(vide supra) had the same NMR spectrum as the hydrogenation product.

Treatment of 11 with Low-Valent Iron. To 25 mL of anhydrous THF at −78 °C under argon was added 0.93 g (5.7 mmol) of anhydrous sublimed ferric chloride, followed by 10 mL of *n*-butyllithium (2.1 M in hexane). After the mixture was stirred for 2 h, a solution of 11 (0.32 g, 0.9 mmol) in 25 mL of THF was added (15 min), and the mixture was stirred at −78 °C for 4 h. Filtration and evaporation of the solvent left a residue which was taken up in methylene chloride, washed with water, and dried (Na_2SO_4). The yellow solid (0.33 g) left after solvent removal was chromatographed on neutral alumina, hexane removed a yellow impurity, and further elution with 9:1 methylene chloride/hexane gave 0.25 g (78%) of 27: mp 233–235 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 0.72 (d, 6 H, *J* = 7 Hz), 1.86 (s, 6 H), 1.89 (s, 6 H), 2.33 (s, 6 H), 2.56 (m, 2 H); mass spectrum, *m*/*e* (relative intensity) 350 (63), 306 (48), 296 (77), 253 (100).

Hydrogenation of 11 and 27. A single isomer of 11 (0.33 g, 0.9 mmol) in 40 mL of absolute ethanol was hydrogenated at atmospheric pressure and room temperature overnight over 0.3 g of 10% palladium on carbon. Removal of the catalyst and solvent gave 0.31 g (93%) of 1,2,3,4,5,6,7,8,9,10-decamethyl-1,2,3,4,5,6,7,8-octahydroanthracene 1,4;5,8-diendoxide: mp 251–252 °C (ethanol); ^{1}H NMR (CCl_4) δ 0.43 (d, 12 H, *J* = 7 Hz), 1.67 (s, 12 H), 1.8–2.3 (m, 4 H), 2.20 (s, 6 H); mass spectrum, *m*/*e* (relative intensity) 298 (31), 242 (100), 122 (17); with chemical ionization *m*/*e* 355 [(M + 1)$^+$]. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.45; H, 9.61.

Similar hydrogenation of 27 gave the same product (melting point, NMR) in 98% yield.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE 77-05956) and the National Institutes of Health (Grant GM 15997) for financial support of this research.

Registry No. 1, 4705-93-5; 2, 571-58-4; 3, 68185-75-1; 4, 2717-39-7; 5, 68437-68-3; 6, 3031-15-0; 7, 76466-54-1; 8, 781-43-1; 9, 76497-63-7; 10, 75670-42-7; 11, 76466-55-2; 12, 76466-56-3; 13, 57188-23-5; 14, 2395-97-3; 15, 76466-57-4; 16, 76466-58-5; 17, 2960-97-6; 18, 76497-64-8; 19, 64094-28-6; 20, 76466-59-6; 21, 76466-60-9; 22, 76479-87-3; 23, 76466-61-0; 24, 76466-62-1; 25, 76479-88-4; 26, 76466-63-2; 27, 76498-71-0; 9,10-dimethoxy-1,4,5,8-tetramethyl-1,4-dihydroanthracene-1,4-endoxide, 76466-64-3; 1,2,3,4,5,6,7,8,9,10-decamethyl-1,2,3,4,5,6,7,8-octahydroanthracene-1,4:5,8-diendoxide, 76466-65-4; $FeCl_3$, 7705-08-0; WCl_6, 13283-01-7; $TiCl_3$, 7705-07-9.

Rates and Mechanism for Oxidation of Paraquat and Diquat Radical Cations by Several Peroxides

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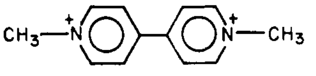
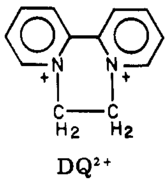
The rates of oxidation of the free radicals $MV^{+}\cdot$ and $DQ^{+}\cdot$ derived from herbicides Paraquat (MV^{2+}) and Diquat (DQ^{2+}) by hydrogen peroxide, peroxodiphosphate species, and peroxodisulfate have been investigated. Where consistent data were obtainable, the reactions are first order each in peroxide and radical. Results for H_2O_2 and $MV^{+}\cdot$ are $k = 2.0$ M^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 92$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 73$ J mol^{-1} K^{-1}; similar results were found with H_2O_2 and $DQ^{+}\cdot$. Although hydroxyl radicals are likely intermediates, the predicted inhibition when methanol is present did not materialize; a mechanistic rationalization is presented. The rates with peroxodiphosphate were pH dependent and could be interpreted as different contributions from $H_2P_2O_8^{2-}$, $HP_2O_8^{3-}$, and $P_2O_8^{4-}$ in the same order as found for peroxodiphosphate and unstable radicals. The rate with $S_2O_8^{2-}$ is fastest, but complications prevented the evaluation of a rate constant.

Methylviologen dichloride (1,1′-dimethyl-4,4′-bipyridylium chloride) and 6,7-dihydrodipyrido[1,2-*a*:1′,2′-*c*]pyrazinium dibromide are marketed as herbicides under the names of Paraquat and Diquat. Both compounds in water as the dications (here symbolized MV^{2+} and DQ^{2+}, respectively) are readily reduced to the stable and persistent radicals $MV^{+}\cdot$ and $DQ^{+}\cdot$ by chemical, electrochemical, and photochemical means.[1] The herbicidal activity appears to be associated with the formation of these stable radicals and with the reduction potentials of the dications as they can substitute for a normal electron acceptor in the photosynthetic pathway.[2] The radicals are air sensitive and can be reoxidized by oxygen.[3] For plant death, both oxygen and light are required;[4] the oxygen intermediates $O_2^{-}\cdot$ and/or H_2O_2 have been considered to be the active lethal agents.[2,5]



MV^{2+}



DQ^{2+}

Paraquat and Diquat are also potent mammalian poisons. The mechanism of mammalian toxicity may be related to herbicidal activity but cannot depend on photochemical activation.[6]

Methylviologen has also been used as an oxygen meter; a solution of the radical cation, buffered at pH 6.5 and prepared by photoreduction of MV^{2+} by using proflavine and EDTA,[7] is reported to react quantitatively with oxygen according to the stoichiometry of eq 1. The system can

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(1) A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **13**, 155–278 (1976).

