

Anionic polyurethane dispersions are more stable than their cationic counterparts toward electrolytes (particularly in the presence of sulfonate groups), and hence have a better pigment tolerance, and they have the additional advantage that they can be combined with commercial polymer dispersions and additives. Cationic products exhibit particularly good adhesion, e.g. even to glass.

There are possibilities for the use of crosslinked redispersible polyurethane ionomer suspensions in the production of microporous sheet materials (synthetic leather).

Our own work in this field has been supported by a number of colleagues from the applications, analytical, engineering, and technological departments. Special contributions were made by Dr. M. Hoffmann (Polymer Analysis) and Dr. Erwin Müller, who directed this development. We are grateful to all those mentioned. Special thanks are due to the former head of the Scientific Laboratories, Prof. Dr. O. Bayer, who initiated this work in 1962 and furthered its progress by numerous discussions.

Received: September 23, 1969 [A 737 IE]

German version: Angew. Chem. 82, 53 (1970)

Translated by Express Translation Service, London

Reactions with Addition Compounds Containing Activated Formic Acid

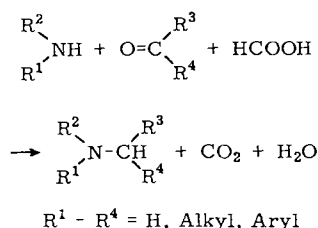
By K. Wagner[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

Addition compounds of formic acid with tertiary organic bases in ratios higher than that required for salt formation (3 : 1 and 2 : 1 adducts) contain formic acid in a highly activated form. In particular, the 3 : 1 adducts of formic acid with trimethylamine and triethylamine are liquid reducing agents that are convenient to handle and are suitable for use in many selective reductions. These addition compounds have a surprisingly strong reducing action on sulfur dioxide, which is rapidly converted, even at low concentrations, into crystalline rhombic sulfur. Sulfones and polysulfones can be prepared in good yields by three-component reactions from activated formic acid, sulfur dioxide, and polarized vinyl compounds.

1. Introduction

In the Leuckart-Wallach reaction, formic acid acts as a strong reducing agent in the presence of carbonyl compounds.



This method of aminoalkylation was greatly extended by Wietzel^[1] and Clarke^[2] with the use of formaldehyde as the carbonyl component in the reduction. The reaction is widely used as an elegant method of permethylation.

[*] Dr. K. Wagner
Wissenschaftliches Hauptlaboratorium
der Farbenfabriken Bayer
509 Leverkusen-Bayerwerk (Germany)

[1] R. Wietzel, German Pat. — 12 q I. 19. 30(5)(1930), I.G. Farben.

[2] H. T. Clarke, J. Amer. chem. Soc. 55, 4571 (1933).

In studies on cleavage reactions of hexamethylenetetramine with acetic anhydride^[3] and phosgene^[4], anhydrous formic acid^[5] was also used. Liquid, distillable cleavage products, whose compositions were unknown at first, but which possessed reducing properties, were isolated. The reducing power of these compounds was much greater than the well-known reducing action of formic acid.

2. Methods for the Preparation of Addition Compounds Containing Activated Formic Acid and their Thermal Behavior

2.1. Preparation and Constitution of the Addition Compounds

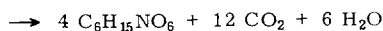
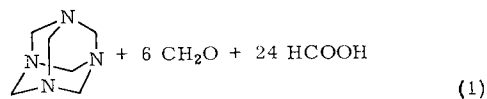
The reaction of concentrated formic acid with hexamethylenetetramine yields a liquid, distillable reaction product having the analytical composition C₆H₁₅NO₆

[3] H. Holtschmidt, unpublished.

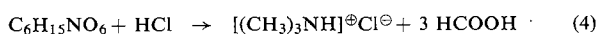
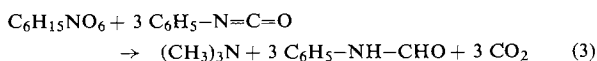
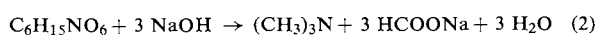
[4] H. Holtschmidt and K. Wagner, DBP 1132118 (Feb. 1, 1961), Farbenfabriken Bayer.

[5] H. Holtschmidt and K. Wagner, unpublished.

