HMnO_{4(aq)} + BaCO_{3(s)} = Ba(MnO_4)_{2(s)} + H_2O_{(l)} + CO_{2(g)} \quad (4b)$$

$$BaCO_{3(s)} + Mn_2O_{7(l)} = Ba(MnO_4)_{2(s)} + CO_{2(g)} \quad (4)$$

Since only a catalytic amount of water is present, the hydration heat of the manganese heptaoxide (0.05 kJ/mol [81-84] (eqn. 4a) is neutralized by the endothermic reaction of the solid barium carbonate and permanganic acid (1.90 kJ/mol) (calculated by us [68] from the heat of formation values obtained for liquid Mn_2O_7, solid barium permanganate and gaseous carbon dioxide [78, 85, 86]) (eqn. 4b), thus local overheating is avoided. Water liberated in (4b) continues the reaction cycle. Permanganyl sulphate is a water sensitive compound and easily hydrolyses:

$$O_3MnOSO_3H + H_2O = HMnO_4 + H_2SO_4 \quad (5)$$

The H_2SO_4 formed is changed into insoluble barium sulphate and does not contaminate the product, barium permanganate. Barium permanganate is extracted from the organic phase with water. The yield of barium permanganate was found to be 39% [80].

The method has been modified to directly prepare some high-valent metal permanganates. Instead of the concentrated sulphuric acid, sulphuric acid monohydrate was reacted with solid potassium permanganate in the presence of CCl_4. The sulphuric acid monohydrate (86% aq. H_2SO_4) reacts instantaneously with the permanganyl sulphate:

$$O_3MnOSO_3H + H_2SO_4.H_2O = HMnO_4 + 2H_2SO_4 \quad (6)$$

When the permanganic acid formed reacts with the appropriate metal oxides, hydroxides or carbonates, catalytic amount of water is generated and the appropriate permanganates are formed in higher yield than in case of concentrated sulphuric acid. In the case of barium permanganate under analogous conditions the yield was 58.7%. Similar reaction with calcium carbonate is exothermic. Since there is no heat absorption, the yield of calcium permanganate is only 33.8%. Using this procedure, aqueous solutions of Mg, Pb, Ni, Zn, Cu, Al, Gd, Fe(III), Y, Ce, Sm, Pr and Cd permanganates have been prepared [80] with moderate yields. It should be noted that the powder X-ray diffractograms of the copper and rare earth permanganates formed in this reaction are different from the powder X-ray diffractograms of the previously prepared $Cu(MnO_4)_2.2H_2O$ [87] and $RE(MnO_4)_3*nH_2O$ [69] compounds. It indicates that other hydrates or other modification of the compounds are formed. The copper salt showed an altered powder X-ray diffractogram after 2 hours in open air while its solubility in water and the purple color remain unaltered. The powder X-ray diffractogram of the newly formed purple compound does not fit with the powder X-ray diffractogram of the dihydrate [87] either.

The retention of purple color and the water solubility indicate that there has been no permanganate decomposition but a hydration or dehydration reaction has taken place. In case of lead compound, a large amount of brown precipitate was also formed, which is probably lead dioxide or basic lead permanganate [88-90]. The solution contained lead and permanganate ions in 1:2 ratio, which indicates the presence of dissolved lead(II) permanganate (not isolated; yield is 18.7%).

Using pyridine as an alkaline compound to prepare pyridinium permanganate was unsuccessful [80] due to the sensitivity of the pyridinium ring towards permanganic acid oxidation. This result is unexpected because of the existence of poly(vinylpyridinium permanganate), as a solid phase oxidant [28].

2.2. Direct metathesis reactions of potassium permanganate

Metathesis reaction of $KMnO_4$ with MX_n type (X=leaving group such as halogenides, nitrate, sulphate, perchlorate, etc.) compounds, means a precipitation reaction or a polytherm fractional crystallization from the $K,M//X,MnO_4\text{-}H_2O$ system. This method can be used directly when the solubility of the formed $M(MnO_4)_n$ compound as low as in the case of silver permanganate [91] or if a hardly soluble KX compound is formed [92-94]. Since the potassium compounds are generally well soluble in water, this method is limited to the preparation of some complex salt, organic permanganates and the three most important precursors, viz. silver, barium and aluminium permanganates.

$$AgMnO_4 + MCl = AgCl + MMnO_4 \quad (7)$$

$$Ba(MnO_4)_2 + M'SO_4 = BaSO_4 + M'(MnO_4)_2 \quad (8)$$

$$Al(MnO_4)_3 + 3MOH = Al(OH)_3 + 3MMnO_4 \quad (9)$$

Silver permanganate can be obtained in a direct reaction of aqueous $KMnO_4$ and $AgNO_3$ solutions at room temperature, when it is precipitated immediately as a purple solid which can be recrystallized from hot water. The main limiting factor of further use of $AgMnO_4$ is its low solubility in water (9 g/l at 25 °C) [91]. Barium permanganate as a stable and soluble compound is an important starting material, but its direct preparation from $KMnO_4$ is not a simple task. There are only two simple KX compounds the solubility of which is low enough, these are the $KClO_4$ and K_2SiF_6. The solubility of the potassium perchlorate is 0.73 and 1.96 g/100 ml water at 0 and 25 °C, respectively [95], therefore, in theory by cooling of a warm saturated solution of the $KMnO_4$ and $Ba(ClO_4)_2$, the $KClO_4$ should be precipitated.

$$Ba(ClO_4)_2 + 2KMnO_4 = Ba(MnO_4)_2 + 2KClO_4 \quad (10)$$

In practice, however, instead of the $KClO_4$, a purple coloured solid solution of $KClO_4/KMnO_4$ is formed due to isomorphous structure of the $KMnO_4$ and the $KClO_4$. According to the studies of Muthmann and Kuntze, from the $K//MnO_4,ClO_4$ system it is not possible to crystallize out either pure $KMnO_4$ or $KClO_4$, only the above mentioned solid solution is obtained [96]. Thus, the preparation of pure $Ba(MnO_4)_2$ is not possible this way. By using stoichiometric amount of $KMnO_4$, the conversion is 80% [68]. The barium permanganate solutions formed cannot be purified (from $KMnO_4$, $KClO_4$ and $Ba(ClO_4)_2$) by fractional crystallization.

By the addition of H_2SiF_6 to a $KMnO_4$ solution, $HMnO_4$ is obtained which can be neutralized immediately with barium hydroxide [92-93] or barium carbonate [94].

$$2KMnO_4 + H_2SiF_6 + Ba(OH)_2 = Ba(MnO_4)_2 \quad (11)$$

Since the commercial H_2SiF_6 is always contaminated with chloride, a part of the formed barium permanganate has to be reacted with H_2SO_4 to form $BaSO_4$ precipitate and free $HMnO_4$. By heating the solution the $HMnO_4$ oxidises the chloride ions to chlorine. In this way, the 90% of the chloride contamination can be removed. This reaction is a formal reaction of barium hexafluorosilicate with $KMnO_4$. Substituting the "barium hexafluorosilicate" with zinc hexafluoro-silicate the zinc permanganate can directly be prepared [97-98]:

$$Zn[SiF_6] + 2KMnO_4 = K_2SiF_6 + Zn(MnO_4)_2 \quad (12)$$

The solubility of alkali metal alums in water is strongly temperature-dependent, thus, by mixing saturated solutions of aluminium sulphate and potassium permanganate at 80 °C, then cooling the mixture, aluminium permanganate solution is formed and potassium alum separates out [8, 99-101]:

$$6KMnO_4 + 4Al_2(SO_4)_3 = 6KAl(SO_4)_2 + 2Al(MnO_4)_3 \quad (13)$$

The aluminium permanganate, however, is contaminated with potassium and sulphate ions because of the residual solubility of the potassium alum. The use of large excess of aluminium sulphate decreases the solubility of the potassium alum. Further, the aluminium permanganate formed and the aluminium sulphate solution can be treated with barium hydroxide at room temperature [102-103]:

$$2Al(MnO_4)_3 + 3Ba(OH)_2 = 2Al(OH)_3 + 3Ba(MnO_4)_2 \quad (14)$$

$$Al_2(SO_4)_3 + 3Ba(OH)_2 = 2Al(OH)_3 + 3BaSO_4 \quad (15)$$

The only water soluble compound formed is the barium permanganate. Since the $KMnO_4$ is isomorphous with the $BaSO_4$, the large amount of $BaSO_4$ intercalates the small amount of $KMnO_4$ present in the solution [104, 105]. The $BaSO_4$ formed has a light purple color which could not be removed with boiling with oxalic acid. This indicates the complete intercalation of the $KMnO_4$ into the insoluble barium sulphate. The method results a highly pure $Ba(MnO_4)_2$, which can be used for the preparation of other permanganate salts in a state of high purity [102].

2.3. Preparation of barium permanganate via manganate(VI) intermediates

Manganate(VI) salts are stable only in strong alkaline medium and H_2MnO_4 disproportionates immediately after its formation. Thus acidification of alkaline solutions of manganate(VI) compounds can be an easy way to prepare permanganates [106-110]:

$$3M_2MnO_4 + 6H_2O = 6MOH + 3H_2MnO_4 \quad (16a)$$

$$3H_2MnO_4 = MnO_2 + 2HMnO_4 + 2H_2O \quad (16b)$$

$$3M_2MnO_4 + 4H_2O = 2MMnO_4 + 4MOH \quad (16)$$

Metal permanganates and hydroxides (or salts formed during their neutralization) are generally soluble in water, therefore the method has limited application. Using water-insoluble barium manganate(VI) ($L=2.46*10^{-10}$ [106]) as a starting material, however, the barium hydroxide formed may be neutralized with acids which forms insoluble barium salts, e.g. carbonate or sulphate. These can be separated from the soluble barium permanganate. By using sulphuric acid, depending on the molar ratio, both barium permanganate and permanganic acid can be prepared [55]:

$$3BaMnO_4 + 2H_2SO_4 = 2BaSO_4 + Ba(MnO_4)_2 + 2H_2O \quad (17)$$

$$3BaMnO_4 + 3H_2SO_4 = 3BaSO_4 + 2HMnO_4 + 2H_2O \quad (18)$$

Barium manganate can be prepared from potassium permanganate with reducing agents, such as cyanides [111], iodides [112], hydrazine [113] or various organic compounds [114-115], in the presence of barium ion which precipitates the manganate(VI) intermediates formed during the reduction reactions [116-117]. The barium manganate(VI) formed, however, is always contaminated mainly with manganese dioxide, therefore it is not easy to calculate the 2/3 amount of sulphuric acid. Excess acid causes $HMnO_4$ formation and decreases the yield of barium permanganate [55].

Using carbonic acid instead of sulphuric acid seems to be a suitable solution. Permanganic acid is a stronger acid than the carbonic acid [118] and no reaction takes place between barium permanganate formed and the excess CO_2. The reaction of barium manganate with CO_2 is known [119-130], but it proceeds under very inconvenient conditions (heating with supersaturated steam and continuous CO_2 bubbling for 10-12 h) [130].

$$3BaMnO_4 + 2H_2CO_3 = 2BaCO_3 + Ba(MnO_4)_2 \quad (19)$$

Results of thermodynamical calculations indicates that free energy changes of the reaction is slightly positive (ΔG = +1.7 kJ/mol) [80], thus the reaction should not proceed directly. In order to find a reason for the contrary result, behaviour of aqueous suspension of barium manganate (saturation concentration is 0.017 mM), was studied in the absence and the presence of CO_2 [80].

Under CO_2 free conditions the freshly prepared suspension of $BaMnO_4$ is colorless and the pH of the solution is 8.8. After 10 min, however, the solution becomes purple and the pH increases to 9.2. The pH increases to 9.3 within 24 h, then no further changes can be observed. These results are the consequence of consecutive hydrolysis and disproportionation reactions of the barium manganate and the manganic acid, respectively [80]:

$$BaMnO_4 + 2H_2O = [Ba(OH)_2 + H_2MnO_4] = Ba^{2+} + 2OH^- + [2H^+ + MnO_4^{2-}] \quad (20)$$

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O \quad (21)$$

The disproportionation equilibrium is pH-dependent, therefore the accumulating hydroxide ion and the permanganate ions formed are in equilibrium with the constant manganate(VI) concentration derived from the solubility of the solid $BaMnO_4$ according to the following equation [106].

$$K = [MnO_4^-]^2[OH^-]^4/[MnO_4^{2-}]^3 \quad (22)$$

Based on the experimentally determined pH, the permanganate concentrations, and the L_{BaMnO4} values [106], only 0.76% of the starting barium manganate decomposed [80] in the aqueous suspension of solid barium manganate. Presuming that the carbon dioxide decreases the pH by reacting with the hydroxide ions formed, resulting in the formation of hydrogen carbonates, the presence of CO_2 shifts the equilibrium towards permanganate formation. This experiment has been repeated in the presence of carbon dioxide. On the addition of barium hydroxide to the purple solution a white precipitate of $BaCO_3$ is formed [106]. This confirms the presence of the presumed barium hydrogen carbonate.

$$3Ba(MnO_4)_2 + 4H_2O + 4CO_2 = 2Ba(HCO_3)_2 + Ba(MnO_4)_2 + MnO_2 \quad (23)$$

Thermodynamic calculations (taking into consideration the barium hydrogen carbonate formation (ΔH = 166.8 kJ/mol, ΔG = -16.8 kJ/mol) suggest an endothermic reaction with negative Gibbs energy. It means that heating is essential to perform this reaction. The relative thermal stability of the barium hydrogen carbonate solution [131-134] explains the required high temperature and long reaction time [130]. Taking into consideration that barium hydrogen carbonate is more stable and well soluble at higher CO_2 pressures (s = 0.727 M (188.3 g/L) at a CO_2 pressure of 22 atm [133]), a hydrothermal synthetic procedure has been developed [80]. At a $BaMnO_4$:H_2O:CO_2 = 1:40:20 molar ratio, by using solid reagents such as ice and dry ice, in a Teflon-lined stainless steel autoclave at 75% filling ratio, the reaction was performed at 100 ^oC for 1.5 h. The yield of the barium permanganate was found to be 93.8%. Due to a concurrent reaction of disproportionation, namely the decomposition of the H_2MnO_4 to MnO_2 and O_2, increasing temperature leads to decreasing yield. Increasing pressure acts against the decomposition reaction and increase the solubility and stability of the barium hydrogen carbonate. Depressurizing of the hot solution leads to immediate decomposition of the $Ba(HCO_3)_2$ into $BaCO_3$, CO_2 and H_2O. When the pH is adjusted to 8 with $Ba(OH)_2$, the residual amount of $Ba(HCO_3)_2$ can be decomposed [80, 133]. One can conclude that this method is a simple and fast way to prepare barium permanganate via the $KMnO_4$-$BaMnO_4$-$Ba(MnO_4)_2$ reaction route.

3. Structure, properties and reactivity of permanganate compounds with inorganic and complex cations

Structure, spectroscopic properties and thermal decomposition reactions of permanganate

compounds other than potassium salts are reviewed in this section. Special attention is paid to the compounds which have oxidisable cationic part, e.g. ammonium salt, organic and complex compounds.

3.1. Alkali metal permanganates

Most alkali metal permanganates exist in anhydrous form. Only the lithium and sodium salts have hydrated forms, namely trihydrates and monohydrates. Alkali metal permanganates can be prepared as purple solids by the reaction of the appropriate metal sulfate and barium permanganate. The thermal stability increases from the lithium salt (100 °C) up to the cesium salt (260 °C). Their decomposition process takes place with oxygen evolution, and has an autocatalytic character. The decomposition products and mechanism strongly depend on the nature of the cation [54]. Calculated crystal lattice energy [135], the heat of formation [136] and the lattice entropy [137] of the crystalline alkali metal permanganates (including the ammonium salt) are presented in Table 1.

With the increase of the atomic weight of the cations some of the properties change monotonically, e.g. the solubility in water, thermal stability, etc. Besides the thermal annealing, the other key factor in the recoil of ^{56}Mn in neutron irradiated alkali permanganates is the compactness of the crystalline lattice [138].

3.1.1. Lithium permanganate

Lithium permanganate trihydrate can be prepared from $AgMnO_4$ and LiCl in aqueous solution [139-140], or from barium permanganate and lithium sulfate [54, 141-143]. The isotope substituted $^7LiMnO_4*3D_2O$ was prepared in a similar way from $AgMnO_4$ and ^7LiCl in D_2O [144]. Lithium permanganate could also be prepared directly (i) by anodic dissolution of ferromanganese in lithium sulphate solutions (the highest current yield was 26.8-32% at 1.5 V and at 15-25 A/dm^2 current density and at 50 g/L lithium sulphate concentration [145]), or (ii) from lithium perchlorate and potassium permanganate [146]. Lithium permanganate trihydrate crystals are stable in air [91], soluble in water (71.43 g salt in 100 g of water at 16 °C [119-121]) with bluish-violet color [144] and completely dissociates in its dilute aqueous solution [147]. The $LiMnO_4$ can be extracted at the alkaline pH range with tributyl phosphate and tert-butanol. Increasing lithium hydroxide concentration results increased extractability, however, at very high pH the formation of lithium manganate(VI) decreases the extraction efficiency [73] (Figure 1).

Dark violet needles of lithium permanganate trihydrate (d = 2.06 g/cm^3) [146] are hexagonal crystals ($P6_3mc$, a = 779.41 pm, c = 542.7 pm, Z = 2, d = 2.1 g/cm^3) which are isostructural with $LiClO_4.3H_2O$ and contains $Li(H_2O)_6$-chains with octahedral environment around the lithium. The regular tetrahedrons of the permanganate ions bound to the cation-chains via hydrogen bonds. The Mn-O distances are 160.7 and 161.8, and the Li-O distances are 209 and 218 pm [140]. The trihydrate can be dehydrated thermally at 363 K for 2 h to produce $LiMnO_4.H_2O$ [141], but decomposes at 373 K with oxygen evolution in an autocatalytic process [54]. The anhydrous salt could be obtained as a violet powder by thermal

Table 1. Calculated crystal lattice energy (kJ/mol), the heat of formation (kJ/mol) and the lattice entropy (J/mol.K) of the crystalline alkali metal permanganates.

M	U [135]	ΔH^0_{cryst} [135]	$\Delta H_f{}^0_{298}$ [136]	S_{298} [137]
Li	587.1	-692.2	-831,3	-
Na	555.5	-731.1	-821,4	160.1
Rb	520.0	-811.3	-832,6	183.1
Cs	522.5	-836.4	-840,6	190.6
NH_4	522.5	-680.9	-	-

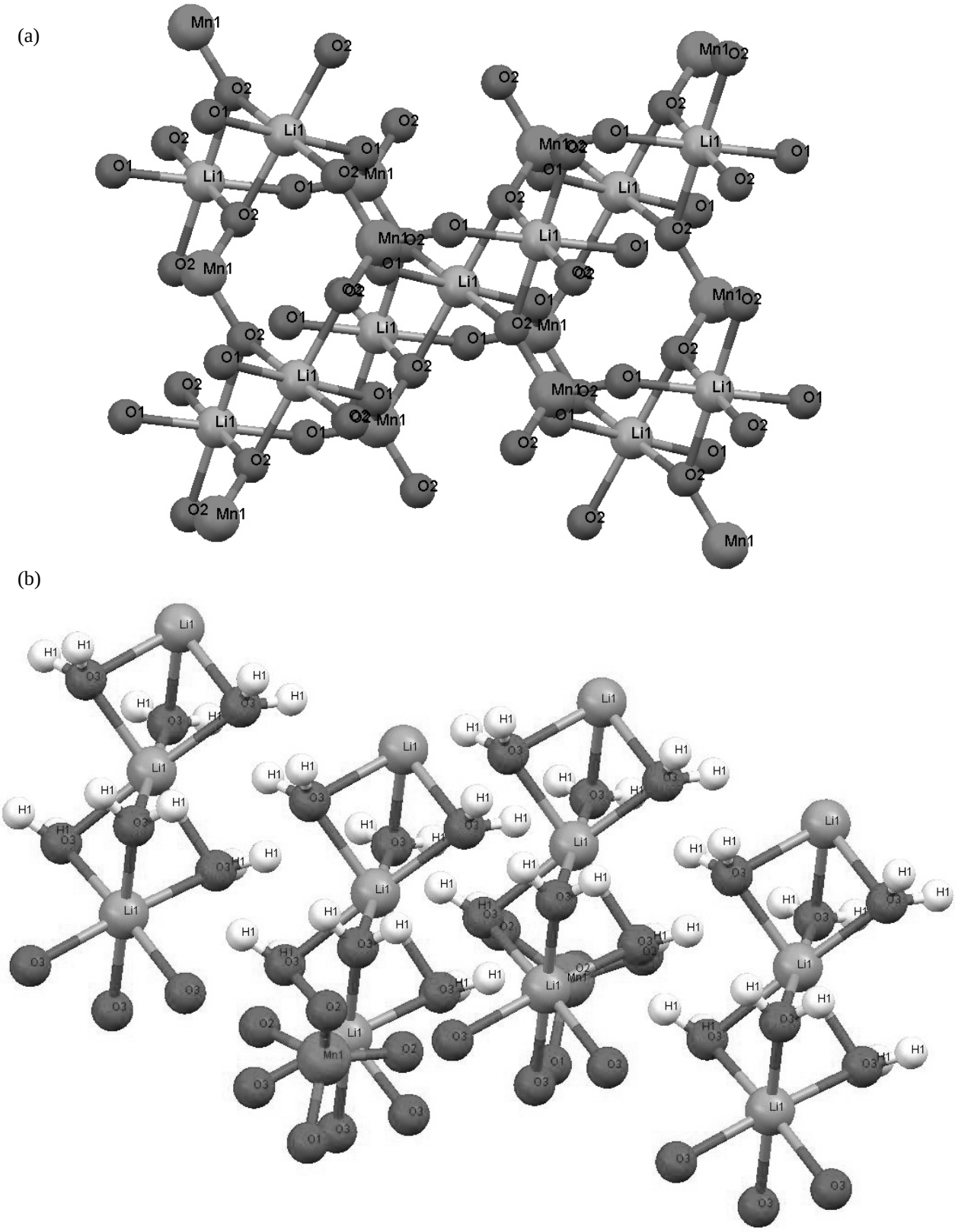


Figure 1. Crystal structure of lithium permanganate (a) and its trihydrate (b).

dehydration at 60 °C above P_4O_{10} in vacuum. The crystal structure of the anhydrous salt has been determined by neutron diffraction (orthorombic, space group Cmcm, a = 551.402 pm, b = 839.754 pm, c = 635.911 pm, Z = 4, $CrVO_4$-type structure), and it were found to have octahedral and tetrahedral environments for lithium and manganese, respectively. The Mn-O and Li-O distances are between 160.5-164.0 and 211.5-214.0, respectively. The Madelung part of the lattice energy is 8720 kcal/mol [144]. It is sensitive to moisture and decomposes above 60 °C or even at room temperature during long storage time (months).

IR characteristics of both the hydrated and the anhydrous form have already been discussed [148]. The permanganate ion site symmetry is C_{3v} in the trihydrate salt. IR spectra of $LiMnO_4.3H_2O$ and its deuterated analogue ($LiMnO_4.3HDO$) confirm the presence of a medium strong hydrogen bond interaction [149]. The symmetry relationships of the water molecules in these compounds have also been determined [150]. Based on the shifting and splitting of the $\nu_3(F_2)$ bands of the lithium permanganate trihydrate and its deuteroanalogue, the presence of relatively strong hydrogen-bonds have also been proposed [151].

Polarized absorption spectrum of $LiMnO_4.3H_2O$ in $LiClO_4.3H_2O$ matrix at 4.2 K and 77 K has been discussed in detail [152]. There are two-two different excitations, and the higher energy absorption spectra are quite broad and unstructured. The polarization data are vitiated by light scattering effects, but the lower energy absorption region at λ>6000 A is structured and appears to contain more than one electronic absorption associable with T_d parent symmetry. The only electronic excitation of the MnO_4^- ion is $^1T_2 - {}^1A_1$, and the $^1T_1$ state exhibits a 548 cm^{-1} splitting producing two states $^1A_1$(parallel) and ^{1}E(perpendicular). The stark effect of the $^1T_1$ state at 726 nm was detected in the lithium perchlorate trihydrate matrix [153]. The modulated spectrum indicates 2nd order electrical field effects. The 0-0 band shifts to lower energy and increases in integrated optical intensity.

The X-ray absorption K edge spectra of $LiMnO_4.3H_2O$ and its aqueous solution have been compared and stated that in the solution the lithium ion has no significant effect on the fine structure of the permanganate ion spectrum [154]. The AlK_α XPS of the $LiMnO_4$ has also been studied and the electron structure and assignations of bands have been provided [155].

Increasing the concentration of ^{55}Mn in D_2O solutions of $LiMnO_4$ shifted the NMR signal linearly to lower frequencies [156].

Lithium permanganate was irradiated with thermal neutrons from ^{252}Cf fission for the $^{55}Mn(n,\gamma)^{56}Mn$ reaction, and the initial retention (7%), the distribution of the active ^{56}Mn-containing species among the various valence states and the activation energies of the annealing process have been determined [138, 157]. The process is pH dependent. Besides $Li^{56}MnO_4$ and $^{56}Mn^{2+}$ some amount of MnO_2 is also formed [139]. The amount of the MnO_2 is the smallest in neutral solution [139-140].

Although the ^{56}Mn distribution among the Mn^{7+}, Mn^{2+} and Mn^{4+} states are the same in the mono and trihydrate (7:93:0), the activation energies have been found to be 12.3 and 28.7 kJ/mol, respectively. Annealing of the mono-hydrate occurs only to a very small extent, while the trihydrate salt anneals to a considerable extent and the time required to reach its saturation is longer. Lower recovery found in the monohydrate may be the consequence of a less tightly packed crystal structure which allows the recoil fragments to move farther away from the parent site, so that the recombination reactions become less probable even on heat treatment. The role played by the water of crystallization in aiding the recovery of the lithium salt is unique. No such recovery over the dehydration temperature range is noted in the case of $NaMnO_4.3H_2O$ and hydrated alkaline earth or transition metal permanganates [159].

Irradiation of dilute solutions of $LiMnO_4.3H_2O$ sorbed on Al_2O_3 resulted in $^{56}MnO_4$ and $^{56}Mn^{2+}$; $^{56}MnO_2$ could not be detected. The effect of the pH, concentration and the type of adsorbent (Al_2O_3 or MnO_2) have also been studied. Around pH = 13 a complex is formed from the permanganate and the hydroxide which does not adsorb on MnO_2 and completely dissociates with a first order kinetics with lowering the pH below 7. This complex has no influence on the distribution of the species when Al_2O_3 was used

as adsorbent [158]. By using MnO_2 adsorbent, the ^{56}Mn activity was distributed in 7:87:6 ratio between permanganate, MnO_2 and Mn^{2+} [159].

The thermal decomposition process has three steps. Two endothermic peaks at 390 and 432 K for the trihydrate refer to the loss of two water molecules. The exothermic peak at 450 K shows a phase transition during the removal of the third water molecule. This step is immediately followed by the decomposition at 570 K, the mass loss is in accordance with the following equation:

$$2LiMnO_4 = Li_2MnO_4 + MnO_2 + O_2 \quad (24)$$

Heat treatment of $LiMnO_4$ in air leads to a mixture of oxides which can be used as cathode active material [160]. Subsequent acidic treatment enables the heat treated lithium permanganate to absorb lithium ions [161].

Lithium permanganate reacts with alkali peroxides, e.g. the solid phase reaction of $RbO_{0.9}$ in an Ag-tube at 660 °C for 56 d leads to the dark green compound of Rb_2MnO_4 [162]. Peroxides of lighter alkalies give manganate(V) compounds, namely K_2O_2 and Na_2O_2 reacts with the formation of $(KNa)K[MnO_4]$ (580 °C for 66 d) and pure Na_2O_2 (Na:Mn = 2.8:1) produces $Na_{10}[Li_2[MnO_4]_4]$ even within 30 h in an Ag bomb at the same temperature [163-164]. The similar reaction of pure K_2O_2 gave $K_{11}[Li[MnO_4]_4]$ [165].

Solution phase reactions are similar to the reactions of potassium permanganate, but the lithium content of the reaction products can affect the properties of the reaction products. For example, lithium permanganate can be reduced in aqueous solution with H_2O_2 with the formation of MnO_2 containing lithium and manganese(2+) ions. This precipitate can absorb lithium radionuclides [166]. Its reaction with lithium hydroxide leads to lithium manganate, Li_2MnO_4 [119-121]. Deoxidation of the alkaline solutions of lithium permanganate has also been studied by Maximoff, A. A. [142-143].

Lithium permanganate reacts with manganese(II) in sulfuric acid solution, especially with the formation of the H^+-form of hollandite type manganese oxides under hydrothermal conditions [167-168]. When the reaction is performed under acidic but normal conditions, α-manganese dioxide containing proton and manganese as principal cations is formed. This means that the α-manganese dioxide formed does not contain cations which adversely affect the performance of a cell. Potassium and ammonium ions and the proton of the α-manganese dioxide can be ion-exchanged for lithium, to prepare lithium doped α-manganese dioxide [169-170].

Lithium permanganate is used as a source of lithium for intercalated manganese oxides used in thermal batteries [171] and cathode materials for electrochemical generators [513]. Its reduction is carried out with carboxylic acid containing 4 carbon atoms so as to obtain a manganese oxide gel in which the degree of oxidation of the manganese is 4. The manganese oxide gel obtained is then dried and calcined in order to obtain a compound with the formula of Li_yMnO_2 where y is a number between 0.5 and 1.

Oxidation of manganese (II) compounds with lithium permanganate in acidic aqueous solution at a temperature of 60-150 °C can be performed to produce manganese dioxide for the hydration reaction of cyanohydrins [173].

Lithium permanganate can be used for the surface treatment of various materials, e.g. aluminium and aluminium alloys [174]. Immersing pre-treated aluminium into lithium permanganate solution results a manganese oxide coated corrosion resistant surface [175]. A mixture of lithium permanganate and aluminium nitrate forms an especially resistant coating on aluminium or aluminium alloys (pH 2.5 to 4.0). The protecting of the aluminium and the aluminium alloys is effective for more than 168 hours in salt fog [175]. Not only metallic but non-metallic materials can be surface treated, e.g. surface modification of carbon powder results battery electrodes with superb battery characteristics [177]. Ceramics coating with high hardness and high adhesion for alloy plating, plasma etching treatment and dry coating [178] can also be performed by using lithium permanganate, and it increases the mechanical strength of porcelain manufacture products [179].

Lithium permanganate can be applied as a reagent to decrease the COD in water [180] and in the preparation of rhodium manganese catalysts used for the selective transformation of CO into acetic

acid [181]. It can be used as an additive in tobacco filters [182], in photosensitive electrostatic photography [183] and to modify various kinds of cationic polymers [184]. Its oxidant ability is used in low-pressure drop filters to purify central forced air systems in residential and commercial constructions containing different kind of adsorbers [185]. Oxidation of harmful components such as H_2S or SO_2 in fluid streams proceeds with an inert fiber matrix or porous substrates bound lithium permanganate or sodium hydrogen carbonate [186-187]. Mixing with a hygroscopic salt ensures capturing water needed for the oxidation of ethylene. The mixture of the permanganate and the hygroscopic salt placed onto the surface of an inert carrier [188] can be used as an ethylene reactive agent in packaging, for example to modify the atmosphere for fresh fruits, vegetables and flowers [189]. Lithium permanganate can be used as a fixation reagent to analyze biogenic monoamines in histochemical samples for electron microscopy. With 6 and 9% $LiMnO_4$, small granular vesicles could be seen in slices from the caudate nucleus after incubation with α-methyldopamine [190].

3.1.2. Sodium permanganate

Deliquescent crystals of sodium permanganate trihydrate was prepared first by Chevillot and Edwards via the dissolution of sodium manganate in water [47-48]. The sodium hydroxide formed was separated by magnesium sulphate [108-110]:

$$3Na_2MnO_4 + 2MgSO_4 + 2H_2O = 2Mg(OH)_2 + MnO_2 + 2Na_2SO_4 + 2NaMnO_4 \quad (25)$$

The amount of the water in the salt has been determined by Raoult, F. M. [191]. The density is 2.47 g/cm^3 [192]. Sodium permanganate can be prepared when sodium chloride and silver permanganate or sodium sulphate and barium permanganate are reacted in aqueous solutions [119-121, 146]. It decomposes at 155 °C with oxygen evolution in an autocatalytic process [54]. Sodium permanganate monohydrate is strongly hygroscopic. The dark purple crystals of the anhydrous sodium permanganate and its mono-hydrate are moderately soluble in water. In its dilute aqueous solution completely dissociates, but in the 1 M solution the dissociation degree is only 0.60 [147]. Sodium permanganate can be extracted from its alkaline aqueous solutions with tributyl phosphate and tert-butanol. With increasing NaOH concentration, however, the extractability is increased only to a point which refers to the formation of sodium manganate(VI) which is not extractable. Therefore a further increase in the pH decreases the amount of the extractable permanganate [73]. Sodium permanganate is freely soluble in liquid ammonia [193-197].