(2) (a) A. A. Akhavein and D. L. Linscott, *Residue Rev.*, **23**, 97 (1968); (b) A. Calderbank and P. Slade in "Herbicides", 2nd ed., P. C. Kearney and D. D. Kaufman, Eds., Marcel Dekker, New York, 1976, pp 501–541.

(3) (a) G. Zweig, N. Shavit, and M. Avron, *Biochim. Biophys. Acta*, **109**, 332 (1965); (b) P. Brune and A. San Pietro, *Arch. Biochem. Biophys.*, **141**, 371 (1970); (c) ref 2a, pp 105–113.

(4) A. D. Dodge, *Endeavour*, **30**, 130 (1971).

(5) E. M. Kosower in "Free Radicals in Biology", Vol. II, W. A. Pryor, Ed., Academic Press, New York, 1976.

(6) L. S. Bus, S. D. Aust, and J. E. Gibson, *EHP, Environ. Health Perspect.*, **16**, 189, (1976).

(7) P. B. Sweetser, *Anal. Chem.*, **39**, 979 (1967).

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$$4MV^{+}\cdot + 4H^{+} + O_2 \rightarrow 4MV^{2+} + 2H_2O \qquad (1)$$

be monitored spectrophotometrically by taking advantage of the intense blue color of $MV^{+}\cdot$. A second oxygen meter technique makes use of the fact that $MV^{+}\cdot$ can be generated by constant-current electrolysis and the oxygen titrated to a "dead-stop" end point.[8]

Stoichiometric consideration indicates that four radical cations must donate one electron each to an oxygen molecule for complete reduction to water; plausible oxygen intermediates in the reactions are the superoxide ion, $O_2^{-}\cdot$, hydrogen peroxide, H_2O_2, and hydroxyl radical, $OH\cdot$. The reactions of $MV^{+}\cdot$ with oxygen and with superoxide are very fast. The process shown in eq 2 has been reported

$$MV^{+}\cdot + O_2 \rightarrow MV^{2+} + O_2^{-}\cdot \qquad (2)$$

to have a rate constant of 7.7×10^8 M^{-1} s^{-1} in water at room temperature.[9] In another investigation,[10] the rate constants in water, methanol, ethanol, 2-propanol, and 1-propanol were found to be 6.0×10^8, 3.3×10^6, 1.3×10^6, 8.7×10^5, and 3.0×10^6 M^{-1} s^{-1}, respectively. A third study[11] again reported rapid rates, but the detailed kinetics were said to differ. There is a striking medium effect, but some unresolved questions remain.

The reaction of $MV^{+}\cdot$ with superoxide ion has a rate constant of 6.5×10^8 M^{-1} s^{-1} in aqueous solution at ambient temperature.[10] The rate constants for reaction of $DQ^{+}\cdot$ with O_2 and $O_2^{-}\cdot$ are comparable: $k = 4.7 \times 10^8$ M^{-1} s^{-1} and 4.8×10^8 M^{-1} s^{-1}, respectively.[12]

It was decided to study the reaction of the Paraquat and Diquat radical cations with hydrogen peroxide and other peroxides as nothing had been reported concerning this particular step in the reduction of oxygen to water. Only one report has appeared in the literature concerning the reaction of a peroxide with these radical cations; namely, that $MV^{+}\cdot$ did not react with di-*tert*-butyl peroxide thermally.[13]

Experimental Section

Paraquat (K & K) was recrystallized from acetone–methanol and dried to give either the dihydrate or almost anhydrous compound. Diquat (Chemical Services, Inc.) was purified in the same fashion. Chemicals for buffers were commercial analytical grade. Water for solutions was glass distilled and passed through an ion-exchange column. FMC Corp. H_2O_2 (90% and 30%) was determined by $KMnO_4$ titration. Potassium persulfate (Merck) was recrystallized twice and shown by ferrous sulfate/dichromate analysis to be 100% pure. Potassium peroxodiphosphate was recrystallized from ethylene glycol/water and then found to be 98% pure.

All stopped-flow kinetic data were obtained on a Durrum-Gibson D-110 instrument equipped with either a 2-cm or 2-mm path length cell. Data were collected by photographing transmittance vs. time or absorbance vs. time traces on an oscilloscope. The photographs were digitized, transmittances converted to absorbance where necessary, and the data fitted to the following equation:

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - kt$$

Before the drive syringes were filled, the flow apparatus was swept out with argon and then filled with deoxygenated, distilled water. Solutions were drawn into the syringes under argon. A connected filling syringe containing radical solution was used to further deoxygenate the flow system. The instrument was considered ready for use when the absorbance of the radical in the spectrophotometer cell remained unchanged for 15 min.

