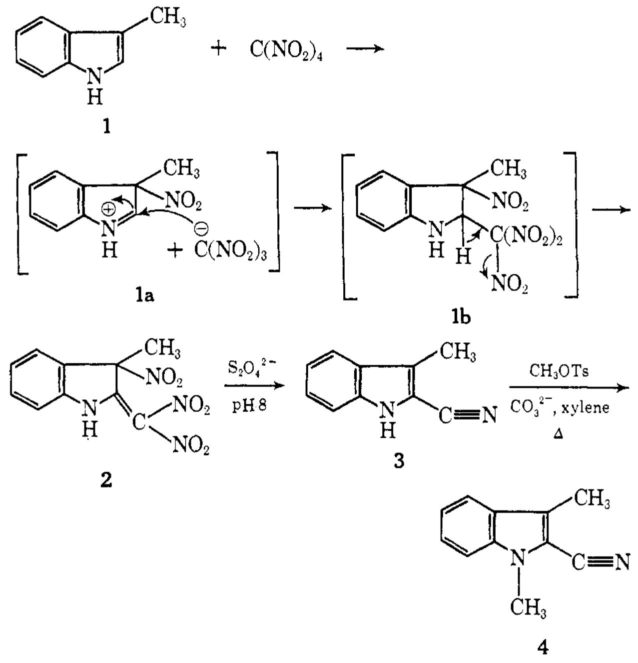

lose ammonia to give a ketenimine, followed by isomerization and expulsion of nitrite

$$=C(NO_2)_2 \longrightarrow =C(NH_2)_2 \xrightarrow{-NH_3} =C=NH$$

When the reaction with TNM was carried out in aqueous ethanol, significantly decreased yields of **2** resulted, suggesting alternate reaction pathways. In preliminary experiments, TNM on tryptophan peptides in aqueous solvents gave a mixture of nitrated products with the spectral characteristics of nitroindoles.[17] We are now looking into the reaction of tryptophan peptides with TNM in organic solvents.

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[17] G. Berti, A. Da Settimo, and D. Segnini, *Gazz. Chim. Ital.*, **90**, 539 (1960).

[18] Associate in the Visiting Program of the U. S. Public Health Service, 1968–1969.

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Preparation and Properties of Crystalline Permanganic Acid[1]

Sir:

Aqueous $KMnO_4$ has been used successfully as an alternative to aqueous OsO_4 for electron microscopy fixation of biological objects.[2] This prompted us to determine if an analog could be prepared that would similarly complement the use of the volatile OsO_4 for vapor-phase fixations.[3] $HMnO_4$ seemed a possibility but had been reported to be too unstable to prepare, and previous attempts at preparation had yielded only products grossly contaminated with MnO_2,[4] or a 2.6 *M* solution which froze at −11° to a mass of ice and $HMnO_4$ crystals.[5]

By analogy with $HClO_4$, it was anticipated that $HMnO_4$ and/or some of its hydrates might be both stable and volatile[6] at low temperature, *e.g.*, 1°. Accordingly, we devised a low-temperature method of preparation depending on fractional, vacuum sublimation of frozen, aqueous $HMnO_4$ which promised to yield both anhydrous and hydrated $HMnO_4$.

Samples of H_2SO_4 and recrystallized $Ba(MnO_4)_2$ were analyzed by the usual gravimetric procedures to ±0.1 %. To 120 ml of 0.3 *M* aqueous $Ba(MnO_4)_2$ at 0° was added a precisely equivalent amount of 0.3 *M* H_2SO_4, care being taken that the temperature remained below 1°, and the resultant precipitate removed by centrifugation. The deep violet, aqueous, $HMnO_4$ was transferred to a 500-ml round-bottom flask, and promptly frozen onto its walls by rotation in a CO_2–acetone bath at −75°. The flask was then connected to a glass and Teflon vacuum system and immersed in an ice bath. The vacuum system, operating through successive −75° CO_2–acetone and −193° liquid N_2 traps, was capable of maintaining a vacuum of 10^{-3} Torr. Ice immediately formed in the −75° trap, indicating removal of water.

After about 10 hr a violet color appeared in the −75° trap, and the system was promptly shunted through a U tube immersed in a −75° bath to collect the violet fraction. This crystallized in the form of fine, deep violet, needles.

After about 30 hr all of the volatile, violet fraction had been removed, and the flask temperature rose to that of the ice bath, indicating an end to vaporization of volatile components. The contents of the flask and the traps were removed for analysis; all operations were conducted at, or below, 1°. In addition, all operations on the flask contents were performed in a drybox, since the material proved quite hygroscopic.

Samples of the rectangular crystals remaining in the flask were extracted with successive portions of cold water. The soluble fraction, on analysis, proved to be pure $HMnO_4$ (see Table I). The insoluble fraction, on analysis, proved to be MnO_2, about 0.1 mole % in all. The U-tube contents were completely water soluble and proved to be $HMnO_4 \cdot 2H_2O$ (Table I). Analyses were performed conventionally except that permanganic acid samples were added quickly to excess reagent, and the

Table I

	$HMnO_4$ 119.944[a]	$HMnO_4 \cdot 2H_2O$ 155.974[a]
Yield, mole %[b]	50.9 ± 0.2	49.0 ± 0.2
Neutralization weight[c]	120.03	156.11
Fe^{2+} titration weight[c]	119.32	155.71
MnO_2 production weight[c]	119.69	156.08
O_2 evolution weight[c]	119.90	156.17
Experimental mean weight	119.74 ± 0.27	156.02 ± 0.18

[a] Theoretical formula weight. [b] Mean of 11 runs. [c] Mean of duplicate determinations.

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[1] Work supported by U. S. Atomic Energy Commission and presented, in part, at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Inorganic Division.

[2] T. N. Tahmisian, R. L. Devine, B. J. Wright, and C. Christiansen, Argonne National Laboratory Report ANL-6971, 1964, p 75.

[3] R. A. Jenkins, *J. Cell Biol.*, **23**, 46 (1964).

[4] M. M. P. Muir, *J. Chem. Soc. Trans.*, 1485 (1907).

[5] P. DuBois, *Compt. Rend.*, **200**, 1107 (1935).

[6] J. Pike and J. Hoste, *Anal. Chim. Acta*, **26**, 501 (1962).

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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[7] O. E. Goehler and G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **3**, 55, 58, 61 (1931).

[8] J. Williams, Proceedings of the Second Materials Research Conference, Special Publication No. 301, National Bureau of Standards, Washington, D. C., 1967.

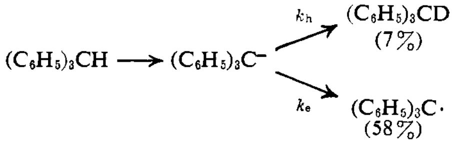
Electron Transfer as an Efficient Carbanion Trapping Reaction

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 $(0.236 \pm 0.008) \times 10^{-5}\ \text{sec}^{-1}$. 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



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[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.

[2] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

[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.