Sodium permanganate decomposes at 120-180 °C with oxygen evolution expressed by the following equation [198]:

$$2NaMnO_4 = Na_2MnO_4 + MnO_2 + O_2 \quad (26)$$

Formation of Na_2MnO_4 and other lower valence sodium manganese oxides are discussed and compared with the thermal behaviour of $NaMnO_x$ and Na_xMnO_y compounds [199]. The isotherm decomposition process at 140 °C has 101 min induction period [200]. Pre-irradiation with γ-rays reduces the length of the induction period and increase the rate of the subsequent salt breakdown. The irradiation increases the number of active nuclei in the salt breakdown in direct proportion with the dose [201].

Boiling the alkaline solution of the sodium permanganate forms Na_2MnO_4 and oxygen [119-121, 142-143]. However, at 80-140 °C under hydrothermal conditions, hollandite type or tunnel-like manganese oxides are formed. Lower or higher temperature leads to the formation of nsutite (γ-MnO_2) (<30 °C) or pyrolusite (β-MnO_2) (>160 °C) [202-203]. Hollandite type of manganese oxides are formed in the reaction of sodium permanganate and manganese(II) sulphate in sulfuric acid solution under hydrothermal conditions [101].

Na_yMnO_2 type compounds, where y is a number between 0.5 and 1 and which are applied for manufacturing cathode materials for electrochemical generators [513], can be prepared from $NaMnO_4$ via reduction with carboxylic acid containing 4 carbon atoms to obtain a manganese oxide gel in which the degree of oxidation of the manganese is 4. The manganese oxide gel obtained is dried at room temperature, then it is subjected to heating between 300 °C and 1000 °C. By using an inorganic salt of manganese(II) as a reducing

agent in acidic environment leads to a proton containing α-manganese dioxide. The proton can be exchanged to lithium to produce lithium doped α-manganese dioxide containing no cation such as potassium ion or ammonium ion having a bad influence on cell performances [170].

Its reaction with oxalate is a 1st order reaction where the kinetic depends on the nature of the cation [204].

Solid sodium permanganate monohydrate can be used as an efficient and selective oxidant for the oxidation of secondary alcohols into ketones, and primary alcohols or aldehydes into carboxylic acids. 1-tridecene as terminal alkene is oxidised into lauric acid in refluxing hexane, n-butyl sulphide and t-butylamine are transformed into n-butyl sulfone and 2-methyl-2-nitropropane, respectively. Water has an essential role, the dried compounds gave very low yields. Adding a few drops of water restores the activity [205, 432].

$NaMnO_4$ reacts with S and O-containing orthocyclophanes, e.g. decahidro-benzotrioxa-dithiociklohéptadecin or dioxa-dithia-azabiciklo-oktadekatrién when chloroform-benzene soluble sodium permanganate derivatives are formed. Formation of some of these derivatives is selective in the case of sodium permanganate, other metal permanganates, e.g. potassium, silver, rubidium or cesium salts do not form such complexes [206].

IR spectroscopic characteristics of anhydrous sodium permanganate and its hydrates are different [148]. Thermal neutron irradiation of $NaMnO_4$ has been studied and the thermal annealing kinetics were determined. The initial retention (16%), the distribution of the active species among the various valence states and the activation energies of the annealing process have been measured [157].

During irradiation of dilute solutions of $NaMnO_4.3H_2O$ retained by Al_2O_3 sorbent, only $^{56}MnO_4$ and $^{56}Mn(II)$ species are formed, no $^{56}MnO_2$ could be detected. There is an influence of pH, concentration and temperature on the distribution of the species when Al_2O_3 is used as adsorbent. Around pH = 13 a complex is formed from the permanganate and hydroxide ion. The complex is not adsorbed on MnO_2 and completely dissociates with a first order kinetics with lowering the pH below 7 [158].

Sodium permanganate can be used as an oxidant in the compositions used for corrosion inhibition of metals towards acidic gases such as H_2S, CO_2 or COS [207]. A mixture of sodium permanganate and copper hydroxide can also be brought into contact with waste gas containing harmful components to provide a detoxification method [208]. It can remove NO from smoke and the volatile components of tobacco [209]. A fiber filter used for the removal of hydrogen sulfide and sulfur dioxide in fluid streams comprises an inert fiber matrix, water, sodium permanganate and sodium hydrogen carbonate bound to the fiber matrix [186]. Improved efficiency of the removal of hydrogen sulfide is achieved by sodium permanganate and sodium bicarbonate loaded onto porous substrates [187].

Sodium permanganate functionalization of metal-substituted (Ca, Ni, Zn) and pure hydrotalcites forms layered permanganates which can absorb ethylene [210]. Numerous other application fields of sodium permanganate are known, e.g. for surface treatment of aluminium, aluminium alloys [174] and chromium metal [211], is used as a combustion improver in civil liquid fuels [212] and as an oxidant in the hydroxylation treatment of acrylate esters to prepare glycerol monoesters [213]. Sodium permanganate can also be used as an additive to prevent adhesion of polymers to the polymerization vessels during the polymerization of various monomers containing an ethylenic double bond [214], or in the fixation to analyze biogenic monoamines in histochemical samples for electron microscopy [190].

3.1.3. Rubidium permanganate

Rhombic bipyramidal crystals of rubidium permanganate was first prepared in a classical way by the interaction of aqueous solutions of barium permanganate and rubidium sulphate [54, 130, 215]. The density of the crystals formed was found to be 3.2348 g/cm^3 [130]. Since its solubility in water is low (0.46 and 4.68 g/100 g of water at 0 and 60 °C, respectively) [216], it can be prepared from potassium permanganate and various rubidium salts such as rubidium sulphate [217], rubidium chloride [87, 218], or rubidium

nitrate [146]. By using a temperature gradient of 60/25 and 60/0 °C, the crystals formed from rubidium chloride [218] or rubidium nitrate [146] decompose at 243-254 [219] and 295 °C [146], respectively, with oxygen evolution [139,146]. The autocatalytic decomposition process, however, could be observed even at 240 °C [54].

Rubidium permanganate can be extracted from its aqueous RbOH solutions with tributyl phosphate and tert-butanol. Increasing RbOH concentration increases the extractability up to the rubidium manganate formation which is not extractable (the extraction curve has a maximum and any further increase in the pH decreases the extractability [73]). Rubidium permanganate is isomorphic with the potassium salt, the average Mn-O distance is 1.63 A, the permanganate tetrahedron is slightly distorted with C_s site symmetry [148]. The calculated lattice energy is 583.5 kJ/mol [85] and the Madelung part of the lattice energy is 36299 kJ/mol [144]. Rubidium permanganate contains some amount of MnO_3OH^- -ion as crystal defect (detected by NMR), which has a role in the decomposition temperature and in the decomposition mechanism [219].

UV-VIS spectrum of the single crystalline $RbMnO_4$ has been studied both at room temperature and at liquid N_2 temperature. Most of the bands measured in solid state are shifted to blue, toward the band positions observed in solution, because of the compression of the permanganate ion in the solid crystalline lattice [220].

Since the ion-exchange interactions between the rubidium permanganate and the KBr matrix is not extended as in the case of other permanganate salts [87], the IR spectrum of the rubidium permanganate only slightly depends on the conditions of the measurement (nujol or KBr matrix). The singlet ν_s Mn-O band and the triplets of ν_{as} and δ_{F2} bands have been observed in nujol suspension [215]. Resonance Raman spectrum of $RbMnO_4$ has been measured and the fundamental and combination bands have been assigned. The progression of ν_1 could be observed up to v = 5, and the value of the ω_1 harmonic frequency and the X_{11} anharmonicity constant have also been determined. The $\nu_1+\nu_3$ combination band has also appeared [221]. The intensities of the permanganate lines have been calculated by using a quantum chemical method [222].

Thermal neutron irradiation of the rubidium permanganate has been studied and the thermal annealing kinetics have also been determined. The initial retention (26%), the distribution of the active species among the various valence states and the activation energies of the annealing processes have been determined [157]. The thermal annealing affects the process, and the other key factor is the compactness of the crystalline lattice [138]. Recovery of the parent form has been found to be 48% at 180 ^oC for 2 h annealing [223]. The activation process is pH dependent. Besides the $Rb^{56}MnO_4$ and $^{56}Mn^{2+}$ some amount of MnO_2 is also formed both in neutral and alkaline solutions. This is due to the oxidation of Mn^{2+} by the permanganate. No $^{56}MnO_2$ has formed in acidic environment [139].

During irradiation of dilute solutions of $RbMnO_4$ on Al_2O_3 sorbent, only $^{56}MnO_4$ and ^{56}Mn(II) species are formed, and no $^{56}MnO_2$ could be detected. The effect of the pH, concentration and the type of adsorbent (Al_2O_3 or MnO_2) have also been studied. Around pH = 13 the complex formed from the permanganate and the hydroxide is not adsorbed on the MnO_2 and completely dissociates with a first order kinetics with lowering the pH below 7. This complex has no influence on the distribution of the species when Al_2O_3 is used as an adsorbent [158].

Comparing the neutron and deuterium activation ($^{55}Mn(n,\gamma)^{56}Mn$ and $^{55}Mn(d,p)^{56}Mn$) processes, the ^{56}Mn activity was higher in the case of neutron irradiated samples [224].

^{87}Rb and ^{55}Mn solid phase NMR studies in the temperature range of 100-440 K showed the presence of two crystallographically non-equivalent Cs-position in the lattice in the ratio of 1:1. The quadruple bond constants, chemical shifts and the symmetric tensor parameters of the gradient electric field have also been determined [156]. The second order quadrupole interactions, the asymmetry parameters and the local gradient of the electric field at the nucleus of each position have also been determined from the room temperature ^{55}Mn and ^{87}Rb NMR spectra of polycrystalline rubidium permanganate [225].

The thermal decomposition of rubidium permanganate starts at 230 °C with a 103 min induction period without irradiation [200]. Keeping $RbMnO_4$ at 230 °C for 20 min then cooling to 50 °C (repeating the experiment twice), the product consists of $Rb_4Mn_7O_{16}$ and Rb_2MnO_4 detected by XRD [226-227]. The presence of MnO_2 has also been mentioned [228]. Others exclude the formation of β-MnO_2 and detected the presence of $Rb_xMn_8O_7$ type cryptomelane compounds [198]. The temperature dependence of the number of the acoustic impulses, electric conductivity and magnetic susceptibility show that $RbMnO_4$ decomposes in an uniform reaction at 513 K [219]. Pre-irradiation with γ-rays reduces the length of the induction period and increase the rate of the subsequent salt breakdown because of the number of active nuclei in the salt breakdown is in direct proportion with the dose [201]. The decomposition temperature was found to be 243-254 °C for the non-irradiated and 233 °C for the γ-irradiated samples (^{60}Co). A combined TG, DTA and DTG study showed that 275 °C is the decomposition peak temperature [228]. The decomposition has an autocatalytic nature [54] and it is an exothermic process.

The rate of the decomposition depends on the age of the sample and the crystalline size. The irradiation does not change the rate of the starting phase but increases the maximal rate to 3-4 times at 243 °C. At lower temperature (233 °C) the starting rate decreases to half, but the rate of the maximal reaction does not change. It shows that the irradiation is the cause of accumulation of products effecting the thermal decomposition. The activation energy is 30.54 kcal/mol [230]. The decomposition in air at 315 °C can be illustrated by the following equation [229].

$$10RbMnO_4 = 3.48Rb_2MnO_4 + (1.52Rb_2O,6.50MnO_{1.93}) + 5.98O_2 \quad (27)$$

Replacing nitrogen with oxygen in the decomposition at 290-330 °C, results in an increase in the decomposition temperature by ca. 40 °C [231]. Isothermal kinetic measurement of the evolved oxygen showed a sigmoid type curve of the conversion and time relationship. The decomposition has an unusually extended acceleratory period. The decomposition is rapid and there is a short deceleration period. The rate equations are not satisfactorily expressed by a solid-solid phase decomposition. A temporary melting of particles is supposed. Some fusion of the products could be detected as a textural change by SEM [218]. The thermal decomposition curve in high vacuum showed a sigmoid pressure-time function at 110 °C. On the basis of this, it is assumed that at the commencement of the acceleratory period strains exist in the crystal at the interface between the product formed before the acceleration and the undecomposed material. This strain produces micro cracks in the reactant surface and the reaction progresses inwards by a mechanism of branching planes of reaction [232].

Rubidium permanganate transforms into rubidium manganate in RbOH solution [227]. Heating in the presence of a large excess of 1 N RbOH leads to the formation of $Rb_3(MnO_4)_2$ [227]. Rubidium permanganate reacts with oxalic acid and hydrazine hydrate at 80 °C with the formation of rubidium carbonate and manganese dioxide [233]. The formation of carbon dioxide from the oxalic acid and easily sedimentable manganese dioxide provide a possibility for preparing pure rubidium carbonate [233].

Mixture of rubidium permanganate and elemental antimony can be used in pyrotechnical compositions [234] and as a manganese source for the preparation of rhodium manganese catalysts for selective transformation of CO into acetic acid [181].

3.1.4. Cesium permanganate

Dark violet rhombic crystals (d = 3.5974 g/cm^3) [130] have been obtained by the reaction of silver permanganate and cesium chloride [87, 139, 235], or from barium permanganate and cesium sulphate [215]. Due to its low solubility in cold water (0.097 g/100 g of water at 0 °C) [216], $CsMnO_4$ can be precipitated from saturated aqueous solutions of potassium permanganate and cesium salts such as cesium nitrate [146, 236], cesium bromide [237], or cesium sulphate [217]. Because of its low solubility, $CsMnO_4$ is an important intermediate for the removal of the cesium-content of the acid-treated pollucite ores [238-239] or from cesium aluminium hydroxide, $Cs[Al(OH)_3]$, containing supernatants in the alkaline digestion of cesium ores [240]. $CsMnO_4$ was also

used to separate cesium and rubidium-salts with crystallization in the $CsMnO_4$-$RbMnO_4$-H_2O system [241].

Cesium permanganate can be extracted from its aqueous CsOH solutions with tributyl phosphate and tert-butanol. Increasing CsOH concentration increases the extractability up to the point of cesium manganate formation, which is not extractable, therefore the extraction curve has a maximum. Further increase in the pH decreases the extractability [73]. This low solubility value ensures the use of cesium permanganate as a co-precipitant for ammonium-ion containing solutions [242]. Flame photometric method has been developed to measure the alkaline and calcium contaminations of the cesium permanganate samples [243].

Crystals of $CsMnO_4$ are orthorombic with a = 10.0692, b = 5.8080 and c = 7.9470 Å, Z = 4 and d = 3.597 g/cm^3. The space group is Pnma [236]. Similar lattice constants (a = 10.143, b = 5.803, c = 7.941 Å) have been determined by Erenburg *et al.* [227] by powder X-ray diffraction. The calculated lattice energy is 563.0 kJ/mol [85] and the Madelung part of the lattice energy is 36274 kJ/mol [144].

UV-VIS spectrum of single crystalline $CsMnO_4$ has been studied at room temperature and at liquid N_2 temperature. Because of the compression of the permanganate ion in the solid crystalline lattice, the position of the bands is blue shifted toward the band positions observed in solution [220].

Permanganate ion in the $CsMnO_4$ has C_s site symmetry [148], the singlet ν_s and triplets of ν_{as} and δ_{F2} Mn-O bands have assigned [215] in nujol suspension. The IR spectrum of cesium permanganate depends only slightly on the conditions of the measurement (nujol or KBr matrix) because of the lack of the ion-exchange interactions between the cesium permanganate and the KBr matrix [87]. Raman spectrum of $CsMnO_4$ has been recorded with He/Ne laser excitation because of the intensive visible color. Some amount of MnO_2 has formed on the surface, therefore the spectrum has always been contaminated with the signals of MnO_2 [244]. Resonance Raman spectrum of $CsMnO_4$ has been measured and the fundamentals and combination bands have been assigned. The progression of ν_1 was observed up to v = 5, and the value of ω_1, harmonic frequency, and X_{11}, anharmonicity constant, have also been determined. The $\nu_1+\nu_3$ combination has also appeared [221].

XPS parameters of cesium permanganate have been measured [245]. The ^{133}Cs and ^{55}Mn solid phase NMR studies have been performed in the 100-440 K temperature range. The NMR results showed the presence of two crystallo-graphically non-equivalent Cs-positon in the lattice ca. in 1:1 ratio. The quadruple bond constants, chemical shifts and the asymmetric tensor parameters of the gradient electric field have also been determined [246]. The parameters of the second order quadruple interactions, the asymmetry parameters and the local gradient of the electric field at the nucleus of each positions have also been determined [225].

Thermal neutron irradiation of $CsMnO_4$ has been studied and the thermal annealing kinetics have been determined. The initial retention (32%), the distribution of the active species among the various valence states and the activation energies of the annealing process have been determined as well [157]. The thermal annealing affect on the process is one and the compactness is the other key factor of the crystalline lattice [138]. The recovery of the parent form was found to be 31% at annealing at 180 °C for 2 h [223]. The activation process is pH dependent. Besides the expected $Cs^{56}MnO_4$ and $^{56}Mn^{2+}$, some amount of MnO_2 has also been formed due to the oxidation of Mn^{2+} by the permanganate [139]. No $^{56}MnO_2$ has formed because of nuclear recoil. The amount of the MnO_2 is zero around pH = 1.5 and high at alkaline conditions. Neutron and deuterium activation of $CsMnO_4$ have been studied and the ^{56}Mn activity was found to be higher in the case of neuron irradiated salts [224].

During irradiation of dilute solutions of $CsMnO_4$ adsorbed by Al_2O_3, only ^{56}MnO4 and ^{56}Mn(II) species have formed and no $^{56}MnO_2$ could be detected. The effect of the pH, concentration and the type of adsorbent (Al_2O_3 or MnO_2) have also been studied. Around pH = 13, a complex formed from the permanganate and the hydroxide ion dissociates completely with a first order kinetics

meanwhile the pH decreases below 7. This complex does not adsorb on MnO_2 and has no influence on the distribution of the species when Al_2O_3 is used as adsorbent [158].

$CsMnO_4$ decomposes with oxygen evolution. The process has been studied with TG, DTA and DTG methods, and the temperature of the autocatalytic and the exothermic decomposition have been reported to be 295 °C [215] and 320 °C. [54, 231]. Isothermal heating at 240 °C leads to a decomposition with a 167-min induction period [200]. Pre-irradiation with γ-rays reduces the length of the induction period and increases the rate of the subsequent salt breakdown. The irradiation increased number of nuclei active in the salt breakdown is directly proportional to the dose [201].

The decomposition carried out at 310-350 °C leads to the formation of cesium manganate and a cesium manganese oxide phase with unknown structure. The decomposition temperature is increased by ca. 40 °C when the nitrogen was replaced with oxygen [231]. DTA studies in air showed the formation of MnO_2 [228]. Formation of β-MnO_2 was excluded, however, the formation of $Cs_xMn_8O_7$ type cryptomelane compounds could be observed [198]. Erenburg confirmed Cs_2MnO_4 formation with XRD [227].

In high vacuum, the thermal decomposition has a sigmoidal pressure vs. time function (110 °C). Based on this, it is suggested that at the commencement of the acceleratory period a strain exists in the crystal at the interface between the product formed before the acceleration and the undecomposed material. This strain produces micro cracks in the reactant surface, and the reaction progresses inwards by a mechanism of branching planes of reaction [232]. Melting during the first phase of the decomposition provides a possibility for the decomposition within the local intracrystalline molten phase resulted from the fusion of $CsMnO_4$:Cs_2MnO_4 eutectic with a

$$2MnO_4^- = MnO_4^{2-} + MnO_2 + O_2 \qquad (28)$$

type process. The decomposition is completed at 502 K without comprehensive melting or extensive disintegration. There was neither extensive nor strongly aligned crack propagation within the reactant crystals. The intracrystalline product structures were irregular with the appearance of rounded and granular textures where the aggregates are often appeared to be composed of smaller particles fused or sintered together. Kinetic investigations, performed between 490 and 560 °C, showed an unexpected effect of crushing. Though there are indications that the initial reaction rate is increased with crushing, at moderate conversions there are no differences in spite of the surface area increased. The thin superficial “egg-shell” like layer of unreactive or already reacted material maintained at the surface by large sized crystals explains the differences between the amount of O_2 evolved in the case of whole crystals or powders. Decomposition products added to a new sample have increased the decomposition rate markedly. No effect of the water vapour or of the potassium permanganate could be observed [237].

The presence of a small amount of MnO_3OH^- -ion as crystal defect in cesium permanganate was detected by NMR. This defect has a role in the decomposition temperature and in the decomposition mechanism. The temperature dependence of the number of acoustic impulses, of the electric conductivity and of the magnetic susceptibility shows unambiguously that $CsMnO_4$ decomposes around 553 K. The curve of the specific magnetic susceptibility is unusual compared to other univalent permanganate compounds, which confirm the presence of an elongated molten phase decomposition with the presence of more than one decomposition intermediate having unpaired electron [219].

Cesium permanganate can be transformed into Cs_2MnO_4 [227] in CsOH solutions, and can be easily reduced in its aqueous solutions with H_2O_2 with the formation of MnO_2 containing Cs^+ and Mn^{2+} ions. This precipitate can absorb cesium radionuclides [166]. The lithium intercalated manganese oxides can be used in thermal batteries [171]. Under hydrothermal conditions in sulfuric acid solutions, the cesium permanganate can be reduced with manganese(II) sulphate to hollandite type manganese oxides [167]. In a similar reaction some metal substituted (Pd, La, Co) octahedral manganese oxides could also be prepared [247]. The hollandite type manganese oxides have been formed between 80 and 140 °C, but below 30 °C

nsuite (γ-MnO_2) and above 160 °C pyrolusite (β-MnO_2) have been formed [202-203].

Cesium permanganate activated silver impregnated supports can be used effectively to prepare epoxides of alkenes, mainly ethylene oxide [248]. This kind of catalyst is especially useful in the epoxidation of carbon-dioxide containing ethylene [249]. Mn-Rh catalyst for selective transformation of CO into acetic acid can also be prepared from $CsMnO_4$ [181].

Using reducing agents [239] or methanol [238] $CsMnO_4$ can be converted into various kinds of cesium compounds, e.g. into cesium carbonate or cesium manganese oxide $Cs_xMn_4O_{8-9}$ [238].

3.1.5. Francium permanganate

Although francium permanganate has not been isolated yet, but some of its thermodynamical characteristics have been calculated. The lattice energy is 498.2 kJ/mol, the heat of formation is ΔH_f^{298} = -828.4 kJ/mol [250]. The calculated lattice entropy is 198.6 J/mol.K [137].

3.2. Ammonium permanganate

Ammonium permanganate was prepared first by Mitserlich by means of the reaction of ammonium sulphate and barium permanganate [91]. Because of isomorphism a light purple solid solution of $(NH_4,Ba)(MnO_4,SO_4)$ is precipitated during the synthesis. The crystal habit strongly depends on the crystallization conditions; most frequently it crystallized out in needle shape from aqueous solutions. The NH_4MnO_4 is orthorhombic (space group is Pnma (No. 62), Z=4) and isomorphous with the potassium permanganate and ammonium perchlorate. Its heat of formation is -684 kJ/mol [251-252], picnometric density is 2.231 g/cm^3 at 25 °C [253]. During storage slowly decomposes. Explosive-decomposition occurs at 55-60 °C, depending on the heating rate and the presence/absence of metal oxides catalyzing the decomposition [254]. Its solubility is 7.936 and 8.576 g/100 ml water at 15 and 25 ^oC, respectively, but it is insoluble in acetone [119-121]. It is completely dissociated in dilute aqueous solution [147], and by illumination with sunlight slowly decomposes with the formation of N_2 and MnO_2 [79]. Its thermal decomposition products are likely candidates as noble-metal free catalyst for fuel cells [255].

The typical method for its preparation is the interaction of potassium permanganate and ammonium chloride [254].

$$NH_4Cl + KMnO_4 = NH_4MnO_4 + KCl \qquad (29)$$

Moles and Crespi [146] modified the original Christensen's method [254] and used double recrystallizations to remove the excess NH_4Cl. The purity of the NH_4MnO_4 prepared by this method was checked by redox-titration, however, the permanganometric titrations have some errors due to self-oxidation of the ammonium ion by the permanganate. This leads to erroneous conclusions about the purity of the salt. Since all of the authors [256] accepted this method for the preparation of pure ammonium permanganate, nobody checked the purity of the product. Thermal studies of the NH_4MnO_4 prepared in this way, however, showed the formation of a residue which had the same lattice constant as the potassium manganese oxide residue formed in the thermal decomposition of $KMnO_4$ [257]. This residue was assigned un-ambiguously as cryptomelane, KMn_8O_{16}. Since Christensen [254] mentioned the presence of some unidentified amount of residual potassium in the formed NH_4MnO_4, we studied this synthesis in detail. By reproducing the Moles and Crespi method [146], excess of ammonium chloride and ice-cooling was used to prepare NH_4MnO_4 with double recrystallizations. The XRD of the products can be seen in Figure 2.

The product believed to be pure ammonium permanganate was found to be a solid solution of $(K,NH_4)MnO_4$ containing 40% $KMnO_4$. The potassium content does not change even after two recrystallizations. It explains the formation of the phase obtained during the thermal decomposition of "NH_4MnO_4". Since the NH_4MnO_4 is better soluble in water than the potassium salt, the composition of the solid solution strongly depends on the $KMnO_4/NH_4Cl$ molar ratio used in the synthesis. Although there is no available literature data about the polytherm solubility of the $KMnO_4$-NH_4MnO_4-H_2O system, data of the analogous $KMnO_4$-$RbMnO_4$-H_2O system might be taken into consideration. The reason for this is that the size of the NH_4-ion lies between the potassium-ion and rubidium-ion sizes, and the $KMnO_4$, $RbMnO_4$ and NH_4MnO_4 are isomorphous

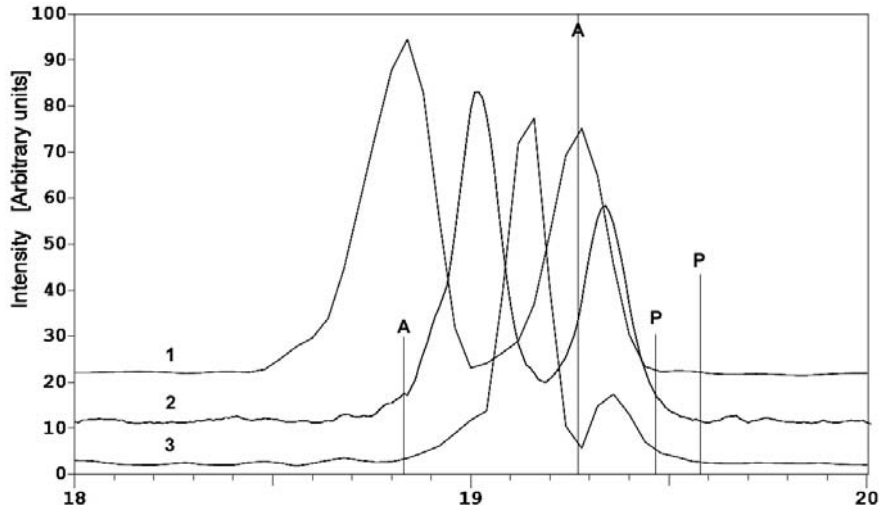


Figure 2. XRD of ammonium permanganate and $(K,NH_4)MnO_4$ solid solutions prepared in the $KMnO_4$-NH_4Cl reaction.

compounds. Since it is not possible to crystallize pure $RbMnO_4$ or $KMnO_4$ from the $RbMnO_4$-$KMnO_4$-H_2O system [96], this situation is probably valid for the $KMnO_4$-NH_4MnO_4-H_2O system as well. By the addition of NH_4Cl to the solutions made from the solid $K_x(NH_4)_{1-x}MnO_4$, the solubility of the NH_4MnO_4 can be suppressed easily. By means of triple recrystallizations with 1-1 equivalent of ammonium chloride which is then followed by a recrystallization to remove the residual NH_4Cl led to pure NH_4MnO_4. As it can be seen in Figure 2, the first recrystallization in the presence of 1 equivalent NH_4Cl at a 75/25 °C temperature gradient removes half of the potassium content, and a solid solution with a composition of $K_{0.20}(NH_4)_{0.80}MnO_4$ is obtained.

Pure NH_4MnO_4 can also be prepared from $NH_4H_2PO_4$ solutions by electrolysis at pH = 2-4 with using a Ni-Mn alloy anode [258].

Ammonium permanganate contains tetrahedral ammonium and permanganate ions, therefore the same four normal vibrations (ν_s, ν_{as}, δ_s and δ_{as}) appear for both ions both in the IR and the Raman spectra. This can be attributed to the C_s site symmetry (space group is Pnma (No. 61), Z = 4) and to the distortion of the tetrahedral environment causing the activation of two forbidden IR stretchings (ν_s and δ_s). There are several combination bands in both the N-H and the Mn-O region [259], and the curve analysis showed that the matrix has important effect on the spectra in the N-H region. Baran and Aymonino compared the IR spectra of the pure NH_4MnO_4 in KBr matrix and the $(NH_4,Ba)(MnO_4,SO_4)$ solid solution (NH_4MnO_4 in $BaSO_4$ matrix), and found only one or four band of δ_{as}, respectively. High resolution IR measurements showed the presence of three bands in KBr and four bands in $BaSO_4$ matrixes [253]. The δ_{as} band has two symmetric in plane and three antisymmetric in plane components ($2B_{1u}$, $2B_{3u}$ and B_{2u}). In diffuse reflection measurement mode complete degeneration and decomposition into three bands in KBr and into four bands in $BaSO_4$ occurred. This phenomenon can be explained by the effect of the N-H….X (X = bromide or sulphate) interactions in the matrixes on the ν_{as} and δ_{as} frequencies of the N-H stretchings [260-263]. The analysis of the N-H vibrations of the NH_4^+-salt in NaCl type matrixes (as KBr) [264-266] showed the presence of N-H...Br hydrogen bond, and there are N-H…O-SO_3 type strong hydrogen bonds in the ammonium sulphate crystals [267-268].

The anion stretchings also depends on the matrix. The ν_s and ν_{as} bands at 840 and 898 cm^{-1} appear as singlet and triplett in KBr [215], but Baran and Aymonino observed only a doublet for ν_{as} in KBr and a doublet with shoulder for the ν_{as} in $BaSO_4$.

The two bands at 848 and 828 cm^{-1} were believed to be B_{1u} and B_{3u} components of the ν_s (Mn-O) [253], but no similar splitting of the permanganate ion in the $KClO_4$ matrix even at 100 K could be observed [269-270]. The $\nu_s+\nu_{as}$ and $2\delta_{as}$ bands as combinations are very typical both in the $KMnO_4$ and in the NH_4MnO_4 spectra [259].

There are only a few permanganate compounds which have Raman spectra due to the intensive color and heat sensitivity [271-274]. Detailed Raman study has been performed on some alkaline-, alkaline earth metal- and lanthanum-permanganates. Using sample rotating and far-IR excitation, the Raman spectrum of NH_4MnO_4 has also been measured [259] and the complete factor group analysis has been performed. The splitting of the bands depends on the temperature, but no crystal structure changes have been detected as it was confirmed by DSC between 153 and 323 K and neutron diffraction experiment done at 2 K [68].

Theoretical interpretation of the reincorporation of the parent form in permanganates based on the retention of the recoil of ^{56}Mn in NH_4MnO_4 in the light of extreme back-diffusion and billiard ball collision as well as hot zone models have been investigated [275]. Ra-Be neutron source activation of ammonium permanganate led to about 4% ^{56}Mn initial retention. Reduction of the recoil fragments by the ammonium ion has been observed during thermal annealing. Pre-heat treatment has effected the fate of the ^{56}Mn. Annealing phenomenon consists of two apparent first order processes both for the heat-treated and the untreated permanganates. It is the reason for the competitive participation of the oxidising/ reducing inherent crystal defects [276].

