Photochemistry of Aqueous Permanganate Ion

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Abstract: The photodecomposition of aqueous MnO_4^- with a broadband source has been investigated. The products of the decomposition have been firmly identified. Trapping studies suggest the existence of a long-lived intermediate in the reaction; a structure for this intermediate and a basis for its long life are proposed.

The photochemistry of coordination compounds has been extensively investigated for many years. The electronic transitions of symmetric inorganic complexes are well understood for the most part and lend themselves extremely well to theoretical explanations and predictions based on group theory, Jahn–Teller theory, ligand field theory, etc. It is therefore somewhat surprising that the possibilities for initiating useful reactions with electronically excited inorganic molecules have been largely undeveloped. It is also surprising that the mechanism of one particular simple photoreaction, the decomposition of the permanganate ion—indeed, even the nature of the products of the reaction—has remained unspecified so far. In this paper we describe experiments which provide answers to some of the remaining questions about this system and also suggest the presence and structure of a reactive intermediate which is a more active oxidant than permanganate itself.

The photodecomposition of MnO_4^- in aqueous solution proceeds with evolution of oxygen, but it has not been unequivocally shown[1] whether the net photochemical reaction follows eq 1 or eq 2. A study using isotopic labels[2] did indicate, however, that the oxygen produced comes from permanganate and not from the solvent, a result later confirmed by an investigation[3] of the photolysis of potassium permanganate in rigid glass solutions at 77 K. The lack of an ESR signal corresponding to the O_2^- ion in the latter study suggested that the products were MnO_2^- and O_2. In any case, a single-step decomposition via eq 1 or eq 2 would involve either a three- or four-electron reduction of the metal, events for which there are no precedents.

$$MnO_4^- \rightarrow MnO_2^- + O_2 \qquad (1)$$

$$MnO_4^- \rightarrow MnO_2 + O_2^- \qquad (2)$$
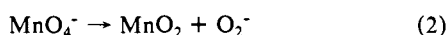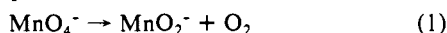
In a careful study under neutral and basic conditions (pH 6.8–13), Zimmerman observed[2] that the quantum yield for oxygen production decreased substantially as the wavelength increased from 254 to 578 nm. Furthermore, he noted that the reaction was temperature dependent at the longest wavelengths. On the basis of these observations, he proposed a mechanism involving internal conversion followed by unimolecular decomposition of the vibrationally excited permanganate. The temperature dependence was rationalized as occurring at wavelengths longer than that corresponding to the activation energy for decomposition, where vibrational energy present before excitation could enable a significantly greater fraction of ions to react.

Adamson et al.[4] have noted that either of two alternative mechanisms could explain the decrease in quantum yield with increasing wavelength. The first mechanism postulates that only the shorter wavelength (311 nm) band is photoactive; reaction induced by wavelengths in the 546-nm band is due to absorption in the overlapping tail of the other band. The second mechanism concerns electron photodetachment from the permanganate ion as the primary photochemical event, followed by fragmentation of neutral MnO_4. Balzani and Carassiti[1] have pointed out, however, that the latter process has been observed only in solid

alkali metal permanganates under radiolytic conditions[5] and is therefore insignificant in UV–visible photochemistry of aqueous permanganate.

It is of substantial interest to ascertain the details of this mechanism and to determine whether the process can be utilized to effect substrate oxidations. Consequently, we have examined the photolytic reduction of aqueous potassium permanganate under neutral, basic, and acidic conditions in both the presence and absence of organic substrates in an effort to develop a better understanding of the reaction mechanism.

Experimental Section

Product identification and kinetic studies were carried out with use of a medium-pressure Hanovia mercury lamp surrounded by a double-walled Pyrex tube through which cold water could be circulated to minimize heat transfer from the lamp to the solution. The products of the reaction were studied by following spectral changes that occurred when the lamp was immersed in a beaker of aqueous potassium permanganate. As the reaction proceeded, aliquots were withdrawn and analyzed spectrophotometrically with use of a Hewlett-Packard Model 8450A UV/vis spectrophotometer. The reaction kinetics were studied in a similar way, except that the vessel containing the permanganate solution was immersed in a bath to maintain constant temperature. It was later found, however, that the constant temperature bath was not necessary because the reaction rate was quite insensitive to temperature between 15 and 20 °C. The water used in all of the experiments was doubly distilled, the final distillation being from basic permanganate,[6] in order to minimize reduction of permanganate by contaminants.

The effect of oxidizable substrates on the rate and quantum yields of the photolysis reaction was studied. This requires soluble, oxidizable compounds that are unreactive toward permanganate in the dark. After testing a large number of compounds, we found that acetone (under acidic conditions) and *p*-toluenesulfonic acid (under all conditions) could be used.

The effect of acetone and three *p*-alkylbenzenesulfonic acids (methyl, ethyl, and isopropyl) on the relative quantum yields was determined from a comparison of the amount of photolysis that occurred in the absence and presence of various amounts of these reactants.

In a typical experiment, eight aliquots of a permanganate solution (3×10^{-4} M $KMnO_4$, 0.13 M $HClO_4$, 1.42×10^{-2} M $Na_4P_2O_7$) were placed in quartz test tubes that had been cooled in an ice bath. (Sodium pyrophosphate was present to stabilize the product, MnO_2^-, by complexation.[7]) Various concentrations of a *p*-alkylbenzenesulfonic acid (0–0.015 M) were added, and the tubes were irradiated for 4 min with use of a Rayonet Merry-Go-Round unit (Southern New England Ultraviolet) fitted with 3000-Å lamps. The decrease in concentration of permanganate in each tube, $\Delta[MnO_4^-]$, was then determined spectrophotometrically by using the band at 546 nm, and relative quantum yields were calculated from the expression $Q_{rel} = \Delta[MnO_4^-]/\Delta[MnO_4^-]_0$, where

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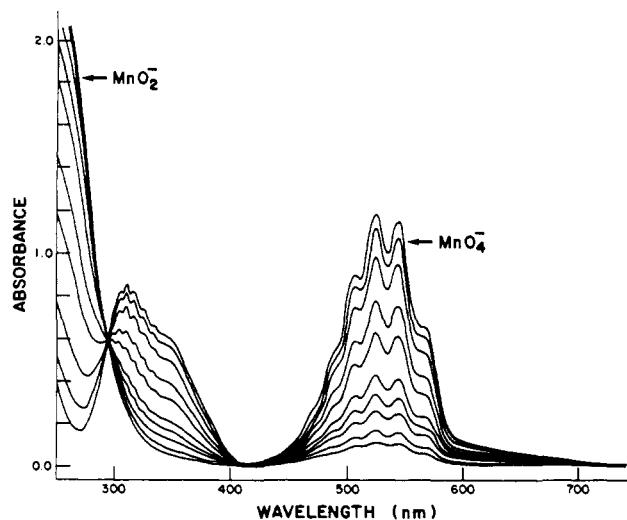
Figure 1. Spectral changes occurring during the photolysis of acidic aqueous permanganate solutions. $[KMnO_4] = 4.95 \times 10^{-4}$ M, $[HClO_4]$ = 0.10 M, $Na_4P_2O_7 = 4.50 \times 10^{-3}$ M.