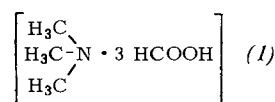
(b.p. 87 °C/14 torr), together with small quantities of dimethylformamide and methylformamide. When this reaction is followed with the aid of gas analysis, it is found that the compound $C_6H_{15}NO_6$ can be obtained in practically quantitative yield and without by-products only if formaldehyde is also present, the proportions being at least 6 moles of formaldehyde and 24 moles of formic acid per mole of hexamethylenetetramine.



The CO_2 balance found under these conditions clearly points to a permethylation corresponding to the Leuckart-Wallach reaction. The unknown compound should therefore contain bound trimethylamine and this is in fact the case as is shown by equations (2) to (4).

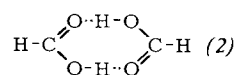


The liquid addition compound $\text{C}_6\text{H}_{15}\text{NO}_6$ [6] has the constitution (1). An identical adduct can be obtained



in quantitative yield by passing one mole of gaseous trimethylamine into three moles of anhydrous formic acid.

The IR spectrum of (1) contains characteristic bands for both the carboxyl and the carboxylate groups. The very pronounced broadening of the OH bands indicates that extremely strong hydrogen bonds must be present. This agrees with the molecular structure found for formic acid, for which an eight-membered cyclic chelate (2) [7,8] with hydrogen bonds has been detected both in the liquid phase and in the vapor within a certain temperature range.



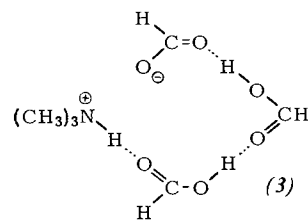
Comparison of the ^1H -NMR spectra of the addition product and of the corresponding 1 : 1 salt of trimethylamine and formic acid shows that the electron density in the position of the alkyl protons is lower in the addition compound than in the salt.

[6] K. Wagner and H. Holtschmidt, German Pat. 1233 398 (March 14, 1964), Farbenfabriken Bayer

[7] J. Karle and L. O. Brockway, J. Amer. chem. Soc. 66, 574 (1944).

[8] R. Hofstadter, J. chem. Physics 6, 540 (1938).

On the basis of IR-spectroscopic observations, elementary analysis, and osmotic molecular weight determinations in halogenated hydrocarbons such as chloroform, the constitution (3) has been proposed for the addition product of three moles of formic acid with one mole of trimethylamine [9].



2.2. Thermal Properties of the 3 : 1 and 2 : 1 Addition Compounds

The formation of these adducts is not restricted to trimethylamine as the organic base. Many tertiary aliphatic, cycloaliphatic, and heterocyclic amines react with formic acid beyond the salt formation stage, often with formation of liquid 1 : 2 or 1 : 3 adducts. The 1 : 3 adducts are the more stable, and are also the more interesting from the chemical point of view. They are stable up to about 140 °C, and can be distilled under reduced pressure (see Table 1); they decompose above 140 °C in the absence of catalysts [eq. (5)] or below 140 °C in the presence of cuprous chloride and noble metals [eq. (6)] [10].

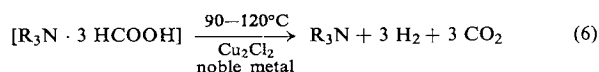
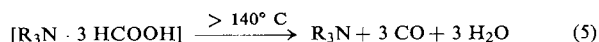


Table 1. Distillable adducts of formic acid and tertiary bases.

	B.p. (°C/14 torr)
$(\text{H}_3\text{C})_3\text{N} + 3 \text{ HCOOH}$	87
$(\text{C}_2\text{H}_5)_3\text{N} + 3 \text{ HCOOH}$	94
$(\text{C}_4\text{H}_9)_3\text{N} + 3 \text{ HCOOH}$	102
$(\text{C}_2\text{H}_5)_3\text{N} + 2 \text{ HCOOH}$	84

The addition compounds with *N*-methylpiperidine, *N*-methylmorpholine, and *N,N*-dimethylbenzylamine readily decompose in accordance with eq. (5) on distillation. Adducts of imidazole and substituted imidazoles and of 1,4-diazabicyclo[2.2.2]octane cannot be distilled.