The crystal structure of the ammonium permanganate shows the presence of hydrogen bond interactions (N-H..O-Mn type, with 2.27-2.80 H..O distances) at 298 K [259]. It is interesting to note, that Chang *et al.* [277] obtained low temperature single crystal diffraction spectra of the ammonium permanganate, but they could not determine the hydrogen positions. The reason for this is that the NH_4MnO_4 studied had been prepared from NH_4Cl and $KMnO_4$, therefore, their measurements were done on the solid solution of $KMnO_4$ and NH_4MnO_4 and not on the pure NH_4MnO_4. Since there are no hydrogens around the potassium cations, the refinement with a model of the NH_4MnO_4 did not enable them to determine the exact hydrogen positions even from the Fourier difference maps. Preparation of ammonium permanganate single crystals in pure form from tetraamminecopper(II) permanganate, provided the possibility to determine the hydrogen positions. Low temperature neutron diffraction experiments showed no polymorphism up to 2 K but there is a strong orientation effect due to hindered rotation of the ammonium ions in the lattice [68] as it was observed in the neutron diffraction experiments of the ammonium perchlorate [278]. The crystal structure of the ammonium permanganate is shown at Figure 3.

The presence of hydrogen bond between the ammonium cation and the permanganate anion determines stability and thermal behaviour. The situation is complex, because the thermal decomposition results the evolution of ammonia, a gas-phase reducing agent, which can react with the unreacted ammonium permanganate and the solid or the gaseous decomposition products [279]. The inner ignition of the ammonium compounds is a well-known phenomenon and may take place if the reaction heat of the decomposition (with N_2 or H_2O formation) is exothermic. Since the reaction heat of the process is ΔH = -309 kJ/mol, thus this type of process may also play a role in the thermal decomposition of the ammonium permanganate.

$$NH_4MnO_4 = 0.5N_2 + 2H_2O + MnO_2 \qquad (30)$$

The decomposition of the ammonium permanganate may be divided into the decomposition of the anionic part with the formation of manganese oxides and oxygen, and of the decomposition of the cationic part with the formation of ammonia or its oxidation products. The redox reaction occurs in solid phase but one cannot exclude gas/solid phase catalytic (manganese oxides) or non-catalytic oxidation reactions. The kinetics of the decomposition, the composition of the solid residue and the effect of the conditions and the additives have been studied in detail [256-257, 280-284]. The ammonium permanganate slowly decomposes even at room temperature because of its sensitivity to light. The bright surface of the crystals turns grey and 4% of

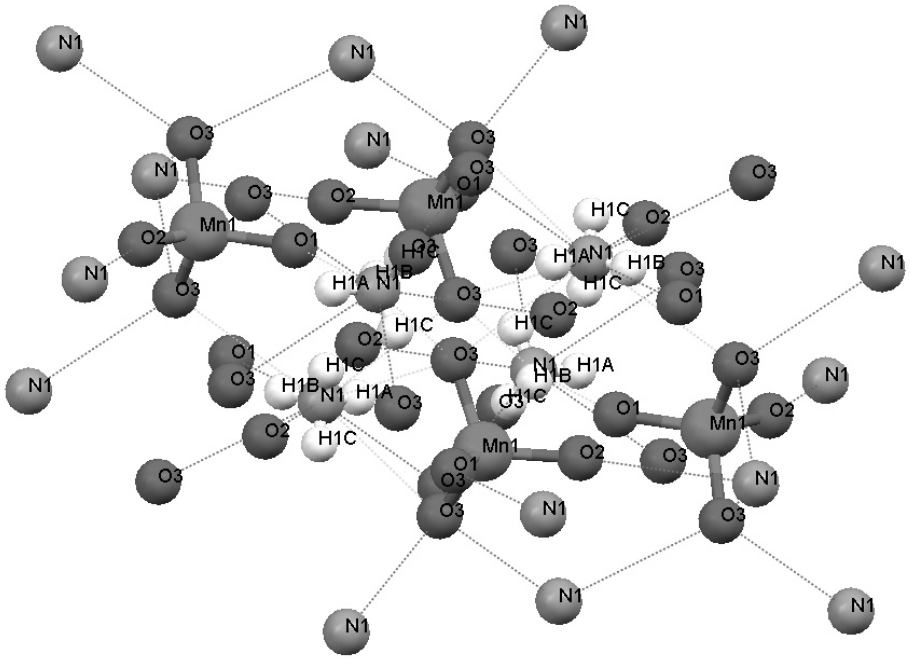


Figure 3. Crystal structure of ammonium permanganate.

the salt decomposes at room temperature in 3 months. After six months, the surface of the crystals is covered with a manganese oxide layer. Nitrogen oxides, ammonium nitrite and ammonium nitrate have also been detected as products [256, 284]. Sonication increases the decomposition rate very much. The rate is inversely proportional to the square of the intensity of the irradiation. If the decomposition is performed in an inert oil [256], the reaction becomes explosion-like after a several minute of induction period. The explosion might be the consequence of the reaction between the ammonium permanganate and the gas bubbles accumulated under the surface of the oil film. Normally, the decomposition process starts at 100 °C with explosion and flame [280-281]. The conditions (temperature, vacuum, UV irradiation and the additives) have an effect on the induction period and the decomposition rate. The complete mechanism is not clear. A radical decomposition reaction induced by the electrons from the cation conduction bands has been proposed. Surface defects also play an important role in the process [282]. The radicals formed in this process can accelerate the decomposition of ammonium perchlorate when NH_4ClO_4 containing 2% NH_4MnO_4 is heated [285]. If the reaction heat is dissipiated and the number of the contacting crystalline surfaces is decreased, the decomposition can take place without explosion. Among the gaseous product formed, the ammonia and the water decrease, and the oxygen increases the rate of the decomposition.

The composition of the solid phase formed during the ammonium permanganate decomposition at 100-120 °C in an inert atmosphere was found to be a 1:1 mixture of MnO and MnO_2 [280-281]. XRD and IR studies, however, showed the presence of α-Mn_2O_3 as a main product with a small amount of MnO_2 [257]. In air, the amount of MnO_2 is increased with increasing temperature. At higher temperatures MnO_2 starts to decompose with Mn_2O_3 formation. The presence of ammonium nitrite [254] and ammonium nitrate [254, 256-257, 280-281, 284] were also confirmed. Among the gaseous decomposition products, H_2O, N_2, NO, NO_2 and N_2O were detected with TG-MS at different temperature ranges [280-283, 286]. In case of ammonium dichromate, hexavanadate and tungstate the same gases were formed. In case of molybdate N_2O could not be detected. The lack of N_2O in the latter case is the consequence of the surface chemistry of the N_2O at various

metal oxides. Decomposition of ammonium permanganate, at 1 °C/min heating rate and under inert atmosphere starts at 70 °C and the maximum was observed at 85 °C. In the first decomposition step, oxygen, nitrogen and water were formed. Ammonia gets partly adsorbed on the solid manganese oxides formed. The presence of N_2 and H_2O in the gas phase, and the NH_4NO_3 and NH_4NO_2 in the solid phase indicates solid phase redox reaction. The classical permanganate decomposition and the redox reactions are concurrent processes:

$$2NH_4MnO_4 = 2NH_3 + 2MnO_2 + H_2O + 1.5O_2 \quad (31)$$

$$2NH_4MnO_4 = NH_4NO_3 + Mn_2O_3 + 2H_2O \quad (32)$$

$$2NH_4MnO_4 = NH_4NO_2 + 2MnO_2 + 2H_2O \quad (33)$$

The main sources of the N_2O and the N_2 are the ammonium nitrate and the ammonium nitrite, respectively. However, small amount of nitrogen and nitrogen oxides can be formed in the reaction of the solid manganese oxides and the adsorbed ammonia.

$$NH_4NO_3 = N_2O + 2H_2O \quad (34)$$

$$NH_4NO_2 = N_2 + 2H_2O \quad (35)$$

The ammonium nitrite decomposes at around 70 °C [256], but some amount of N_2 appears as a fragmentation product of the N_2O [286]. Redox reaction between the adsorbed ammonia and the manganese oxides can be confirmed by the N_2 and NO signals increased simultaneously with the decrease of the NH_3 signals.

Burning of NH_4MnO_4 [287-288] and the parameters of the ignition have been determined at 1-700 bar O_2 pressure. The ignition starts at 130 °C. The reaction heat found was 2299 kJ/mole and the ignition temperature measured was 1400 °C [289].

The cation has important effect on the oxidation ability of the various permanganate salts and the ammonium ion can act as an amination agent towards the starting/intermediate or the oxidation products, therefore the ammonium permanganate is a potential ammoxidation reagent. Oxidation of alcohols and aldehydes in the presence of ammonia lead to nitriles [290-294].

Benzyl alcohol could easily be oxidized with various permanganate compounds into benzaldehyde or benzoic acid. The selectivity depends on the solvent, counter-ion, temperature, sonication, etc. [7, 19, 45, 295-303]. Solid ammonium permanganate oxidizes benzyl alcohol into benzaldehyde even at room temperature, but the conversion is not completed even after 48 h. Increasing temperature, however, leads to complete conversion at 50 °C in 48 h.

$$3Ph\text{-}CH_2OH + 2NH_4MnO_4 = 3Ph\text{-}CHO + 2NH_3 + 2MnO_2 + 4H_2O \quad (36)$$

If the reaction mixture is heated up to 60 °C, the reaction rate is increased but traces of benzonitrile could also be detected. At 80 °C the benzonitril/ benzaldehyde molar ratio were 2:1 in 48 h, but traces of benzyl benzoate was also formed. By changing the benzyl alcohol/ammonium permanganate molar ratio between 0.4 and 4, the benzonitril/benzaldehyde ratio and amount did not change [304].

$$Ph\text{-}CHO + NH_3 + \text{‘O’} = Ph\text{-}CN + 2H_2O \quad (37)$$

It shows, that the source of the ammonium ion is the NH_3 derived from the first oxidation step (only 2/3 of ammonia is liberated compared to the amount of benzaldehyde), therefore, the conversion into benzonitrile cannot be higher than 67%. The oxidant in the benzaldimine oxidation step might be the colloidal manganese dioxide which might be partly regenerated with air [304].

Depending on the experimental conditions, various kinds of manganese oxide catalyst can be prepared by using NH_4MnO_4. For example, Mn-nitrate and $Mn(OH)_2$ can be reacted with NH_4MnO_4 to prepare alumina supported Mn-oxide catalysts [305]. The effect of the K-contamination on the surface texture of the Mn-oxide prepared from K-containing NH_4MnO_4 has also been studied [306].

Ammonium permanganate is used widely in various kind of industrial process, e.g. in surface treatment of aluminium and aluminium alloys [174], in water sterilization [307], as an oxidant in hair-dyeing composition [308], or as an additive to prevent adhesion of a polymer to the polymerization vessel [214]. If fibrous multi-filamentary acrylic material is contacted with hydroxylamine solution and subsequently with ammonium permanganate solution and the resulting fibrous material is heated in an

oxygen-containing atmosphere, a thermally stabilized acrylic fibrous material is formed which is capable of undergoing carbonization and is non-burning when subjected to an ordinary match flame [309].

Ammonium permanganate containing corrosion inhibitors are widely used in aqueous gas-liquid contacting processes for recovering carbon dioxide (CO_2) from industrial gases and oil combustion flue gases [310]. In order to reduce the corrosion during the removal of CO_2 from industrial combustion gases containing O_2 as well, the gas is contacted with an aqueous solution of alkanolamine and NH_4MnO_4 [311]. Ammonium permanganate is also used in the preparation of microcapsules comprising polymerizing urea and formaldehyde with forming a wall membrane of a urea/formaldehyde resin around the droplets of a hydrophobic oily liquid [312] or in the preparation of high quality priming devices by treating suitable pieces of cellulose with NH_4MnO_4 [313].

Calcination products of the NH_4MnO_4 catalyses the decomposition of H_2O_2 [314]. Ammonium permanganate is used for the preparation of manganese oxides via its reduction with carboxylic acid containing 4 carbon atoms. The reaction is carried out to obtain a manganese oxide gel in which the degree of oxidation of the manganese is 4. The manganese oxide gel obtained is dried at room temperature then it is subjected to a temperature of 300 ^oC - 1000 ^oC in order to obtain Mn_2O_3, which is used as a cathode material in electrochemical generators [513].

3.3. Permanganates of alkaline earth metals

Alkaline earth metal permanganates have been prepared from $Al(MnO_4)_3$ and the appropriate alkaline earth metal hydroxides (Ca, Sr and Ba). The calcium-salt could be crystallized out from 75-80% solution as tetrahydrate [100]. Calculated heat of formation (kJ/mole) and the lattice entropy (J/mol.K) of the crystalline alkaline earth metal permanganates are presented in Table 2.

3.3.1. Beryllium permanganate

Beryllium permanganate has been first prepared by Moles and Crespi from the aqueous solution of beryllium chloride and a calculated amount of silver permanganate. Crystallization led to pentahydrate [315]. Anodic dissolution of ferromanganese in a 100 g/l beryllium sulphate solution at 1.7 V potential and 10 A/dm^2 current density led to the same compound with 23.9% current yield [145]. The salt begins to decompose at 60 °C [315], and the decomposition has autocatalytic character [54]. Karapetyants and Lin gave the lattice energy as 606 kcal/mol [316].

Table 2. Calculated heat of formation (kJ/mol) and the lattice entropy (J/mol.K) of the crystalline alkaline earth metal permanganates.

M	$\Delta H_{f\ 298}^{0}$ [136]	S_{298} [137]
Be	-1533.6	-
Mg	-1629.3	259.6
Ca	-1708.5	272.1
Sr	-1717.3	286.7
Ba	-1688.4	296.4
Ra	-1694.4	305.1

3.3.2. Magnesium permanganate

Magnesium permanganate hexahydrate has been prepared by E. Mitserlich [91] and H. Aschoff [54, 87, 119-121] by means of the reaction of $AgMnO_4$ with magnesium chloride or $Ba(MnO_4)_2$ with magnesium sulphate. Its density was found to be 2.18 [192]. It decomposes at 130 °C with oxygen evolution in an autocatalytic decomposition process [54]. Starting from $AgMnO_4$ and $MgCl_2$ a slow crystallization and drying has led to the tetrahydrate [315]. The density was found to be the same as it has been found for the hexahydrate, and the salt decomposes with oxygen evolution at 150 °C. The deliquescent crystals are insoluble in $CHCl_3$, CCl_4, benzene, toluene, nitrobenzene ether, ligroin and CS_2, but they are soluble in MeOH, acetone, pyridine and glacial acetic acid. It dissolves in water and completely dissociates in dilute solutions [147]. The acetic acid solution has stronger oxidation activity than the pyridine solution [317]. The anhydrous salt can be prepared by thermal dehydration of the hexahydrate [148].

Magnesium permanganate has also been prepared by anodic dissolution of ferromanganese in magnesium sulphate solution (the highest current yield was 26.8% at 1.5 V and 1050 A/dm^2 current

density). By the addition of MgO as neutralization agent (20 or 40 g/L amount), a double salt, $MgSO_4*Mg(MnO_4)_2*6H_2O$ has formed. The chemical nature of this salt has not been elucidated yet [145].

IR spectra of the hydrated and the anhydrous salts showed that the permanganate ion has C_s site symmetry in both compounds [148]. The IR spectrum of the magnesium permanganate hexahydrate due to the ion-exchange interactions of the hydrated permanganates and the KBr matrix strongly depends on the measuring (nujol or KBr matrix) conditions [87].

Neutron irradiation and the studies on the distribution of the ^{56}Mn-species among the MnO_4^-, MnO_2 and Mn^{2+} species, respectively, showed anomaly in solution in reference to the solid state. It is attributed to the change of the retention depending on the concentration influenced by colloidal MnO_2 formation and the adsorption of Mn^{2+} on this colloid [318]. During irradiation of dilute solutions of $Mg(MnO_4)_2.6H_2O$ on Al_2O_3 sorbent, only $^{56}MnO_4^-$ and $^{56}Mn^{2+}$ species have formed and no $^{56}MnO_2$ could detected. The effect of pH, concentration and the type of the adsorbent (Al_2O_3 or MnO_2) have also been studied. Around pH = 13 a complex is formed, which does not adsorb on the MnO_2. The complex is formed from the permanganate and the hydroxide ion and completely dissociates with a first order kinetics on lowering the pH below 7. In the case of Al_2O_3 this complex has no influence on the distribution of the species [158].

Magnesium permanganate reacts with manganese(II) chloride under hydrothermal conditions, but the distribution of the products strongly depends on the pH and the temperature. Under markedly alkaline conditions, 3x3 type manganese oxide octahedral molecular sieves of todorokite type [319] are obtained, while in sulfuric acid solution hollandite type manganese oxides [167] are formed. Between 80 and 140 °C, these hollandite type or tunnel-like manganese oxides are produced, but below 30 °C nsutite (γ-MnO_2) and above 160 °C pyrolusite (β-MnO_2) can be obtained [202-203]. Octahedral molecular sieves in which a portion of the framework manganese is substituted by a transition metal can also be prepared in this way [320]. The manganese dioxide formation under acidic conditions can be performed to prepare proton substituted α-manganese dioxide. The proton of the α-manganese dioxide can be ion exchanged with lithium and thus producing lithium doped α-manganese dioxide containing no cell-damaging cations such as potassium or ammonium ions [170].

In organic solvents such as ethanol a new class of manganese oxide octahedral molecular sieves possessing a (4x4) tunnel structure could be prepared. The molecular sieves formed in this way are useful as oxidation catalysts in hydrocarbon conversion and in the preparation of electrochemical sensors [599]. Not only the manganese salts but the manganese(II) hydroxide can also be oxidized with magnesium permanganate to obtain manganese oxides with about 6.9 A tunnel size [172].

Magnesium permanganate oxidises a series of organic compounds [25]. It instantly reacts (in some cases with fire) with common solvents, such as THF, ethanol, methanol, t-butanol, acetone and acetic acid. Diphenylacetylene is oxidized into benzyl with 67% yield.

Magnesium permanganate is used in various branches of the industry and technology, e.g. as wood impregnating and colouring agents [321], as an additive in tobacco filters [182], as a catalyst in the aerial oxidation of toluene to benzoic acid without the formation of coloured by-products [322], for transesterification reactions of dicarboxylic acid esters and glycol to prepare high molecular weight polyesters [323] and as an ignition compound for insecticidal fumigants [324], especially to produce domestic fumigants of polyhydric alcohols as heat generating agents [325].

Successive treatment of multifilamentary acrylic fibrous material with a solution of hydroxylamine and magnesium permanganate results a fibrous material which possesses a chemically altered structure which can be carbonized in an oxygen-containing atmosphere into a stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame [309].

A fiber filter or porous substance comprising of an inert fiber or porous matrix, water, magnesium

permanganate and $NaHCO_3$ is capable of oxidizing or neutralizing hydrogen sulfide and sulfur dioxide from fluid streams [186-187, 323]. Magnesium hydroxide particulates with a given crystalline structure and a thickness of 30 to 200 Å, and a median particle size of up to about 1 micron are prepared by a process in which an alkaline material is reacted with concentrated aqueous solution of the magnesium permanganate [326].

Magnesium permanganate can be used as an additive in flexible polymeric films useful in the modified atmosphere packaging of fresh fruits, vegetables and flowers and acts as an ethylene reactive agent [189]. Its mixture with hygroscopic salts that captures the water needed for the oxidation of the ethylene by the permanganate absorbed on the surface of an inert carrier can also be used [188]. Residential and commercial constructions containing magnesium permanganate are issued in low-pressure drop filters to purify the central forced air systems [185]. Mixing a blend of magnesium permanganate and iron powder in a specific ratio with a given amount of silicon (ferrosilicon) powder leads to a safe composition for heating foods and drinks [327].

3.3.3. Calcium permanganate

Calcium permanganate exists as pentahydrate, tetrahydrate and anhydrous salt. The pentahydrate is obtained under normal conditions by the reaction of calcium sulphate and barium permanganate, or from calcium chloride and silver permanganate [54, 315]. It decomposes at 140 °C with oxygen evolution in an autocatalytic decomposition process [54]. The hydrated forms may thermally be dehydrated [148] in two stages between 50 and 100 °C [328]. The first two molecules of water can be removed swiftly, the third only during a longer dehydration time. The anhydrous salt decomposes at 130-150 °C in air. The sigmoidal isothermal fractional decomposition *vs.* time curves are reproducible. The decomposition starts with a slow induction period followed by an acceleratory and a decay period. The induction period and the decay period can be shortened with ^{60}Co γ-irradiation [328]. The calculated lattice energy and the heat of formation are 1935 and -1434 kJ/mol, respectively [85]. The IR spectra of the pentahydrate and the anhydrous salt have been discussed previously [148].

During irradiation of dilute solutions of $Ca(MnO_4)_2.5H_2O$ adsorbed on Al_2O_3, only $^{56}MnO_4^-$ and $^{56}Mn^{2+}$ species are formed and $^{56}MnO_2$ is not detected. The effect of pH, concentration and the type of the adsorbent (Al_2O_3 or MnO_2) have also been studied. A complex is formed from the permanganate and the hydroxide ion around pH = 13 which does not adsorb on the MnO_2. It completely dissociates with a first order kinetics at a pH below 7. This complex has no influence on the distribution of the species when Al_2O_3 is used as adsorbent [158].

Calcium permanganate reacts with manganese(II) in sulfuric acid solution under hydrothermal conditions with the formation of hollandite type manganese oxides [167]. These tunnel-like manganese oxides have been formed between 80 and 140 °C. Below 30 °C nsutite (γ-MnO_2) and above 160 °C pyrolusite (β-MnO_2) have been formed [202-203]. Metal substituted (Pd, La, Co) octahedral manganese oxides could also be prepared from manganese sulphate and calcium permanganate under similar conditions [247].

Calcium permanganate is widely used as an oxidant in compositions used for corrosion inhibition of metals induced by acidic gases such as H_2S, CO_2 or COS [207, 329-330], for the removal of NO from smoke [209], in the removal of arsenic from shale oil [331], as a combustion improver [212] or as an additive in lubricating oil for motors [332]. Asphalt fibers are treated with calcium permanganate before carbonization [333], and fumes can be generated with calcium permanganate from hydrazine absorbed in an inert porous support material [334]. It can be used as an ignition compound for insecticidal fumigants [324-325]. Calcium permanganate can be used as an oxidant in low-pressure drop filters to purify central forced air systems in residential and commercial constructions containing different kind of adsorbers and chemicals [185]. It can be used in the preparation of lithographic supports [335], and in the impregnation of zeolites to obtain a sorbent for formaldehyde and other toxic gases emitted from furniture [336].

It can also be used as a catalyst in the preparation of arylalkyl hydroperoxides by oxidizing hydrocarbons with air [337], for the aerial oxidation of toluene to benzoic acid without the formation of colourful by-products [322], in the preparation of polyethylene terephthalate from dimethyl terephtalate and glycol [338], in the transesterification reactions of dicarboxylic acid esters and glycol to prepare high molecular weight polyesters [323], and as a fixation reagent to analyze biogenic monoamines in histochemical samples for electron microscopy. Tissue fixed with calcium permanganate revealed very distinct membranes [190]. It can be used as an additive in chitosan based calcium agent to enhance the absorbability of calcium into living plant [339], as an ascuring agent in polysulfide type polymers [340], as an additive in tobacco filters [182] or in the surface treatment of aluminium and aluminium alloys [174, 341].

Calcium permanganate additive in polymeric films acts as an ethylene reactive agent and can be used as an additive in flexible polymeric films useful in the modified atmosphere packaging of fresh fruits, vegetables and flowers [189]. Its mixtures with hygroscopic salts that captures the water needed for the oxidation of the ethylene in an inert carrier [188]. Impregnation of porous substrates is also known [187]. During impregnation, an inert fiber matrix bound reagent is formed which is capable of oxidizing or neutralizing contaminants such as hydrogen sulfide and sulfur dioxide from fluid streams [186].

Fibrous multifilamentary acrylic materials can be modified by treating fibers with a solution of hydroxylamine and subsequently with a solution of calcium permanganate. The resulting fibrous material which possesses a chemically altered structure is heated in an oxygen-containing atmosphere until a thermally stabilized acrylic fibrous material is formed capable of undergoing carbonization and it does not burn when subjected to an ordinary match flame [309]. It can be used as a permanganate constituent of the composite conductive crystals containing graphite or other carbonaceous material for the use of cathodic material in a galvanic cell [342].

3.3.4. Strontium permanganate

Hygroscopic dark violet crystals of strontium permanganate trihydrate has been prepared from $AgMnO_4$ and $SrCl_2$ [91, 119-121, 315, 343] as quadratic columns and cubes. Reaction of aluminium permanganate and strontium hydroxide, strontium oxide or strontium carbonate led to strontium permanganate solution [100, 102]. Barium permanganate and strontium sulphate has also been reacted due to the two order of magnitude difference between the solubility product of the strontium and the barium sulphate [55, 102]:

$$Ba(MnO_4)_2 + SrSO_4(s) = Sr(MnO_4)_2(aq) + BaSO_4(s) \quad (38)$$

Electrolysis of Mn-containing anodes in concentrated strontium hydroxide solutions also produced strontium permanganate [344]. Its decomposition temperature depends on the heating conditions. The values of 155 and 175 °C have been provided by Elovich and Moles and Crespi, respectively [54, 315]. The decomposition has an autocatalytic character [54]. Its density has been found determined to be 2.88, 2.95, 2.81 g/cm^3 by Saslawsky [192], Moles and Crespi [315], and Ferarri [345], respectively. Calculated density of the trihydrate is 2.84 g/cm^3 and of the tetrahydrate is 2.97 g/cm^3, which confirm the existence of the trihydrate [345]. Its solubility in H_2O is 2700 times higher than the solubility of the $CsMnO_4$ [216]. Equivalent conductivity in 0.0005-0.005 M solutions has been determined by Franke and Falkenhagen [346, 347], calculated contraction has been obtained by Saslawsky [192], heat of formation was calculated to be -1492 kJ/mol [85]. The lattice energy is -1852 kJ/mol and the lattice entropy is 478.7 J/mol.K [85] (Figure 4).

$Sr(MnO_4)_2.3H_2O$ has a cubic lattice (space group: $P2_13$, Z = 4, a = 9.611, d_{calc} = 2.84, d_{exp} = 2.78 g/cm^3), the average Mn-O distance is 1.605 Å. Each strontium cation is surrounded with ten oxygen atoms (seven oxygen atoms from permanganate anions and thee from the water molecules), the three average Sr-O distance is 2.68 Å. No well defined hydrogen bonds could be observed. The site symmetry of the permanganate ion in the

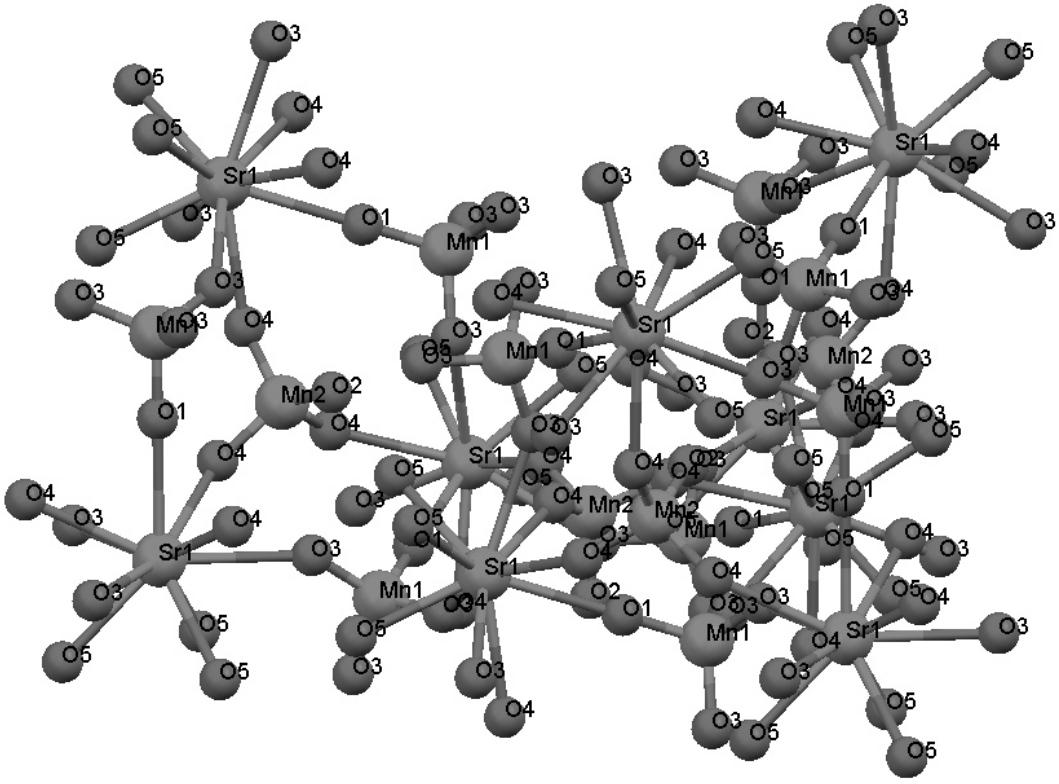


Figure 4. Crystal structure of strontium permanganate trihydrate.

trihydrate is C_3. The IR spectrum is not completely consistent with this, because three strong bands at 945, 930 and 920 cm^{-1} have been observed in the ν_{as} region, whereas only two components, A and E are allowed in C_3. The weak band at 845 cm^{-1} could be assigned as ν_s (A) [148]. Resonance Raman spectrum of the $Sr(MnO_4)_2{*}3H_2O$ has been measured and the assignation of the fundamentals and the combination bands have been performed as well. The progression of ν_1 was observed up to v = 3, and the values of ω_1 harmonic frequency and X_{11} anharmonicity constant have also been determined [221].

Radiochemistry (n,γ) of the strontium permanganate trihydrate and its aqueous solution has been studied in detail. In dilute solutions of $Sr(MnO_4)_2.3H_2O$ on Al_2O_3 sorbent, only $^{56}MnO_4^-$ and $^{56}Mn^{2+}$ species are formed and $^{56}MnO_2$ could not been detected. The effect of pH, concentration and the type of the adsorbent (Al_2O_3 or MnO_2) have also been determined [158]. The pH has an influence on the retention only at low (1-2) and high (9.5-12.5) pH values [348]. At higher pH a complex is formed from the permanganate and the hydroxide ion, which does not adsorb on MnO_2 and completely dissociates with a first order kinetics at a pH below 7. This complex has no influence on the distribution of the species when Al_2O_3 was used as adsorbent. In solid state, the retention has been found to be higher at higher temperatures, however, preactivation heating gave lower retention values, comparing with the post-activation heating of the targets, due to the presence of crystal defects and to the transition reactions of the lattice stable precursors in the parent reformation [349].

The anhydrous salt has been prepared by dehydration of the trihydrate at room temperature in vacuum desiccator in several days or by heating up to 100 °C [148]. The dehydration process has two stages between 50 and 100 °C. This includes a single step nucleation process followed by a growing process without nuclei overlap. Two and one water can be removed in each step. The anhydrous salt can be decomposed at 120-145 °C

in air. The sigmoidal isothermal fractional decomposition *vs.* time curves are reproducible. The decomposition starts with a slow induction period, which is then followed by an acceleratory and a decay period. The induction period can be shortened with ^{60}Co γ-irradiation [328].

Its violet aqueous solution becomes pale green when treated with excess strontium hydroxide [123-125]. This is the consequence of the formation of colloidal strontium manganate [68].

$$Sr(MnO_4)_2 + Sr(OH)_2 = 2SrMnO_4 + H_2O + 1/2O_2 \quad (39)$$

Strontium permanganate catalyses the transesterification reactions of dicarboxylic acid esters and glycol to obtain high molecular weight polyesters [323], or the preparation of arylalkyl hydroperoxides from hydrocarbons and air [330, 337]. It can be used in surface treatment of aluminium and aluminium alloys [174] and as an oxidant in compositions used for corrosion inhibiton of metals toward acidic gases such as H_2S, CO_2 or COS [207, 329].