$\Delta[MnO_4^-]_0$ is the decrease in concentration in a solution which contained no p-alkylbenzenesulfonic acid.

In order to minimize the thermal reduction of permanganate by the p-alkylbenzenesulfonic acids, the Merry-Go-Round unit was placed in a cold room thermostated at 6 °C. After irradiation, the tubes were again placed in an ice bath until absorbance measurements could be completed. In this way it was possible to carry out the entire experiment below 10 °C. Furthermore, each step was timed and a series of control experiments were done in order to estimate the amount of thermal reaction that would occur in each experiment. Appropriate corrections (never in excess of 14%) were then applied and the relative quantum yield calculated. Each experiment was repeated four to ten times.

The effect of p-alkylbenzenesulfonic acids on the relative quantum yields was studied in buffered solutions (0.25 M Na_2HPO_4, 0.25 M $KHPO_4$, pH 6.89) and basic solutions (0.097 M NaOH). The effect of acetone on the relative quantum yields was studied only under acidic conditions; under basic conditions, acetone reduces permanganate in a thermal reaction that cannot be sufficiently suppressed at 0 °C.

Results

Product Identification. In order to determine whether reaction 1 or reaction 2 is the dominant process, identification of the manganese-containing product was undertaken. This was done by studying the photolysis under acidic conditions (0.1 to 1.0 M $HClO_4$) in the presence of sodium pyrophosphate. Zimmerman[2] confined his work to neutral and basic solutions because he felt that under acidic conditions other compounds such as $HMnO_4$, $H_2MnO_4^+$, and Mn_2O_7 might interfere. From a consideration of the pK_a's of $HMnO_4$ and its conjugate acid, $H_2MnO_4^+$, it can be shown, however, that these compounds cannot be present in significant quantities at moderate acidities. For example, if the value of -2.25 is accepted[8] as the pK_a of $HMnO_4$, one finds[9] that a 1.0 $\times 10^{-3}$ M solution of MnO_4^- in 1.0 M perchloric acid would have an equilibrium concentration of $HMnO_4$ of about 10^{-6} M, with the concentration of $H_2MnO_4^+$ being several orders of magnitude smaller. Furthermore, since Mn_2O_7 is the anhydride of permanganic acid, its concentration would also be very small in dilute aqueous solutions.

Under such conditions it is easy to distinguish between the two possibilities represented by eq 1 and 2. Both products would be stable under acidic conditions; MnO_2 would gradually coagulate and eventually precipitate,[10] while MnO_2^-, complexed by pyrophosphate, should form a stable pink solution.[11] The latter was

Table I. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Toluenesulfonic Acid[a]

| [p-toluenesulfonic acid], M	Q_{rel}	[p-toluenesulfonic acid], M	Q_{rel}
0	1.00	5.02×10^{-3}	1.30 ± 0.09
5.30×10^{-4}	0.96 ± 0.11	6.51×10^{-3}	1.34 ± 0.03
1.01×10^{-3}	1.07 ± 0.14	8.50×10^{-3}	1.38 ± 0.09
1.51×10^{-3}	1.15 ± 0.12	9.98×10^{-3}	1.29 ± 0.09
2.51×10^{-3}	1.21 ± 0.03	1.24×10^{-2}	1.36 ± 0.15
3.52×10^{-3}	1.28 ± 0.09	1.50×10^{-2}	1.38 ± 0.14

^{a} $[HClO_4] = 0.13$ M. $[Na_4P_2O_7] = 1.42 \times 10^{-2}$ M.

Table II. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Ethylbenzenesulfonic Acid[a]

[p-ethylbenzene-sulfonic acid], M	Q_{rel}	[p-ethylbenzene-sulfonic acid], M	Q_{rel}
0	1.00	8.43×10^{-3}	1.43 ± 0.18
1.50×10^{-3}	1.11 ± 0.10	9.90×10^{-3}	1.46 ± 0.08
2.49×10^{-3}	1.13 ± 0.10	1.14×10^{-2}	1.51 ± 0.11
3.49×10^{-3}	1.16 ± 0.14	1.23×10^{-2}	1.52 ± 0.14
4.98×10^{-3}	1.20 ± 0.10	1.48×10^{-2}	1.58 ± 0.15
6.46×10^{-3}	1.36 ± 0.15		

^{a} $[HClO_4] = 0.13$ M. $[Na_4P_2O_7] = 1.42 \times 10^{-2}$ M.

Table III. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Isopropylbenzenesulfonic Acid[a]

[p-isopropylbenzene-sulfonic acid], M	Q_{rel}	[p-isopropylbenzene-sulfonic acid], M	Q_{rel}
0	1.00	6.46×10^{-3}	1.23 ± 0.15
5.00×10^{-4}	1.07 ± 0.06	8.43×10^{-3}	1.24 ± 0.06
9.99×10^{-4}	1.10 ± 0.12	9.90×10^{-3}	1.32 ± 0.09
1.50×10^{-3}	1.10 ± 0.10	1.23×10^{-2}	1.38 ± 0.02
2.49×10^{-3}	1.11 ± 0.07	1.48×10^{-2}	1.55 ± 0.11
3.49×10^{-3}	1.26 ± 0.06	1.62×10^{-2}	1.46 ± 0.20
4.98×10^{-3}	1.19 ± 0.11	1.82×10^{-2}	1.47 ± 0.11

^{a} $[HClO_4] = 0.13$ M. $[Na_4P_2O_7] = 1.42 \times 10^{-2}$ M.

observed to occur. As the concentration of permanganate fell, a new species with an intense absorption above 300 nm formed (Figure 1). Two absorption maxima centered at 240 and 260 nm, each with an extinction coefficient of about 4000, were also observed. Iodometric titrations[12] indicated that the oxidation state of this final product was +3. Addition of base caused manganese dioxide to precipitate in accordance with the known properties of manganese(III) in aqueous alkaline solutions[13] (eq 3).

$$2MnO_2^- + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4OH^- \qquad (3)$$
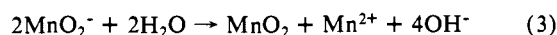
Under basic conditions, the product of the reaction could be identified from its spectrum to be manganate(VI) ion, MnO_4^{2-} (Figure 2). This ion is most likely formed from the oxidation of the initial product, MnO_2^-, by permanganate (eq 4).

$$MnO_2^- + 3MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + 2H_2O \qquad (4)$$
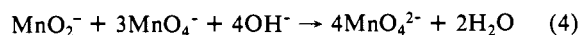
Under neutral conditions, the product was observed to be a brown precipitate resembling MnO_2, which is known to be formed from the oxidation of MnO_2^- in the absence of complexing agents (eq 5).

