system was back-titrated to avoid decomposition during titrations. Titrations were done by mass, rather than volume, for increased speed and precision. A closed gas manometer system containing sample was very cautiously warmed until gas evolution began (about 3° for $HMnO_4$, about 18° for the dihydrate). The system was then held at a temperature just adequate to maintain reaction until O_2 evolution ceased. Despite an occasional explosion a number of successful decompositions were obtained in this way to yield the MnO_2 and O_2 values of Table I.

$HMnO_4$ proved to be a violent oxidant. Every organic material tried (alcohols, alkanes, arylhydrocarbons, greases, cycloalkanes, alkylamines, amides, ethers, etc.) exploded into flame on contact, except CCl_4, $CHCl_3$, and CH_2Cl_2. The latter was not as inert as the other two and reacted completely over a period of 30 min. $HMnO_4$ is quite hygroscopic, very soluble in water, slightly soluble in perfluorodecalin and CCl_3CF_3, and insoluble in CCl_4 or $CHCl_3$.

At −75° less than 1% decomposition was observed after 9 days. Above 3°, however, it often decomposed violently, albeit not as explosively as might be feared. Often the stopper would be blown into the air, but the flask remained intact. On the few occasions where violent explosions occurred, it is suspected that traces of organic matter had been inadvertently introduced.

The reactions of the dihydrate were very similar, but less violent. At room temperature the dihydrate was stable for 10–30 min. In fact, when cold crystals of $HMnO_4$ were exposed to air, enough water condensed on them to delay decomposition considerably.

In many ways $HMnO_4$ resembles $HClO_4$.[7] Thus, low-pressure distillation yields both the dihydrate and the anhydrous forms, in that order. The dihydrate is more stable, and a less vigorous oxidant, than the anhydrous form. For $HClO_4$ a distinct fraction, shown to be $H_3O^+ClO_4^-$, can be obtained during distillation. For permanganic acid, on the other hand, no monohydrate was observed. In fact, the nearly equivalent molar yields of $HMnO_4$ and $HMnO_4 \cdot 2H_2O$ suggest that the system loses water until its composition approximates $HMnO_4 \cdot H_2O$, then disproportionates to yield $HMnO_4$ and $HMnO_4 \cdot 2H_2O$. This is supported by the visual observation that a violet color appeared very suddenly on the −75° trap, just at the point where all of the excess seemed to have been removed. This corresponds to the known[7] partial disproportionation of $H_3O^+ClO_4^-$ to $HClO_4$ and $HClO_4 \cdot 2H_2O$ with the exception that $HMnO_4 \cdot H_2O$ does not appear to be stable enough to be isolated. This may simply reflect a lessened tendency for $HMnO_4 \cdot H_2O$ to form $H_3O^+MnO_4^-$ and for $HMnO_4 \cdot 2H_2O$ to form $H_3O^+MnO_4^- \cdot H_2O$ or $H_5O_2^+MnO_4^-$, analogous to the known[7,8] oxonium perchlorates. This might explain why $HMnO_4$ and $HMnO_4 \cdot 2H_2O$ differ less in their chemical and physical properties than the corresponding perchloric acids.

While much intriguing chemistry remains to be done with this compound, it is now at least possible to produce and store it. Its solubility, albeit slight, in such low freezing point, nonaqueous, unreactive solvents as perfluorodecalin and the Freons raises the possibility of synthesis of yet another "impossible" compound, manganic acid, by controlled reduction of $HMnO_4$. Attempts in this direction are currently under way. Attempts are also being made to utilize it for the vapor fixation of tissues for comparison with OsO_4 and $KMnO_4$, although it does not seem adaptable for general use in tissue fixation.

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Received July 7, 1969

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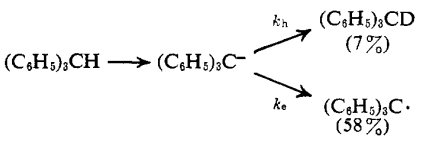
Electron Transfer as an Efficient Carbanion Trapping Reaction

Sir:

We wish to report some preliminary results in an investigation of the efficiency of electron transfer as a device for trapping carbanions.[1] Russell has shown that a variety of carbanions will transfer electrons to nitrobenzene.[2] Triphenylmethide ion, which must have been present at lower concentration than most of the donors in Russell's study,[3] nevertheless showed evidence of electron transfer. This indicated a relatively facile electron transfer and suggested triphenylmethane as substrate for study of base-catalyzed hydrogen–deuterium exchange in the presence and absence of nitroaromatics.

Triphenylmethane undergoes exchange of hydrogen for deuterium (mass spectral analysis) at 50° in *t*-butyl alcohol-O-*d* catalyzed by 0.471 *N* potassium *t*-butoxide with a pseudo-first-order rate constant of $(0.236 \pm 0.008) \times 10^{-5}$ sec^{-1}. With nitrobenzene added to the reaction mixture at concentrations between 0.2 and 0.6 *M*, triphenylmethane was lost at a rate very nearly equal to the rate of exchange in the absence of nitrobenzene. In a typical experiment, a 0.059 *M* solution of triphenylmethane was sealed in an evacuated ampoule with 0.48 *N* potassium *t*-butoxide, 0.25 *M* nitrobenzene, and 0.018 *M* hexadecane in *t*-butyl alcohol-O-*d*. After 4.33×10^5 sec gas chromatography showed 63% of triphenylmethane had been lost. Deuterium incorporation under these conditions in the absence of nitrobenzene can be calculated as 65% of one atom of D. Recovered triphenylmethane (by silica gel chromatography) from the nitrobenzene-containing reaction mixture contained 16.5% of one atom of D. Taken by itself, the effect of nitrobenzene on deuterium incorporation can be analyzed in terms of Scheme I where the

Scheme I



(1) Some of these results have been presented earlier: R. D. Guthrie, Abstracts of the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

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(3) Based on comparison of pK_a's: D. J. Cram in "Fundamentals of Carbanion Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1965, p 19.