3.3.5. Barium permanganate

Barium permanganate has only anhydrous form under normal conditions. Barium permanganate is an essential compound in the preparation of other permanganate salts, therefore, numerous efforts have been done to find simple and easy methods for its preparation [55, 80, 102]. Highly pure barium permanganate can be prepared from $KMnO_4$ and $Al_2(SO_4)_3$ via using excess Al-salt, and reacting the excess Al-salt and the formed aluminium permanganate with stoichiometric amount of $Ba(OH)_2$ to obtain $Ba(MnO_4)_2$, $BaSO_4$ and $Al(OH)_3$ with 68% yield [102, 350]. Because of the formation of barium manganate the yield is less than the expected. In boiling solution, only barium manganate is formed:

$$2Al(MnO_4)_3 + 3Ba(OH)_2 = 2Al(OH)_3 + 3BaMnO_4 + 3MnO_2 + 3O_2 \quad (40)$$

Silicomanganese and phosphor-doped silico-manganese anodes can electrochemically be dissolved in $Ba(OH)_2$ solution. Silicon is a necessary component, however, more than 10-20% Si content impairs the process. The presence of Fe in the alloy has a negative effect on the current efficiency [351]. Instead of barium hydroxide, barium carbonate can be used as a neutralization agent to bind the permanganic acid formed. Depending on the pH, between 0.5 and 14 the primary product is permanganic acid or barium permanganate. Some anodic sludge is formed in the alkaline pH range which is a decomposition product of the formed permanganate ion. The optimal pH range is from 3.5 to 10.5. The isolation of barium in the solution formed performed by ion-exchange with nitrate ions on AV-17 anion exchanger, and the barium nitrate solution is analyzed with a complexometric method [352]. Besides this, a gravimetric method has also been developed [353]. Pure metallic manganese can also be dissolved electro-chemically in barium hydroxide solution with the formation of barium manganate and permanganate. Increasing temperature (up to 70 °C) decreases the overall yield, but increases permanganate: manganate ratio. The optimal conditions are: saturated barium hydroxide solution, 15-30 °C, 3.5-7.5 A/dm^2 current density and 0.5-1.0 V potential [354]. Barium permanganate can also be prepared from $AgMnO_4$ and $BaCl_2$ [139]. It is very soluble in water and dissociates completely in dilute aqueous solution. In 1 M solution the degree of dissociation is only 0.50 [147].

Barium permanganate has orthorhombic structure (Fddd, a = 14,749, b = 11,896 Å, c = 7,414, Z = 8), d = 3.78 g/ml, the average O-Mn distances are 1.74 and 1.61 Å [355], the calculated lattice energy and the heat of formation are 1776.5 and 1559.1 kJ/mol, respectively [85].

The IR spectrum of barium permanganate has been studied in detail, and the permanganate ion site symmetry has given as C_2 [148]. In KBr four IR bands of ν_{as} were observed, while only three bands were observed by Guerchais [356]. In nujol suspension two singlets of ν_s and δ_E, Mn-O band, a quartet and a triplet of ν_{as} and δ_{F2} bands, respectively, were observed [215]. Neither ion exchange nor redox reactions could be observed in the KBr under the IR measurement conditions [87]. The factor group analysis and assignation of its Raman bands measured with NIR excitation at 100 and 300 K have been discussed [221].

The barium permanganate trihydrate exists only as a mixed crystal component in $Ba(ClO_4)_2.3H_2O$ matrix. Its polarized electronic absorption spectrum bands have been assigned and evaluated in detail. The transitions and the effects of the environment on these band shifts have been discussed [357]. XPS [245] and NMR parameters [156] have also been given. With increasing concentration in D_2O solutions the ^{55}Mn NMR signal shifts linearly to lower frequencies [156].

Preparation of ^{56}Mn isotope containing compounds by neutron irradiation is pH dependent. Besides the expected $Ba(^{56}MnO_4)_2$ and $^{56}Mn^{2+}$ some amount of MnO_2 also forms in neutral solution, because of the oxidation of Mn^{2+} by the permanganate [139, 158, 358]. Due to the nuclear recoil no $^{56}MnO_2$ forms, on the other hand, there is no MnO_2 formation in acidic solution. The effect of the pH, concentration and the type of the adsorbent (Al_2O_3 or MnO_2) have also been studied. Around pH = 13, a complex is formed from the permanganate and the hydroxide ion. It does not adsorb on MnO_2 and completely dissociates with a first order kinetics at pH below 7. This complex has no influence on the distribution of the species when Al_2O_3 is used as an adsorbent [158].

Pre-heat treatment slightly increases the initial ^{56}Mn retention and decreases the extent of the subsequent thermal annealing. Annealing phenomenon consists of two apparent first order processes for both heat-treated and untreated permanganates. It is the reason for the competitive participation of the oxidising/reducing inherent crystal defects [276].

Barium permanganate is stable thermally up to 180 °C, and decomposes in two stages between 180-350 and 500-700 °C. The decomposition is fast at 200-220 °C, exothermic and the activation energy is 113 kJ/mol. The decomposition can be described as it follows:

$$Ba(MnO_4)_2 = BaMnO_3 + MnO_2 + 1.5O_2 \quad (41)$$

$$2BaMnO_3 = 2BaO + Mn_2O_3 + 0.5O_2 \quad (42)$$

$$2MnO_2 = Mn_2O_3 + 0.5O_2 \quad (43)$$

A small amount of MnO_3OH^- -ion was detected by NMR in the barium permanganate as crystal defect. This defect has a role in the decomposition temperature and in the decomposition mechanism. The temperature dependence of the number of acoustic impulses, electric conductivity and magnetic susceptibility shows unambiguously that $Ba(MnO_4)_2$ decomposes in an uniform reaction [219]. DTA studies in air showed the formation of MnO_2 [228]. Endothermic peak of the DTA curve at 575 °C is assigned to the decomposition of MnO_2 into Mn_2O_3, and the exothermic peak at 630 °C refers to the decomposition of $BaMnO_3$. Normally, $BaMnO_3$ can be prepared from $BaMnO_4$ at 900 °C [359], therefore its formation at lower temperature might be the effect of the catalytic power of the formed Mn_2O_3 [360]. Because of the formation of catalytically active intermediates due to radiolysis, X-ray irradiation at the moment of the thermal decomposition increases the decomposition rate of the barium permanganate [360-361]. TG, gas-evolution, dielectric and XRD measurements have also been studied and provided the kinetics of the decomposition which has an activation energy of 34 kcal/mol [53].

The thermal decomposition curve in high vacuum shows a sigmoid pressure-time function (110 °C). Based on this, it is assumed that at the commencement of the acceleratory period, strains exist in the crystal at the interface between the product formed before the acceleration and the undecomposed material. This strain produces micro cracks in the reactant surface and the reaction progresses inwards by a mechanism of branching planes of reaction [232].

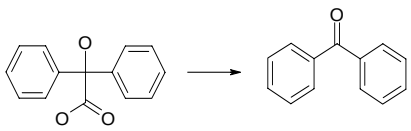
Barium permanganate reacts with manganese(II) in sulfuric acid and hollandite type or tunnel-like manganese oxides are formed at 80-140 °C under hydrothermal conditions [167]. Nsutite (γ-MnO_2) or pyrolusite (β-MnO_2) are formed below 30 and above 160 °C, respectively [202]. The same method can be used to prepare metal substituted (Pd, La, Co) octahedral manganese oxides [247]. Barium permanganate reacts with sulfur dioxide in its aqueous solution. This oxidation process partly leads to sulphate but dithionate also forms:

$$4Ba(MnO_4)_2 + 21H_2SO_3 = 4BaSO_4 + 8MnSO_4 + H_2S_2O_6 + 7H_2SO_4 + 13H_2O \quad (44)$$

Thiosulphate, higher thionates or sulfites could not be detected [362].

Barium permanganate as a solid reagent can oxidize various organic compounds, e.g. sulfides to sulfoxides [23], and regenerates aldoximes and ketoximes to the corresponding carbonyl compounds [18]. Thioles are oxidized into disulfides, and vicinal aromatic hydroxyketones are oxidized into diketones [8] under reflux in MeCN.

Barium permanganate selectively oxidizes secondary benzylic C-H bonds. In toluene solution, e.g. ethylbenzene and diphenylmethane are converted into acetophenone and benzophenone respectively [302], without oxidizing the toluene. Diphenylacetylene, benzoin and 1,2-diphenylethane are oxidized to benzil with good yield. Condensed aromatic hydrocarbons such as naphthalene, phenanthrene are oxidized to the appropriate quinones. Unsaturated alcohols transform into unsaturated aldehydes, but styrene is oxidized to benzaldehyde. Benzylic alcohols are transformed into carboxylic acids, but primary alcohols such as 3-phenylpropanol or 1-octanol are converted only to aldehydes [302]. Secondary alcohols are oxidized to the appropriate ketones, while the double bond functionalities are retained. Benzylic acid, however, is cleavaged to benzophenone [8]:



(45)

Benzyl halides are transformed to a mixture of aldehydes and carboxylic acids; aldehydes are transformed into the corresponding carboxylic acids [302]. Arylamines are transformed into the corresponding azo-compounds, except o-nitroaniline which does not react [302]. Barium permanganate is selective in oxidative cleavage of benzylic type C-N bonds, e.g. 2,4-dinitrophenylhydrozones and semicarbazones are oxidized to the corresponding carbonyl compounds, however, benzaldehyde or cyclohexanone derivatives remain unchanged in this reaction.

Barium permanganate acts as corrosion inhibitor of aluminium [174] and chromium [211]. It is added to epoxy resin encapsulants for various microcircuits with Al conductors to improve their reliability [363].

Barium permanganate can be used for the preparation of lithographic supports [335], for the generation of gases in compositions used as disintegration assistants in casting molds [364], as a polymerization catalyst in the polyphenylene-oxide polymers preparation [365], as an oxidant in hardening SH-functional polymers like polymeric ditihiocarbamates [366] and in the transformation of 2-t-butyldimethylsilyl-3-methylfuranol to the corresponding furaldehyde [367].

Barium permanganate can be used itself or in a mixture containing a hygroscopic salt that captures water needed for the oxidation of ethylene in flexible polymeric films useful in the modified atmosphere packaging of fresh fruits, vegetables and flowers and acts as an ethylene reactive agent. [188-189]. It catalyses the transesterification reactions of dicarboxylic acid esters and glycol to prepare high molecular weight polyesters [323]. In the preparation of arylalkyl hydroperoxides it can catalyze hydrocarbons oxidation with air [337], and in the presence of barium permanganate the aerial oxidation of toluene to benzoic acid can be performed without the formation of colourful by-products [322].

Barium permanganate impregnated porous substrates are effective hydrogen sulfide removing agents [187]. Fiber filters, comprising barium permanganate bound to the fiber matrix, are capable of oxidizing or neutralizing contaminants like hydrogen sulfide and sulfur dioxide in fluid streams [186].

It can be used as a permanganate constituent of composite conductive crystals containing graphite or other carbonaceous material used as cathodic material in a galvanic cell [342]. It can be used to purify central forced air systems in residential and commercial constructions [185].

3.4. Permangnates of p-elements

Only lead and aluminium permanganates have been synthesized so far. The properties of the pure salts have not been studied in detail.

3.4.1. Aluminium permanganate

Aqueous solution of aluminium permanganate has been prepared by the reaction of hot aqueous solutions of potassium permanganate and aluminium sulphate, followed by the removal of potassium alum after cooling the solution [99-102]. It dissociates completely in its dilute aqueous solutions [147]. The pure aluminium permanganate is a deep purple crystalline mass which contains crystallization water. Its composition and properties are under study [68].

3.4.2. Lead(II) permanganate

Lead permanganate has been prepared by the reaction of the dilute aqueous solutions of $PbCl_2$ and $AgMnO_4$. The $1.07*10^{-3}$ M solution formed was treated with alkali, when a brownish precipitate was formed in which the Pb:Mn ratio has proved to be 2. The compound has been defined as basic lead(II) permanganate, $3PbO*Pb(MnO_4)_2$. Its solubility product has been found to be $1.35*10^{-19}$ [89-90, 368]. Lead permanganate can be used for the removal of interfering redox-active substances from liquid samples e.g. for the treatment of blood, serum, plasma or other bodily fluids [369].

3.5. Transition metal permanganates

Numerous transition metal permanganates have been prepared, and their inorganic and organic reactions have also been studied. These compounds are purple water-soluble compounds, which with the exception of the silver salt have various crystalline water content.

3.5.1. Silver permanganate

$AgMnO_4$ prepared from $KMnO_4$ and $AgNO_3$ is a dark purple, nearly black, stable and non-hygroscopic crystalline material [139, 215]. Application of excess $AgNO_3$ at 0 °C prevents co-precipitation of the $KMnO_4$ with the $AgMnO_4$ [39]. Silver permanganate has also been prepared by the reaction of silver sulphate with barium permanganate [54, 215]. It can be stored (in dark) at room temperature for 5 months without decomposition, and pre-irradiation with visible flash light has no influence on its magnetic and optical data [39]. Solubility in water is $0.966x10^{-5}$ M and $1.420x10^{-5}$ M at 15 and 35 °C, respectively. The temperature dependence of the solubility product between 15 and 35 °C has been described as it follows [370]:

$$\log L = -37.3958 + 0.053788T + 3419.9/T \quad (46)$$

The values of the thermodynamical properties at room temperature have been found to be ΔG^0_{298} = -407,6 kJ/mol, ΔS^0_{298} = 42,66 J/mol.K [371]. Its solubility product has been determined in the temperature range of 25-35 °C both in aqueous [370] and DMF solutions [234].

The crystal structure of $AgMnO_4$ has been re-determined by Boonstra [372]. The average Mn-O bond length was found to be 1.60 Å. The needle-shaped crystals belongs to monoclinic system, $P2_1/n$, with a = 5.64, b = 8.33 and c = 7.12 Å with β = 92.25°. The thermal motion of the permanganate is isotropic while the silver ion has anisotropic motion. On the contrary to Sasvari's results [373], the structure cannot be regarded as a slightly deformed barite structure. Although there is a formal correspondence in the heavy atom positions, the orientation of the oxygen tetrahedron is quite different [372]. Single crystal X-ray diffraction studies have been performed on needle shaped single crystals grown from water. The average Mn-O distance has been found to be 1.633 A, d = 4.500 g/cm^3, Z = 4 at 298 K. Only one oxygen is bound to the silver, thus resulting a significant deviation from the regular tetrahedral geometry of the permanganate anion [374] (Figure 5).

The silver permanganate, $AgMnO_4$ can be formulated as $Ag^{I}Mn^{VII}O_4$, however, thermo-dynamic calculations [40] show very small difference in the heats of formation of the $Ag^{I}Mn^{VII}O_4$ and the $Ag^{II}Mn^{VI}O_4$. The UV-Vis spectrum of the $AgMnO_4$ is typical for the permanganate ion, however, in frozen solution or in powdered state the UV spectra differs from the spectrum obtained in solution [375]. The electronic spectra measured in H_2O, $AgNO_3$ solutions and in solid KBr, K_2SO_4, Li_2CO_3 and Ag_2SO_4 pellets indicate the role of the Ag^+-ion exchange in the solid matrixes [376]. Although permanganate cannot oxidize the silver(I) in aqueous solutions, but in solid state an electron transfer promoted by the increased lattice energy

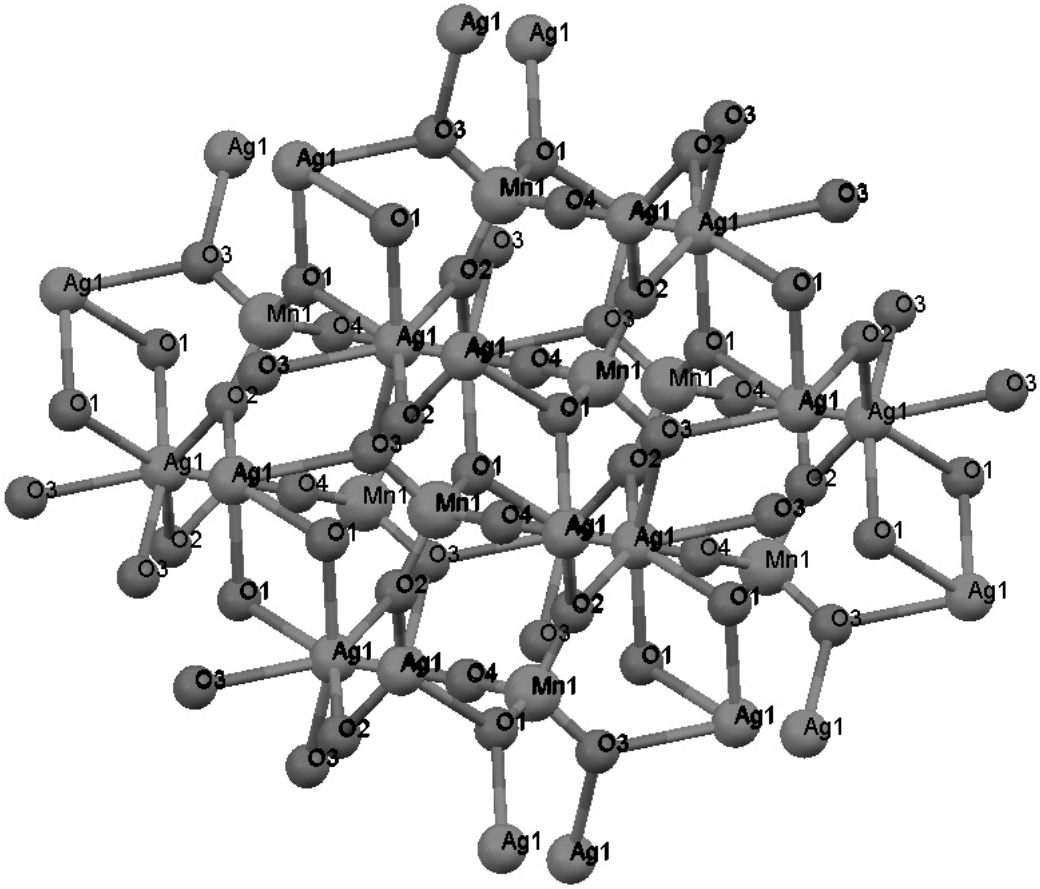


Figure 5. Crystal structure of silver permanganate.

is possible. The broad diffuse electronic spectrum of the $AgMnO_4$ is consistent with a general multicenter interaction in which the electron delocalization would cause cooperative effects between the MnO_4 sites, thus the integrity of the individual ions is lost. Since an electron can enter into the permanganate ion at the 2*e* level, which is antibonding with respect to the Mn-O bond, this reduces the magnitude of the Mn-O stretching force constant. Comparing the force constant for the ideal tetrahedral MnO_4^{n-} (n=1-3) ions, the f_d force constant found for the $AgMnO_4$ has an intermediate value between the force constant determined for the +6 and for the +7 oxidation state of the manganese in the MnO_4 ions. The formal oxidation state can be estimated to be 6.2 for the MnO_4-ion in the $AgMnO_4$. This indicates that substantial electron redistribution occurs in the formation of the solid $AgMnO_4$ [375]. On the bases of magnetic measurements, however, the

$$Ag^{+}MnO_4^{-} = Ag^{2+}MnO_4^{2-} \quad (47)$$

equilibrium in the solid state produces $Ag^{II}Mn^{VI}O_4$ form only in very small amount, because the paramagnetic contribution of the unpaired electrons of MnO_4^{2-} and Ag^{2+} should be at least two orders of magnitude larger than the observed value [39].

Photoelectron spectrum of the silver permanganate was analyzed [377] in detail. The silver $3d_{5/2}$ binding energy (XPS) is 368.9 eV [378], the $Mn2p_{3/2}$ binding energy is 642.3 eV and the surface composition was found to be $Ag_{1.28}MnO_{4.1}$. The charge of the manganese is small compared to the formal oxidation states, and this indicates that the formal charge on the oxygen is much smaller than -2, approx. -0.5 [376].

IR spectrum of the silver permanganate strongly depends on the measuring conditions (nujol or

KBr matrix). This can be attributed to the ion-exchange interactions between the silver permanganates and the KBr matrix [87]. In nujol suspension the permanganate ion (in the silver permanganate) has C_1 site symmetry with a ν_s Mn-O band at 800 cm^{-1} and a triplet of ν_{as} [215] around 900 cm^{-1} [87].

Resonance Raman spectrum of $AgMnO_4$ has been measured and the assignation of the fundamental and the combination bands have been performed [221, 379]. Progression of ν_1 could be observed up to $\nu = 3$, and the values of the ω_1 harmonic frequency and the X_{11} anharmonicity constants have also been determined. This electron redistribution generates some cooperative effects between the various permanganate sites in the crystal lattice and therefore causes a change in the vibrational characteristics of the individual ions. Although the ν_1 frequency is sensitive to the nature of the cation, but its strong shift from the 840-850 cm^{-1} range, and the splitting of the ν_1 bands components (799.0 amd 808.4 cm^{-1}) may be the consequences of this electron redistribution. These results show that the compound has important covalent character, and there is an electron redistribution in the solid lattice [379]. Due to the intensive visible color of the permanganate ion He/Ne laser excitation has been applied. A small amount of MnO_2 always forms on the surface, therefore these spectra are contaminated by the signals of the MnO_2 [244].

^{55}Mn NMR spectra of polycrystalline silver permanganate has been recorded at room temperature. The parameters of the second order quadruple interactions, the asymmetry parameters and the local gradient of the electric field at each positions of the nucleus have also been determined [225]. As crystal defect detected by the NMR, silver permanganate contains a small amount of MnO_3OH^- -ion which has a role in the decomposition mechanism (including decomposition temperature) [219].

The effect of the silver 1st ionization potential on capturing thermal neutrons by the Mn in silver permanganate has been determined, and the distribution of the radioactive Mn between the species formed were found to be similar to the other permanganate salts examined. Its neutron irradiation to prepare ^{56}Mn isotope containing compounds is pH dependent. Besides $Ag^{56}MnO_4$ and $^{56}Mn^{2+}$ some amount of MnO_2 has also been formed both in neutral and acidic solutions. This is attributed to the oxidation of Mn^{2+} by the permanganate [139]. Because of nuclear recoil no $^{56}MnO_2$ has been formed.

Silver permanganate decomposes at 100 °C in an autocatalytic decomposition process with oxygen evolution [54]. Because of the highly active catalytic properties of its solid decomposition products, the thermal decomposition process of the silver permanganate has been studied in detail [380]. Prout and Tompkins [381]:

$$2AgMnO_4 = Ag_2O + 2MnO_2 + 1.5O_2 \quad (48)$$

described a classical permanganate decomposition process which has 124 kJ/mol activation energy [379]. Since the oxygen balance is higher than the expected, Grant and Katz supposed the presence of metallic silver as well [382]. Later, the detailed studies showed the formation of a mixture with the $AgMnO_{2.60\text{-}2.76}$ formula [232], and DTA studies in air showed the formation of MnO_2 [228].

The rate of isothermal decomposition at 115 °C strongly depends on the atmosphere, the rate is decreased in the O_2, N_2 and CO_2 order. Since the donor acceptor properties are not correlated with it, the presence of an ionic-radical process is the probable reason [383]. The rate of the thermal decomposition at this temperature is increased by ZnO or ThO_2 additives, does not affected by Co_3O_4 and NiO, and strongly decreased by TiO_2. Since the reaction product is mainly metallic silver, the decomposition of the permanganate ion can be described as

$$MnO_4^- = MnO_4 + e^- \quad (49a)$$

$$MnO_2 + O_2 \quad (49b)$$

The liberated free electron has an important role in the process. Its interaction with the additives, however, does not explain completely the observed decomposition characteristics, since the formed Ag_2O and β-MnO_2 have reaction rate depressing action [384]. Irradiation with X-rays

also increase the rate of decomposition because of the formation of auto-catalysing intermediates [361].

The thermal decomposition curve in high vacuum gives a sigmoid pressure-time function at 110 °C. Based on this, it is assumed that at the commencement of the acceleratory period strain exists in the crystal at the interface between the product formed before the acceleration and the material not yet decomposed. This strain produces micro cracks in the reactant surface and the reaction progresses inwards by a mechanism of branching planes reaction. Silver permanganate does not disintegrate during the decomposition. Asterism is not exceptionally pronounced immediately prior to the acceleration but there is a marked increase in the lattice distortion after this, detected by XRD. It is seen that the amount of strain is extremely high at the end of the induction period [232]. Thermal decomposition of $AgMnO_4$ single crystal has been studied after irradiation with UV light at 110 °C [385]. It was stated, that there is some increase in the acceleratory and a decrease in the decay region, however, the difference between the rate constants of UV irradiated and non-irradiated samples were insufficiently large to suggest that the UV light had any effect on the reaction kinetics. Furthermore, based on thermal studies of $AgMnO_4$ and $KMnO_4$, some correlation was found between the longest wavelength O-Mn CT band and the activation energy of the decomposition. This relationship, however, is valid only if the rate determining step is an electron transfer [376].

Saturated aqueous solution of silver permanganate can be reduced with metallic silver in 10 h with the formation of Ag_2MnO_4 (silver(I) manganate(VI)) [600].

$$AgMnO_4 + Ag = Ag_2MnO_4 \quad (50)$$

Solid $AgMnO_4$ reacts with Ag_2O at 1:1 molar ratio with the formation of a hollandite type mixed silver manganese oxide of $Ag_{1.8}Mn_8O_{16}$ and a small amount of Mn_2O_3 at 970 °C and under 5 kbar O_2 pressure in an autoclave for 7d [386].

Silver permanganate reacts with sulphur dioxide with the formation of sulphate and dithionate which precipitate as insoluble silver salts:

$$8AgMnO_4 + 21H_2SO_3 = 3Ag_2SO_4 + 8MnSO_4 + Ag_2S_2O_6 + 8H_2SO_4 + 13H_2O \quad (51)$$

Any thiosulphate, sulfite or higher thionate could not be detected [362]. Thermal decomposition products of silver permanganate, however, give only manganese(II) and silver sulphates [387]. Its reaction with oxalate is a 1st order reaction and the kinetic features strongly differs from the values given for K, Na and NH_4 salts [204].

Silver permanganate can be used as a starting material to prepare $AgCF_3$, $Ag(CF_3)_2$ or $Ag[Ag(CF_3)_4]$ by the reaction of $AgMnO_4$ and $Cd(CF_3)_2$ at -30 °C [388].

Silver permanganate and its thermal decomposition products (Körbl catalysts) are widely used catalyst in the determination of elemental composition of various kinds of organic compounds [389-396], especially in the presence of sulfur, halogens, phosphorus, arsenic and mercury [397-401]. These decomposition products were tested for almost all kind of organic compounds, e.g. for volatiles [402] such as benzene or n-heptane [403], ethylene [404], organometallic compounds, [405-406], plastics [407] and hardly ignitable halogen-containing compounds such as organofluoro compounds [408], polyhalogenated organic compounds [409] or chlorine substituted maleinimides [410]. It can be effectively used in the oxidation of carbon monoxide [392, 403, 411], but the catalytic activity strongly depends on the surface area of the support used [412]. Phosphorus removal from the combustion train during elemental analysis [413], and promotion of the MnO_2 catalyst in the oxidation of acetylene [414] are well known application fields. Some other application fields are also known, including the determination of tritium and ^{14}C isotopes in labelled compounds [415] or the oxidation of harmful constituents in tobacco filters [416-417].

It can also be used as permanganate constituent of composite conductive crystals containing permanganate oxidants and graphite or other carbonaceous material for use as a cathodic material in a galvanic cell [342], and as a catalyst in fuel cells [418], batteries and likes [419]. It is a reagent to modify the atmosphere for preservation of fruits and vegetables [420]. Silver permanganate is widely used as aqueous primers for plastics in electroless plating [421] and for pretreatment or

activation of plastics surface before metallization [422-423]. It is a starting material in semi-conductor type ceramic preparation [424].

3.5.2. Copper permanganate

Copper permanganate is a deliquescent purple crystalline material, dissolves in water, and in its dilute aqueous solution completely dissociates [147]. Easily decomposes even at 80 °C with oxygen evolution in an autocatalytic process [54]. It can be prepared by the reaction of barium permanganate with copper(II) sulphate at stoichiometric ratio in water [54, 87, 148, 318, 425-426]. Depending on the synthesis and the isolation conditions the molar water content of the product varies (2, 3, 6, 7 and 8). Reaction of silver permanganate with copper(II) choride is also an easy way to prepare the title compound [427].

The IR spectra of the hydrated copper(II) permanganates (dihydrate [87, 318] or hexahydrate [148]) strongly depends on the conditions of the measurement (nujol or KBr matrix). This phenomenon can be attributed to the ion-exchange interactions of the hydrated permanganates and the KBr matrix [87]. Its X-ray powder diffractogram is complicated [318]. Our experiments indicated, that the XRD of the hydrated copper(II) permanganate changes during the measurement [68]. The powder X-ray diffractogramms of the starting or the de/re-hydrated species do not fit in the XRD results of the copper(II) permanganate dehydrate [148]. The formed compound dissolves completely in water with purple color without the formation of insolubles, consequently it can be presumed that only the number of water molecules in the hydrated salt has changed during the XRD experiment.

The water content of the salt formed is determined by the conditions of the synthesis. When the solution has been partially evaporated at 290-330 K and the crystals have been filtered off, the amount of the water (after a vacuum dehydration) varied between 1.7 and 4.1. The first step of the decomposition led to a mixed phase with a composition of $CuMn_2O_{5.45}$ [425]. Kinetic study has been performed in the range of 335 and 370 K. During the median region of the decomposition the dominant feature has been a constant reaction rate. Acceleratory or deceleratory behaviour was not prominent and the induction period was found to be very short. Water vapour had no influence on the decomposition rate. Anion breakdown occurred at the interface between the crystalline reactant and an ill-crystallized disorganized mixture of the residual products.

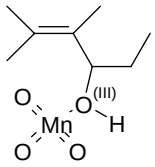
By increasing the temperature up to 695 K, only one phase, $CuMn_2O_5$ could be detected. In the range of 695-1175 K two other phases, $CuMn_2O_4$ and Mn_2O_3 have formed. Magnetic susceptibility measurements showed unambiguously, that above 725 K the copper transforms into Cu(I) valence state. The magnetic moment values of the amorphous $CuMn_2O_5$ showed that it is not a simple mixture of $CuO+2MnO_2$ or $CuO+Mn_2O_3$. This result provides an evidence of a more complicated interactions between the constituent cations of this poorly crystallized material. The presence of copper(2+) can be concluded from the XPS results indicating that Cu is on the two-valent state in this amorphous material [426].

The $Cu^{I}Mn^{III}Mn^{IV}O_4$ formula for the $CuMn_2O_4$ formed in this reaction corresponds to the XPS and magnetic susceptibility measurements. The existence of $Cu^{II}Mn_2{}^{III}O_4$ normal spinel in this system is not possible. It is a simple reduction of Cu^{II} and oxidation of the Mn^{III} into Mn^{IV} at this temperature. Permanganate breakdown is believed to follow an electron transfer to a copper(II) with the formation of copper(I) which can be subsequently re-oxidized. The decomposition products are potential catalysts of heterogeneous reactions [425].

The initial retentions following $^{55}Mn(n,\gamma)^{56}Mn$ recoil in Cu-permanganate was 6% [428]. The distribution of the ^{56}Mn-species between MnO_4^-, MnO_2 and Mn^{2+} is anomalous in solution (referring to solid state (dihydrate)). It can be attributed to colloidal MnO_2 formation and to the adsorption of Mn^{2+} on this colloid [318].