$$3MnO_2^- + MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 4OH^- \qquad (5)$$
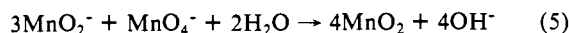
When acidic permanganate solutions were irradiated in an inverted burette resting in a pneumatic trough, almost quantitative yields of oxygen could be obtained if the solution was carefully saturated with O_2 before the lamp was turned on. Because of the relatively high solubility of oxygen in water, low yields were obtained if solutions unsaturated with O_2 were irradiated. This

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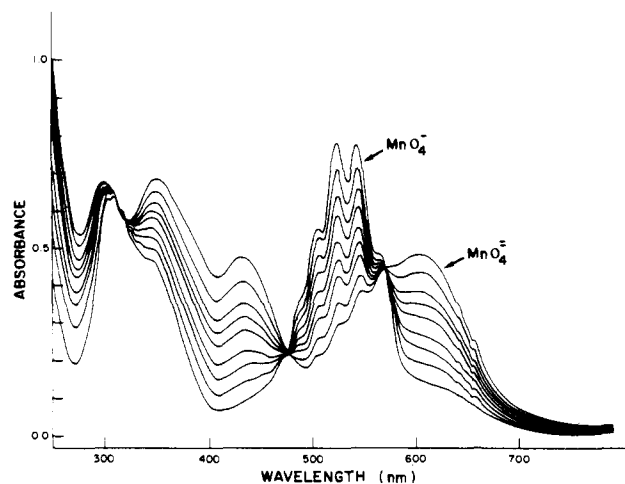
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Figure 2. Spectral changes occurring during the photolysis of alkaline aqueous permanganate solutions. $[KMnO_4] = 3.2 \times 10^{-4}$ M, $[NaOH] = 1.0$ M.

Table IV. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Toluenesulfonic Acid[a]

[p-toluenesulfonic acid], M	Q_{rel}	[p-toluenesulfonic acid], M	Q_{rel}
0	1.00	5.02×10^{-3}	1.58 ± 0.09
5.03×10^{-4}	1.39 ± 0.15	8.50×10^{-3}	1.57 ± 0.14
1.01×10^{-3}	1.41 ± 0.08	9.98×10^{-3}	1.62 ± 0.17
1.51×10^{-3}	1.34 ± 0.05	1.24×10^{-2}	1.75 ± 0.08
2.51×10^{-3}	1.39 ± 0.05	1.49×10^{-2}	1.69 ± 0.09
3.52×10^{-3}	1.43 ± 0.10		

[a] $[Na_2HPO_4] = 0.25$ M. $[KH_2PO_4] = 0.25$ M. pH 6.89.

Table V. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Ethylbenzenesulfonic Acid[a]

[p-ethylbenzenesulfonic acid], M	Q_{rel}	[p-ethylbenzenesulfonic acid], M	Q_{rel}
0	1.00	4.98×10^{-3}	1.65 ± 0.14
5.00×10^{-4}	1.29 ± 0.16	5.96×10^{-3}	1.55 ± 0.08
9.99×10^{-4}	1.39 ± 0.20	7.44×10^{-3}	1.62 ± 0.10
1.50×10^{-3}	1.17 ± 0.09	9.90×10^{-3}	1.70 ± 0.17
2.49×10^{-3}	1.46 ± 0.18	1.19×10^{-2}	1.65 ± 0.10
3.00×10^{-3}	1.43 ± 0.21	1.48×10^{-2}	1.74 ± 0.12
3.98×10^{-3}	1.59 ± 0.08		

[a] $[Na_2HPO_4] = 0.25$ M. $[KH_2PO_4] = 0.25$ M. pH 6.89.

Table VI. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Isopropylbenzenesulfonic Acid[a]

[p-isopropylbenzenesulfonic acid], M	Q_{rel}	[p-isopropylbenzenesulfonic acid], M	Q_{rel}
0	1.00	5.00×10^{-3}	1.35 ± 0.17
5.00×10^{-4}	1.05×0.08	6.46×10^{-3}	1.44 ± 0.09
9.99×10^{-4}	1.31 ± 0.11	8.43×10^{-3}	1.56 ± 0.12
1.50×10^{-3}	1.17 ± 0.12	9.90×10^{-3}	1.50 ± 0.15
2.50×10^{-3}	1.31 ± 0.15	1.23×10^{-2}	1.58 ± 0.11
3.50×10^{-3}	1.36 ± 0.19	1.48×10^{-2}	1.59 ± 0.13

[a] $[Na_2HPO_4] = 0.24$ M. $[KH_2PO_4] = 0.24$ M. pH 6.89.

Table VII. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Toluenesulfonate[a]

[p-toluenesulfonate], M	Q_{rel}	[p-toluenesulfonate], M	Q_{rel}
0	1.00	5.02×10^{-3}	1.16 ± 0.12
5.03×10^{-4}	1.09 ± 0.13	6.51×10^{-3}	1.20 ± 0.01
1.01×10^{-3}	1.15 ± 0.11	8.50×10^{-3}	1.21 ± 0.07
1.51×10^{-3}	1.12 ± 0.09	9.98×10^{-3}	1.23 ± 0.14
2.51×10^{-3}	1.13 ± 0.13	1.24×10^{-2}	1.30 ± 0.16
3.52×10^{-3}	1.17 ± 0.08	1.50×10^{-2}	1.28 ± 0.11

[a] $[NaOH] = 0.097$ M.

Table VIII. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Ethylbenzenesulfonate[a]

[p-ethylbenzenesulfonate], M	Q_{rel}	[p-ethylbenzenesulfonate], M	Q_{rel}
0	1.00	6.46×10^{-3}	2.00 ± 0.10
5.00×10^{-4}	1.45 ± 0.14	8.43×10^{-3}	1.96 ± 0.12
9.99×10^{-4}	1.57 ± 0.12	9.90×10^{-3}	1.98 ± 0.11
1.50×10^{-3}	1.61 ± 0.21	1.23×10^{-2}	2.05 ± 0.14
2.49×10^{-3}	1.66 ± 0.16	1.48×10^{-2}	2.11 ± 0.11
3.49×10^{-3}	1.66 ± 0.15	1.62×10^{-2}	2.12 ± 0.16
4.98×10^{-3}	1.88 ± 0.23		

[a] $[NaOH] = 0.097$ M.

Table IX. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing p-Isopropylbenzenesulfonate[a]

[p-isopropylbenzenesulfonate], M	Q_{rel}	[p-isopropylbenzenesulfonate], M	Q_{rel}
0	1.00	6.46×10^{-3}	1.37 ± 0.09
5.00×10^{-4}	1.08 ± 0.12	8.43×10^{-3}	1.45 ± 0.09
9.99×10^{-4}	1.16 ± 0.04	9.90×10^{-3}	1.36 ± 0.07
1.50×10^{-3}	1.13 ± 0.06	1.23×10^{-2}	1.43 ± 0.06
2.49×10^{-3}	1.25 ± 0.10	1.48×10^{-2}	1.52 ± 0.03
3.49×10^{-3}	1.34 ± 0.08	1.62×10^{-2}	1.49 ± 0.08
4.98×10^{-3}	1.33 ± 0.04		

[a] $[NaOH] = 0.097$ M.