3. Reductions with Addition Compounds containing Activated Formic Acid

The study of the decomposition of the adducts containing activated formic acid by traces of Cu_2Cl_2 and palladium in accordance with eq. (6) led to two reduction methods based on different reactions.

[9] M. Pestemer, N. Joop, and K. Wagner, unpublished.

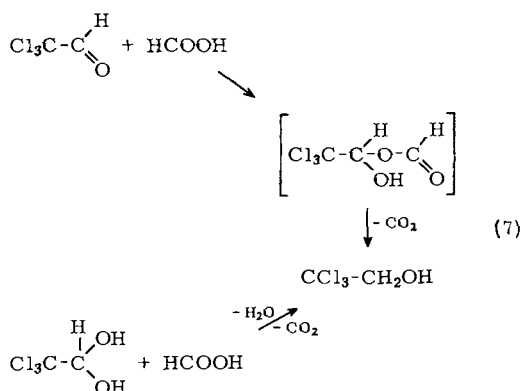
[10] K. Wagner, unpublished.

One of these reductions (cf. Section 3.2) is a true hydrogenation, in which the actual reducing agent is hydrogen formed from the adducts in accordance with eq (6) and then catalytically activated by copper(I) chloride and noble metals. The other method, in which no free hydrogen occurs (see Section 3.1), allows the selective reduction of α -halogenated carbonyl compounds in good yields.

3.1. Selective Reduction of Polarized Carbonyl Compounds with Activated Formic Acid

The selective reduction of α -halogeno aldehydes and ketones to the alcohols does not proceed by hydrogenation following reaction (6); there is consequently no need to add copper(I) chloride, noble metals, or hydrogenation catalysts such as Raney nickel. On the contrary, these additives greatly reduce the yield, since they make the reduction less selective, and reductive dehalogenation occurs.

A simple laboratory method will be described for the selective reduction of chloral hydrate to trichloroethanol [11] [*].



The driving force for this reaction is probably the tendency of formic acid to add to polarized double bonds; in the case of carbonyl compounds this yields hemiacylals of aldehydes, which are then decarboxylated by nucleophilic attack by the tertiary base.

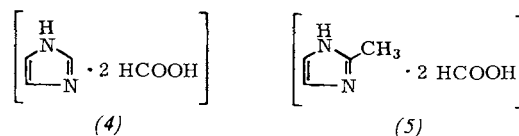
Application of this reduction to chloral, chloral hydrate, or chloral-ethanol adduct yields trichloroethanol in yields of more than 87%. This reduction is simpler and much faster than the classical method for the preparation of trichloroethanol, *i.e.* the *Meerwein-Ponndorf* reduction of anhydrous chloral.

The preferred reducing agents are the liquid 3 : 1 adducts of formic acid with trimethylamine, triethylamine, dimethylethylamine, or diethylmethylamine, since these can be purified by distillation. The compound to be reduced is largely dissolved in the liquid addition compound, and fresh formic acid is continuously added to the system at a rate corresponding to the rate of liberation of CO_2 at 95 to 100 °C, so that the 3 : 1 adduct is still present in the reaction mixture at the end of the reaction.

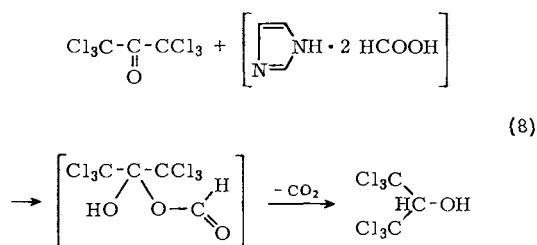
[11] K. Wagner, US-Pat. 3397963 (April 1, 1965), Farbenfabriken Bayer.

[*] The abbreviation HCOOH_a is used for $[(\text{CH}_3)_3\text{N} \cdot 3 \text{HCOOH}]$ and $[(\text{C}_2\text{H}_5)_3\text{N} \cdot 3 \text{HCOOH}]$.

Even unstable ketones such as hexachloroacetone and fluorinated ketones can be reduced to the secondary alcohols in good yields and under mild conditions by activation of formic acid with imidazole or 2-methylimidazole. The resulting adducts (4) and (5) are remarkably fluid, and have a viscosity of about 34 cp at room temperature.