The radicals were prepared by deoxygenating solutions 3.0×10^{-4} to 3.0×10^{-3} M in dication with argon and either drawing them through a Jones reductor column[14,15] into an argon-purged syringe or introducing the parent compound in deoxygenated solution into the side arm of a Schlenk filter apparatus with amalgamated zinc in the other side arm, reducing the radical, filtering the zinc, and withdrawing the solution with an argon-purged syringe. Some decay of radical color with time occurred, but it was far too slow to interfere with the kinetic observations. The radical concentration was determined from absorbance measurements; for $MV^{+}\cdot$, readings were taken at 603 nm, with the literature value[16] of ϵ 1.2×10^4 M^{-1} cm^{-1}, and for $DQ^{+}\cdot$, absorbances were measured at 760 nm, with the literature value[17] of ϵ 3.11×10^3 M^{-1} cm^{-1}.

In order to minimize the usual difficulties in obtaining rates at various temperatures,[18] we used traces that gave correlation coefficients of 0.999 or better, allowed adequate time for temperature equilibration, and selected days when the difference between ambient and instrument temperatures was small enough that resonably reliable values could be obtained.

In the reactions of $MV^{+}\cdot$ with H_2O_2, the pH was adjusted by use of HCl or NaOH or set by means of phthalate or borate buffers. In the reactions of $MV^{+}\cdot$ with disubstituted peroxides, phthalate, carbonate, or phosphate buffers were used.

Because of the rapid reaction of $DQ^{+}\cdot$ with acid, experiments were carried out in phosphate buffers in neutral or alkaline solution.

The variable-temperature runs for $MV^{+}\cdot$ and $DQ^{+}\cdot$ with H_2O_2 were performed in pure water because of the absence of a pH influence on rate.

Pulse radiolysis experiments were performed by using the LINAC at Argonne National Laboratory. The pulses consisted of approximately 1.25 A of 15-MeV electrons and were from 4 to 10 ns in duration. Radiation doses received by the samples were in the range of 600–2000 rads with most in the lower part of that range. When methanol was present, each 100 rads produced approximately 0.6 μM radical cation concentration. The electron pulse produces approximately equal numbers of solvated electrons and hydroxyl radicals. In the presence of 1 M methanol, the latter reacts on a very short time scale with methanol to produce $\cdot CH_2OH$ which in turn reacts with MV^{2+} to yield additional $MV^{+}\cdot$. This conversion from $\cdot OH$ to $MV^{+}\cdot$ is essentially complete in several microseconds. (In the absence of methanol, a new absorption spectrum is produced; it was shown to be formed from $\cdot OH$ and MV^{2+}, and it was found to be moderately persistent.[10])

The peroxodiphosphate radiolysis experiments involved the use of solutions containing 1 M methanol and were buffered at appropriate pH values (4.2, 6.5, and 10.5) so that the primary species present in each case was $H_2P_2O_8^{2-}$, $HP_2O_8^{3-}$, or $P_2O_8^{4-}$. The $P_2O_8^{4-}$ solutions were buffered by carbonate–bicarbonate and the $HP_2O_8^{3-}$ solutions were buffered by phosphate buffers. The $H_2P_2O_8^{2-}$ solutions contained 0.10 M $H_2PO_4^{-}$ which resulted in a pH of 4.2 prior to addition of the $P_4O_8^{4-}$ species. As the concentration of the latter was increased, the pH increased to a maximum of 5.6 at which point an appreciable fraction of the peroxodiphosphate was in the singly rather than the doubly protonated form.

Solutions were thoroughly deoxygenated with helium and were stored in 100-mL syringes until transferred to the cylindrical quartz cells fitted with Suprasil windows. Following the pulse of electrons, the pulse from a sychronized xenon lamp was used as analyzing radiation, with the concentration of $MV^{+}\cdot$ being followed by use of the 603-nm absorbance maximum.

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[8] R. E. V. D. Leest, *J. Electroanal. Chem.*, **43**, 251 (1973).

[9] L. A. Farrington, M. Ebert, E. Y. Land, and F. Fletcher, *Biochim. Biophys. Acta*, **314**, 372 (1973).

[10] L. K. Patterson, R. D. Small, Jr., and L. C. Scaiano, *Radiat. Res.*, **72**, 218 (1977).

[11] A. G. Evans, N. F. Dodson, and N. H. Rees, *J. Chem. Soc., Perkin Trans. 2*, 859 (1976).

[12] J. A. Farrington, M. Ebert, and E. Y. Land, *J. Chem. Soc., Faraday Trans. 1*, 74, 665 (1978).

[13] A. S. Hopkins and A. Ledwith, *J. Chem. Soc., Chem. Commun.*, 830 (1971).

[14] D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", 2nd ed., Holt, Rinehart, and Winston, New York, 1969, p 415.

[15] R. Elofson and R. Edsberg, *Can. J. Chem.*, **35**, 646 (1957).

[16] R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **80**, 828 (1977).

[17] Reference 1, p 254.

[18] For a brief discussion on this point, see D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, **76**, 2733 (1974).

Results

Stoichiometry of Reaction with H_2O_2. It has been reported[19] that the reaction of $MV^{+}\cdot$ with excess H_2O_2 gave a product which could not be re-reduced to the radical cation. It has also been reported[20] that Paraquat and Diquat are slowly oxidized by alkaline hydrogen peroxide and other alkaline oxidizing agents. The following experiment showed that, at least under mild conditions, MV^{2+} is produced quantitatively from $MV^{+}\cdot$ by reaction with H_2O_2 and that unreduced MV^{2+} is not oxidized. A 3.0×10^{-3} M deoxygenated solution of MV^{2+} was drawn through the Jones reductor column into a flow cell mounted in a Hitachi Perkin-Elmer spectrophotometer; the concentration of $MV^{+}\cdot$ was found to be 3.9×10^{-4} M. A deoxygenated hydrogen peroxide solution (8.8×10^{-3}M) was mixed with 50 mL of the reduced solution under argon. The blue radical color disappeared in approximately 45 min, at which time 5 mL of the original MV^{2+} solution was treated with sodium dithionite (to regenerate $MV^{+}\cdot$) in carbonate–bicarbonate buffer as was 5 mL of the peroxide-treated solution. After correction for dilution effects, the absorbances at 603 nm of the two solutions were identical within experimental error.