Table X. Relative Quantum Yields for the Irradiation of Permanganate Solutions Containing Acetone[a]

[acetone], M	Q_{rel}	[acetone], M	Q_{rel}
6.78×10^{-2}	1.35 ± 0.06[b]	5.24×10^{-1}	2.32 ± 0.18
1.35×10^{-1}	1.65 ± 0.11	7.71×10^{-1}	2.93 ± 0.26
2.67×10^{-1}	1.86 ± 0.07	1.01	3.19 ± 0.32
3.96×10^{-1}	2.15 ± 0.07	1.24	2.94 ± 0.24

[a] $[HClO_4] = 0.13$ M, $[Na_4P_2O_7] = 1.42 \times 10^{-2}$ M. [b] Uncertainties are expressed in terms of the standard deviation of the values obtained from several experiments.

phenomenon was also observed by earlier workers.[14] The direct observation of both MnO_2^- and O_2 upon irradiation demonstrates conclusively that eq 1, and not eq 2, describes the photodecomposition of MnO_4^-.

For photolyses carried out in the presence of reductants, oxidation products were separated from the aqueous solution and identified by NMR and/or melting points of p-toluidine derivatives. These were found to be the para carboxylic acid, methyl ketone, and dimethylcarbinol for the p-methyl, -ethyl, and -isopropylbenzenesulfonic acids, respectively.

Kinetics. Relative quantum yields for the reaction in acidic permanganate are listed in Tables I–III. Relative quantum yields for buffered and basic solutions are listed in Tables IV–IX. The effect of acetone is shown in Table X.

The rate of the reaction was found to be zero order in permanganate at high concentrations (Figure 3) and first order at low concentrations (Figure 4). A zero-order rate is expected at high concentrations because all of the light is absorbed, and the rate of reaction will appear to be independent of the concentration of absorbing species. At low concentration, where a large fraction of the light passes through the solution, the rate of reaction depends on the number of photons absorbed and is proportional to the

concentration of permanganate. Identical rates were obtained by both spectrophotometric and iodometric[12] determinations of the permanganate concentrations.

The rate of disappearance of permanganate was found to increase when a reductant such as acetone or p-toluenesulfonic acid was present in the solution (Figure 5). The dark (thermal) oxidation of the reductants proved to be negligibly slow at these concentrations; the permanganate concentration dropped only when the solutions were irradiated. Furthermore, the yield of oxygen decreased when photolysis of permanganate was carried out in the presence of acetone or p-toluenesulfonic acid.

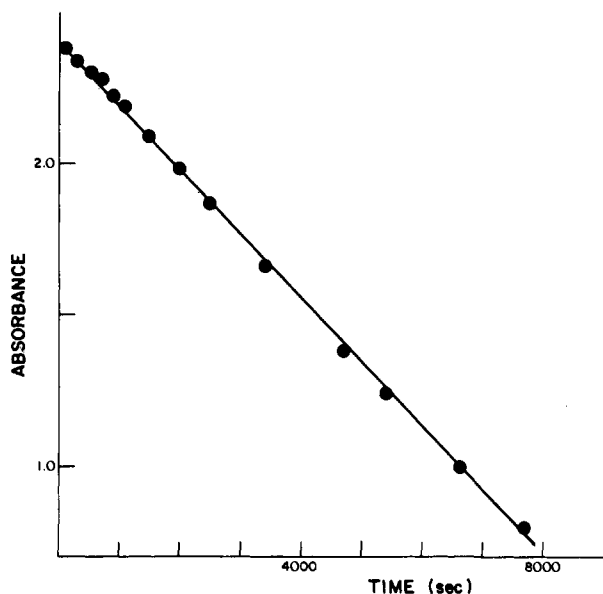(14) Rideal, E. K.; Norrish, R. G. W. *Proc. R. Soc. London* **1923**, *103A*, 342–366; **1923**, *103A*, 366–382.

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Figure 3. Typical zero-order plot for the photolysis of concentrated permanganate solutions. $[KMnO_4] = 1.10 \times 10^{-3}$ M, $[HClO_4] = 0.10$ M, $Na_4P_2O_7 = 4.50 \times 10^{-3}$ M.

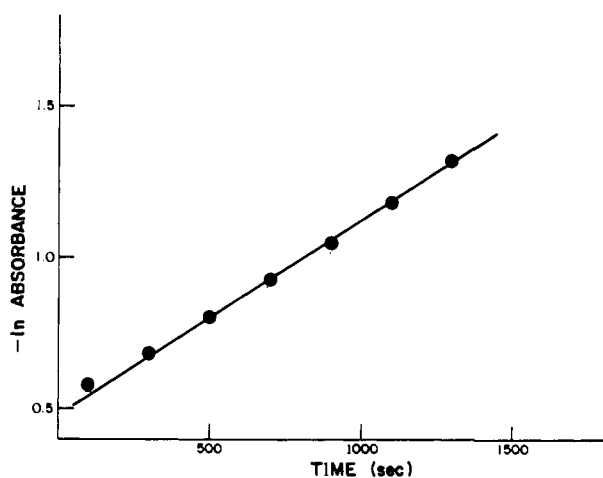**Figure 4.** Typical first-order plot for the photolysis of dilute permanganate solutions. $[KMnO_4] = 2.38 \times 10^{-4}$ M, $[HClO_4] = 0.10$ M, $Na_4P_2O_7 = 4.50 \times 10^{-3}$ M.
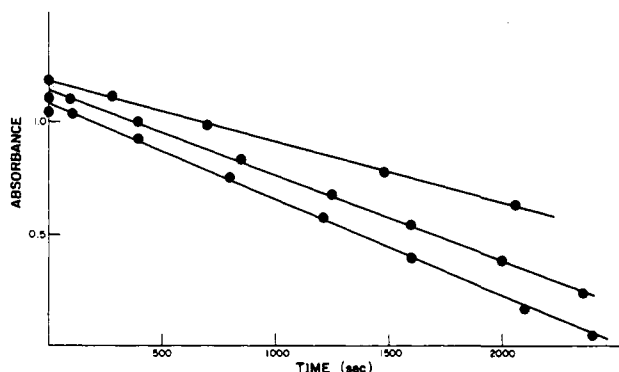
Figure 5. Effect of acetone on the rate of the photochemical reduction of permanganate. $[KMnO_4] = 4.95 \times 10^{-4}$ M, $[HClO_4] = 0.11$ M, $Na_4P_2O_7 = 4.50 \times 10^{-3}$ M. Upper curve: no acetone, slope $= 2.7 \times 10^{-4}$ s^{-1}. Middle curve: [acetone] $= 0.195$ M, slope $= -3.83 \times 10^{-4}$ s^{-1}. Lower curve: [acetone] $= 0.390$ M, slope $= -4.38 \times 10^{-4}$ s^{-1}.