Hexachloro-2-propanol has only recently been described [12]. It was prepared, not by reduction of hexachloroacetone, but by reaction of anhydrous chloral with alkali metal trichloroacetates; the yields are low (35–36%) and the purity of the compound (m.p. 85–86 °C) is only moderate. The selective reduction in accordance with eq. (8) [13], on the other hand, can be carried out very simply.



Hexachloroacetone is added dropwise over about 2 hours to the imidazole-formic acid adduct at 55 to 65 °C. Concentrated formic acid is added continuously at a rate of about 2.1 g of formic acid per liter of carbon dioxide liberated. After the reduction the water-soluble imidazole adduct is removed by extraction with water, and hexachloro-2-propanol crystallizes out immediately (m.p. 89 °C); the yield is about 89%.

3.2. Hydrogenations by Catalytic Decomposition of the Addition Compounds

Under the influence of catalysts such as platinum, rhodium, and iridium, formic acid slowly decomposes even at room temperature into hydrogen and carbon dioxide [14]. This decomposition of formic acid can be greatly accelerated in the addition compounds by the use of copper(I) chloride and palladium on active charcoal as the catalyst.

The hydrogen formed in this case is activated by the noble metal catalyst, so that many aldehydes, ketones, and functional groups such as $-\text{NO}_2$, $-\text{NO}$, $-\text{NHOH}$, $-\text{N}(\rightarrow\text{O})=\text{N}-$, $-\text{N}=\text{N}-$, $-\text{NH}-\text{NH}-$, $-\text{NH}-\text{NH}_2$, $=\text{NOH}$, $=\text{NH}$, and $=\text{N}-\text{R}$ can be hydrogenated in good yields, or $\text{>N}-\text{N}<$ bonds can be reductively broken. This reduction method practically corre-

[12] R. Haszeldine, R. Farmer, and H. Goldwhite, Brit. Pat. 1019891 (Feb. 9, 1966); Chem. Abstr. 64, 12549 (1966).

[13] K. Wagner, German Pat. Appl. P 1793243.3 (April 21, 1968), Farbenfabriken Bayer.

[14] I. E. Adadurov, Ž. fiz. Chim. 2, 142 (1931); Chem. Zbl. 1933, I 1240.

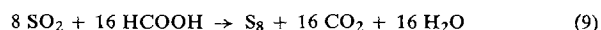
sponds to the conventional hydrogenation methods, but proceeds at atmospheric pressure. It is recommended in the laboratory for the reduction of sparingly soluble compounds or for cases where it is desirable to obtain the *N*- or *O*-formylated derivatives of the hydrogenation products in a single operation. Nitriles, dinitriles, and polyacrylonitrile cannot be hydrogenated, since addition of the activated formic acid to the nitrile group predominates over hydrogenation.

4. Reactions of Addition Compounds Containing Activated Formic Acid with Sulfur Dioxide

4.1. Reduction of Sulfur Dioxide to Crystalline Sulfur

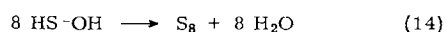
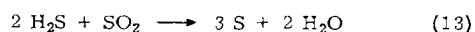
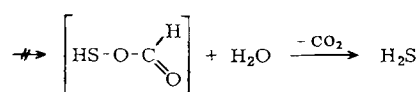
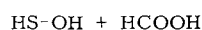
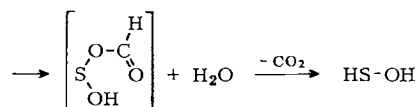
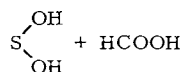
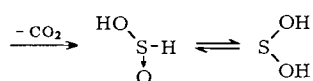
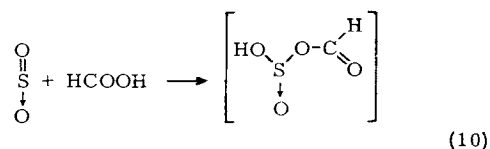
Probably the most striking example of the high activity of the formic acid in the addition compounds is the fast and practically quantitative reduction of sulfur dioxide to crystalline rhombic sulfur^[15]. Sulfur dioxide itself is well known to be a relatively strong reducing agent; however, it behaves as a strong oxidizing agent toward these addition compounds. Since even very dilute sulfur dioxide can be readily reduced and the resulting crystalline sulfur can always be filtered out extremely easily, this reaction has been investigated in connection with the cleaning of industrial waste gases.