Rates with H_2O_2. The reaction of H_2O_2 with $MV^{+}\cdot$ was studied by stopped-flow and pulse radiolysis techniques, and the results indicated that H_2O_2 reacted with $MV^{+}\cdot$ much more slowly than did O_2 or $O_2^{-}\cdot$. By stopped-flow measurements, the rate was found to be first order each in $MV^{+}\cdot$ and H_2O_2.

Stopped-flow determinations of rates were found to give pseudo-first-order plots which are linear over at least 2 half-lives, and the rate constants for a similar set of conditions were quite reproducible; e.g., $k_2 = 2.0 \pm 0.2$ M^{-1} s^{-1} for one group of runs at 27 °C, and $[H_2O_2] = 5.18 \times 10^{-2}$ M.

Noninfluence of pH. It is known that the radical is unstable in the presence of strong acid, so a study of the pH effect on rate was warranted. At pH values near 2, the initial linear portion of the plot was followed by a drop in the absorbance, indicating the intervention of another mode of reaction of $MV^{+}\cdot$ (see Discussion); despite this complication, the initial portion of the curve is reproducible and agrees in rate with results found at higher pH. At pH 3 and 25 °C, two determinations of the order and rate at three H_2O_2 concentrations (0.011, 0.052, and 0.26 M) gave linear pseudo-first-order plots and $k_2 = 2.6 \pm 0.4$ M^{-1} s^{-1}. At pH 10 and 25 °C, two determinations (at the same three H_2O_2 concentrations) again gave linear pseudo-first-order plots and $k_2 = 2.2 \pm 0.3$ M^{-1} s^{-1}. The rate constant was found to be independent of pH, with data being obtained at pH values of 2, 3, 9, 10, and 12 plus many unbuffered runs. A compilation of rate constants is given in Table I. Runs at very high radical concentration (>10^{-3} M) gave abnormal rates; possible reasons for these are pointed out in the Discussion.

Table I. Rate Constants for the H_2O_2 and $MV^{+}\cdot$ Reaction

$[H_2O_2]$, M	pH	temp, °C	no. of runs	k_2, M^{-1} s^{-1}
1.05×10^{-2}	10	25	1	2.92
5.29×10^{-2}	10	25	2	2.08
2.64×10^{-1}	10	25	2	1.94
1.05×10^{-2}	3	25	2	3.21
5.29×10^{-2}	3	25	2	1.80
2.64×10^{-1}	3	25	2	2.79
5.18×10^{-2}	2	27	4	1.78
5.18×10^{-2}	9	27	2	1.86
5.18×10^{-2}	10	27	2	2.28
5.18×10^{-2}	12	27	2	2.57
3.92×10^{-2}		15.4	1	0.394
3.92×10^{-2}		22.6	3	2.02
1.78×10^{-2}		29.6	2	5.25
1.78×10^{-1}		33.2	1	8.25
1.78×10^{-2}		33.6	2	6.95
1.78×10^{-1}		38.7	1	16.0
1.78×10^{-1}		43.2	3	21.7
1.30×10^{-1}		26.5	2	3.23
1.30×10^{-1}		28	1	4.28
1.30×10^{-1}		34	1	13.0
1.50×10^{-1}		40	1	17.2
1.50×10^{-1}		41.5	1	19.7
1.92×10^{-2}		25.5	1	3.40
1.30×10^{-2}		25.5	1	3.06
6.52×10^{-2}		25.5	1	2.34
2.99×10^{-2}		23	1	3.13
1.44×10^{-2}		23	1	2.82

Table II. Rate Constants for the H_2O_2 and $DQ^{+}\cdot$ Reaction[a]

$[H_2O_2]$, M	pH	temp, °C	k_2, M^{-1} s^{-1}
4.45×10^{-2}	6.85	23.5	3.48
2.23×10^{-2}	6.85	23.5	2.36
2.23×10^{-2}	6.85	23.5	3.95
1.57×10^{-1}	9.18	26.3	5.31
4.45×10^{-2}	6.85	23.5	3.84
1.57×10^{-1}	9.18	26.3	6.74
3.04×10^{-1}	9.18	25	3.77[b]
1.76×10^{-1}		21.8	3.83[c]
9.08×10^{-2}		26.5	5.73[b]
1.76×10^{-1}		13.3	2.12
1.76×10^{-1}		16.0	2.00
1.76×10^{-1}		18.5	3.11[c]
9.08×10^{-2}		19.4	3.34
3.65×10^{-2}		31.4	16.5
9.08×10^{-2}		31.4	15.6
3.65×10^{-2}		36.7	18.2
3.65×10^{-2}		40.5	24.6
3.65×10^{-2}		44	19.6
3.65×10^{-2}		46.4	24.1

[a] Values of $[DQ^{+}\cdot]$ ranged from 1.60×10^{-5} to 8.84×10^{-5} M in the first six runs. [b] Average of three runs. [c] Average of two runs.