Relative Quantum Yields. The relative quantum yields obtained under acidic, basic, or neutral conditions were approximately linear in the concentration of added substrate so long as it remained low. At higher concentrations, however, the relative quantum yield became almost independent of added substrate in every case. A
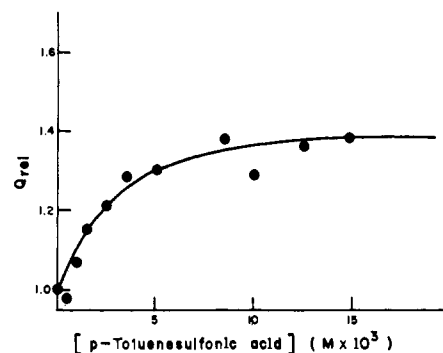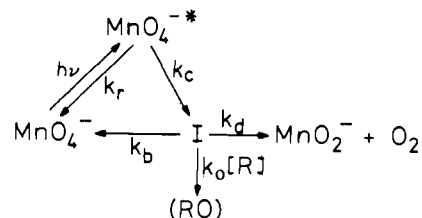

Figure 6. Plot of relative quantum yield as a function of p-toluenesulfonic acid concentration in 0.13 M $HClO_4$.

Scheme I

typical plot of relative quantum yield vs. concentration of added substrate is shown in Figure 6.

Discussion

The observation that addition of either acetone or p-toluenesulfonic acid increases the rate of photolysis while decreasing the yield of dioxygen is consistent with a photochemically prepared intermediate being trapped by an oxidizable substrate. Furthermore, the intermediate must have the capability of returning back to reactant. Inasmuch as the dark reaction for oxidizing these substrates is slow, the intermediate must be a kinetically more effective oxidizing agent than is permanganate.

Determination of the relative quantum yield for reaction as a function of reductant (quencher) normally makes it possible to calculate the product of the lifetime of the excited reactant, τ, and the bimolecular rate constant, k_q, from the slope of a Stern–Volmer plot.[15]

The data in Tables I–X, however, show a pronounced curvature under all conditions; the relative quantum yields level off at high reductant concentrations (Figure 6). The curvature indicates that something other than the initially formed electronically excited permanganate is being trapped. If the initially formed electronically excited permanganate were being trapped by the reductant, the Stern–Volmer plots would be linear at these quantum yields.

The Reaction Mechanism. The observation that addition of reductants causes an increase in the rate of disappearance of the permanganate and a concomitant decrease in the yield of oxygen suggests that the reaction mechanism involves formation of an intermediate of high oxidation potential that can react in three different ways, as outlined in Scheme I: (i) it can return to permanganate, (ii) it can decompose to MnO_2^- and O_2, or (iii) it can react with an oxidizable substrate (reductant).

The mechanism is also consistent with the observed kinetic behavior. At low concentrations of reductant, R, the relative quantum yield will depend on both the structure and concentration of R, while at sufficiently high concentrations, it will be independent of both. That is, at high concentration of R, all of I which is formed will be trapped. The low concentration data do show a linear dependence on R concentration, but because of the very high reactivity of I, its reaction rate appears to be fairly insensitive to the structure of R.

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On the basis of this mechanism, we can calculate a lower limit for the lifetime of the intermediate in the absence of reductant. The quantum yield for reaction (disappearance of MnO_4^-) at reductant concentration [R] is given by eq 6. The relative quantum yield, Φ_R/Φ_R^0, is therefore given by eq 7; the curve-crossing (k_c) and relaxation (k_r) terms drop out. The relative

$$\Phi_R = \left(\frac{k_d + k_0[R]}{k_b + k_d + k_0[R]}\right)\left(\frac{k_c}{k_r + k_c}\right) \quad (6)$$

$$\frac{\Phi_R}{\Phi_R^0} = \left(\frac{k_d + k_0[R]}{k_b + k_d + k_0[R]}\right)\left(\frac{k_b + k_d}{k_d}\right) \quad (7)$$

quantum yield levels off at large [R], and its maximum value is equal to $(k_b + k_d)/k_d$. This value is about 1.7 (Table IV). In the absence of reductant, therefore, 60% of the intermediates follow the decomposition path (k_d), and 40% rearrange back to ground-state permanganate (k_b).

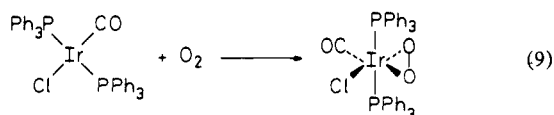The absolute quantum yield in the absence of reductant is given by eq 8. Under neutral conditions, this quantum yield is[2] 2 ×

$$\Phi_R^0 = \left(\frac{k_d}{k_b + k_d}\right)\left(\frac{k_c}{k_r + k_c}\right) \quad (8)$$

10^{-4}, which we have confirmed. Substitution of the decomposition/back reaction branching ratio and the quantum yield value into eq 8 yields the curve-crossing/relaxation branching ratio. Under these conditions, $k_c/(k_r + k_c)$ is equal to 3.4×10^{-4}.

Since k_b and k_d have comparable magnitudes and since concentrations of reductant of about 10^{-3} M can trap a significant amount of the intermediate, a limit on the lifetime of the intermediate can be set by assuming k_0 to be diffusion controlled, i.e., about 10^{10} M^{-1} s^{-1}. Substitution of this value into eq 7 gives values of about 10^{-7} s for the lifetime. If the trapping reaction rate is less than diffusion controlled, the lifetime must be proportionally greater. These observations rule out electronically excited permanganate as the intermediate, since its lifetime has been estimated to be in the picosecond range due to the lack of both observable fluorescence[2] and observable excited-state absorption.[16]

The radiative lifetime for an electronically excited state, which is an upper limit for the true lifetime, may be calculated from the oscillator strength and frequency of the spectral transition producing the excitation.[17] For the $^1T_2$ excited state of permanganate produced by light in the 311-nm band, which is responsible for most of the photochemistry, this lifetime is 20 ns. The discrepancy between this upper limit and the experimental lower limit for the intermediate's lifetime supports the conclusion that excited permanganate does not live long enough to account for our trapping rates.