Overall reaction:



Under normal conditions, 44.8 liters of CO_2 are liberated per g-atom of sulfur.

Reaction steps:



It can be concluded from the investigation of the reaction by gas analysis that sulfur dioxide is not reduced to hydrogen sulfide, and therefore that the sulfur formation cannot be explained by the well known reduction in accordance with eq. (13). When the reduction is carried out at various temperatures and with simultaneous checking of the CO_2 balance, it is found that the reduction leads first in accordance with eq. (10) to sulfoxylic acid (H_2SO_2), which it in turn reduced to the very unstable hydroxysulfane (H_2SO) [eq. (11)]. The hydroxysulfane is so unstable that instead of undergoing further reduction in accordance with eq. (12) it decomposes readily, as a sulfur homolog of hydrogen peroxide, into water and probably free-radical sulfur, which achieves stability by formation of S_8 and is obtained as rhombic sulfur eq. (14).

4.2. Interception of Short-Lived Intermediates of the Reduction of Sulfur Dioxide by Three-Component Reactions

The intermediates involved in the reduction, such as sulfoxylic acid and hydroxysulfane, can be used for a simple preparation of organic sulfinic acids, sulfenic acids, and sulfoxides, and particularly of monosulfones and polysulfones (see Table 2)^[16]. These preparations can be carried out very readily and in excellent yields by dissolving vinyl compounds in the adducts containing activated formic acid before the introduction of sulfur dioxide, adding small quantities of polymerization inhibitors, and introducing SO_2 into the reaction mixture at 90°C .

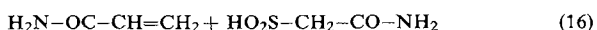
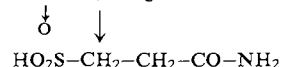
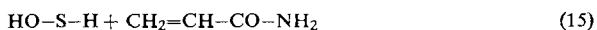


Table 2. Monosulfones prepared by three-component reactions.

Vinyl compound	Monosulfone	M. p. ($^\circ\text{C}$)
$\text{CH}_2=\text{CH}-\text{COOH}$	$(\text{HOOC}-\text{CH}_2-\text{CH}_2)_2\text{SO}_2$	220
$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$	$(\text{H}_2\text{N}-\text{OC}-\text{CH}_2-\text{CH}_2)_2\text{SO}_2$	228
$\text{CH}_2=\text{C}-\text{CO}-\text{NH}_2$ CH_3	$(\text{H}_2\text{N}-\text{OC}-\text{CH}(\text{CH}_3)-\text{CH}_2)_2\text{SO}_2$	178
$\text{CH}_2=\text{CH}-\text{COOC}_2\text{H}_5$	$(\text{C}_2\text{H}_5\text{OOC}-\text{CH}_2)_2\text{SO}_2$	86
$\text{CH}_2=\text{CH}-\text{CN}$	$(\text{NC}-\text{CH}_2-\text{CH}_2)_2\text{SO}_2$	86–87
$\text{CH}_2=\text{CH}-\text{SO}_2-\text{CH}_3$	$(\text{CH}_3-\text{SO}_2-\text{CH}_2)_2\text{SO}_2$	268

The sulfones listed can in most cases be very readily isolated, whereas the primary products, *i.e.* the organic sulfuric acids, can be obtained only with difficulty because of their instability.

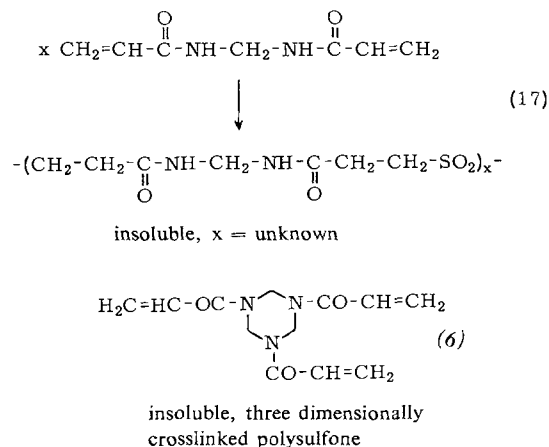
4.3. Interception of Short-Lived Intermediates of the Reduction of Sulfur Dioxide for the Synthesis of High Molecular Weight Polysulfones

As is shown by equations (15) and (16), sulfoxylic acid (H_2SO_2) reacts as a bifunctional compound. It reacts

[15] K. Wagner, German Pat. Appl. P 1442692.7 (April 4, 1964); US-Pat. 3397963 (April 1, 1965).