Rates of DQ^{+} with H_2O_2. Stopped-flow studies of the reaction of $DQ^{+}\cdot$ and H_2O_2 showed a rate comparable in magnitude to that of $MV^{+}\cdot$. At 26.7 °C, k_2 was 5.9 ± 0.4 M^{-1} s^{-1} in unbuffered water; at pH 9.2 and 26.3 °C, $k_2 = 6.0 \pm 0.7$ M^{-1} s^{-1}. The results of many experiments are presented in Table II. It should be noted that although the rate constant is independent of pH from 6.85 to 9.2, the reaction could not be studied at pH 2 or 4 due to side reactions. Attempts to generate $DQ^{+}\cdot$ in phthalate buffer or hydrochloric acid resulted in red or yellow solutions. Further, generation of the radical in water and addition of deoxygenated 0.01 M HCl led to immediate disappearance of the green radical color.

Other Results. Activation parameters for reaction of both radicals were determined in unbuffered aqueous solution (see Figure 1). For $DQ^{+}\cdot$, $\Delta H^{\ddagger} = 73 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = 14 \pm 21$ J mol^{-1} K^{-1}; for $MV^{+}\cdot$, $\Delta H^{\ddagger} = 92 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger} = 73 \pm 16$ J mol^{-1} K^{-1}. The large positive entropy, particularly as seen in the latter case, was unexpected (see below).

Study of the H_2O_2 oxidations of the cation radicals by pulse radiolysis at ambient temperature gave some results that matched the stopped-flow data; for example, for $[MV^{2+}] = 1 \times 10^{-3}$ M and $[H_2O_2] = 6.14 \times 10^{-2}$ M, the value $k_2 = 2.8 \pm 0.2$ M^{-1} s^{-1} was obtained. In the presence of additives such as *tert*-butyl alcohol and EDTA, much

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(19) J. S. Bellin, R. Alexander, and R. Mahoney, *Photochem. Photobiol.*, 17, 17 (1973).

(20) A. Calderbank, D. F. Charlton, J. A. Farrington, and R. James, *J. Chem. Soc., Perkin Trans. 1*, 138 (1972).

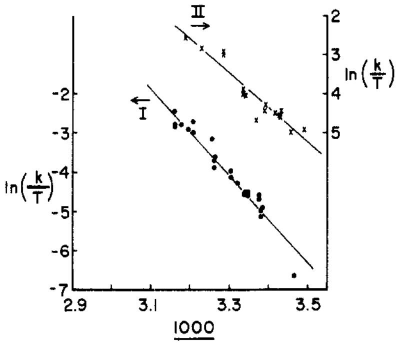

Figure 1. Eyring plots of rate data: (I) $MV^{+}\cdot$ and H_2O_2; (II) $DQ^{+}\cdot$ and H_2O_2.

Table III. Rates of H_2O_2 and $MV^{+}\cdot$ with Methanol Present[a]

$[H_2O_2]$, M	$[CH_3OH]$	temp, °C	k_2, $M^{-1}\ s^{-1}$
3.74×10^{-2}	1 M	21.5	2.50
3.74×10^{-2}	1 M	22.9	1.65
7.68×10^{-2}	83%	26.2	3.56
1.24×10^{-1}	100%	26.2	0.784

[a] Each k_2 is an average of two values in neutral, unbuffered solution.

Table IV. Rates for H_2O_2 and $DQ^{+}\cdot$ with Methanol Present[a]

$[H_2O_2]$, M	temp, °C	k_2, $M^{-1}\ s^{-1}$
3.75×10^{-2}	24.3	0.722
7.51×10^{-2}	25	0.877
1.5×10^{-1}	27	0.833
1.5×10^{-1}	28	1.11

[a] Each k_2 is an average of two values in neutral unbuffered solution. The concentration of methanol was 1 M in every case.

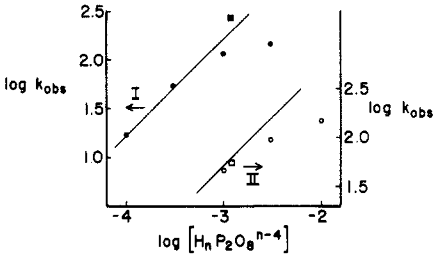

Figure 2. Variation of the observed first-order rate constant of $MV^{+}\cdot$ oxidation with peroxodiphosphate concentration: (I) $H_2P_2O_8^{2-}$; (II) $HP_2O_8^{3-}$. The lines are drawn with a slope of 1.0. The circles are pulse radiolysis data and the squares are stopped-flow average rate constants.

Table V. Temperature Dependence of Peroxodiphosphate Oxidation of $MV^{+}\cdot$ Rates[a]

temp, °C	pH	no. of runs	$10^{-4}k_2$, $M^{-1}\ s^{-1}$
14.6	4.2	4	17.8 ± 1.3
14.6	6.5	6	3.60 ± 0.40
14.6	10.5	5	0.147 ± 0.009
25	4.2	5	22.8 ± 0.6
25	6.5	4	4.58 ± 0.07
25	10.5	4	0.176 ± 0.008
35	4.2	2	36.7 ± 0.1
35	6.5	2	9.2 ± 0.2
35	10.5	3	0.453 ± 0.002

[a] The results are given in terms of the second-order constant k_2, but it is to be remembered that the apparent ion-pairing (see Figure 2) means that the constant is somewhat concentration dependent.

larger rate values were obtained; we presume that these species form interfering radicals. The addition of 1 M methanol, which increases the amount of $MV^{+}\cdot$ formed by the initial pulse, did not have a large influence on the rate as may be seen in Table III. We obtained similar results with $DQ^{+}\cdot$ and H_2O_2, but in this reaction the presence of methanol did seem to reduce the rate by about a factor of 4 (see Table IV).