Some insight into the possible structure of intermediate I can be obtained from a consideration of the hypothetical reaction between MnO_2^- and O_2, which, according to the principle of microscopic reversibility, should follow the same pathway as the decomposition of I but in the reverse direction. There is a great deal of information available concerning the reactions between low-valent transition-metal complexes and oxygen.[18] In almost all cases, these reactions are believed to yield dihapto dioxygen complexes as, for example,[19] reaction 9. If the same sort of

$$ \quad (9)$$

reaction occurs between MnO_2^- and O_2, the product would be a manganese peroxide with a formal oxidation state of +5 as in eq 10.

$$MnO_2^- + O_2 \rightarrow \quad (10)$$

Although manganate(V) ions are not usually considered to be stable species,[20] it is known that they are formed as intermediates when permanganate is reduced by alkenes,[21] and they were recently identified as the products obtained from a pulsed radiolysis study of manganate(VI) ion in 0.1 M sodium hydroxide solutions.[22]

To our knowledge, there has been only one previous report of the formation of a peroxo manganese compound,[23] and although the structure of that particular compound has not been well characterized, numerous transition-metal peroxo compounds are known[24,25] and a few have been subjected to X-ray crystallographic studies.[25] For example, hydrogen chromate reacts with hydrogen peroxide to give a blue compound, $CrO(O_2)_2$, which forms several well-characterized solid derivatives when complexed with an additional ligand such as pyridine:[26]

$$HCrO_4^- \xrightarrow{H_2O_2} CrO(O_2)_2 \xrightarrow{py} \quad (11)$$
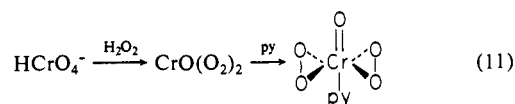
Furthermore, it is known (in analogy with the proposed properties of $MnO_2(O_2)^-$) that the typical reactions of these peroxo compounds are either decomposition with the evolution of oxygen[24] or reduction by organic compounds.[27]

Another product that could be obtained from the addition of oxygen to manganate(III) ion would be a monohapto dioxygen manganese(IV) complex as in eq 12. Such a three-coordinate MnO_4^- could conceivably solvate at the vacant tetrahedral coordination site, thereby hindering rearrangement back to tetrahedral permanganate and accounting for the intermediate's long lifetime. Superoxide complexes are usually formed, however, from porphyrin complexes of transition metals such as chromium(II), iron(II), ruthenium(II), or cobalt(II) having a single axial ligand.[18] Although we are unaware of any similar structural studies with manganese(III) complexes, Hoffman and co-workers[28] have found, in contrast to the above examples, that manganese(II) porphyrins form dihapto dioxygen compounds.

$$MnO_2^- + O_2 \rightarrow \quad (12)$$
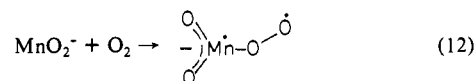
Thus it seems logical to postulate a peroxo manganese(V) complex (as in eq 10) as the long-lived intermediate, I, in the photochemical reactions of permanganate (Scheme I). For this explanation to be plausible, however, the intermediate's rearrangement back to tetrahedral permanganate should be slow in
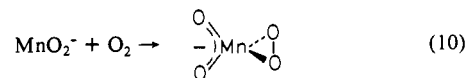
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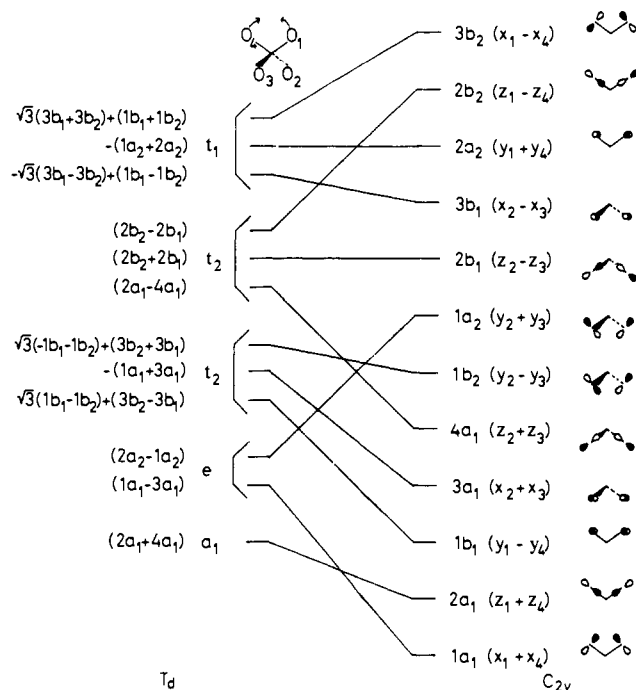
Figure 7. Proposed reduction of the ligand group orbitals for tetrahedral permanganate into C_{2v} symmetry. Normalization factors of $^1/_2$ and $^1/_4$ have been omitted from both sides of the figure.

Figure 8. Proposed frontier orbitals for permanganate ion under reduced (C_{2v}) symmetry: (a) HOMO; (b) ground orbital in 311-nm spectral transition; and (c) LUMO.

order to account for its long lifetime.

Molecular Orbital Correlation. The most logical cause for a slow rearrangement would be an energy barrier to the thermal reaction due to an avoided crossing of two electronic states with the same symmetry (a Woodward–Hoffmann barrier). Such a situation would explain the facile photochemical formation of the peroxo intermediate as well as its long lifetime. Symmetry barriers commonly appear as a result of HOMO–LUMO energy reversals along reaction coordinates. Searching for a symmetry barrier,[29] we therefore consider the molecular orbitals of the permanganate ion and how their energies are affected by decreases in the O–Mn–O bond angle. If the orbital from which an electron is promoted by irradiation increases dramatically in energy with the deformation, and if it eventually becomes higher in energy than the orbital occupied by the excited electron, the A_1 ground state of the reactant MnO_4^- will correlate with an A_1 doubly excited state of the peroxo complex and vice versa. An avoided crossing will occur, leading to the proposed energy barrier between the two species.

The problem is complicated by the change in symmetry from T_d to C_{2v} that occurs as the tetrahedral permanganate deforms. The molecular orbital correlation must be constructed under the symmetry elements that are conserved during the reaction[29]—in this case, the elements of the C_{2v} point group. Since the ligand orbital basis functions of the tetrahedral ion are known,[30] however, and since both of the electronic transitions undergone by permanganate in the visible are ligand-to-metal charge transfers whose energies and orbital assignments are known,[31,32] reduction of the tetrahedral symmetry to produce HOMO and LUMO orbitals under C_{2v} symmetry is a tractable problem.
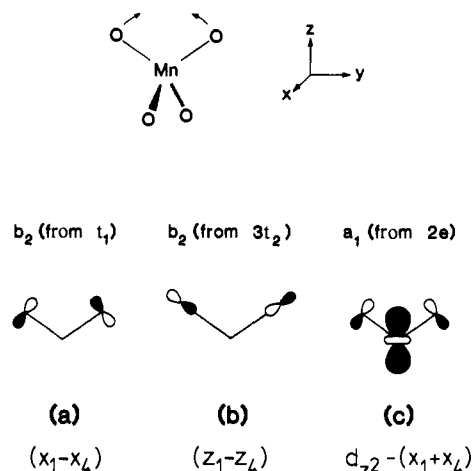
Since there are no degenerate representations in C_{2v} symmetry, deformed MnO_4^- has no degenerate orbitals. Each ligand symmetry orbital is a normalized combination of two oxygen p orbitals in either a bonding or an antibonding fashion. Using the coordinate system given by Ballhausen,[30] we can construct a reasonable

energy ordering for the ligand orbitals based on the extent of overlap of each type of p orbital. First, p orbitals on the two oxygens that are close together (say, using Ballhausen's notation, ligands 1 and 4) interact more than the orbitals on ligands 2 and 3. Second, p_x orbitals overlap the most, because they point at each other. The p_y orbitals interact the least, because their overlap has a π orientation. Therefore, the lowest-energy ligand orbital is the $p_x(1) + p_x(4)$ bonding combination, which we will refer to as $(x_1 + x_4)$; the most antibonding combination is $(x_1 - x_4)$. The s orbitals on the oxygen atoms are lower in energy and do not contribute significantly to the frontier orbitals of permanganate, so a ladder of the 12 symmetry orbitals based on p functions (Figure 7) will be sufficient for our purposes.