Hydrated copper(II) permanganate (octahydrate) seems to be a very versatile oxidant in organic chemistry, oxidizes cyclohexanols into cyclo-hexanones [303], secondary saturated and unsaturated alcohols into the appropriate ketones with extremely short periods of time in methylene

chloride even at room temperature [296]. Saturated primary alcohols like benzyl alcohol or decanol are oxidized into benzoic acid or decanoic acid [296]. Alkyl and aryl sulfides or selenides are readily converted into the appropriate sulfones or selenones [429]. It is supposed that alkenes inhibits the oxidation of sulfides and the competition between the sulfides and the alkenes to adsorb on the active sites of the oxidant surface [429]. The reaction is initiated by the formation of a coordinative covalent bond between the sulfur and the manganese. The sulfur would thereby acquire a partial positive charge and therefore it is attracted to an oppositely charged oxygen ligand, leading to the formation of a new bond. The rearrangement is similar to the rearrangement of the coordinated C=C double bond in the oxidation of alkenes [429, 582]. An interesting feature of the oxidation reactions of the hydrated copper(II) permanganate is the oxidation of unsaturated alcohols into unsaturated ketones without the oxidation of alkene part, since the C=C double bond instantly reacts with the permanganate anion in solutions. Addition of alkenes, e.g. cyclohexene or 5-decene inhibits the oxidation reaction of alcohols [24]. It indicates that certain reactive sites on the surface of the oxidant can bind rather firmly carbon-carbon double bonds and thus prevent binding and subsequent oxidation of the alcohols. Neither cyclohexene nor 5-decene are oxidized with solid copper(II) permanganate, however, a substituted alkene, e.g. 2,3-dimethyl-2-butene slowly oxidizes under the same conditions [24]. Saturated secondary alcohols are oxidized easily with solid hydrated copper(II) permanganate, while allyl alcohols are oxidized slower. In the mixture of saturated and allylic alcohols, the allylic alcohol oxidation is the preferred reaction. It indicates, that the double bond of allylic alcohols is attached first to the oxidant by a π-bond and oxidized subsequently. Non-allylic unsaturated alcohols, however, are not oxidized under the conditions that lead to good yields of ketones from secondary allylic alcohols. This indicates unambiguously that, if the hydroxyl group of the alcohol is not close to the point at which the π-bond forms, it does not interact with the oxidant, possibly because it cannot come into the coordination shell of the manganese(VII). A possible reaction mechanism has already been published [24].



(52)

The reason for this unusual behaviour has been pointed out as the coordination of the double bond to the manganese [24]. This mechanism, however, is inconsistent. First of all, the coordination of the double bond to the permanganate manganese with closed d-shell seems to be very unusual. The mechanism of the permanganate oxidation of alkenes has been studied by means of high-level quantum chemical calculations and the probability of [3+2] and [2+2] (with C-O bond formation) addition compounds have been found to be possible intermediates. The five-membered $O_2Mn(O\text{-}CHR\text{-}CHR\text{-}O)(-)$ compounds proved to be the energetically favoured ones. No evidence of manganese-double bond coordination could be established at all [430].

Second times, not only the hydrated copper(II) permanganate but the mixture of the solid copper(II) sulphate pentahydrate and $KMnO_4$ also oxidises the unsaturated allyl-type alcohols without oxidation of the double bond [431, 555]. Pure $KMnO_4$ does not give this reaction which shows that the copper blocks the alkene part oxidation.

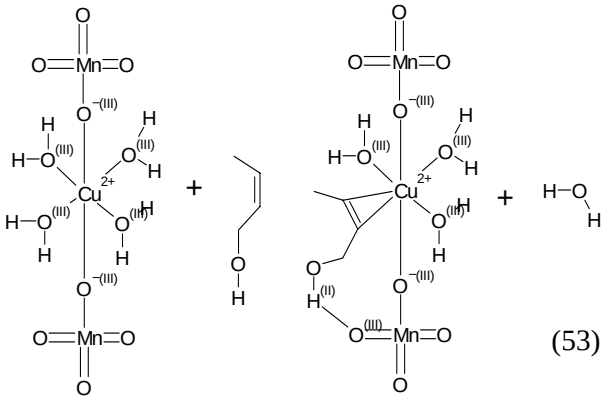
Since solid copper(II) compounds react with alkenes [433-435] easily, the coordination of the double bonds at another coordination site, namely on the copper center can be assumed. Surprisingly, the coordination ability of the solid copper(II) compounds is strong enough. Solid $CuCl_2$ or $CuSO_4$ reacts with 2-chloro-2-butene meanwhile producing $CuCl_2$.L and $CuSO_4$.L type adducts which can be isolated as stable solids. These adducts are coordinatively unsaturated and can absorb H_2O, NH_3 or pyridine to form $CuSO_4$.L. A type adducts (A = H_2O, NH_3 or pyridine), which decompose on heating by loosing the H_2O, NH_3 or pyridine and regenerating the starting alkene complex. It indicates that the binding of an alkene via the π-system can be

much stronger than the binding of a classical Lewis-base donor ligand as H_2O, NH_3 or pyridine. Furthermore, the reversible bonding of the H_2O and other donor ligands shows a possible catalytic role of the solid copper salts in H_2O (NH_3, pyridine) - alkene ligand exchange reactions. In the light of the abovementioned facts, the following mechanism can be presumed:

(1) The alkene part is coordinated to the copper(II) coordination sphere, e.g. by substituting a weakly bound coordinated H_2O. The binding of H_2O is not strong in copper(II) permanganate. The water content depending on the drying conditions and varies between 2 and 8. The easy exchangeability of the water in the coordination sphere fixes the unsaturated ligand in a given position, thus the distance between the allyl-position of the ligand and the oxygen atom of the Cu-Mn=O linkage is optimal to oxidize the oxidable group located at the allyl-position. The vinyl type or δ-positons are to far from the oxidant group immobilized in the solid reagent.

(2) Considering the temperature dependence of the water content of the hydrated copper(II) permanganate, the supposed mechanism explains the role of the temperature in the oxidation of 1-phenyl-1-buten-3-ol with hydrated copper(II) permanganate [24]. If the oxidation of the alcohol is carried out at low temperature, cleavage of the double bond is the predominant reaction, however, as the temperature is increased, the relative amount of non-cleavaged products increases dramatically and eventually predominates at reflux temperature. On the bases of our assumption, with increasing the temperature, the substitution of the water in the coordination sphere with the alkene part of the substrate is completed or becomes predominant because the bound of the water to the copper center is weaker than the alkenes. The possible mechanism is showed at Figure 6.

Presuming the reliability of this mechanism and the alkene-exchangeability of other ligands than water, ammonia or pyridine, e.g. optically active O- or N-coordinating ligands (alcohols, amines and likes), this type of alkene coordination could regulate the coordination of the re or si-side



(53)

Figure 6. Supposed mechanism of the hydrated copper-permanganate oxidation of allyl alcohols.

because of the steric hindrance of the optically active ligands remain in he coordination sphere. It seems to be a perspective research area to perform optical resolution during oxidation reactions. This supposed mechanism induced our efforts to study the preparation of anhydrous copper(II) permanganate and amin-type copper(II) permanganate complexes [68]. As it was declared [24] previously the role of the water in these type of reactions is an interesting question. The dried copper permanganate does not give the reactions of the hydrated ones. The drying leads not only to complete dewatering, but sometimes to the complete decomposition of the permanganate anion. Because of the lack of the permanganate ion the oxidation power of the dried “copper permanganate” [68] misses.

3.5.3. Basic copper(II) permanganate

Basic copper(II) permanganate, $Cu_2(OH)_3MnO_4$ can be prepared by an anion exchange reaction between the layered $Cu_2(OH)_3OAc$ basic acetate and 1 M $KMnO_4$ in one day [38]. The ion exchange keeps the layered structure of the acetate compound (the basal spacing is 7.22 Å). The thermal decomposition of the compound formed proceeds in the following way:

$$Cu_2(OH)_3MnO_4 = 0.5CuMn_2O_4 + 1.5CuO + 1.5H_2O + O_2 \quad (54)$$

The formed mixed copper manganese phase catalyzes the oxidation of CO even at 30 °C. The amorphous spinel crystallizes at 440 °C and

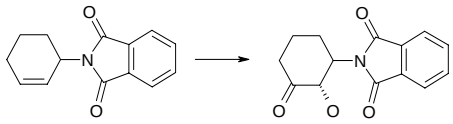
decomposes at 940 °C into $CuMnO_2$. If heated above 500 °C, the activity of the $CuMn_2O_4$ is lost but it can be reactivated in oxygen at 400 °C. This is the consequence of various Cu(I)-Mn(IV) and Cu(II)-Mn(III) redox reactions [38].

3.5.4. Zinc permanganate

Purple crystals of zinc(II) permanganate hexahydrate have been prepared by the reaction of barium permanganate and zinc(II) suphate at a stoichiometric ratio in water [87, 318]. It easily dissolves in water and in its dilute aqueous solution completely dissociates [147]. Zinc-permanganate hexahydrate starts to dehydrate at 40 °C and decomposes with oxygen evolution at 100 °C. The amorphous product formed ($ZnMn_2O_{4.59}$*$0.7H_2O$) decomposes further at 300 °C with the formation of $ZnMn_2O_4$*$0.7H_2O$ which crystallizes at 420 °C (with water loosing), and turns into pure $ZnMn_2O_4$ at 750 °C. Hydro-thermal decomposition of zinc(II) permanganate hexahydrate leads to $ZnMn_2O_4.2.5H_2O$ at 300 °C [116]. The decomposition proceeds with oxygen evolution in an autocatalytic process [54]. Due to the ion-exchange interactions of the hydrated permanganates and the KBr matrix the IR spectrum of the zinc permanganate hexahydrate strongly depends on the conditions of the measurement (nujol or KBr matrix) [87]. In this compound, the permanganate site symmetry is C_s [148].

Neutron irradiation and the studies on the ^{56}Mn-species among the MnO_4^-, MnO_2 and Mn^{2+} showed an anomalous distribution in solution, because of the colloidal MnO_2 formation and the adsorption of Mn^{2+} on this colloid [318]. The initial retention following the $^{55}Mn(n,\gamma)^{56}Mn$ recoil in Zn-permanganate was found to be 8%, but only 2% could be observed after an isochronal heating for 30 min in the temperature range of 25-120 °C (with the characteristics distribution of activity among the Mn^{2+}, Mn^{4+} and Mn^{7+} states). In the decomposition region, both Mn^{2+} and Mn^{7+} diminished to give Mn^{4+} [428] .

Zinc permanganate can be used as an useful oxidant in organic chemistry [25]. It reacts instantly, in some cases with fire, with common solvents, such as THF, ethanol, methanol, t-butanol, acetone and acetic acid. Diphenyl-acetylene is oxidized into benzyl with a yield of 67%, lactones form from THF and tetrahydro-pyrane, and the appropriate ketones can be regenerated from 1,3-dioxolanes [25]. Cyclo-hexanone produces adipic acid, Boc-susbtituted amines gives the appropriate amides, N-phenyl-sulfonyl pyrrolidine gives the 2-pyrrolidone derivative, 3-ftalimidocyclohexene transforms into the appropriate hydroxyketone:



(55)

Synthesis of N-acyl-N-alkylcarboxylates can be performed by means of $Zn(MnO_4)_2$ oxidation of substituted amides formed from carboxylic acid esters and an N-alkyl-N-alkanolamine [436]. Zinc(II) permanganate catalyses the trans-esterification reactions of dicarboxylic acid esters and glycol to prepare high molecular weight polyesters [323]. It can also be used as a catalyst in tobacco smoke filters, [182] or in curable polysulfide compositions [340]. Its strong oxidation ability can be utilized in various fields and compositions, respectively, e.g. in corrosion inhibition of metals towards acidic gases such as H_2S, CO_2 or COS [207, 329-330], in surface modifying during annealing of non-porous insulators [438], in electrochemical reactor components for transporting oxygen in partial oxidation of methane to produce unsaturated compounds or synthesis gas, in partial oxidation of ethane, in substitution reactions of aromatic compounds, extraction oxygen from oxygen-containing gases including oxidized gases, ammoxidation of methane and likes [439]. It can also be used for the preparation of pharmaceutical compositions containing zinc compound of cyclodextrin to treat gastric disorders and Helicobacter pylori in the stomach or duodenum [440]. Zinc-manganite and its cobalt-substituted solid solutions prepared from zinc(II) permanganate are active catalysts for CO oxidation [441]. Zinc(II) permanganate was tested as a histochemical fixation agent, but destroyed the tissues [190].

3.5.5. Cadmium permanganate

Cadmium permanganate hexahydrate, $Cd(MnO_4)_2.6H_2O$, has been prepared by the reaction of barium permanganate and cadmium(II) sulphate at a stoichiometric ratio in water [54, 87, 325, 442], or by the reaction of $Cd(OH)_2$ with the CCl_4 solution of freshly prepared Mn_2O_7 [70]. Purple rhombohedral crystalline substance, isomorphous with the appropriate Mg- and Ni-permanganate hexahydrates [442], ($C7_{2v}$ ($Pmn2_1$) a = 8.04, b = 13.91, c = 5.34 Å, d = 2.49 g/ml, Z = 2) [442]. It is soluble in water and completely dissociates in its dilute aqueous solutions [147]. The IR spectrum of the cadmium permanganate hexahydrate strongly depends on the measurement conditions (nujol or KBr matrix). It can be attributed to the ion-exchange interactions of the hydrated permanganates and the KBr matrix [87]. The four IR stretching of the permanganate ion are active [87, 442]. Cadmium permanganate was also defined as heptahydrate and its IR spectrum was also discussed [148].

Neutron irradiation and the studies on the ^{56}Mn-species among MnO_4^-, MnO_2 and Mn^{2+} showed anomalous distribution in solution. Depending on the concentration, the retention is changed due to the colloidal MnO_2 formation and to the adsorption of Mn^{2+} on this colloid [325]. The initial retention following the $^{55}Mn(n,\gamma)^{56}Mn$ recoil in Cd-permanganate was found to be 7%, but only 2% could be observed after an isochronal heating for 30 min in the temperature range of 25-120 °C. No reaction of the Mn^{2+} was observed, the Mn^{4+} was obtained only from Mn^{7+} [428].

Decomposition temperature strongly depends on the conditions and the heating rate. The dehydration proceeds in two steps, and the anhydrous salt decomposes around 100 °C with oxygen evolution in an autocatalytic decomposition process [54]. The dehydration temperatures have found to be 30 and 60 [328], 61 and 82 [70] and 75 and 147 °C [442]. Both dehydration steps are based on a single step nucleation process followed by a growing process with nuclei overlap [328]. Based on DSC studies, the two endothermic dehydration steps is followed with an exothermic peak which belongs to the decomposition step of the anhydrous salt (108 °C). The decomposition product proved to be a mixture of MnO_2 and $CdMnO_3$.

$$Cd(MnO_4)_2 = CdMnO_3 + MnO_2 + 1.5O_2 \qquad (56)$$

The kinetics of the decomposition has also been determined [70]. The temperature of the exo-thermic decomposition is 164 °C [442]. This value is much higher than the values obtained by others [54, 70, 328]. The decomposition of the anhydrous salt in air was studied in the temperature range of 80-110 °C. The sigmoidal isothermal fractional decomposition *vs.* time curves are reproducible. Dehydration starts without induction period, but the thermal decomposition has induction, acceleratory and decay period. The acceleratory and the decay periods can be shortened with ^{60}Co γ-irradiation [328].

Cadmium permanganate catalyses the transesterification reactions of dicarboxylic acid esters and glycol (to prepare high molecular weight polyesters) [323].

3.5.6. Nickel permanganate

$Ni(MnO_4)_2.6H_2O$ has been prepared by the reaction of barium permanganate and nickel(II) sulphate at a stoichiometric ratio in water [54, 87, 116, 318, 443]. It is a dark purple crystalline substance, soluble in water, and in its dilute aqueous solution completely dissociates [147].

IR spectrum of the nickel permanganate hexahydrate strongly depends on the measurement conditions (nujol or KBr matrix). It is due to the ion-exchange interactions of the hydrated permanganates and the KBr matrix [87]. The permanganate ion site symmetry is C_s [148].

The initial retention following the $^{55}Mn(n,\gamma)^{56}Mn$ recoil in Ni-permanganate was found to be 16% [428]. Neutron irradiation and the studies on the ^{56}Mn-species among MnO_4^-, MnO_2 and Mn^{2+} showed an anomalous distribution in solution. The retention is changed because of the colloidal MnO_2 formation and the adsorption of Mn^{2+} on this colloid [318].

It decomposes with oxygen evolution in an autocatalytic process [54]. The hexahydrate readily losts a part of its water and $Ni(MnO_4)_2*4.5H_2O$ is formed. Heating the salt in vacuum above 360 K releases all water and a bit more than 1.5 O_2:

$$Ni(MnO_4)_2*4.5H_2O = NiMn_2O_5 + 1.5O_2 + 4.5H_2O \quad (57)$$

Isothermal decomposition kinetics was studied between 361 and 393 K. An initial deceleratory process (up to 3.5% conversion) preceeds the induction period followed by an acceleratory process. The value of the activation energy is close to the values of similar permanganates and can be identified as the activation energy of the

$$2MnO_4^- = MnO_4^{2-} + MnO_4 \quad (58a)$$

$$MnO_4 = MnO_2 + O_2 \quad (58b)$$

process. Under dry conditions this process is relatively rapid compared to the reaction performed in the presence of small amount of water vapour. Due to the same activation energies both reactions seem to be rate-controlling step. The overall rate of the salt decomposition is controlled by the amount of electronic imperfections. It is surprising that a solid phase reaction is faster than the analogous homogeneous solution phase decomposition. The forces of the crystal coherence cannot stabilize the anion in this particular reaction. The mechanism of the effect of the water vapour is not clear. If the reaction proceeds in the solid state exclusively, adsorption of water may influence the reactivity of the potential nucleation sites. Presuming local and temporary melting, the involvement of the surface water may similarly influence the concentration of the electronic imperfections in the surface zone [443]. Dehydration starts at 60 °C and the decomposition starts at 100 °C [116, 426]. The first intermediate product of the decomposition is $Ni_2Mn_2O_5$ [426]. At 300 °C an amorphous compound $Ni(HMnO_{2.495})_2*0.6H_2O$ forms which transforms to $NiMnO_3$ and α-Mn_2O_3 at around 400 °C. The latter process is accompanied with oxygen evolution [116, 426]. Above 1075 K $NiMn_2O_4$ is formed which has an inverse spinel structure $Mn^{II}Ni^{II}Mn^{IV}O_4$ [426]. This reaction can be used to prepare $NiMn_2O_4$ type sintered ceramics for thermistors [444].

In solution (0.01 M) the decomposition is much slower than in solid state, and the reaction rate almost the same as in the case of the potassium salt. It means, that the hydrated nickel ion has no promoting effect in the breakdown of the permanganate in its aqueous solution [443]. The amorphous $Ni(HMnO_3).4H_2O$ could be isolated as a decomposition product obtained by the evaporation of aqueous $Ni(MnO_4)_2$ solution over H_2SO_4 [116].

3.5.7. Mercury(II) permanganate

Mercury(II) permanganate is used as a cathode material in electrochemical cells [559].

3.6. Permanganates of f-elements

Only a few papers dealt with the permanganate salts of rare earth elements. $Re(MnO_4)_3.4H_2O$ (where Re = La, Pr, Nd, Sm and Y), $Re(MnO_4)_3.5H_2O$ (where Re = Gd and Dy), $Er(MnO_4)_3.7H_2O$ and $Yb(MnO_4)_3.9H_2O$ were prepared in the reaction of CCl_4 solution of Mn_2O_7 and Re_2O_3 type rare earth oxides. These compounds are formed as purple crystalline solids. All of the compounds showed the same ν_1 and ν_3 stretchings (843 and 899 cm^{-1}) [69] which indicates that these compounds probably ion-exchanged with the KBr in the pellet [xx, notpubl]. All of the compounds dehydrates at 80-90 °C and decomposes at 137-140 °C. Their decomposition products are rare earth oxides and MnO_2. The XRD results of the compounds prepared by us (Re = La, Sm, Gd, Y, Pr) [80] do not agree with the XRDs measured previously [69].

3.6.1. Lanthanum permanganate

Resonance Raman spectrum of $La(MnO_4)_{3*}3H_2O$ was measured and the assignation of the fundamentals and the combination bands were accomplished. The progression of ν_1 was observed up to $\nu = 3$, and the value of the ω_1 harmonic frequency and the X_{11} anharmonicity constants were also determined [221] and compared with the analogous X_{11} values of the monovalent and the divalent metal

permanganates. The X_{11} value strongly depends on the polarizing action (charge) of the cation [273].

Radiochemistry (n,γ) of the lanthanum permanganate and its aqueous solution were studied in detail. The pH has an influence on the retention of the ^{56}Mn-containing species only at low (1-2) and high (9.5-12.5) values [348]. In solid state the retention was found to be high at higher temperatures, however pre-activation heating gave lower retention comparing with post-activation heating of the targets. This is the consequence of the crystal defects and the transition reactions of the lattice stable precursors in the parent reformation [349].

The standard Gibbs free energy of the aqueous solutions of lanthanum, actinium and all of the rare earth and actinide elements permanganates ($Ln(MnO_4)_3$) have been calculated [445]. These values are significantly lower than the analogous values of other LnX_3 type compounds, where X = ClO_2, ClO_3 or ClO_4, NO_2, NO_3 and BrO_3.

3.7. Complex permanganates

Although a few complexes containing coordinated perrhenate and perchlorate anions are known [446-448], but the $[Cu(bipy)_2(MnO_4)]MnO_4$), which was believed to be the first coordinated permanganate ion containing compound [9-12], proved to be $[Cu(bipy)Cl]MnO_4$ without a coordinated permanganate anion [68]. Consequently, "permanganate complexes" discussed here are essentially permanganate salts with complex cations.

3.7.1. Ammonia complexes

The first complex permanganate salts, namely ammine complexes of Ag, Cu, Ni, Cd, Zn, and Co were prepared by adding aqueous ammonia to a mixture of potassium permanganate and the appropriate metal salts at 8-10 °C and subsequently cooling the mixture to 2 °C [446-447]. The low temperature and a large excess of ammonia (pH is shifted to alkaline region) are essential to avoid oxidation of the ammonia by the permanganate ion. Reaction of the metal permanganates with ammonia [449-450], or the reaction of the appropriate amminemetal sulphate or nitrate complexes with $KMnO_4$ leads to the same products [44, 451-454].

Three silver complexes, namely $[Ag(NH_3)_2]MnO_4$, $Ag(NH_3)_2MnO_4.H_2O$ [68, 456] and $[Ag(NH_3)_3]MnO_4$ have been described [449-450]. $[Ag(NH_3)_2]MnO_4$ is a violet powder consisting of microscopic rhombic plates, sparingly soluble in cold water, its solubility is 3.6 g/100 ml of H_2O at 20 °C. The salt explodes by percussion, and gradually decomposes in air by loosing ammonia [449-450]. Bruni and Levi have described the compound as $[Ag(NH_3)_3]MnO_4$ [455]. Reproducing their experiments, the product has been found to be $[Ag(NH_3)_2]MnO_4.H_2O$ [68]. The silver and permanganate contents of this compound almost the same as of the $[Ag(NH_3)_3]MnO_4$ [455]. This purple complex contains non-coordinated water and chain-like $Ag(NH_3)_2$ units with close Ag-Ag contacts [68]. Exothermic decomposition of the complex can be observed at 85 °C with the liberation of one mol of ammonia, then a second decomposition step occurs at 204 °C. Water also forms in both the steps. The formal decomposition can be written as it follows:

$$2[Ag(NH_3)_2]MnO_4.H_2O = 2[AgMnO_2] + 3H_2O + NH_4NO_3 + 2NH_3 \quad (59)$$

The decomposition temperature of the pure NH_4NO_3 is 260 °C, therefore the lower temperature of the second decomposition step may be attributed to the catalytic effect of the silver-manganese oxide. Based on the weight loss, the most probable amorphous decomposition product is $AgMnO_2$ which is a known and stable compound of silver-manganese-oxygen system.

Three [tetraamminemetal(II)] permanganate have been prepared. The [tetraammincopper(II)]-permanganate [44, 449-451, 456-457], the isomorphous [tetraamminezinc(II)]-[451, 458] and [tetraamminecadmium(II)] permanganates [68, 451]. The [tetraamminecopper(II)] permanganate was obtained in pure form by means of the reaction of [tetraamminecopper(II)] sulphate and potassium permanganate at a 5/2 °C temperature gradient [451, 457]. When ammoniacal copper(II) sulphate solution (excess of ammonia) or pure

$[Cu(NH_3)_4]SO_4$ and $KMnO_4$ were used at room temperature (with consequent cooling) the reaction always led to contaminated product. The contaminant has proved to be NH_4MnO_4 [457], the formation of which is the consequence of the temperature dependent hydrolysis of the complex cation [459-460]. The pH of the saturated aqueous solution of the $[Cu(NH_3)_4](MnO_4)_2$ is 9.60, which indicates that the [tetraamminecopper(II)] cation dissociates into Cu^{2+}, NH_3 and $[Cu(NH_3)_n]^{2+}$, n = 1-3, and the ammonia formed is protonated by the water (with NH_4^+ and OH^- ions formation). Since the vapour pressure of the ammonia is higher than that of the water, the concentrations of these species strongly depend on the temperature and change with the time on contact with air. Ammonia is lost from the solution continuously on standing, heating or keeping under vacuum [457]. Due to these processes, the accumulating copper and hydroxide ions precipitate as copper (II) hydroxide, and the remaining ammonium and permanganate ions can crystallized out as ammonium permanganate:

$$[Cu(NH_3)_4](MnO_4)_2 + 2H_2O = Cu(OH)_2 + 2NH_3 + 2NH_4MnO_4 \quad (60)$$

Elimination of the ammonia (by heating or in vacuum) is favourable for the formation of $Cu(OH)_2$ and ammonium permanganate. Due to the temperature-dependent complex equilibrium situations including the solubility relationships of the complex cation and the formed species, the starting compound may crystallize out (solubility product of $[Cu(NH_3)_4](MnO_4)_2$ is $L = 7.81*10^{-3}$ [457, 459-460],) or the sparingly soluble $Cu(OH)_2$ may precipitate, depending on the conditions. Below 5 °C only the expected $[Cu(NH_3)_4](MnO_4)_2$ [456-457] crystallizes out, but above 8 °C only $Cu(OH)_2$ is formed together with the ammonium permanganate solution. This reaction can be generalized for ammonia (and some other) complexes of metal permanganates with basic ligand (or complexes with other metal salts e.g. perchlorates) and provides a method for the preparation of pure ammonium permanganate or other onium type permanganates [459-460].

The [tetraamminecopper(II)] permanganate is a violet crystalline substance, soluble in H_2O, DMF and Ac_2O, insoluble in hydrocarbons and chlorinated solvents. In dry state it is stable for several weeks, but over a longer period of time decomposes with the formation of MnO_2. Its wet crystals decompose above 10 °C. Sunlight increases the decomposition rate. It also decomposes in its solutions, the decomposition product is NH_4MnO_4 in H_2O, MnO_2 in DMF and an unidentified green compound in Ac_2O [457]. In DMF it dissociates completely, the permanganate ion ν_{as} band at 900 cm^{-1} appears as a very sharp band which indicates the symmetrically and completely solvated free permanganate anion. The Cu-N band region contains a wide band system, showing the solvation of the complex cation and the formation of various Cu-N bound species. The DMF solution loses its purple color within half an hour.

The [tetraamminecopper(II)] permanganate crystallizes in monoclinic symmetry, with lattice parameters a = 5.413, b = 9.9093, c = 10.749 Å and b = 96.18° at 293 K (Z = 2, $P2_1/m$) [456]. The central Cu-atom lies in a near-regular tetragonal place of an octahedron, and the two axial permanganate ions are crystallographically non-equivalent [456-457] (Figure 7).

The ESR g-factors ($g_{zz} = 2.273$, $g_{xx} = g_{yy} = 2.090$) are typical of the O-ligation with a square-planar Cu-environment. The ESR spectrum has sharp parallel and perpendicular bands. The sharpness of the lines and the lack of the copper hyperfine-structure show that the exchange interactions between the magnetically equivalent Cu-centers are much stronger than the dipole couplings [457].

Due to the two crystallographically non-equivalent permanganate ions two singlets (ν_s, A_1), two doublets (δ_s, E), and twice two triplets ($\nu_{as}(F_2)$ and d_{as} (F_2)) should appear both in the IR and the Raman spectra. The splitting of the bands in the IR spectra depends on the measuring conditions (KBr, nujol, temperature) [451, 457]. By means of the results of the factor group analysis and the quantum chemical calculations performed on the permanganate anion and the $[Cu(NH_3)_4]^{2+}$ cation, as well as taking into consideration the IR and Raman results of the isomorphous [tetraamminecopper(II)] perchlorate and -perrhenate and their isotope substituted

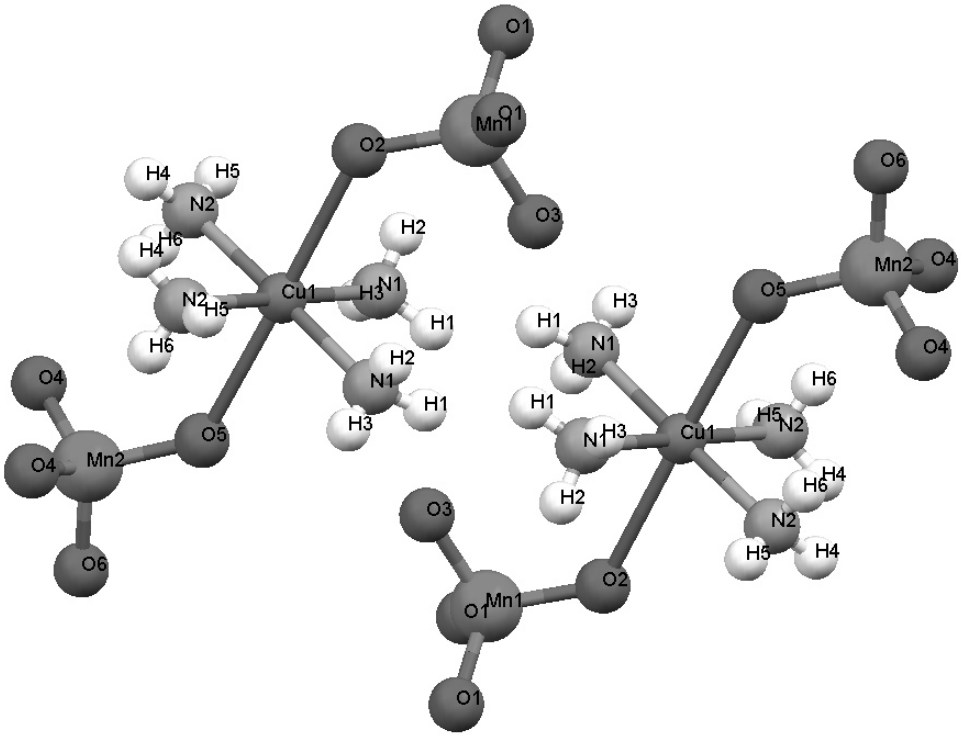


Figure 7. Crystal structure of [tetraamminecopper(II)] permanganate.

derivatives [447, 451, 461-462], all of the bands observed in the IR and Raman spectra were assigned. Since the $[Cu(NH_3)_4](MnO_4)_2$ contains dark blue cation and dark violet anion, and very sensitive to heat, its Raman spectrum could be measured by means of near-IR excitation and continuous and fast rotation of the sample in a ring like holder. The Raman spectra of the $[Cu(NH_3)_4](MnO_4)_2$ can be seen in Figure 8 [457].

The position of ν_{as} N-H stretching bands is usually used for the evaluation of the H-bonding ability of the N-H-bond, but it cannot unambiguously prove the presence of the N-H…O hydrogen bonds. The shift of the ρ_r(NH) band in the ammine-complexes, however, is very sensitive to the presence of H-bond [602]. The position of this splitted band in the [tetraamminecopper(II)] permanganate unambiguously indicates the presence of a weak hydrogen bond along the N-H…O-Mn linkage. The presence of this hydrogen bond is the cause of the unusual thermal behaviour of this complex, when an N-H...O-Mn centered redox reaction occurs instead of the expected ammonia releasing process [286].

The [tetraamminecopper(II)] permanganate explodes during fast heating or on mechanical impact, and ignites above 8 atm oxygen pressure in an explosion-like reaction with dark red flame and 1500 K combustion temperature [44].

$$[Cu(NH_3)_4](MnO_4)_2 = Cu(l) + 0.66Mn_3O_4(l) + 5.34H_2O(g) + 0.44NH_3 + 1.78N_2 \quad (61)$$

The reaction heat and the ignition rate at 100 atm oxygen pressure were found to be $\Delta H_r = 638{,}4$ kJ/mol and $\nu = 16$ g/cm^2.s [183]. On fast heating, the explosion like decomposition has occurred at 65 °C. The gas phase decomposition products were found to be NH_3, H_2O, O_2, N_2, NO and NO_2. The presence of N_2O could not be detected. The solid residue contained manganese (MnO and Mn_3O_4) and copper (Cu and Cu_2O) species. The heat of reaction is high, $\Delta H_r = 308.6$ kJ/mol [44].