Rates with Peroxodiphosphates. The two radicals react with the several protonated forms of peroxodiphosphate more rapidly than with hydrogen peroxide. Good pseudo-first-order plots were obtained, but the values of k_{obsd} were not linear with peroxide even though obviously dependent on peroxide concentration. The deviation from first-order dependence on peroxodiphosphate falls in the order $P_2O_8^{4-} > HP_2O_8^{3-} > H_2P_2O_8^{2-}$, with the deviation in the last case being barely detectable. Given this correlation with anion charge and the fact that $MV^{+}\cdot$ is a cation, we ascribe the divergence from first-order in peroxide to ion pairing, and we make the reasonable assumption that in the absence of ion pairing the rate law would be first order each in peroxide and radical.

Kinetic data were obtained both in the presence and absence of methanol, and the rate was not obviously dependent on the presence of this additive.

A partial summary of the data (obtained with both techniques) is presented in Figure 2 and Table V for $MV^{+}\cdot$ oxidation. In principle, it should be possible to separate the observed rate constant into two constants (first-order decomposition constant and ion-pair formation constant). We feel, however, that our data are not so precise or numerous as to warrant such detailed treatment.

In Table V, rate constants at the three pH values (4.2, 6.5, and 10.5) where the three species $H_2P_2O_8^{2-}$, $HP_2O_8^{3-}$, and $P_2O_8^{4-}$ predominate, respectively, are given. From these data, we calculated the following activation parameters: for $P_2O_8^{4-}$, $\Delta H^{\ddagger} = 35$ kJ mol^{-1} and $\Delta S^{\ddagger} = -63$ J mol^{-1} K^{-1}; for $HP_2O_8^{3-}$, $\Delta H^{\ddagger} = 28$ kJ mol^{-1} and $\Delta S^{\ddagger} = -59$ J mol^{-1} K^{-1}; for $H_2P_2O_8^{2-}$, $\Delta H^{\ddagger} = 22$ kJ mol^{-1} and $\Delta S^{\ddagger} = -67$ J mol^{-1} K^{-1}. The entropies of activation are negative and all of the same magnitude; the variation in rate seems to be dominated by the enthalpy changes.

Rates with Peroxodisulfate. The reactions of $MV^{+}\cdot$ and $DQ^{+}\cdot$ with peroxodisulfate were too fast to follow with the stopped-flow apparatus; all radical color was gone by the time mixing was complete. In the pulse radiolysis experiments, rate phenomena were observed; however, the results were complicated by the presence of unexpected absorptions not attributable to the reactants or ultimate products. Suffice it to say here that k for $MV^{+}\cdot$ and $S_2O_8^{2-}$ seems to be about 10^6 M^{-1} s^{-1} and that the results were the same whether methanol was present or absent.

Discussion

We have shown that the reactions of $MV^{+}\cdot$ and $DQ^{+}\cdot$ with hydrogen peroxide are relatively slow. The rate constants at ambient temperature are about 2.0 and 6.0 M^{-1} s^{-1}, respectively, about eight powers of ten smaller than the corresponding rate constants for the reactions with oxygen and with superoxide ion.

One-electron transfer from $MV^{+}\cdot$ to H_2O_2 would be expected to produce hydroxyl radical (eq 3), with the $\cdot OH$

$$MV^{+}\cdot + H_2O_2 \rightarrow MV^{2+} + OH^{-} + \cdot OH \qquad (3)$$

intermediate reacting rapidly with another $MV^{+}\cdot$ to complete the known sequence of reductions of oxygen to water (eq 4). For several reasons, however, it is necessary to

$$MV^{+}\cdot + \cdot OH \rightarrow MV^{2+} + OH^{-} \qquad (4)$$

consider an alternative path for reduction of hydrogen peroxide, specifically one which does not postulate the presence of free hydroxyl radical. The strongest reason, to be discussed below, is the absence of methanol inhibition.

It is known that ·OH can react with MV^{2+} itself to give a relatively long-lived (on the pulse radiolysis time scale) intermediate with a distinct ultraviolet spectrum.[10] We obtained a large positive entropy of activation for the reaction of $MV^{+}\cdot$ and H_2O_2, whereas we had expected a negative value similar to those obtained with the peroxodiphosphates. A positive entropy of activation for a second-order process might be explicable if a dissociation were an integral part of the activation process. Transfer of an electron from $MV^{+}\cdot$ (in the same solvent cage) to H_2O_2 could cause dissociation (eq 5). The ·OH is formed near

$$H_2O_2 + e^{-} \rightarrow OH^{-} + \cdot OH \qquad (5)$$

MV^{2+} (from $MV^{+}\cdot$ by loss of the electron), and combination of these two species by in-cage collision is reasonable in light of the earlier discovery of the intermediate.[10] The usual magnitude of the cage effect[21] would allow some HO· escape from the cage, but the methanol results obtained here indicate little escape. This suggests that H_2O_2 is hydrogen bonded to $MV^{+}\cdot$, and the nearby OH group becomes the radical which because of its immobilization near the newly developed MV^{2+} has a facilitated attachment.

Happily this mechanism resolves what was for us a serious paradox. If the hydroxyl radical were free, it should have reacted preferentially with methanol. Reaction 4 can proceed no faster than the diffusion rate (about 3×10^{10} M^{-1} s^{-1}), and the reaction of ·OH with methanol (eq 6) is

$$\cdot OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH \qquad (6)$$

known[22] to have a rate constant of 9×10^{8} M^{-1} s^{-1}. In many of our experiments, the concentration of methanol was 10^{3}–10^{5} times greater than that of $MV^{+}\cdot$. Therefore step 6 would compete very successfully with step 4, and this would be followed by the known process of eq 7, which

$$\cdot CH_2OH + MV^{2+} \rightarrow CH_2O + H^{+} + MV^{+}\cdot \qquad (7)$$

re-forms the reactant free radical. The net consequence of reactions 6 and 7 on the H_2O_2–$MV^{+}\cdot$ reaction would be significant inhibition, from one to three powers of ten, of the rate.