The explicit functions for the 12 tetrahedral ligand orbitals based on p orbitals are also given by Ballhausen[30] and can be expressed as combinations of the C_{2v} pairs. The energy ordering of these ligand functions is diagrammed by Ballhausen and Gray,[31] as is the ordering of the molecular orbitals created by their interaction with the metal. The HOMO is the triply degenerate t_1 set; the next lower level is a t_2 set formed from combinations of the two different t_2 ligand sets (the σ set based on z orbitals and the π set based on x and y orbitals). These two molecular orbital sets are the initial orbitals for the two allowed electronic transitions of permanganate.[31]

The correlation may now be carried out for the nonbonding molecular orbitals, since they consist solely of the ligand sets we have. The HOMO of C_{2v} permanganate is the $3b_2$ ($x_1 - x_4$) combination; it must correlate with the highest-energy tetrahedral orbital that has $3b_2$ as a component. This orbital turns out to be one of the t_1 set (Figure 7).

The remaining ligand orbitals may be correlated in the same manner. Since the t_2 and e ligand orbitals are apparently degenerate,[31] the e set is placed lower because it interacts with the metal to a much greater extent. This ordering leads to a correlation between the e pair and the $1a_1$ and $1a_2$ combinations. The LUMO of tetrahedral permanganate is an e pair consisting mostly of metal d orbitals with ligand orbitals contributing to a lesser extent in an antibonding fashion. Under C_{2v} symmetry, this pair splits into an a_1 and an a_2; the question then arises as to which one is lower in energy (and is therefore the LUMO). The a_1 component is known[33] to be the LUMO for some other four-coordinate C_{2v} compounds, so we choose it here as well. The LUMO for C_{2v} MnO_4^- is thus the metal d_{z^2} orbital combined with the $1a_1$ ligand orbital in an antibonding manner.

The three relevant frontier orbitals for C_{2v} permanganate (Figure 8) have thus been determined by symmetry reduction of the known molecular orbitals. The next step is to estimate what

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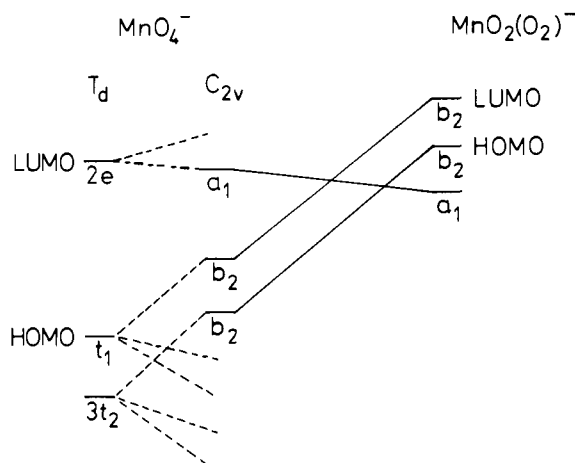
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Figure 9. Hypothetical molecular orbital correlation diagram for rearrangement of tetrahedral MnO_4^- to a peroxo complex.

happens to the relative energies of these orbitals as the two oxygens are bent together; if the LUMO drops below either of the others, the basis of a Woodward–Hoffmann barrier has been found.

The proposed frontier orbital correlation is shown in Figure 9. Both of the nonbonding b_2 orbitals become antibonding as the two oxygen atoms move together, while the LUMO is slightly stabilized by the interaction of its p-orbital components. It is entirely likely that both b_2 orbitals become higher in energy than the LUMO when the O–O bond is fully formed. Breaking the O–O bond of the peroxo complex while keeping the electrons in the same orbitals therefore results in an electronically excited state of permanganate. The avoided crossing that ensues produces a barrier to the thermal rearrangement.

This double crossing also implies that photoexcitation from *both* the $3t_2$ and the t_1 orbitals to the 2e LUMO can produce the peroxo complex and subsequent decomposition. If the energies of both singly excited states lie above the barrier caused by the avoided crossing, permanganate in each excited state may undergo curve crossing and produce the peroxo complex. Zimmerman's absolute yield[2] did in fact increase by a small amount in the 546-nm (t_1) band, although the yield is much greater in the 311-nm ($3t_2$) band. Why the shorter wavelength band should be so much more photoactive than the longer wavelength one cannot be rigorously determined from this simple analysis; some knowledge of the energies of the various excited states as a function of O–Mn–O bond angle would be necessary before the wavelength dependence of the quantum yield could be fully understood. Symmetry considerations merely suggest that both bands could in fact be photoactive, and the data provide a modicum of support for this conclusion.

The electronic state correlation diagram presented in Figure 10 is consistent with all the data. The $^1T_2$ state corresponding to the visible absorption band (a $^1B_2$ state in C_{2v} symmetry) lies just below the doubly excited state curve at some O–Mn–O bond angle. Only a few vibrationally excited ions possess enough internal energy to perform the curve crossing; most of the electronically excited ions will return to ground-state permanganate by radiationless processes. The low probability of curve-crossing accounts for the inability[16] to bleach ground-state permanganate absorption by photolysis at 530 nm. The higher excited state populated by absorption in the ultraviolet (also a $^1B_2$) has sufficient energy to cross onto the surface leading to products. Although the relative energies depicted in Figure 10 are conjectural, they successfully explain the greater photoactivity of the 311-nm band as well as the temperature-dependent quantum yield of the 546-nm band. Although such a temperature dependence could conceivably arise from different activation energies for the competing isomerization and elimination reactions of the intermediate, the observed wavelength dependence of this temperature dependence[2] indicates that additional vibrational energy affects the probability of forming the intermediate via curve crossing rather than affecting the branching ratio of the intermediate once formed.
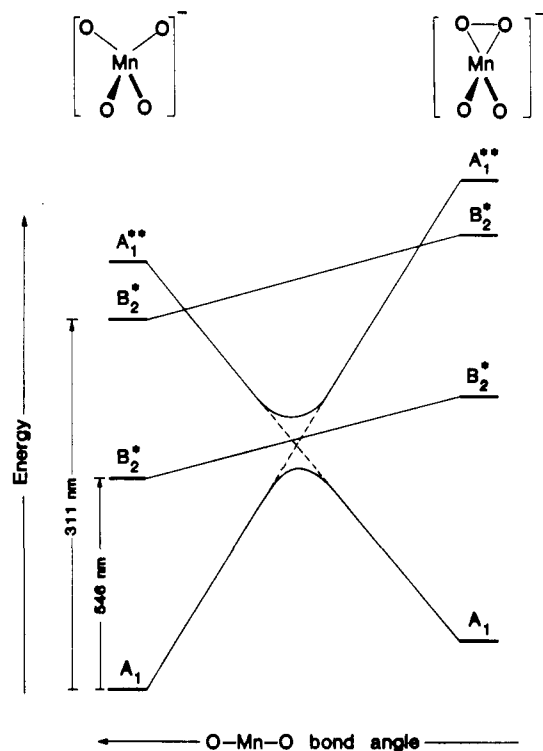

Figure 10. Hypothetical electronic state correlation diagram for the rearrangement reaction.