Preliminary thermal studies have been performed on [tetraamminecopper(II)] permanganate with TG method [456]. In accordance with the

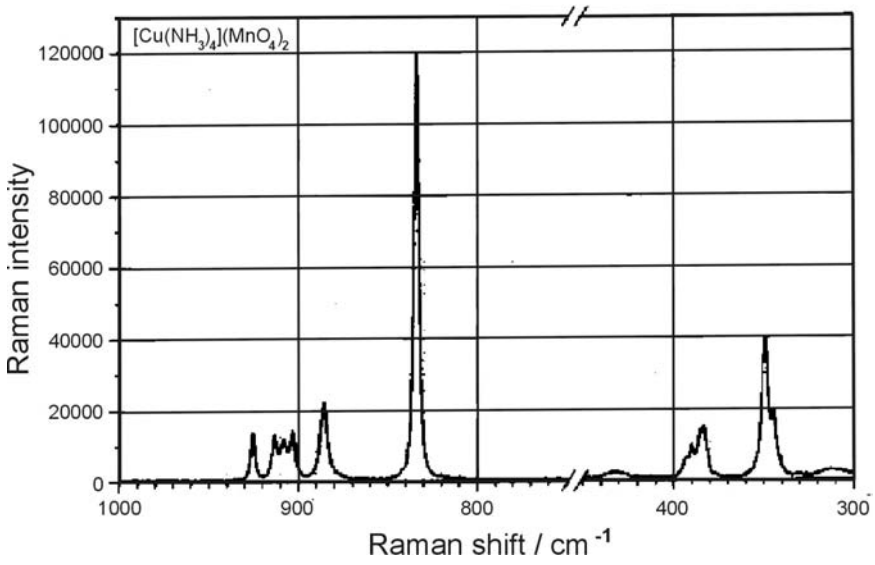


Figure 8. Raman spectrum of $[Cu(NH_3)_4](MnO_4)_2$ at room temperature. Reproduced from [457] with permission from Helvetica Chimica Acta.

stepwise weight loss data and with the identity of the solid decomposition product ($CuMn_2O_4$), the following decomposition mechanism has been suggested:

$$[Cu(NH_3)_4](MnO_4)_2 = 2NH_3 + Cu(NH_3)_2](MnO_4)_2 \quad (62a)$$

$$[Cu(NH_3)_2](MnO_4)_2 = 2NH_3 + Cu(MnO_4)_2 + 2NH_3 \quad (62b)$$

$$Cu(MnO_4)_2 = CuMn_2O_4 + 2O_2 \quad (62c)$$

During the heating of the tetraammine complexes of oxidising anions such as perchlorate or nitrate, explosion-like decomposition have occurred [461]. Only three ammonia could be liberated even from the [tetraamminecopper(II)] sulphate, and a part of the fourth ammonia reacts with the sulphate anion with the formation of SO_2 [463]. The [tetraamminecopper(II)] sulphate loses its three ammonia in an endothermic reaction, however, DTA results show that the decomposition of the $[Cu(NH_3)_4](MnO_4)_2$ is exothermic [457]. Furthermore, IR studies of the intermediates formed during the thermal decomposition of the $[Cu(NH_3)_4](MnO_4)_2$ did not show the presence of the permanganate ion. The IR spectra of the intermediate formed around 250 °C, however, contains a sharp peak appearing around 2200 cm^{-1} (Figure 9).

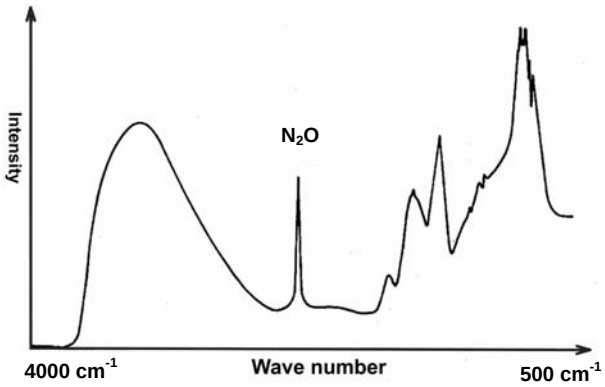
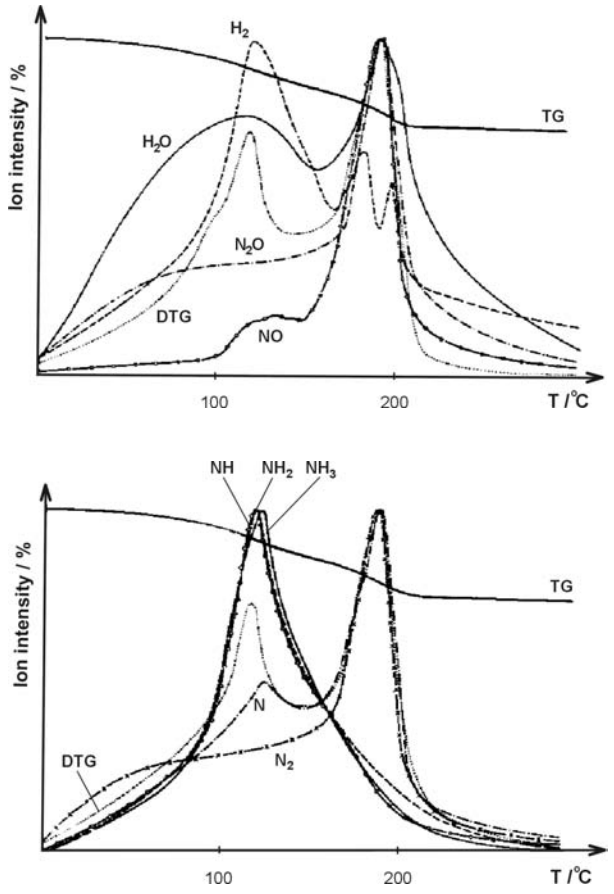


Figure 9. IR spectrum of the intermediate formed during heating of [tetraamminecopper(II)] permanganate.

The strong shift of the Mn-O bands to the lower wave-number region unambiguously indicates decreasing oxidation number of the manganese [464]. This results points to the formation of $[Cu(NH_3)_2](MnO_4)_2$ and $Cu(MnO_4)_2$ intermediates. Thus, anhydrous copper (II) permanganate could not be prepared either by thermal dehydration or by thermal deammoniation of the appropriate aquo- or ammonia-complexes of the copper(II) permanganate [457, 459-460].

TG-MS and TG-gas titrimetry showed that two well-defined steps occur during the decomposition (Figure 10). The most unambiguous feature of



Figures 10a and 10b. TG-MS curves of [tetraammine-copper(II)] permanganate. Reproduced from [457] with permission from Helvetica Chimica Acta.

these decomposition steps is the lack of oxygen formation. In the first step two mols of ammonia are released, and ammonia is not evolved in the second step. Water is released in each decomposition step. The residue is amorphous $CuMn_2O_4$, which does not dissolve in nitric acid at all, therefore, the $CuO+Mn_2O_3$ phase composition can be discounted. Further heating leads to crystallization, and at 500 °C crystalline cubic $CuMn_2O_4$ appears as the final decomposition product.

The IR spectra of the decomposition intermediates showed the presence of N-H and nitrate bands, and the sharp band observed in the IR spectrum was identified as N_2O gas inclusion. In view of the lack of the ammonia and the appearance of N_2O as decomposition product in the 2nd stage, the two-step process can be described as follows [457]:

$$[Cu(NH_3)_4](MnO_4)_2 = CuMn_2O_4 + 2NH_3 + NH_4NO_3 + H_2O \quad (63)$$

$$NH_4NO_3 = N_2O + 2H_2O \quad (64)$$

In the first step, the oxidation of one ammonia ligand into nitrate and H_2O overcomes the endothermicity of the release of two ammonia molecules, thus the overall reaction is exothermic. The facts that the reaction starts at 65 °C, which is lower than the deammoniation temperature of the [tetraamminecopper(II)] sulphate (75 °C) and the decomposition temperature of the permanganate anion (97 °C) [54], further N_2O gas is present among the decomposition products indicate that the oxidation of the ammonia takes place in the solid phase. The DSC studies showed the presence of an intermediate decomposition step which has been attributed to the decomposition of the ammonium permanganate formed during the storage of the wet sample [457].

Dark purple microcrystalline $[M(NH_3)_4](MnO_4)_2$ (M = Cd, Zn) complexes can be prepared by the reaction of saturated aqueous [tetraammine-metal(II)] sulfates and potassium permanganate in the presence of excess ammonia, and simultaneously cooling of the solution from +5 to +2 °C [449-451, 458].

$$[M(NH_3)_4]SO_{4(aq)} + 2\ KMnO_{4(aq)} \rightarrow M(NH_3)_4](MnO_4)_{2(s)} + K_2SO_{4(aq)}\ (M = Cd,Zn) \quad (65)$$

Higher ammonia concentration or larger temperature gradient decreases the purity of the complexes formed. The zinc complex is slightly soluble in water (0.91 g/100 ml H_2O at 19 °C) and is stable in solid form under dry conditions. In wet form, however, it quickly decomposes, especially when exposed to light [458]. The cadmium complex forms purplish black crystals, slightly soluble in water and decomposes during drying [68]. These complexes decompose in aqueous solution, partly with the formation of MnO_2 and oxygen and partly by a temperature-dependent hydrolysis [459-460] in which metal(II) hydroxides and ammonium permanganate are formed (similar to the analogus copper-compound). Inspite of the

existence of the $[Zn(NH_3)_2(ReO_4)_2]$ complex [447], the analogous permanganate complex, [diamminezinc(II)] bis(permanganate) ($[Zn(NH_3)_2(MnO_4)_2]$) could not be prepared either in solid phase or in solution phase by partial de-ammoniation of [tetraammine-zinc(II)] permanganate [458].

Due to the decomposition of [tetraamminezinc(II)] and [tetraamminecadmium(II)] permanganates during crystallization, growing of single crystals have not been successful. Therefore, their structures have been solved by Rietveld refinement of the XRD data [68, 458]. These complexes crystallize in a closely packed cubic structure of $[M(NH_3)_4]^{2+}$-ions with MnO_4^- anions occupying all the octahedral interstices and half of the tetrahedral interstices. The main feature of the structure is a three-dimensional M-N-H....O-Mn hydrogen-bonded network built from block like structural motifs of 4-4 $M(NH_3)_4^{2+}$ and MnO_4^--ions. The stoichiometry of this building element indicates that only one of the two permanganates (type 1) takes part in the 3D network. The other permanganate (type 2) is captured in the cavities enclosed by the connection of the tetramer building blocks of the 3D-network (Figure 11). The

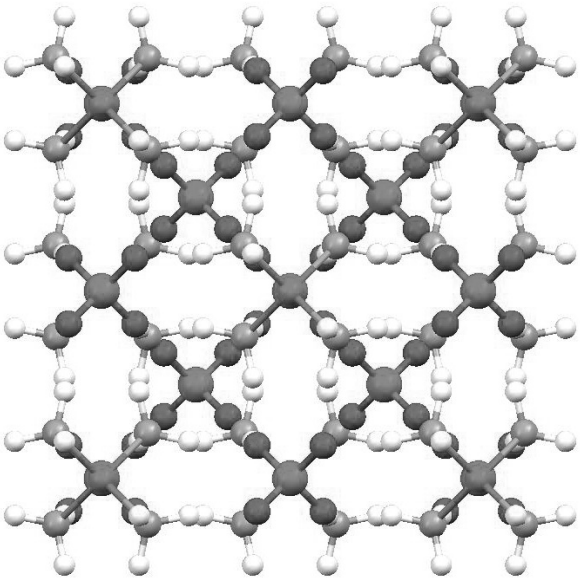


Figure 11. Crystal structure of tetraammine-cadmium(II) permanganate.

N...O distances and the strength of the hydrogen bond in the 3D-networks formed by the permanganate type 1 in the compounds are not the same as the strength of the hydrogen bonds formed by the permanganate type 2. The permanganate-ion located in the cavities (type 2) are bound with ammonia hydrogens, and its free rotation is hindered within the cavities, although its freedom is higher than that of the permanganate type 1 ion. The structures and packings of the analogous zinc and cadmium complexes in solid state can be seen in Figure 11.

Based on factor group analysis, in this cubic lattice (a = 104.32 (Cd) and a = 103.35 nm (Zn)), space group: F-43m Z = 4) all four vibrations of the $[M(NH_3)_4]^{2+}$ and MnO_4^- tetrahedral species are Raman active, but only the two triply degenerated vibrations are IR active [68, 458]. There are two crystallographically different permanganate ions in the cubic lattice, therefore the IR and the Raman bands should appear twice for the two (ν_{F2} and δ_{F2}) and all four ($\nu_{s,}$ $\delta_{E,}$ ν_{F2} and δ_{F2}) vibrational normal modes in the IR and the Raman spectra, respectively. The degeneration of the F_2 bands in this symmetric crystallographical environment does not cease, thus splitting of the ν_{as} asymmetric stretching bands is an unusual phenomenon. The appearance of the IR forbidden vibrations (ν_s and δ_E) as singlets and the splitting of the triply degenerated ν_{as} bands into three components in the Raman spectrum are inconsistent with the factor group analysis results. There are several possible reasons for the appearance of the forbidden IR bands of the tetrahedral oxo-anions [262]. One of them is a dynamic lattice distortion as it was supposed in the case of [tetraamminezinc(II)] perchlorate [465], or some orientational effect which has been observed several times in the N-H hydrogen bonded compounds, e.g. in ammoniumperchlorate [278]. Both the dynamic lattice distortion and the permanganate orientation depend on the temperature, but with opposite sign. Decreasing temperature can freeze one of the orientations, and this should increase the intensity of the forbidden band. In the case of a dynamic lattice distortion, however, the decreasing temperature decreases the extent of the distortion, because the

anisotropic thermal motions are slowing down. Increasing the ratio of the ν_{as}(Mn-O)/ν_s(Mn-O) integrated intensity values by decreasing the temperature (293/173 K) indicates the appearence of the permanganate-ion orientation. Based on this consideration, the forbidden ν_s and δ_E IR bands probably belong to the cavity-embedded permanganate (type 2) [68, 458]. The $[M(NH_3)_4]^{2+}$ complex cations (M = Cd and Zn) have 17 atoms and there are 11 Raman active ($3A_1$+8E) and 21 (F_2) IR and Raman active band that can be taken into consideration among the 45 possible vibrational modes. All vibrations belonging to the coordinated ammonia are IR and Raman active. The bands in the IR spectra of the zinc complex at 421, 388 and 381 cm^{-1} may belong to any of the $\nu_s(ZnN_4)$, $\nu_{as}(ZnN_4)$ and $\delta_{F2}(MnO_4)$ modes [458]. Based on the IR data of the analogous [tetraamminezinc(II)] perchlorate and perrhenate complexes and of an isotope substituted derivative ($[Zn(^{15}NH_3)_4](ReO_4)_2$) [451, 465-467], the band appearing at 421 cm^{-1} belongs to the $\nu_s(ZnN_4)$. Since the $\delta_E(ZnN_4)$ and the δ_{F2} (ZnN_4) are assigned at 232 cm^{-1} and 179 cm^{-1}, respectively, the bands at 388 and 381 cm^{-1} do not belong to the ZnN_4 vibrations but have to belong to the two different permanganate ions and can be assigned as a pair of the $\delta_{F2}(MnO_4)$ bands.

Thermal decomposition of the [tetraammine-zinc(II)] permanganate and the [tetraammine-cadmium(II)] permanganate under inert atmosphere occurs in 2+1 steps [458]. On the basis of the weight loss data the amorphous product is estimated to have a $[MO+Mn_2O_3]$ formula. In the case of the zinc complex, the first decomposition step occurrs at 107 °C, however, depending on the heating rate, the decomposition-peak temperature varies in the 100-130 °C range. This temperature is lower than the deammoniation temperature of the analogous perrhenate salt (150-195 °C, in which range the intermediate $[Zn(NH_3)_2(ReO_4)_2]$ complex [466] was formed). Thermo-gas titrimetric investigation indicates that 2 moles of ammonia are released in the first decomposition step, and no ammonia formation in the second or third step can be observed. As it has been observed in the case of copper(II) complex [457], water forms in both steps and no O_2 evolution occurs in the whole thermal decomposition process. Mainly N_2O and its fragmentation products could be detected in the second step. Similar features were observed in the case of [tetraamminecadmium(II)] permanganate (with 100 and 224 °C decomposition temperatures) [68]. The final decomposition products at 500 °C are MMn_2O_4 (M = Cd, Zn) spinels. Summarizing these results, the main decomposition processes can be illustrated with the following equation:

$$[M(NH_3)_4](MnO_4)_2 = MMn_2O_4 + NH_4NO_3 + 2NH_3 + H_2O \ (M = Cd, Zn) \quad (66)$$

In case of Zn and Cd complexes, respectively, the second decomposition step (T_{peak} = 231 °C and 224 °C) indicates a catalytic action of the MMn_2O_4 in the decomposition of the ammonium nitrate. DSC studies showed that each decomposition step is exothermic. The reaction heats are ΔH = -169 kJ/mol and -318,29 kJ/mol for the Zn- and Cd-compound, respectively. These values indicate that exothermic solid phase quasi-intramolecular redox reactions preceed the deammoniation of the complex cations. Therefore, the [diamminemetal(II)] bis(permanganate) complexes cannot be prepared by the partial deammoniation of $[M(NH_3)_4](MnO_4)_2$ (M = Cd, Zn) compounds. Since the [diamminezinc(II)] perrhenate can be prepared in this way [466], the higher redox activity of the permanganate may be one of the reasons for these redox reactions [68, 458].

In chloroform or in toluene as a heat convecting media each of the three [tetraamminemetal(II)] permanganate (M = Cu, Zn or Cd) can be decomposed between 80 and 100 °C to obtain MMn_2O_4 type catalyst precursors. The ammonium nitrate formed can be removed with water then the precursors can be heat treated at 100-500 °C. The amorphous metal-manganese oxides crystallize into cubic $CuMn_2O_4$, tetragonal $ZnMn_2O_4$ and $CdMn_2O_4$, respectively [68, 457-458]. The amorphous decomposition products formed at 80-100 °C contains some excess lattice oxygens, MMn_2O_{4+x}, (x = 0-0.35). These products are potential catalyst, e.g. in the CO oxidation (M = Cu).

Only the [tetraamminecopper(II)] permanganate has already been used in organic oxidation

reactions, namely for the oxidative regeneration of oximes and phenylhydrazones. The oxidative deoximation of several aldo- and keto-oximes by [tetraamminecopper(II)] permanganate in aqueous acetic acid exhibits a first order dependence both on the oxime and the copper complex. The oxidation of the ketoximes is slower than that of the aldoximes. The rates of oxidation of the aldoximes are well correlated in terms of the Pavelich-Taft dual substituent-parameter equation. The low positive value of the polar reaction constant indicates a nucleophilic attack by a permanganate-oxygen on the carbon. The reaction is subject to steric hindrance by the alkyl groups [468]. Similar kinetic features have been observed in the regeneration of phenylhydrazines in aqueous acetic acid. The rate-determining step is the formation of the cyclic activated complex in both processes [469].

Since the ammonium permanganate can not assure a yield higher than 67% of benzonitrile in the oxidation of benzyl alcohol (due to the 1:1 NH_3:MnO_4^- and 3:2 $PhCH_2OH$:MnO_4^- stoichiometries), several experiments were performed to measure the capability of the [tetraamminecopper(II)] permanganate at the 2:1 NH_3:MnO_4 ratio [68]. The [tetraamminecopper(II)] permanganate as a heterogeneous oxidant oxidizes benzyl alcohol to benzaldehyde with 67% yield after 3 h reflux in chloroform. Only a small amount of nitrile (4%) forms. Increasing temperature (reflux in CCl_4 for 3 h) increases the nitrile yield only to 14%. This indicates that the ammonia could not be liberated from the coordination sphere to react with the aldehyde formed. The addition of strongly coordinating solvents to substitute ammonia in the primary coordination sphere of the complex cation (DMF or CH_3CN) suppresses the nitrile formation. It might be the consequence of the formation of the more stable outer-sphere solvated ammine complexes [68].

Several [hexaamminemetal] permanganate, e.g. $[Ni(NH_3)_6](MnO_4)_2$, $[Co(NH_3)_6](MnO_4)_3$, $[Cr(NH_3)_6](MnO_4)_3$ have already been prepared [449-450, 452-454]. Chloride and bromide containing $[Co(NH_3)_6]X_2(MnO_4)$ compounds (X = Br and Cl) and a double salt with potassium chloride, $K_2[Co(NH_3)_6]Cl_3(MnO_4)$, also exist [453]. XPS of $[Co(1,2\text{-ethylendiamine})_2Cl_2]MnO_4$ has been published [245].

The nickel complex, $[Ni(NH_3)_6](MnO_4)_2$ was prepared first by adding of nickel(II) nitrate to an aqueous potassium permanganate solution saturated with ammonia at 0 °C [449-450]. Klobb defined the compound obtained as a dihydrate, however, the real composition was found to be $[Ni(NH_3)_6](MnO_4)_2$ as an anhydrous salt by Wilke Dörfurt *et al.* [454]. The same anhydrous compound was formed from [hexaammine-nickel(II)] sulphate and potassium permanganate [68]. The complex is a dark violet crystalline mass, decomposes easily during storage, its solubility is 3.5 g/100 ml H_2O at 20 °C. At 78 °C, it decomposes with the liberation of two mols of ammonia. The decomposition process is exothermic, and water is also formed in each step. The rocking Ni-NH_3 stretching [452], which is a structure sensitive mode of the amminemetal-compounds, was observed as a doublet in KBr matrix [68].

[Hexamminechromium(III)]- and [hexa-amminecobalt(III)] permanganates have been obtained as purple precipitates from the reaction of the appropriate sulphate complexes and potassium permanganate [449-450, 452-454]. The [hexa-amminecobalt(III)] permanganate (luteo-cobaltic permanganate) can also be prepared by mixing the warm concentrated solution of [hexa-amminocobalt(III)] chloride with 12 equivalent of potassium permanganate [449-450, 454]. It precipitates as hexagonal plates. A second crop can be recovered with cooling and recrystallizing the precipitate from warm (60 °C) water. Decreasing the excess of the $KMnO_4$ ensures purer crystals [454]. It forms brilliant black tetrahedral crystals, which are slightly soluble in cold water, more soluble in hot water, but partly decomposes. It detonates on heating, and also explodes if it is struck. It has cubic lattice with a = 11.39 Å and Z = 4. It starts to decompose at 108 °C and explodes at 116 °C. It reacts with hydrochloric acid with the formation of manganous chloride and [hexaamminocobalt(III)] chloride.

In warm aqueous solution it reacts with 8 equivalent of [hexaamminecobalt(III)] chloride, when $[Co(NH_3)_6Cl_2]MnO_4$ precipitates during cooling as a black lamellea with the form of regular hexagons, which are red or brown in transmitted light.

$$[Co(NH_3)_6](MnO_4)_3 + 6[Co(NH_3)_6]Cl_3 = 9[Co(NH_3)_6]Cl_2MnO_4 \quad (67)$$

This compound is very unstable, decomposes by water, but dissolves in [hexamminocobalt(II)] chloride solutions. Detonates on heating but does not explode on percussion. The analogous bromide compound, $[Co(NH_3)_6Br_2]MnO_4$, can be prepared by mixing [hexaamminocobalt(III)] bromide with 3 equivalent of potassium permanganate. The salt furnishes hexagonal plates, which are more stable than the analogous chloride compound, e.g. does not decompose in its hot aqueous solution. Potassium [hexaamminocobalt(III)] trichloro dipermanganate, $K_2[Co(NH_3)_6]Cl_3(MnO_4)_2$, can be crystallized out from cold saturated solutions, when [hexaamminocobalt(III)] chloride is mixed with 3 equivalent of potassium permanganate [454]. It furnishes violet hexagonal lamellae which dissolve easily in H_2O, but partly decomposes. On heating it explodes immediately. It can also be prepared if [hexaamminocobalt(III)] permanganate reacts with a large excess of potassium chloride.

The only representative of the platinum metal permanganate complexes is the [tetraammineplatinum(II)] permanganate, $[Pt(NH_3)_4](MnO_4)_2$ [470]. The appropriate [tetraammineplatinum(II)] chloride complex has been reacted with potassium permanganate in ice-cooled water. The triclinic crystals (a = 51,76 nm, b = 75.861 nm, 77.217 nm, a = 69.313 Å, b = 79.656 Å, c = 76.883, space group is P1, d = 2.50 g/cm^3, Z = 1) contain distorted square planar tetraammineplatinum cations and distorted tetrahedral permanganate anions linked by hydrogen bonds.

3.7.2. Pyridine complexes

Tetrakis(pyridine)metal(II) permanganate complexes were prepared by Klobb [471, 472] as purple crystalline compounds ($[Mpy_4](MnO_4)_2$, M = Cu, Ni, Cd, Zn). Two pyridine complexes of silver(I) permanganate, namely $[Agpy_2]MnO_4$ (decomposition point is 65 °C) and a compound with $Ag_2py_5(MnO_4)_2$ formula (decomposition point is 103 °C) were also synthesized. All of these compounds could be prepared in two ways: 1) by the reaction of the appropriate metal permanganate salts with aqueous pyridine or 2) by means of the interaction of the appropriate metal sulphate, pyridine and potassium permanganate in cooled solution [471-472]. The tetrakis(pyridine) metal(II) permanganates are isostructural with the analogous tetrakis(pyridine)metal(II) perchlorate, fluorosulfonate and tetrafluoroborate complexes [454]. The tetrakis(pyridine) complexes are unstable, slightly soluble in water and decompose at 65 °C [471-472].

There are some controversial information about the pyridine complexes of silver permanganate [19, 471-472]. The purple monoclinic crystals of $[Agpy_2]MnO_4$ is prepared by the reaction of silver sulphate with 0.1 M $KMnO_4$ and 10% aqueous pyridine solutions. Its decomposition temperature strongly depends on the purity of the complex and on the heating rate. By using 20% aq. pyridine solution a compound with the formula of $Agpy_{2.5}MnO_4$ is obtained. This decomposed 103 °C [471-472]. Reaction of silver nitrate with pyridine and potassium permanganate led to a compound defined as $[Agpy_2]MnO_4$ (decomposition temperature was 104-105 °C) [19]. Elemental analysis of the compound obtained by the Klobb's method with 20% pyridine [471-472] proved to be $Agpy_{2.25}MnO_4$ [473]. Single crystal X-ray diffractometric elucidation of the structure of this product, however, showed that the real composition is $Agpy_{2.4}MnO_4$ which is analogous with the previously described $Agpy_{2.4}ClO_4$ [474]. This means, that this compound retains its crystal structure during the initial stage of the pyridine loss (from 2.4 to 2.25). The structure consists of an $Agpy_4^+$ and $3Agpy_2^+$ unit with permanganate counter ions (Figure 12).

XRD studies showed that the primary product prepared from $AgNO_3$ and $KMnO_4$ and believed to be $[Agpy_2]MnO_4$ is a mixture of $[Agpy_2]MnO_4$ and $Agpy_{2.4}MnO_4$ [473]. Recrystallization of the abovementioned mixture from benzene-acetone

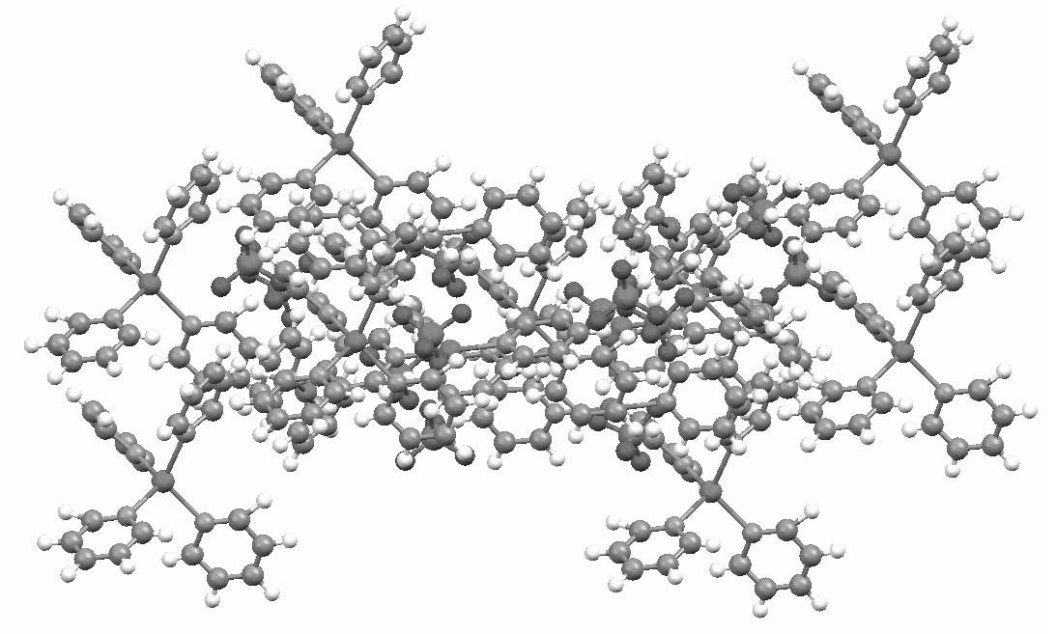


Figure 12. Crystal structure of $Agpy_{2.4}MnO_4$.

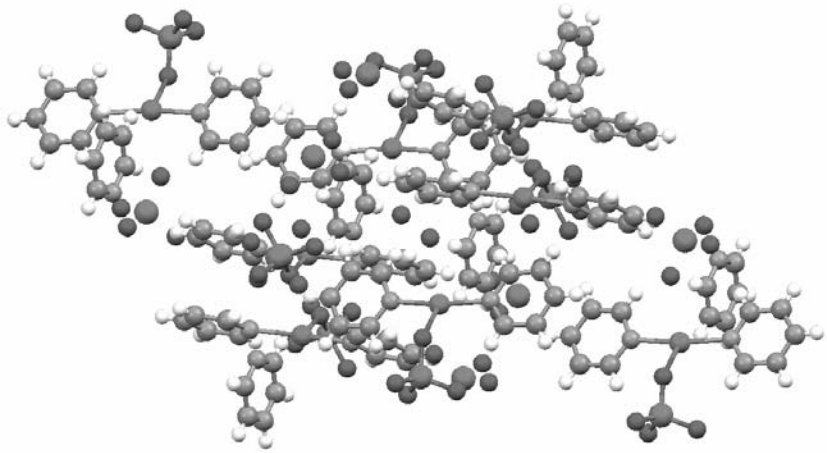


Figure 13. Crystal structure of $Agpy_2MnO_4$.0.5py.

(1:1, v/v) mixture leads to a compound with the $[Agpy_{2.5}]MnO_4$ formula. This compound is the hemipyridine solvate of the $[Agpy_2]MnO_4$. Formation of the $[Agpy_2]MnO_4$*0.5py solvate from the $Agpy_{2.4}MnO_4$ in a pyridine free solvent system is a special feature of the $AgMnO_4$-py system. The purple needle-like monoclinic crystals are stable only in the presence of the mother liquor and decompose at 78 °C. Its structure can be seen in Figure 13 [68].

This compound slowly transforms into $[Agpy_2]MnO_4$ even at room temperature [473], thus the method described by Firouzabadi [19] can be used to prepare this compound besides the formation of two new compounds.

$$4AgNO_3 + 4KMnO_4 + 10py = [Agpy_4]MnO_4*3[Agpy_2]MnO_4 \quad (68)$$

$$[Agpy_4]MnO_4*3[Agpy_2]MnO_4 = 4[Agpy_2]MnO_4.0.5py \quad (69)$$

$[Agpy_2]MnO_4*0.5py = [Agpy_2]MnO_4 + 0.5py$ (70)

The mechanism of the formation of the $[Agpy_2]MnO_4*0.5py$ solvate from the mixture of $[Agpy_2]MnO_4$ and $[Agpy_4]MnO_4*3[Agpy_2]MnO_4$ during the recrystallization from acetone-benzene is an interesting question. The source of the pyridine is the decomposition of the $Agpy_4$-cation (which is less stable than the $Agpy_2^+$-cation). The other possibility is the hydrolysis of the complex cations [459-460] with the liberation of free pyridine and the formation of Ag_2O precipitate. The TG-MS of the $[Agpy_2]MnO_4.0.5py$ shows the presence of a small amount of benzene substituting the solvate pyridine [475]. Preceding the decomposition of the $[Agpy_2]^+$ cation, benzene is liberated disrupting the crystalline lattice. This process in turn promotes the decomposition of the complex before the decomposition temperature of the pure $[Agpy_2]MnO_4$ (103-104 °C) is reached. The thermal decomposition products are metallic silver, Mn_3O_4 and MnO. The low valence manganese compounds indicate reductive processes. The silver manganese oxides (possible intermediates of the decomposition) catalyze the oxidation of the pyridine ring, which leads to unusual features of the thermal decomposition process. First of all, exothermic decomposition takes place below the decomposition point of the $Agpy_2^+$ cation (decomposition temperature of the $[Agpy_2]ClO_4$ is 147 °C). Besides pyridine, its degradation products, e.g. CO, CO_2 and nitrogen oxides are formed, and oxygen is not evolved in the whole process. The proposed mechanism of the redox reaction is as follows [475] (Figure 14).