In fact, the addition of 1 M methanol does not have a discernible effect on the rate constant. This lack of inhibition by methanol caused us considerable concern since the known rate constants for steps 6 and 7 formed the basis for a very compelling prediction. Suffice it to say now, the fact that the hydroxyl radical can be tied up by MV^{2+} means that reaction 6 is no longer mandatory, and the lack of inhibition by methanol is explicable. This does not mean that zero effect by methanol is now predicted. Indeed, the observed rate when $DQ^{+}\cdot$ reacts with H_2O_2 decreases slightly when methanol is present. The $DQ^{+}\cdot$ reaction also differs from that for $MV^{+}\cdot$ in that the entropy of activation is near zero, suggesting less dissociation in the transition state. On the other hand, no methanol effect was seen in the oxidations by peroxodiphosphates and peroxodisulfate, but we have no data for $SO_4^{-}\cdot$ and $HPO_4^{-}\cdot$ comparable to that for ·OH.

All three peroxodiphosphate species ($P_2O_8^{4-}$, $HP_2O_8^{3-}$, and $H_2P_2O_8^{2-}$) react with $MV^{+}\cdot$ much faster than does H_2O_2, and all of their reactions exhibit the expected negative entropies of activation. It was noted that there is a dependence of second-order rate constant on the concentration of peroxodiphosphate species. At the lower limit, the rate constants follow the expected second-order kinetic pattern, whereas there is a decrease of k_2 as peroxodiphosphate concentration increases. This type of behavior is consistent with ion-pair formation between reactants (eq 8). The ion-pairing could slightly influence

$$P_2O_8^{4-} + MV^{+}\cdot \rightleftarrows [P_2O_8 \cdot MV]^{3-} \qquad (8)$$

the activation parameters. Since no new bonds are made or broken, no great change in $\Delta H^{\ddagger}$ is expected. The prime effect on $\Delta S^{\ddagger}$ would be due to desolvation because the sum of absolute charges on the separate reactants is greater than on the ion pair. It can be concluded that $\Delta S^{\ddagger}$ would be more negative if ion-pair formation had not occurred.

It is worthy of note that the reactivity order for the three peroxodiphosphates is $H_2P_2O_8^{2-} > HP_2O_8^{3-} > P_2O_8^{4-}$. This correlates with the known order of susceptibility to attack on these three peroxoanions by the very reactive radical $\cdot C(CH_3)_2OH$[23] and by the hydrated electron.[24]

Peroxodisulfate reacts extremely rapidly with $MV^{+}\cdot$. As mentioned above, we found it difficult to sort out a rate constant under pulse radiolysis conditions and estimate it to be about 10^{6} M^{-1} s^{-1} or slightly larger. Again this correlates with known susceptibility of organic radical (e.g., $\cdot C(CH_3)_2OH$) attack on peroxide; a long-chain oxidation mechanism involving the step shown in eq 9 has been

$$\cdot C(CH_3)_2OH + S_2O_8^{2-} \rightarrow SO_4^{-}\cdot + {}^{-}O_3SOC(CH_3)_2OH \qquad (9)$$

observed. By analogy, some ion pairing between $MV^{+}\cdot$ and $S_2O_8^{2-}$ might be expected; our data do not, however, give any information relative to this question.

As noted above, we were unable to prepare $DQ^{+}\cdot$ in acidic solution. We found $MV^{+}\cdot$ to be stable in dilute acid, but during the course of reaction with acidic H_2O_2 a deviation toward more rapid radical loss was observed toward the end of the run. Some qualitatively similar problems have been reported[1] for $MV^{+}\cdot$, with an explanation being based on the disproportionation equilibrium of eq 10,

$$2MV^{+}\cdot \rightleftarrows MV^{0} + MV^{2+} \qquad (10)$$

normally shifted toward the left, being shifted to the right by acid reacting with MV^{0}. This could pertain for $DQ^{+}\cdot$ under our conditions, but it does not pertain to our $MV^{+}\cdot$ results because the observed deviation is more serious at low $[MV^{+}\cdot]$ and higher $[MV^{2+}]$.

There are two ancillary observations that should be mentioned.

(1) Most of the hydrogen peroxide kinetic runs involved low concentrations of reactant radicals, and the rate constants were reasonably reproducible. This situation changed dramatically when the radical concentration was increased. For example, when $[MV^{+}\cdot]$ was estimated from the absorbance to be 5×10^{-3} M or greater, apparent second-order rate constants from 40 to 400 M^{-1} s^{-1} were obtained. The pseudo-first-order plots were no longer linear, indicating a mechanism change. We believe that the faster rate probably is due to the presence of significant amounts of $(MV)_2^{2+}$, the "pi-mer" of Kosower.[5,25] At high concentrations of radical (and at high concentrations of salts) the radical is known not to obey Beer's law. The

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[21] J. P. Lorand, *Prog. Inorg. Chem.*, 17, 207–325 (1972).

[22] P. Neta and L. M. Dorfman *Adv. Chem. Ser.*, No. 81, 222 (1968).

[23] R. J. Lussier, W. M. Risen, Jr., and J. O. Edwards, *J. Phys. Chem.*, 74, 4039 (1970).

[24] G. Levey and E. J. Hart, *J. Phys. Chem.*, 79, 1642 (1975).