[16] K. Wagner, DBP 1222048 (Dec. 8, 1964), Farbenfabriken Bayer.

with suitable vinyl compounds to form sulfinic acids, and if the reaction mixture still contains activated vinyl compounds, sulfones are very rapidly formed. High molecular weight polysulfones can thus be readily prepared by polyaddition reactions with sulfoxylic acid if suitable divinyl compounds are used as acceptors.



With introduction of sulfur dioxide at a suitable rate during the preparation of polysulfones, water-soluble polysulfones with sulfinic acid end groups can also be prepared by this method.

The results obtained in the reduction of sulfur dioxide have led to the investigation of the action of activated formic acid

on nitrous gases, dinitrogen trioxide, and nitrous acid. It is difficult to isolate intermediates of the reduction. The utmost care is necessary in the treatment of even small reaction mixtures from the reduction of potassium and sodium nitrites, since violent decompositions have sometimes been observed.

5. Addition Compounds Containing Activated Formic Acid as Formylating Agents and as Solvents

Many of the liquid adducts, particularly those of one mole of trimethylamine or triethylamine with three moles of formic acid can be used as formylating agents for *N*- and *O*-formylations, since the addition compounds are generally good solvents for high molecular weight polyols and polyamines, and the formylations are accelerated in these solvents. Reductive degradations of natural polymers such as cellulose and polypeptides proceed particularly readily.

I am grateful to Professor Dr. Holtschmidt for the use of his unpublished experimental results on the hexamethylenetetramine-formic acid cleavage reaction, to Professor Dr. Pestemer for spectroscopic studies, to Dr. Joop for NMR measurements, to Dr. Fauss for osmotic molecular weight determinations, and to Dr. Klauke for the preparation of partly fluorinated ketones.

Received: May 30, 1969

[A 736 IE]

German version: Angew. Chem. 82, 73 (1969)

Translated by Express Translation Service, London

Chlorosulfonylated Carbonic Acid Derivatives

By G. Zumach and E. Kühle^[*]

Dedicated to Professor K. Hansen on the occasion of his 60th birthday

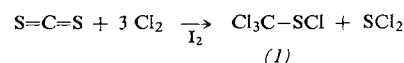
The present article deals first with the synthesis of chlorocarbonylsulfonyl chloride and its imino analogs. The chemical behavior of these bifunctional compounds is illustrated for selected examples. Special attention is given to the syntheses of five-membered heterocycles containing sulfur, oxygen, and/or nitrogen.

1. Introduction

The present article deals with compounds that can be regarded both as carbonic acid derivatives and as sulfinic acid derivatives. Two compounds of this series, *i.e.* trichloromethanesulfonyl chloride (1) and *N*-dichloromethylenesulfonylamide chloride (2), have been known for a long time.

Trichloromethanesulfonyl chloride (1) consists formally of an orthocarbonyl trichloride group and a sulfonyl chloride

group. It was first synthesized more than 100 years ago by Rathke^[1] by chlorination of carbon disulfide in the presence of iodine, and is still produced on the large scale by the same method.



In 1924, Kaufmann and Liepe^[2] obtained "thiocyanogen trichloride" by chlorination of thiocyanogen; this product was later found to be (2)^[3].

[1] B. Rathke, Ber. dtsch. chem. Ges. 3, 858 (1870).

[2] H. P. Kaufmann and J. Liepe, Ber. dtsch. chem. Ges. 57, 923 (1924).

[3] E. Kühle, B. Anders, and G. Zumach, Angew. Chem. 79, 663 1967; Angew. Chem. internat. Edit. 6, 649 (1969).

[*] Dr. G. Zumach and Dr. E. Kühle
Wissenschaftliches Hauptlaboratorium
der Farbenfabriken Bayer AG
509 Leverkusen-Bayerwerk (Germany)