The initiation of the redox reaction below the decomposition temperature of the $Agpy_2$ unit starts at the α-hydrogen of the pyridine ring. The distance of the N=C-H…O=Mn linkage corresponds to ca. 2 Å O…H distance, (it is shorter than the 2.7 Å H…O distance of the β-CH O…H distance) and the reactivity of the α-C-H is higher than of the β-C-H [68, 475].

The rearrangement of the TS_1 transition state gives a 2-hydroxypyridine derivative (TS_2). This is supported by the known oxidation process of the six-membered aromatic rings [476-477]. The pyridine state is more stable than of the hydroxypyridine, thus the formation of TS_3

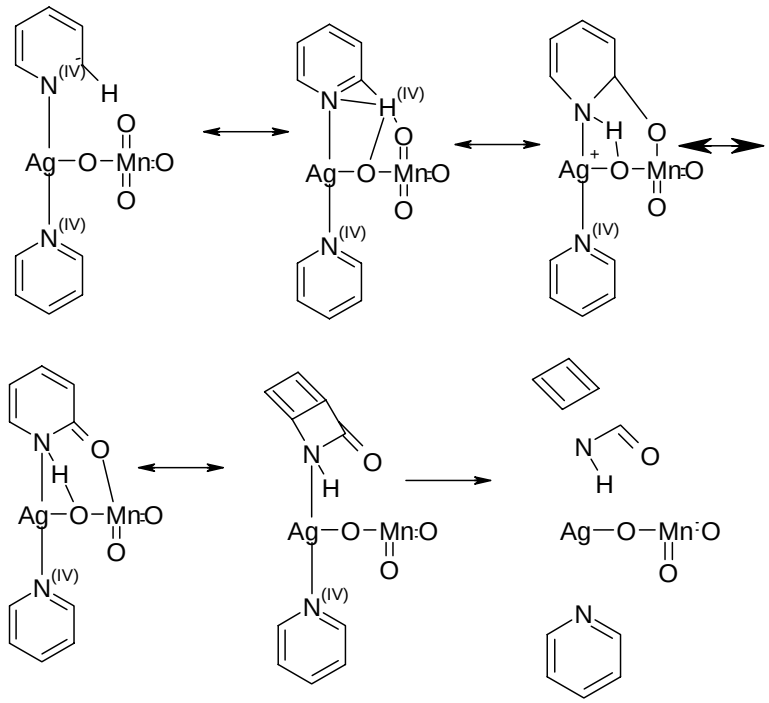
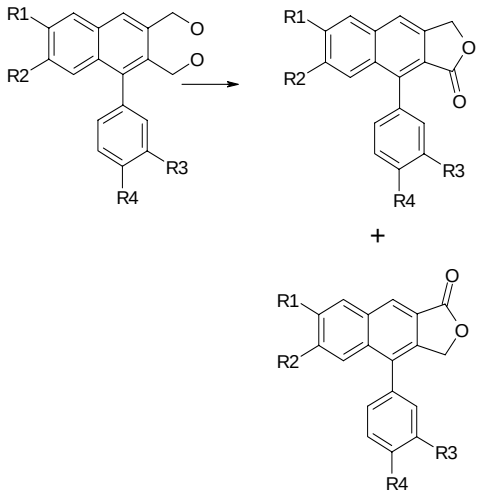


Figure 14. Reaction mechanism of the thermal decomposition of $[Agpy_2]MnO_4$.

intermediate and its transformation via a Dewar-benzene type ring to HNCO and "C_4H_4" type fragment is well known [478-481]. The decomposition and oxidation products of the HNCO are CO, CO_2, H_2O and NO_x. The loss of the other pyridine completes the reaction. This reaction is an example of an aromatic C-H hydrogen-bond mediated molecular level differentiation between the coordinated pyridines. While one of the pyridine is completely destroyed in the reaction the other is liberated without any damage.

The [bis(pyridine)silver(I)] permanganate ($[Agpy_2]MnO_4$, BPSP), is a weak, chemo- and regio-selective oxidizing agent of the organic chemistry. It oxidizes alcohols and diols to aldehydes and dialdehydes under mild conditions [19]. The substituents, however, have major influence on the product distribution. For example, diarylthiophene-2,5-dimethanol is oxidized into the appropriate dicarboxylic acid, although the product distribution depends on the amount of the oxidant used [482]. If the dimethanol groups are located on a condensed aromatic ring, the main products are aryl-substituted lactones [483].



(71)

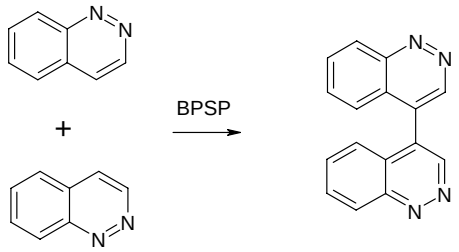
R_1R_2 and R_3R_4 are OCH_2O, R_1-R_4=OMe, R_1R_2=OCH_2O, R_3 and R_4 are OMe, R_1 and R_2=OMe and R_3R_4=OCH_2O.

Most of the aromatic amines transform into the appropriate azo-compounds, however, steric and electronic factors have strong influence on the reaction, e.g. m-nitroaniline and 1-amino-naphthalene do not react at all. Benzylamine can be oxidized into benzaldehyde [19]. BPSP easily oxidizes phenanthrene or anthracene to the corresponding 9,10-quinone or naphthalene to 1,4-naphtoquinone [484]:



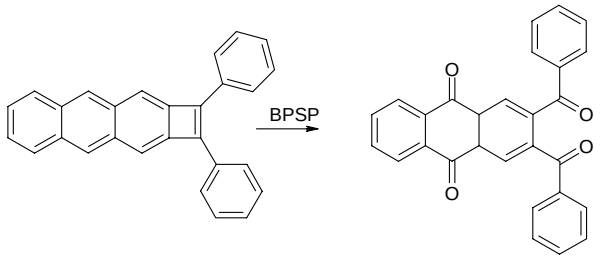
(72)

It can be used as an effective deoximation agent for various kind of aldoximes and ketoximes with high yield [485], and oxidizes diphenylacetylene to benzil [484]. Oxidative coupling of hydro-carbons is a convenient way for C-C and C-N bond formation. Aromatic acetylene hydro-carbons with C-H functions can be oxidized into diacetylene derivatives [484]. Cinnoline can be dimerized by BPSP via a regioselective C-C coupling [26]:



(73)

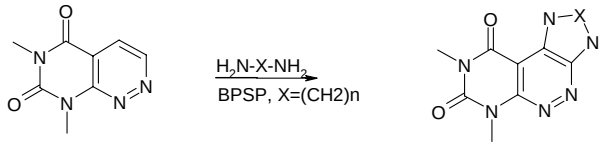
Depending on the number of condensed rings in the structure, the aromatic cyclobutanes (naphtalene or anthracene) are oxidized into diaroyl-aromatic hydrocarbons or to the corresponding diaroyl-quinones [484].



(74)

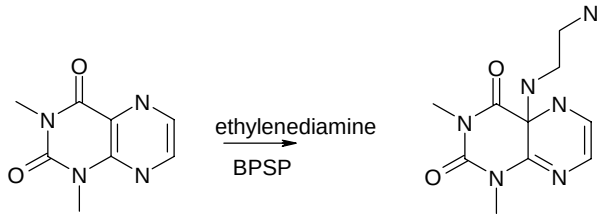
A selective tandem oxidative substitution of pyridazine ring at C-H sites, e.g. in 6,8-dimethyl-pyrimido[4,5-c]pyridazine-5,7(6H,8H)-dione with α,ω-diamines is a new tool to prepare new

heterocycles. Similar reaction was observed with 1,2-diaminocyclohexane [26]



(75)

A nucleophilic addition reaction can be observed when 1,3-dimethyllumazine reacts with various amines, e.g. ethylenediamine [26], ammonia, di-tert-butylamine, piperidine or morpholine [486] in the presence of BPSP with the formation of 7-amino-1,3-dimethyllumazine or its N-substituted deriva-tives. Similar C-H amination was observed in the case of 1,3,5-triazines when the amination or alkylamination were performed in a nucleophilic-type oxidative amination without opening the triazine ring [487].

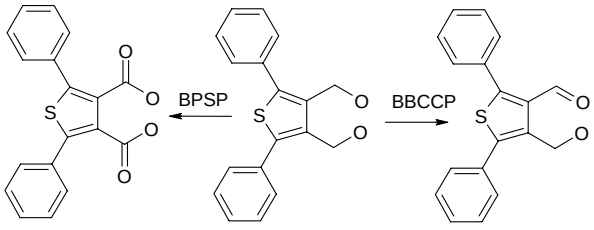


(76)

3.7.3. 2,2'-Bipyridine complexes

Reaction of $[Cu(bipy)_2]Cl_2$ and $KMnO_4$ gives a light purple compound which was believed to be [bis(2,2'-bipyridine)copper(II)] dipermanganate (BBCP), and used widely as a selective and specific oxidant of organic compounds [7, 9-11, 13-14, 17, 488]. The starting complex, however, is the [chlorobis(2,2'-bipyridine)copper(II)] chloride and contains only one ionic exchangeable chlorine ($[Cu(bipy)_2Cl]Cl.6H_2O$) [489]. Furthermore, the amount of the used $KMnO_4$ is only 0.25 equivalent [305] related to the chlorine content of the starting copper complex. In the repeated synthetic experiments (following the given procedure [7]), the compound formed was found to be $[Cu(bipy)_2Cl]MnO_4$ (BBCCP) and not the expected BBCP $[Cu(bipy)_2MnO_4]MnO_4$. This explains the surprising results obtained by using "BBCP" in oxidation reactions, namely, the "BBCP" oxidized only with one permanganate equivalent power [9-10]. Since the BBCCP contains only one permanganate ion, this result is explained. BBCCP belongs to the series of pentacoordinated $[Cu(bipy)_2X]MO_4$ type complexes (X = I, Br, Cl, M = Cl [490-492] and Mn), and its elemental analysis confirmed the presence of one equivalent of chlorine [68]. The perchlorate analog of the BBCP exists ($[Cu(bipy)_2ClO_4]ClO_4$ [493]), however, increasing amount of potassium permanganate did not give pure BBCP. It indicates that the coordinated chlorine cannot be exchanged easily with weakly coordinating permanganate anion, and the preparation of BBCP requires an other synthetic procedure (probably the reaction of $Cu(MnO_4)_2$ with 2,2'-bipyridine). The compound believed to be BBCP prepared by the reaction of $[Cu(bipy)_2](OAc)_2$ and 2 equivalent of $KMnO_4$ has a decomposition point of 105-110 °C, the same as obtained for BBCCP [484]. This compound and the BBCCP have purple color, dissolve in dichloromethane and acetone. TG-MS shows the formation of various kind of carbon and nitrogen containing oxidation products indicating a solid phase redox reaction.

The BBCCP easily oxidizes primary and secondary alcohols to aldehydes [7, 13] and ketones [7, 17] respectively. The first order oxidation reactions have important deuterium kinetic isotope effects and the reaction proceeds with a non-radical mechanism [13, 17]. Similar substantial deuterium isotope effect was observed in the oxidation of various substituted benzyl alcohols [12] and hydroxy acids [16] with BBCCP. Aromatic ortho-dimethanols and non-vicinal diols transform into the appropriate hydroxy-aldehydes or hydroxyketones [7, 488].



(77)

2,5-Diphenylthiophene-3,4-dimethanol are oxidized to hydroxyaldehyde with BBCCP. With $[Agpy_2]MnO_4$ (BPSP) [7, 488] the same compound

transforms to the appropriate dicarboxylic acid. BBCCP has several bond cleavage reaction, e.g. 1) in its reaction with vicinal glycols [488] (deuterium kinetic isotope effect could not be observed), 2) in the oxidation of formic acid [494] and 3) in cleavages both C-C and N-H bond of the pentamminecobalt(III) coordinated amino acids [495]. Monoethers of vicinal diols are oxidized to the corresponding oxo-compounds without bond cleavage [488], and no reaction occurs with 1,4-dihydroxyanthraquinone, toluene, diphenylmethane and alkenes like cyclohexene or oxo-arylalkenes [7].

BBCCP oxidizes aromatic amines to azo-compounds, except o-nitroaniline, but contrast with the BPSP the BBCCP easily reacts with 1-naphthylamine and p-nitroaniline. BBCCP can be used as an effective deoximation agent for aldoximes and ketoximes [7], and oxidizes phosphorus acid and phosphinic acids in aqueous acetic acid to the appropriate pentavelent phosphorus and phosphonic acids [10]. BBCCP also oxidizes thiols and thioacids to the corresponding disulfide dimers (via the formation of a sulphenium cation which is the rate-determining step) [7, 15].

The oxidation of diorganil sulfides [11] and methionine [14] with BBCCP leads to the formation of the appropriate sulfoxide. The oxidation rate of the substituted phenyl methyl sulfides strongly depends on the type and on the site of the substituents. The oxidation of ortho and para substituted compounds is more susceptible to delocalization effect, in case of ortho groups with an important steric inhibition. The oxidation of the meta-substituted ones exhibits a greater dependence of the field effect. The oxidation of the alkyl phenyl sulfides is a subject to both polar and steric effects of the alkyl groups. The polar reaction constants are negative, which indicates an electron-deficient sulphur center in the rate-determining step [11]. Similar kinetic features were observed in the oxidation of various aliphatic aldehydes [496] and substituted benzaldehydes [9].

Similarly to the BPSP, the BBCP also oxidizes polycyclic arenes to the appropriate quinone or ketone compounds or the C-H function of the acetylene hydrocarbons to diacetylenes [484]. Diphenylacetylene is oxidized into benzil. In analogy with the BPSP, the 1,2-diphenyl-naphto[b]cyclobutadiene is converted to 2,3-dibenzoylnaphthalene. The analogous anthracene derivatives are oxidized not only at the cyclobutane but at the anthracene ring as well [448].

3.7.4. Triphenylphosphine-complexes

Triphenylphosphine is an oxidation sensitive compound, but it can be stabilized via complex formation in [tris(triphenylphoshinegold)oxonium] permanganate, $[(Ph_3PAu)_3O]MnO_4$. This compound has been isolated as a purple crystalline powder with a 131-131.5 °C melting point (accompanied by decomposition). The complex could be obtained by the reaction of Ph_3AuCl and $KMnO_4$ in the presence of Ag_2O (yield 70%) [497-499]. The same compound is formed in the reaction of triphenylphosphine complexes of vinyl or cyclohexylgold with $KMnO_4$ in acetone at -30 °C. During storage it easily decomposes both in solid state and in solution. The [tris(triphenyl-phosphinegold)oxonium] permanganate is well soluble in CH_2Cl_2, $CHCl_3$, MeCN alcohols, pyridine, ketones and organic nitro-compounds and insoluble in ether, benzene and hexane. Its structure elucidated with IR and UV spectroscopy shows the presence of an ionic permanganate anion [497-498]. Steric hindrance of the Ph_3PAu-groups around the oxygen atom causes some increase in the bond angles. The effect of the Au-Au interactions could not be observed in the Mössbauer spectrum [500].

It reacts with nucleophiles, e.g. reaction with NaCl results Ph_3AuCl in quantitative yield:

$$[(Ph_3PAu)_3O]MnO_4 + 3NaCl + H_2O = 3Ph_3PAuCl + NaMnO_4 + 2NaOH \quad (78)$$

The solubility of the complex in organic solvents provides a possibility for oxidative auration of acidic C-H groups, as the CH_3 groups at neighbouring oxo-group, e.g. acetone, methyl-ethylketone or acetophenone:

$$R\text{-}C(=O)\text{-}CH_3 + [(Ph_3Au)_3O]MnO_4 = R\text{-}C(=O)\text{-}CH_2\text{-}AuPPh_3 \quad (79)$$

R=CH_3 (60%), R=Et (33), R=Ph (35%), ferrocenyl (5%) [497-499].

3.7.5. Other complexes

There is only one paper published on urotropine containing complexes of Mg, Cu and Ni-permanganates with the composition of $[MU_2](MnO_4)_2*8H_2O$ [501]. These compounds, however, not urotropine but aqua-complexes [68]. On the basis of our XRD studies they are isomorphous with the $[M(H_2O)_6](ClO_4)_2*2U*2H_2O$ complexes (M = Cd, Ni, Zn, Mn [502-504]). These compounds have three-dimensional hydrogen bound structure without coordinated urotropines. The copper-compound is very explosive even in wet state, and decomposes by the touch of a pencil. The redox properties of the copper cation might be responsible for this sensitivity. This type of behaviour of other complex metal permanganates (e.g. in the case of ammine complexes) could also be observed.

Hexaantipyrine-complexes of calcium, aluminium and chromium(III) were prepared by the reaction of hexaantipyrinemetal chlorides and $KMnO_4$ in aqueous solution as purple needles (Ca), and dark purple powders (Al or Cr(III)) which are stable in air only for a short time (5 h and 24 h for the Al and Cr(III) salts, respectively) [505].

Hexacoordinated urea complexes of chromium(III) permanganate is isomorphous with the analogous perchlorate, tetrafluoroborate and fluorosulphonate [505]. It is a purple precipitate formed by the reaction of $[Cr(H_2NCONH_2)_6]Cl_3$ and $KMnO_4$ [506]. Besides the [hexaurea-chromium(III)] permanganate, some mixed salts were also prepared, e.g. $[Cr(H_2NCONH_2)_6]SO_4(MnO_4)*3H_2O$ as purple needles from the [hexaureachromium(III)] chloride sulphate and calculated amount of $KMnO_4$. The crystals are dichroic (red and blue), instable in air and decomposes within one hour. It contains three mol of crystalline water. The analogous dichromate permanganate could be prepared from the saturated solution of [hexaureachromium(III)] chloride by potassium permanganate and sodium dichromate under strong cooling as dark violet slightly dichroic crystals, decomposing during isolation [507]. It is slightly soluble in water and explodes on heating with the formation of manganese dioxide.

Complexes of lithium, rubidium and cesium permanganate with cis-trioxa-tris-σ-homobenzene and cis-triaza-tris-σ-homobenzenes ($[C_6X_3]_2MMnO_4$, X = O or NH, M = Li, Rb and Cs) have been prepared but not characterized in detail [508]. Strontium and barium permanganates form complexes with the $[(C_6X_3)_nM](MnO_4)_2$ M = Sr, Ba, X = O, n = 2 or X = NH, n = 4) formula with different stoichiometry depending on the heteroatom [508].

4. Permanganates of organic cations

4.1. Tetraorganylammonium permanganates

Quaternary ammonium permanganates (R_4N=(C_{2-8} alkyl)4N, $MeBu_3N$, Me(n-Okt)$_3$N, Bu(n-Pr)$_3$N, $BzEt_3N$, Bz(n-Bu)$_3$N, p-nitrobenzyl(n-Bu)$_3$N, (p-fluorobenzyl)Et_3N and p-fluorobenzyl(n-Bu)$_3$N) have been prepared by the reaction of the appropriate halides with solid $KMnO_4$ in CH_2Cl_2, or by the aqueous metathesis reaction of these compounds. These compounds exist in their solutions as either ion pairs or aggregates promoted by high concentrations, low temperatures and the low polarity of the solvent. The high solubility, e.g. in case of Me(n-Oktyl)$_3$$NMnO_4$ permits the anion to penetrate the organic cation. These compounds have low thermal stability, but the benzyltriethylammonium and p-fluoro-benzyltri(n-butyl)ammonium permanganates have good shelf lives under cooling [6] (Table 3).

Depending on the temperature, the concentration and the solvent, different kind of aggregates have been detected by NMR [6]. The C_{2-8} tetraalkyl-ammonium, cetyltrimethylammonium, benzyl-triethylammonium, p-fluorobenzyltrimethyl-ammonium, n-butyltri-n-propylammonium, methyl-tributylammonium, p-fluorobenzyltributyl-ammonium, p-nitrobenzyltributylammonium, and methyl-tri-n-octylammonium permanganates are soluble in dichloromethane and chlorofom, but the C_{2-4} tetralkylammonium salts decompose in $CHCl_3$ and the solubility of benzyltriethyl-ammonium permanganate is less (with two order of magnitudes) than the others. The C_{2-3} alkyl, cetyltrimethylammonium, benzyltriethylammonium,

Table 3. Synthesis conditions and decomposition temperatures of quaternary ammonium permanganates [6].

R_4N	Solvent	Yield, %	Dec. temp., °C
Et_4N	aq.	17	113
n-Pr_4N	aq.	97	104
n-Bu_4N	aq.	89	98
n-$Pent_4N$	aq	97	92
n-Hex_4N	CH_2Cl_2	93	-
n-$Hept_4N$	CH_2Cl_2	87	91
n-Oct_4N	CH_2Cl_2	60	90
Me(n-Bu)$_3$N	aq.	88	107
Me(n-Oct)$_3$N	CH_2Cl_2	60	66
(n-Bu)(n-Pr)$_3$N	aq.	92	104
BzEt$_3$N	CH_2Cl_2	80	114
Bz(n-Bu)$_3$N	aq.	97	101
(n-hexadecyl)Me$_3$N	aq.	78	98
p-NO_2Bz(n-Bu)$_3$N	CH_2Cl_2	90	-
p-FBz(n-Bu)$_3$N	CH_2Cl_2	74	96
p-FBzEt$_3$N	aq.	68	109

p-fluorobenzyltriethylammonium and n-butyl-tri-n-propylammonium permanganates are not soluble in toluene and CCl_4. The C_{6-8} tetralkyl salts are not soluble while others are slightly soluble in water [6].

Several tetraalkylammonium salts (tetraalkyl = tetrabutyl, tetra-n-octyl, methyl-tri-n-octyl, methyltributyl) oxidize various substituted styrene derivatives such as substituted (E)-methyl cinnamates and alkyl, halo and alkoxy substituted styrenes in different solvents. In polar organic solvents such as in acetone the cation has no effect on the reaction rate. In less polar solvents, such as in methylene chloride or in toluene, the reaction rates, however, depend on the identity of the quaternary ammonium ion. Thus it appears as if the reacting species in polar solvents may exist as solvent separated ion pairs and in non-polar solvents as intimate ion pairs. The reaction rates are sensitive to substituent effects. The mechanism can be visualized as the proceeding of transition states that varies from electron rich to electron poor depending on the capacity of the substrate to accommodate either negative or positive charges [509-510].

Tetraalkylammonium permanganates (R_4NMnO_4, R=Me, Et, n-Pr, nBu) oxidize primary alcohols to acids and secondary alcohols to ketones in a partly autocatalytic reaction involving colloidal manganese dioxide formation. The temperature dependence of the reaction kinetics have been determined for each oxidant and substrate, and the activation energies have also been determined [511].

Tetraalkylammonium permanganates (R_4NMnO_4, $R_4=C_{3-8}$, methyltri-n-butyl and methyl-tri-n-octyl) oxidize methyl (E)-cinnamate to the appropriate cis-dihydroxylated derivatives [510]. If one of the alkyl groups is methyl the rate is higher as in the case of longer chain-length tetraalkylammonium cations. Comparing the oxidation rate, the methyl-trialkyl (alkyl = n-butyl or n-octyl) permanganates react with the same high rate which suggest that these two cations can adopt similar orientation with respect to the anions (in both ground and transition states). Introduction of substituents into

the phenyl ring causes marked changes in the reaction rate, which indicates that the transition state contains a greater concentration of the negative charge near to the aromatic ring than does the ground state. The reaction is initiated by an electrophilic attack followed by a slower step in which the organometallic complexes convert into cyclic manganese(V) diester [510]. Inverse secondary deuterium isotope effect has been observed at the β-position.

The lower (C_{3-6}) tetralkylammonium permanganates can be used as cathodes in alkaline dry cells [512].

4.1.1. Tetramethylammonium permanganate

Tetramethylammonium permanganate can be used for the preparation of manganese oxides by means of its reduction with carboxylic acid containing 4 carbon atoms. The reaction is carried out to obtain a manganese oxide gel in which the oxidation state of the manganese is 4. The manganese oxide gel is dried at room temperature and then it is heated to 300 and 1000 °C to obtain Mn_2O_3 applied to manufacturing cathode materials for electro-chemical generators [513]. Solid state ^{55}Mn NMR spectra of polycrystalline tetramethyl-ammonium permanganate has been recorded at room temperature and the parameters of the first order quadruple interactions, the asymmetry parameters and the local gradient of the electric field at the nucleus of each positions have also been determined [225].

4.1.2.Tetraethylammonium permanganate

Tetraethylammonium permanganate could be prepared by the reaction of $KMnO_4$ and $[Et_4N]Cl$ [514] or tetraethylammonium hydroxide [515] in aqueous solution. The dark violet precipitate formed was dried at room temperature. It forms also if $MnCl_2$ is reacted with $KMnO_4$ in aqueous solution containing Et_4NBr. It decomposes at 80-100 °C without explosion. Both the IR and Raman spectra have been measured and evaluated including the resonance and the pre-resonance Raman effect in detail. Only the ν_{as} band is splitted in the Raman spectrum and a lot of bands belonging to the cationic part appeared in the IR spectrum. The electronic spectrum has complicated vibrational fine-structure, the t_1+e* bands have been assigned for $^1T_1$ (I), $^1T_2$(II) and $^3T_2$(III). The electronic origin for the states t_2-e* charge transfer was determined for $^1T_1$(IV) and $^1T_2$(V). The vibrational coupling has been observed only with the totally symmetric Mn-O stretching vibration. The t_1,t_2-t_2* charge transfer bands have also been assigned [514]. The solid state ^{55}Mn NMR spectra of the polycrystalline tetraethylammonium permanganate has been recorded at room temperature, and the parameters of the first order quadrupole interactions, the asymmetry parameters and the local gradient of the electric field at the nucleus of each positions have also been determined [225]. Et_4NMnO_4 has monoclinic crystals, $P2_1/c$, a = 7.512, b = 11.103, c = 14.764 Å, β = 91.44, Z = 4, D = 1.34, T = 295. The average Mn-O distance is 1.610 Å.

Et_4NMnO_4 reacts with MCl_2 type halides (M = Mn, Cd) and 2,2'-bipyridine and forms $Mn_3O_4(bipy_4Cl_2[MCl_4]$ (M = Mn, Cd) cluster type complexes in DMF solution [516].

This compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515]. It oxidises cis and trans-decalin to the appropriate cis and trans decalol, or in the case of trans isomer into trans-1-decalone and trans-2-decalone. Methylcyclohexane and tetraline could hardly be oxidised, but cymene has been transformed to 2-phenyl-2-propanol and acetophenone [515].

4.1.3. Tetrabutylammonium permanganate

Tetrabutylammonium permanganate precipitates as purple crystalline mass in the reaction of cold aqueous solutions of excess tetrabutylammonium hydroxide and $KMnO_4$. In solid state it can be stored for a prolonged period at time without decomposition, Mp.120-121 °C (dec.), in the case of blocks it is 115 °C [517]. Because of its intrinsically pyrophoric properties, self-ignition has occurred in case of a one week old sample. It has ignited violently when tipped onto glassine paper or during weighting [518-519]. It dissolves in pyridine and can be purified by crystallization from CH_2Cl_2-benzene [517]. nBu_4NMnO_4 is sparingly soluble in benzene, easily soluble in polar solvents such as acetone, CH_2Cl_2 and

$CHCl_3$, very soluble and stable in pyridine (1.4M) [517]. In order to prepare an unexplosive reagent containing tetrabutylammonium permanganate, potassium permanganate and Bu_4NCl have been reacted in aqueous solution and the precipitate formed has been dried at room temperature. This compound is dissolved in dichloromethane and adsorbed onto alumina [514]. Based on the studies of the solid-liquid and the liquid-liquid system of tetrabutylammonium permanganate and H_2O, the formation of clathrate hydrates has been proposed. The reason of this behaviour, which is opposite to the other monovalent cations like fluoride, nitrite or bromate, is the large molar volume of the permanganate anion [520].

The ν_{as} Mn-O IR band appears at 900 cm^{-1}, the UV-VIS spectrum in pyridine similar to the UV spectrum of the $KMnO_4$ in H_2O [517]. Raman measurement has been performed with rotating sample in order to avoid decomposition due to local overheating. The Raman spectrum measured at liquid N_2 temperature contains 9 overtones of the totally symmetrical A vibrational mode [522-523]. The vibronic fine structure has been determined using optically isotropic KBr pellets [524]. In order to compare the spectra, a room temperature and a low temperature (-196 °C) measurement have been made and the room temperature spectrum of the aqueous solution has also been recorded. The Raman and the resonance Raman spectra have been measured and the complete assignation of the normal stretchings and the combination bands have been made. The X_{11} anharmonicity constant for the ν_s Mn-O band has also been determined [274].

Formation or reactions of tetrabutyl-ammonium permanganate are valuable techniques in chemical analysis. It can be used for the determination of DDT in the presence of various polyhalogenated compounds via converting them into 4,4'-dichlorobenzylic acid [525]. Tetrabutylammonium permanganate can be used for photometric titration of unsaturated hydrocarbons in organic medium such as chloro- or bromobenzene. The by-product of the reaction is MnO_2 [526]. n-Bu_4NMnO_4 can be used for the determination of permanganate ion by precipitating it with n-Bu_4NCl, and determining gravimetrically, or dissolving (extracting) the precipitate in CH_2Cl_2 and using spectrophotometry at 525 or 545 nm [527]. Extraction constant of n-Bu_4NMnO_4 between water and chlorobenzene has been determined as a function of the temperature and of the acidity of the solution [528]. Ion-pair formation selectivity has been measured towards hydroxide ion in chlorobenzene-H_2O system comparing it with various anions [529].

The reactions of the tetrabutylammonium permanganate in various solvents with lower valence manganese compounds lead to various dinuclear Mn(III) and Mn(II)-complexes [530]. Dinuclear Mn_2O type complexes as catalase models have been synthesized from manganese(II) choride, tetrabutyalammonium permanganate, 2,2'-bipyridine, benzoic acid and NaN_3 in MeCN [531]. Due to the thermodynamical instability of the permanganate ion in alkaline aqueous solutions, its reactions with biologically important basic ligands like phenoxide or imidazolate is not easy. Tetrabutylammonium permanganate is, however, highly soluble in MeCN, EtOH, Me_2CO and DMF in which these reactions are easily performed. In this way, discrete manganese(III) and manganese(IV) complexes have been prepared by the reaction of $Mn(OAc)_2.2H_2O$, organic ligands (picolinic acid, salicylic acid and pyridine) and tetrabutylammonium permanganate [532]. Tetrabutylammonium permanganate reacts with benzoic acid and manganese(II) acetate in pyridine, which is then followed by the addition of sodium perchlorate to obtain $[Mn_4O_2(benzoate)_7(bipy)_2]ClO_4$ [533]. The acetate analog with Br_3^- counter ion has also been prepared and a series of binuclear $Mn_2O(OR)X_2(bipy_2)_2$ type complexes (X = Cl, N_3, OAc) (OR = acetate, propionate, benzoate) can also be prepared from n-Bu_4NMnO_4 [533]. Comproportionation of manganese benzoate with n-Bu_4NMnO_4 in 1:2.5 ratio in EtOH/MeCN has yielded $Bu_4N[Mn_4O_2(H_2O)(OPh)_9]$ in 90-95% yield [534]. A decanuclear $Mn_{10}O_8(OAc)_6(picolinate)_8$ cluster containing an Mn^{3+} core has been prepared by the reaction of tetrabutylammonium permanganate with $Mn_3O(OAc)_6(py)_3$*py and picolinic acid in MeCN [535]. Substituted

benzoic acid analogous of the starting trinuclear complexes can be prepared as well from tetrabutylammonium permanganate, $Mn(OAc)_2.4H_2O$, and the halo-substituted benzoic acids in EtOH-pyridine and MeCN at room temperature. These complexes have mixed valence character (Mn^{4+}, Mn^{3+}, Mn^{2+}) [536].