[25] A. G. Evans, N. K. Dodson, and N. H. Rees, *J. Chem. Soc., Perkin Trans. 2*, 859 (1976).

association reaction (eq 11) is apparently the reason for

$$2MV^{+\cdot} \rightleftarrows (MV)_2^{2+} \qquad (11)$$

the absorbance shift, and it appears that $(MV)_2^{2+}$ reacts more rapidly with H_2O_2 than does the monomeric $MV^{+\cdot}$. Unfortunately, further study of this fast rate must await resolution of another problem with solutions having higher radical concentrations.

(2) When the concentrations of $MV^{+\cdot}$ and of added salt are raised, insoluble dark-colored materials were formed in most reactions. Precipitation is often very slow, and the darkness of these concentrated solutions so obscures the process of deposition that one may be unaware of the presence of a suspended solid. This can, of course, seriously interfere with rate measurements at high concentrations. We plan to investigate the nature of these interesting solids.

Many bipyridylium salts are efficient herbicides. The formation of radical cations, persistent and stable in the absence of air, is a prerequisite for this activity. In addition, the parent cations must have a reduction potential comparable to those electron acceptors natural to the photosynthetic assembly plus a certain size and shape.[26-28]

The rate constants obtained in aqueous solution are not necessarily the same as those which may obtain in chloroplast assemblies. We have found that the rate constant for H_2O_2 and $MV^{+\cdot}$ is significantly lower in pure methanol than in water or aqueous methanol, and the reaction of O_2 with $MV^{+\cdot}$ has a solvent-dependent rate.[10] Further the reaction of MV^{2+} with a solvated electron has a rate which changes with micelle concentration in an aqueous solution containing sodium dodecyl sulfate.[29] It seems certain that extrapolating rates from aqueous in vitro studies to real photosynthetic systems is not a reliable procedure.

Nevertheless, the fact that H_2O_2 reacts with $MV^{+\cdot}$ and $DQ^{+\cdot}$ by eight powers of ten more slowly than O_2 and $O_2^{-\cdot}$ react suggests that a buildup of hydrogen peroxide is an important possibility in chloroplasts containing the herbicidal dications under light, particularly since the catalase in plant cells is believed to be located at sites spacially separated from the chloroplast stack.[30] Thus H_2O_2 may indeed be able to oxidize plant tissue and thereby cause plant death.

Finally, the rate of reaction of H_2O_2 and $MV^{+\cdot}$ is sufficiently slow so that deviations from the usual 4:1 stoichiometry for $MV^{+\cdot}/O_2$ in the oxygen analysis techniques are to be expected under some conditions.

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Registry No. $MV^{+\cdot}$, 25239-55-8; $DQ^{+\cdot}$, 59079-66-2; H_2O_2, 7722-84-1; $H_2P_2O_8^{2-}$, 20824-76-4; $HP_2O_8^{3-}$, 56795-74-5; $P_2O_8^{4-}$, 15538-83-7.

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[26] R. F. Homer, G. C. Mees, and T. G. Y. Tomlinson, *J. Sci. Food Agric.*, 11, 309 (1960).

[27] N. H. Porzada, P. M. Pojir, and L. A. Summers, *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.*, **31B**, 1115 (1976).

[28] K. J. Schmalz and L. A. Summers, *Aust. J. Chem.*, **30**, 657 (1977).

[29] M. A. J. Rodgers, D. C. Foyt, and Z. A. Zimek, *Radiat. Res.*, **75**, 296 (1978).

[30] R. P. F. Gregory, *Biochim. Biophys. Acta*, **159**, 429 (1968).

Photooxidation of Alcohols by Ferric Ion

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Near-UV photolysis (through Pyrex) of 0.15 M solutions of $Fe(ClO_4)_3$ in a series of primary alcohols, RCH_2OH, leads to a variety of products, RCHO, CH_2O, RH, RR, RCH_2OR, alkenes, and tetrahydrofurans. Both the products and the variation in their distribution with structure are consistent with the initial production of alkoxy radicals from the alcohols. Photolysis rates parallel the importance of a charge-transfer band in the near UV, implying that it is involved in the primary photochemical process.

The photooxidation of organic substrates by aqueous ferric ion with concomitant reduction of the iron has been studied intermittently for over 30 years.[1] For uncomplexed Fe^{3+}, data are consistent with the formation of hydroxyl radicals, e.g., eq 1, and their subsequent reactions.

$$Fe^{3+}\,(H_2O) \overset{h\nu}{\rightleftharpoons} Fe^{2+} + H^+ + \cdot OH \qquad (1)$$

In the absence of organic substrates O_2 is evolved, but quantum yields are very low due to the reversibility of eq 1. In the presence of organic substrates, hydroxyl radicals are scavanged, and primary quantum yields of the order of 0.065 have been reported.[2] The oxidation products reported for such photooxidations are typical of hydroxyl radical reactions. Aromatics undergo ring hydroxylation or side-chain oxidation, and alcohols are oxidized to carbonyl compounds.[3] In cases where the substrate complexes with Fe^{3+}, photooxidation may occur at longer wavelengths, and it appears that the photoexcited state

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[1] For a review of early work: Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: London, 1970; Chapter 10.

[2] Langford, C. H.; Carey, C. H. *Can. J. Chem.* **1975**, *53*, 2430–2435.

[3] Bates, H. G. C.; Evans, M. G.; Uri, N. *Nature* **1950**, *166*, 869. Bates, H. G. C.; Uri, N. *J. Am. Chem. Soc.* **1953**, *75*, 2754–2759. Baxendale, J. H.; Magee, J. *Trans. Faraday Soc.* **1955**, *51*, 205–213.

0022-3263/81/1946-1260$01.25/0