Evidence for symmetry barriers to a similar reaction, the deformation of a metal dicarbene into a metal alkene, has been found by Hoffmann and co-workers.[34] Their extended Hückel calculation reveals not one but two a_1-b_2 orbital crossings, which result in symmetry barriers for every d-orbital occupation except d^2.

The possible involvement of singlet excited oxygen in the mechanism deserves comment. Oxygen produced by the decomposition of a number of peroxo compounds, including perchromate ion (CrO_8^{3-}), is known[35] to be formed in the singlet state. Furthermore, singlet oxygen is a good oxidizing agent.[36] This raises the possibility that the product oxygen is responsible for the oxidation of the organic substrates. That reaction, however, is not observed directly; it is inferred from the accelerated disappearance of permanganate. Reaction with $^1O_2$ could be responsible for this accelerated disappearance only if (1) no intermediate exists in the decomposition and (2) the reverse recombination is extremely rapid. In that case, the decomposition could not be observed to the extent that it has been. It should also be pointed out that the lifetime of singlet oxygen in water is shorter than in any other solvent[37]—between 1.5 and 4 μs.

Conclusions

Photochemical evidence and theoretical considerations suggest that reaction 1 occurs by light-induced formation of a Mn(V) peroxo complex, which then undergoes a reductive elimination to yield products. This mechanism is compatible with the generally held idea[38] that changes in the oxidation state of metals occur in increments of one or two units. The peroxo intermediate is a faster oxidizing agent than permanganate and could be used to effect substrate oxidations at dilute concentrations with reasonable rates. The intermediate has a long (microsecond) lifetime due to a

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symmetry barrier to rearrangement to tetrahedral MnO_4^-. The photochemistry may be induced by both of the electronic transitions of permanganate occurring in the visible, but the quantum yield for the shorter wavelength band is significantly greater. Both the structure of the intermediate and its symmetry barrier to thermal decomposition have literature precedents.

New Entry to the C-Glycosilation by means of Carbenoid Displacement Reaction. Its Application to the Synthesis of Showdomycin

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Abstract: The novel and stereoselective carbon–carbon bond-forming reaction at the anomeric center of carbohydrates has been developed by means of a carbenoid displacement reaction with phenyl thioglycosides. This reaction was suggested to proceed via the oxonium ion intermediates and has the following advantages: (i) the preferential participation of a carbenoid with a sulfur atom can restrict the reaction site; (ii) the reaction can be carried out under neutral reaction condition; and (iii) the introduction of various functionalities can be accomplished by manipulation of the organosulfur groups of the products. This synthetic strategy was successfully applied to the synthesis of antitumor agent, (+)-showdomycin, and would provide a general route to the other C-glycosides.

In recent years much attention has been focussed on the formation of carbon–carbon (C–C) bonds[1] at the anomeric center of carbohydrates directed at synthesizing physiologically interesting or naturally occurring C-nucleosides[2] and C-glycosides[3] and also at evaluating their synthetic potential as chiral templates.[4] During the course of our studies on the new C–C bond-forming reactions by employing a carbenoid displacement reaction,[5] we became interested in developing a method for the efficient C-glycosilation reaction.

Scheme I

Scheme II

A

Our design using a carbenoid displacement reaction for the C-glycosilation is based on the following considerations: (i) the use of phenyl thioglycosides as starting materials can restrict the reaction site by the preferential participation[6] of the sulfur atom with the carbenoid, (ii) the introduction of various functionalities can be accomplished by manipulation of the organosulfur groups

(1) For examples, see: (a) Kunz, H.; Weissmüller, J.; Müller, B. *Tetrahedron Lett.* **1984**, *25*, 3571. (b) Yougai, S.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1983**, 68. (c) Martin, O. R.; Mahnken, R. E. *Ibid.* **1986**, 497. (d) Kozikowski, A. P.; Sorgi, K. L. *Tetrahedron Lett.* **1982**, *23*, 2281. (e) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (f) Schmidt, R. R.; Hoffmann, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 406. (g) Dawe, R. D.; Reid, B. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1180. (h) Stewart, A. O.; Williams, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 4289. (i) DeShong, P.; Slough, G. A.; Elango, V. *Ibid.* **1985**, *107*, 7788. (j) Cohen, T.; Lin, M.-T. *Ibid.* **1984**, *106*, 1130. (k) Rosenthal, A. *Adv. Carbohydr. Chem.* **1968**, *23*, 59. (l) Trainor, G. L.; Smart, B. E. *J. Org. Chem.* **1983**, *48*, 2447. (m) Dunkerton, L. V.; Serino, A. J. *Ibid.* **1982**, *47*, 2812. (n) Arai, I.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 287. (o) Arai, I.; Lee, T. D.; Hanna, R.; Daves, G. D., Jr. *Organometallics* **1982**, *1*, 742. (p) Dupuis, J.; Giese, B.; Hartung, J.; Leising, M. *J. Am. Chem. Soc.* **1985**, *107*, 4332. (q) Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622.
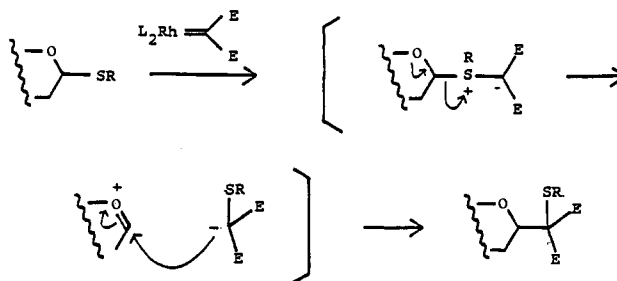
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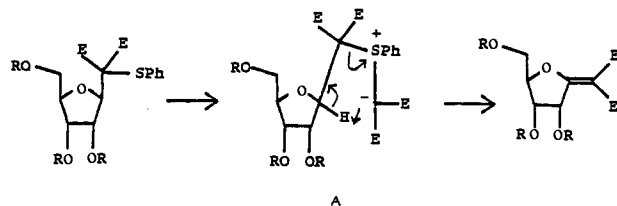
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