Tetrabutylammonium permanganate, depending on the solvent and the reaction conditions, oxidizes various kinds of organic compounds. Toluene is oxidized to benzoic acid in toluene as solvent together with the formation of colloidal MnO_2 [537]. The rate constant has been determined. Significant isotope effect has been observed during the oxidation of deuterated toluene. No induction period could be observed in the reaction. The oxidation in neat toluene is slower with 3 order of magnitude than in water. In the aqueous medium the rate determining step is the oxidation of the benzylic C-H bond. The nature of this reaction, however, is different in toluene because of the difficulties in generating charged species [538]. Other arylalkanes are also oxidized in toluene or dichlorobenzene by dehydrogenation or oxidation. Xanthene is converted to xanthone and dihydroanthracene to anthracene. The reactions are first-order reactions without induction periods. There are primary isotope effects in the oxidation of dihydroanthracene. The reactions have radical mechanism, the rate-limiting step is the H radical transfer from the substrate to the permanganate group [537]. Both the alumina supported and the unsupported forms are active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively. It transforms trans-decaline into trans-9-decalol, trans-1-decalon and trans-2-decalon [514]. Kinetics of the oxidation of alkynes e.g. ethyl tetrolate or 2-heptyne in CH_2Cl_2 have been studied. The reaction has been found to be first order with respect both to the oxidant and the alkyne, and the reaction rate was greatly accelerated by electron withdrawing substituents [539]. Alkynes and tetrabutylammonium permanganate reacts at room temperature in dichloromethane with the formation of α-diones in a second order reaction. On the rates of the reactions the steric factors seem to be not so important as the electronic effects [540].

Substituted benzaldehydes and benzyl alcohols are oxidized to acids in high yields, cis-stilbene and p-nitrotoluene are oxidized into the appropriate benzoic acid [517]. The 4- and 5-nitro-2-methoxycarbonylthiophenes have been prepared by the oxidation of the appropriate nitrothiophene carbaldehydes in pyridine solution [541]. Primary and secondary ferrocenyl alcohols can be oxidized to the corresponding oxo compounds under mild conditions with 48-72% yield [542]. Depending on the solvent (CH_2Cl_2, $CHCl_3$ or pyridine) and the temperature, the extent of the competitive ether forming reactions are different [542]. Oxidation of saturated higher primary and secondary alcohols into acids and ketones have been performed under solvent free conditions. Tetrabutylammonium permanganate oxidizes bromomethyl substituted polyaryletherketones into the appropriate esters (CH_2Br into $COOCH_3$) [543]. The specificity of the tetrabutylammonium permanganate in the oxidation of lignin and carbohydrate model compounds has been studied [544]. It catalyzes the oxidation of isophorone into ketoisophorone with t-butylhydroperoxide, but the mass balance is poor [437].

Vinylferrocene can be oxidized even at 0 °C with tetrabutylammonium permanganate in dichloromethane with the formation of $FcCH(OH)$-CH_2OH as the main product together with some amount of Fc-CH_2OH and $FcCH_2OOCFc$ [545]. Reactivity of the tetrabutylammonium permanganate towards stannylene derivatives of vicinal glycols depends on the structure of the stannylene-compounds, and proved to be ineffective in the cleavage of bicyclic stannylene derivatives of vicinal glycols. However, benzaldehyde is obtained from dibutylstannylene derivative of benzil [546].

Tetrabutylammonium permanganate can be used in various fields of chemistry as phase transfer oxidant [521]. The reaction of the appropriate bromide and $KMnO_4$ in aqueous benzene/toluene two-phase system, with NaCl as catalyst, oxidizes olefins (the formed benzene/toluene solutions are

purple) [547]. This purple solution oxidizes polyethylene and hydroxyl terminated polybutadiene at room temperature with the formation of C=O and C-O-C functions, mainly acids. Ion pair formations have been detected by NMR in $CDCl_3$ and with UV in benzene/toluene [547]. Ethylene-propylene-diene rubber is oxidized from room temperature up to reflux temperature in toluene, when the saturation of the diene type bonds and changes in the plastic properties of the formed polymers have been observed [548]. Oxidation of polypropylene by using phase transfer conditions leads to a change in the surface properties and the adhesive strength [549]. Tetrabutylammonium permanganate can be used as a two-phase oxidant in the degradation of coal, in order to oxidize aliphatic structures particularly benzylic, methylene or methine groups carbon attached to hetero atoms and functional groups [550]. Tetrabutylammonium permanganate have both catalytic and non-catalytic characters. The colloid manganese dioxide formed has some auotocatalytic effect in the oxidation process [551].

4.1.4. Tetra-n-amylammonium permanganate

The reaction of the appropriate bromide and $KMnO_4$ in aqueous-benzene/toluene system containing NaCl as catalyst leads to tetra-n-amylammonium permanganate which can oxidize olefins. The benzene/toluene solutions formed are purple [547]. These solutions oxidize polyethylene and hydroxyl terminated polybutadiene at room temperature with the formation of C=O and C-O-C functions, mainly acids. Ion pair formations have been detected by NMR in $CDCl_3$ solutions and with UV-VIS in benzene/toluene solutions [547].

4.1.5. Tetra-n-heptylammonium permanganate

It has been prepared from tetra-n-heptylammonium chloride (dissolved in 1,2-dichloroethane) with aqueous $KMnO_4$. Its UV spectra in 1,2-dichloromethane shows a band at 525 nm [552].

4.1.6. Benzyltrimethylammonium permanganate

Potassium permanganate and $BzMe_3NCl$ have been reacted in aqueous solution and the precipitate formed was dried at room temperature. It decomposes violently at 80-90 °C. This compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515].

4.1.7. Benzyltriethylammonium permanganate

Potassium permanganate and $BzEt_3NCl$ have been reacted in aqueous solution and the dark purple precipitate formed was dried at room temperature [515, 553]. It decomposes violently after 7 min at 100 °C, explodes after 25 min at 90 °C or after 90 min at 80 °C [554]. Its dichloromethane solution can be adsorbed onto alumina, thus provide a supported and unexplosive reagent [515]. Recrystallization from a minimal amount of hot CH_2Cl_2 by the addition of CCl_4 leads to a solid with a melting point of 125-127.5 °C. NMR shows multiplied signals. In the UV-VIS spectrum four peaks have been observed between 500 and 575 nm in [533]. It can be dried in vacuum at 40 °C and at high vacuum at 20 °C in a time period of 36 h. It can explode during pouring into another flask with explosive ignition and formation of a flame of about 1 m in length [555]. It also explodes at 80 °C during drying at 1 Torr. It is not resistant to shock at all [556-557] and sensitive to heavy blows (30 Nm) [558]. It is readily soluble in CH_2Cl_2 and glacial acetic acid (1.3-0.5 M), and is relatively stable in these solutions [556].

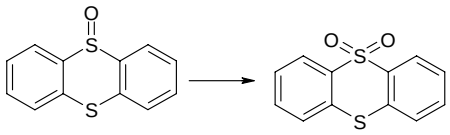
Benzyltriethylammonium permanganate oxidises numerous classes of organic compounds. Alkanes can be oxidized in dichloromethane or glacial acetic acid to alcohols, ketones or esters. Benzylic methylene groups are oxidized to ketones, cleavage to benzoic acid is suppressed. Tertiary benzylic CH groups are smoothly transformed to tertiary alcohols. Aliphatic methin groups require higher temperatures and glacial acetic acid as solvent. The formed alcohol partially decomposed/dehydrated and the secondary methylene groups are also oxidized. Hydroxylation of decalins proceeds stereo-specifically with the retention of the original configuration [556]. Both the supported and unsupported forms are active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane,

respectively [515]. It transforms trans-decaline into trans-9-decalol, trans-1-decalon and trans-2-decalon [515]. Acetoxytoluenes and substituted acetoxytoluenes are converted into acetoxy-benzoic acids via oxidation of the benzylic CH_2 group [557] in glacial acetic acid at 30 °C. Strongly cytotoxic canthin-6-one alkaloids can be prepared by regioselective oxidation of the parent canthines prepared by the Diels-alder reactions of indole and 1,2,4-triazine compounds without the formation of canthin-4-ones with 58-67% yield in CH_2Cl_2-acetic acid solution at 70 °C [558].

Primary alcohols can be oxidized mainly to methylene diesters, which are formed by nucleophilic attack of the carboxylates formed on the solvent dichloromethane. Secondary alcohols furnish high yields of ketones, accompanied by carboxylic acids formed by α-cleavage [554]. Oxidation of aldehydes with benzyltriethyl-ammonium permanganate leads to carboxylic acids at room temperature [560]. Methoxymethyl substituted polyaryletherketones are oxidized to the appropriate esters (CH_2OCH_3 into $COOCH_3$) [543]. Other ethers, e.g. dibutylether transforms to butylbutyrate, benzyl methyl ether to benzyl benzoate, butyl phenyl ether to phenyl butyrate and dibenzyl ether to benzyl benzoate, but a small amount (8%) of methylenedibenzoate is also formed. The ester formation of unsymmetrical ethers show the following reactivity order towards $BzEt_3NMnO_4$ [561]

benzyl>phenylalkyl>primaryalkyl>secondaryalkyl> methyl>phenyl.

Linear sulfides can be oxidized with good yield to the corresponding sulfones in CH_2Cl_2/acetic acid mixture at -10 ^oC [562]. Thianthrene-5-oxide is oxidised selectively to the corresponding sulfone, thianthrene-5,5-dioxide in dichloromethane [553].



(80)

Benzyltriethylamonium permanganate and oxalyl chloride proved to be an effective agent in the stereoselective dichlorination of olefins. The reaction gives trans-dichloro isomers with high selectivity [563].

4.1.8. Benzyltributylammonium permanganate

Benzyltributylammonium permanganate has been prepared from the appropriate chloride by sodium permanganate in o-dichlorobenzene in the presence of NaOH. Its melting point is 107-110 °C [564]. The compound can be used as an oxidant in the preparation of toners for electrostatic image development [565].

4.1.9. Cetylbenzyldimethylammonium permanganate

Cetylbenzyldimethylammonium permanganate ion associate is an electroactive material in the first permanganate ion selective electrode prepared from PVC membrane and dibutylphthalate plasticizer. The response of the electrode is linear between $5E^{-7}$ to $1E^{-1}$ M permanganate concentration [566].

4.1.10. Trioctylmethylammonium permanganate

Extraction of trioctylmethylammonium permanganate from aqueous solutions by organic solvents has been studied, and ion pair formation was observed via dipole-dipole aggregation [567].

4.1.11. Tetradecyltrimethylammonium permanganate

It can be prepared from the CH_2Cl_2 solution of tetradecyltrimethylammonium bromide by aqueous potassium permanganate as a violet solid with 80% yield [568]. Stable at room temperature for a few days, can be stored at 0 °C in a brown bottle for months. It has a violet coloured solution in methylene chloride at 0 °C, and this solution can be used for the dibromination of olefins with Me_2SiBr_2. This reaction can be used in the preparation of pregnenolon and stigmasterol derivatives [271]. Cyclohexene is trans-dibrominated. The linear double bond bromination is preferred to the ring double bond, or the chain-end CH_2=C part bromination is preferred to the CO-CH=CH-type double bond [271].

4.1.12. Cetyltrimethylammonium permanganate

The title compound has been prepared by means of the reaction of the aqueous solution of cetyltrimethylammonium bromide with potassium permanganate with a yield of 92%. The analogous chloride compound can also be used for

starting material. It decomposes at 80-100 °C without explosion [515]. Decomposition has occurred even at 98 °C in a capillary and it violently decomposes at 115 °C. The compound is stable at room temperature if it is kept in dark. It has a phase transition around 50 °C [6].

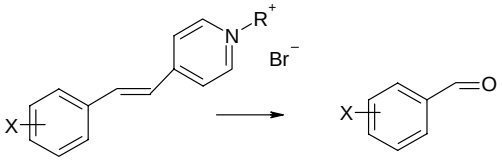
The UV spectra were monitored in various solvents such as $CHCl_3$, CCl_4, benzene and benzonitrile and a self-oxidation process could be detected with the formation of pentadecanal. The rate of the self-oxidation decreases in the benzonitrile > benzene > chloroform > CCl_4 order. The mechanism is a proton transfer from the β-methylene group to the permanganate ion through the formation of an olefinic intermediate [45].

Cetyltrimethylammonium permanganate acts as a 1,3-dipole in the oxidation of cycloalkenes in CH_2Cl_2 at room temperature [569]. The reaction products are cis-hydroxylated compounds. The oxidation of bicyclo[2.2.1]hept-2-ene leads to the formation of exo-diol [569]. This compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515]. It can be used as a selective cis-dihydroxylation agent of alkenes [568]. When the olefin contains aryl-substituted parts, e.g. 1,2-diphenylethylene or tetraphenyl-ethylene, in dichloromethane the cetyltrimethyl-ammonium permanganate cleavages the C=C double bond to the appropriate oxo-compound at room temperature. Nitro-group has similar effect, e.g. Ph-CH=CH-NO_2 gives PhCHO. From alkyl substituted aromatic alkenes, aldehydes are obtained with 1 equivalent of cetyltrimethyl-ammonium permanganate without the formation of carboxylic acid [570]. Trans-stilbene, however, leads to benzaldehyde. C – C bond cleavage has been observed for Ph-CH(OH)-CH(OH)-Ph as well [568]. Diphenylacetylene is converted to benzil [568].

Cetyltrimethylammonium permanganate oxidizes the lower primary and secondary alcohols to acids and ketones in a reaction autocatalysed by colloidal MnO_2 in the appropriate alcohol solvent at 20-40 °C. The kinetic parameters of these processes have been determined [571]. Primary and secondary benzylic alcohols provide the appropriate aldehydes and ketones in dichloro-methane at room temperature [298], but no reaction occurrs with allylic alcohols [298]. Oxidation of C_{6-8} aliphatic alcohols with cetyltri-methylammonium permanganate has led to the corresponding ketones (secondary alcohols) or carboxylic acids (primary alcohols) via the formation of colloidal manganese dioxide [572]. Kinetics of the benzyl alcohol oxidation has been determined [45]. The activation energy was found to be almost the same (49 kJ/mol) as that of the self-oxidation (51 kJ/mol) [45].

In dichloromethane solution primary, secondary and tertiary γ- and δ-hydroxy-olefins can be cyclised with 52-78% yield to γ- and δ-lactones containing one carbon less than the starting alcohol. Vitamin D_2 can be oxidized to the Windaus ketone in yields higher than with other commonly used oxidants like ozone or OsO_4 [573].

Long chain alkyl allyl thioethers have been hydroxylated in aqueous alkaline solutions with cetyltrimethlammonium permanganate into rac-1-S-alkylglycerols [574]. Cetyltrimethyl-ammonium permanganate can be used as a facile reagent for the preparation of 1(3)-acylglycerols through the hydroxylation of allyl esters of fatty acids in dichloromethane at room temperature [575]. It also oxidizes nitroalkanes into the corresponding oxo-compound with the same carbon number [576]. N-alkyl substituted styrylpyridinium bromides are oxidized in chloroform with cetyltrimethyl-ammonium permanganate with the formation of substituted benzaldehydes. The mechanism of the reaction is the same as it is in the case of the acid catalyzed $KMnO_4$ oxidation of these compounds in aqueous medium. From the substituent effect a transition state with low electron density at the olefinic carbon has been proposed [577]:



(81)

R = C_{3-16} alkyl, X = Me, C_{4-16} alkyl, o and p-Cl, OMe, Me_2N.

Dichloromethane solution of cetyltrimethyl-ammonium permanganate can be used to the oxidative opening of the D-ring of 16-dehydroprogesterone which is then followed by rearrangement even at room temperature [578].

Oxime and 2,4-dinitrophenylhydrazone protecting groups can be removed in CH_2Cl_2 with moderate-high yield at room temperature without the oxidation of the sensitive groups like imidazole function, neighbouring methylenes, primary alcohols, condensed aromatic CH-s, chain-end alkene groups, etc. The 2,4-dinitrophenyl-hydrazones react slower than the oximes and the chain-end alkenes can be converted into diols. [579]. The oxidative deoximination of several aldo- or ketoximes in dichloromethane proceeds through the formation of a cyclic intermediate as the rate determining step [580].

4.1.13. Cetylpyridinium permanganate

Potassium permanganate and $[C_{16}H_{35}NC_5H_5]Cl$ were reacted in aqueous solution and the precipitate formed was dried at room temperature to yield the title compound. The title compound decomposes violently at 80-90 °C. This compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515].

4.1.14. Methyltributylammonium permanganate

This salt is formed during the spectrophotometric determination of the permanganate anion obtained by extraction from aqueous solutions with the chloroform solution of benzyltributylammonium chloride [601]. It is precipitates in the reaction of concentrated aqueous solutions of $MeBu_3NBr$ and $KMnO_4$, respectively [581].

Methyltributylammonium permanganate oxidizes different kind of unsaturated alkene type hydrocarbons and butylvinyl ether in dichloromethane. The colloidal manganese dioxide formed absorbs the alkene and stabilizes it, which decreases the solvent polarity at the solvent interphase. The solubility of the colloid is therefore a function of the concentration and the identity of the alkene: when acidic compounds are present, the manganese dioxide is reduced further to manganese(III) [580]. Similar autocatalysis has also been detected in the oxidation of tetradecene with methyltributylammonium permanganate in methylene chloride. The colloidal manganese dioxide formed adsorbs the permanganate and catalyses the reaction. The activated species formed react with the alkene or thermally decompose [583]. The oxidation of 1-octene in dichloromethane is a first order reaction catalyzed by carboxylic acids. A correlation has been observed between the pK_a value of the acids and the logarithm of the catalytic rate constants. The probable pathway is the formation of permanganic acid as an active oxidant [584].

Unsaturated carboxylic acids, for example excess cinnamic acid reduces the methyltributyl-ammonium permanganate to Mn(III) in methylene chloride. The reaction is first order for both the cinnamic acid and the oxidant, electron donating substituents in o-and p-positions increase the activation enthalpy, while the electron withdrawing substituents have the opposite effect. An isokinetic temperature 587 K has been obtained. Deuterium substitution at the α- and β-positions had negligible effect on the activation parameters [585]. Oxidation of lower carboxylic acids as acetic acid in CH_2Cl_2 shows anomalous behaviour, the rate first decreases, remains stationary for a long time and finally increases suddenly until the permanganate is consumed [586]. The reaction has an autocatalytic character inhibited by one of the reactants whose concentration must be decreased under a certain limit that the autocatalysis should become evident [586]. The oxidation of formic acid in methylene chloride is strongly autocatalyzed by colloidal manganese dioxide. The reaction is first order with respect to the catalyst, and the adsorption of both the oxidizing and reducing agents follow the Langmuir isotherm. The reaction is dramatically inhibited by water and exhibits a primary kinetic isotope effect for the oxidation of DCOOH [581].

4.2. Tetraorganylphosphonium permanganates

The quaternary $[RPh_3P]MnO_4$ type phosphonium permanganates, (R = C_{1-7} alkyl, Bz, Cl_3C, p-FBz, 1,2-ethylenebis-) and $[(p\text{-}FC_6H_4)_3BzP]MnO_4$ or $[2,6\text{-}Cl_2Bz(p\text{-}ClPh)_3P]MnO_4$ have been prepared in CH_2Cl_2 from the appropriate halides and solid

$KMnO_4$, or in aqueous metathesis reaction of these compounds [6]. These compounds exist in their solutions as either ion pairs or aggregates promoted by high concentrations, low temperatures and low solvent polarity. Thermally they are not stable and their NMR characteristics have been discussed [6]. Tetraorganylphosphonium salts (R_4 = $MePh_3$, $MeBu_3$, $Me(n\text{-octyl})_3$) oxidize various substituted styrene derivatives such as substituted (E)-methyl cinnamates, as well as alkyl, halo and alkoxy substituted styrenes in different solvents. In polar organic solvents such as in acetone no cationic effect on the reaction rates has been experienced. In less polar solvents, such as in methylene chloride or toluene, the reaction rates depend on the identity of the quaternary phosphonium ion. It thus appears as if the reacting species may exist as solvent separated ion pairs in polar solvents, and as intimate ion pairs in nonpolar solvents. The reaction rates are sensitive to substituent effects. The mechanism can be visualized as a proceeding continuum of transition states that can vary from the electron rich to the electron poor depending on the capacity of the substrate structures to accommodate either negative or positive charges [6]. All of the phosphonium permanganates dissolve in CH_2Cl_2 and $CHCl_3$, although the $BzPh_3$ and 2,6-Cl_2Bz(p-ClPh)$_3$P-salts are slightly soluble. The compounds do not dissolve in CCl_4, the 2,6-Cl_2Bz(p-ClPh)3P-salt does not dissolve in H_2O and toluene. The $BzPh_3P$ and Cl_3CPh_3P salts do not dissolve in toluene, the others are slightly soluble in toluene and H_2O [6] (Table 4).

4.2.1. Tetraphenylphosphonium permanganate

When tetraphenylphosphonium chloride and the warm solution of $KMnO_4$ are mixed tetraphenyl-phosphonium permanganate forms as a slightly soluble precipitate [587]. Raman and resonance Raman spectra of Ph_4PMnO_4 have been measured and complete assignation of the normal stretchings and the combination bands have been performed. The X_{11} anharmonicity constant for the ν_s Mn-O band has also been determined [274].

4.2.2. Triphenylmethylphosphonium permanganate

Potassium permanganate and $[Ph_3MeP]Cl$ was reacted in aqueous solution and the precipitate formed was dried at room temperature. The analogous bromide compounds gave 86% yield in cold water. The compound can be stored in cold and in dark for weeks. Decomposition with explosion occurs over 70 °C [588]. It decomposes violently at 80-90 °C. Triphenylmethyl-phosphonium permanganate is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triaadamantane, respectively [515]. It transforms trans-decaline into trans-9-decalol, trans-1-decalon and trans-2-decalon [515]. Cholesten and

Table 4. Synthesis conditions and decomposition temperatures of quaternary phosphonium permanganates [6].

Compound	Method	Yield, %	Dec. temp., °C
$MePh_3P$	aq	91	102
$EtPh_3P$	aq	97	89
$nPrPh_3P$	aq	98	94
$nBuPh_3P$	aq	98	70
$nPentPh_3P$	aq	92	68
$nHexPh_3$	aq	91	76
$nHeptPh_3P$	aq	69	66
$BzPh_3P$	aq	85	56
Cl_3CPh_3P	CH_2Cl_2	83	86
2,6-Cl_2Bz(p-ClPh)$_3$P	CH_2Cl_2	87	64

cholesterin acetate do not react, but cholesten-3-on produces the appropriate cis-diol in 46% yield [588]. Similarly, unsaturated ketones and olefins can be cis-dihydroxylated in CH_2Cl_2 even at -70 °C. Cyclohexene provides diol instead of the expected adipic acid obtained with $KMnO_4$ under phase transfer conditions [588]. This compound has two crystalline modifications, the α-form is rhombic (a = 12.626, b = 14.320, c = 19.806 Å, Space group is Pbc_2a or Pbcm, Z = 8, D_c = 1.420), the β form is monoclinic, $P2_1c$, Z = 4, D_c = 1.408, a = 10.637, b = 13.424, c = 15.036 Å, β = 119.44 [6].

4.2.3. Heptyltriphenylphosphonium permanganate

It forms rhombic purple crystals (a = 13.122, b = 10.801, c = 17.154 Å, $P2_12_12_1$, Z = 4, D_c = 1.313), soluble in CH_2Cl_2, $CHCl_3$, slightly soluble in H_2O and toluene, and insoluble in CCl_4 [6]. The cation has propeller like geometry around the P-atom. The cations are surrounded by four anions. One of the permanganate ions is distinctly closer to the phosphorus atom as compared to the other three ones. This permanganate ion is "nestled" under the n-heptyl chain. Some penetration effect is responsible for the solubility properties of this compound. It exists in solvents as ion pairs or as ion quadruples and different conformation of the ions are formed during crystallization from different solvents [6]. When the solution is rich in a non-polar solvent, e.g. in CCl_4, the quadruple species is dominating, and the α form will crystallize out. If the solvent mixture is rich in polar solvent, e.g. in CH_2Cl_2, the single ion pairs will be the dominant species and the β form will crystallize out [6] (Figure 15).

4.2.4. Triphenylbenzylphosphonium permanganate

The reaction of the appropriate bromide and $KMnO_4$ in a two-phase aqueous-benzene/toluene system in the presence of NaCl as a catalyst, leads to the purple benzene/toluene solution of the title compound which can oxidise olefins. It also oxidizes polyethylene and hydroxyl terminated polybutadiene at room temperature with the formation of C=O and C-O-C functions, mainly acids. Ion pair formations have been detected by NMR in $CDCl_3$ and with UV spectroscopy in benzene/toluene [589].

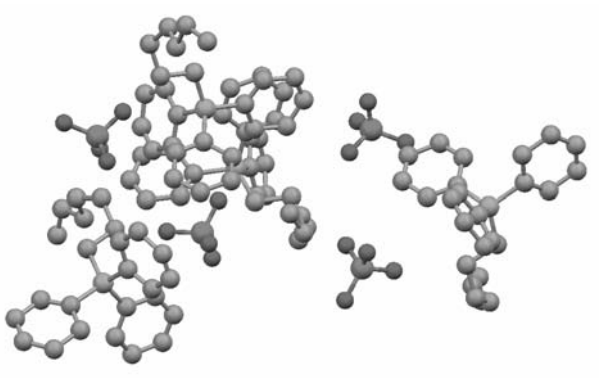


Figure 15. Molecular structure of heptyltriphenyl-phosphonium permanganate.

4.2.5. 1,2-bis(triphenylphosphonium)ethane permanganate

To prepare the title compound potassium permanganate and $[Ph_3PCH_2CH_2PPh_3]Cl_2$ were reacted in aqueous solution and the precipitate formed was dried at room temperature. It decomposes violently at 80-90 °C. This compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515], and can be used for the spectrophotometric determination of permanganate anion after its extraction from aqueous solutions with the chloroform solution of the free diphosphine [590].

4.2.6. 1,3-bis(triphenylphosphonium)propane permanganate

This compound forms an ion-pair associate at pH = 6 with naphthalene and can be extracted to chloroform. The formed compound can be analyzed spectrophotometrically at 548 nm [591].

4.3. Tetraorganylarsonium permanganates

4.3.1. Tetraphenylarsonium permanganate

When tetraphenylarsonium chloride and the warm solution of $KMnO_4$ were mixed, tetraphenyl-arsonium permanganate was formed as a slightly soluble purple precipitate [587], which was then dried at room temperature. The compound decomposes violently at 120-130 °C. This

compound is active in the oxidative hydroxylation of 1 or 3 and 4 bridgehead positions of diadamantane and triadamantane, respectively [515]. Raman and resonance Raman spectra of $[Ph_4As]MnO_4$ have been measured, and complete assignation of the normal modes and the combination bands have been performed. The X_{11} anharmonicity constant for the ν_s Mn-O band has also been determined [587].

4.4. Iminium permanganates

4.4.1. Bis(triphenylphosphine)iminium permanganate

The bis(triphenylphosphine)iminium permanganate is non-hygroscopic and soluble in a number of dipolar aprotic organic solvents, thus it seems to be a real alternative of the tetraalkylammonium permanganate salts [592]. Since the [PNP]Cl (PNP = bis(triphenylphosphine)iminium cation) is well soluble in water (ca. 100 g/L at 80 °C and 7.1 g/L at 25 °C), its warm solution reacts with $KMnO_4$ with the formation of a hardly water-soluble permanganate salt [592]. It melts at 155 °C with violent decomposition. It is very well soluble in acetone, acetonitrile, DMSO, DMF, benzyl cyanide, nitromethane, nitrobenzene, CH_2Cl_2 and sym-tetrachloroethane.

4.5. Organic oxonium permanganates

4.5.1. Triphenylpyrilium permanganate

On reacting triphenylpyrilium chloride, $[Ph_3C_5H_2O]Cl$ in 2% aq. HCl with 1% aqueous solution of $KMnO_4$, the appropriate permanganate salt is precipitated [30].

4.6. Organic sulfonium permanganates

4.6.1. Triphenylsulfonium permanganate

Triphenylsulfonium permanganate is formed in the extraction of permanganate ion with triphenylsulfonium cation to chloroform. This compound can be used for the determination of manganese (after its oxidation to permanganate) via spectrophotometry at 548 nm [176]. This compound can also be prepared by flow-injection extraction of Ph_3SCl and $KMnO_4$ with $CHCl_3$ as solvent. The $[Ph_3S]MnO_4$ is an ion-associate [593].

4.7. Other permanganate-salts of organic cations

1-Phenyl-2-(1-piperidinyl)ethyl-4-nitrobenzoate, 2-(1-piperidinyl)-1-(4-pyridyl)ethyl-4-nitrobenzoate-N-oxid, and 2-diethylamino-1-(4-pyridyl)-ethyl-4-nitrobenzoate-N-oxide easily form permanganate precipitates. The solubility products of these compounds have been determined. All of these permanganates transform to manganese dioxide during storage at room temperature [594]. The 3,7-diamino-2,8-dimetyl-5-phenyl-phenazinium cation (safranine) also forms permanganate, which can be isolated and analyzed [595]. The complex has two new absorption bands in its UV spectrum, at 241 and 540 nm [595]. Similar compound is obtained from $KMnO_4$ and Neutral Red (3-amino-6-dimethylamino-2-methylphenazine [596].

Poly(vinyl)ammonium permanganate resins have been prepared and used for the oxidation of alcohols to carbonyl compounds in cyclohexane. The crosslinking has an influence on the oxidation reaction, 5% crosslinking (DVB) is the optimal. Since the catalytic resin is insoluble in the medium, thus it is a heterogeneous reagent. The IR spectrum of the resin formed has an IR band at 900 cm^{-1}. Primary alcohols are transformed into aldehydes, and it is an easy way to prepare benzaldehyde, n-butanal or 1-pentanal [27].

The permanganate-exchanged forms of anionites with Me_3N^+-group and chelate-forming $-(R)N(CH_2COOH)_2$ groups have been prepared, and their densities have been measured in swelled and dried form [597]. Our measurements [68], however, indicated that some of these oxidable groups have reacted during the functionalization of the ion-exchangers, and this reaction can proceed during storage of the water-containing swelled resins. The oxidation ability of these polymers consists the sum of the oxidation ability of the permanganate and the formed manganese-dioxide in acidic environment. Thus, the results of the density measurements are doubtful to estimate the amount of the exchanged permanganate ion. Since the pyridine ring is more stable to oxidation as the Me-N functionalized organic groups, co-polymers of vinyl-pyridine with divinylbenzene or poly(vinyl alcohol) have been functionalized with permanganate ion. The free-base polymer has been mixed with sulphuric acid solution of the

potassium permanganate. The formed poly(4-vinylpyridinium)permanganate as a solid phase heterogeneous oxidant has been used for the oxidation of primary and secondary alcohols to obtain aldehydes and ketones, respectively, in 80-100% yield. When the hydroxyl group is attached directly to a ring, e.g. in the case of menthol, cyclohexanol and cholesterol, the oxidation could not be performed with the crosslinked heterogeneous vinylpyridine type permanganate resin. The advantage of the polymer supported permanganate reactants are that the oxidation stops at the oxo-compound stage and there is no carboxylic acid formation. The yield and the reactivity is solvent dependent, the best solvent is the cyclohexane. The spent resin can be regenerated with sulfuric acid solution of ferrous ammonium sulphate [28].

Hydroxide forms of the trimethylammonium-based styrene-divinyl-benzene ion exchangers can be converted to permanganate form with $KMnO_4$ at 40 °C with 1.5 g/60 ml $KMnO_4$ solution. Drying at 100 °C leads to a ion-exchanger with permanganate functionality which has been used to detect hydrogen-peroxide [35]. The anion exchange ability on the 4 and 8% divinylbenzene containing styrene resins with trimethyl-ammonium type functional groups have been studied and the diffusion coefficient values for the permanganate ions have also been determined. The kinetics of the ion-exchange between OH and permanganate ions have been determined [598].

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