of ethyl acetate was found in the crystal lattice. The absolute configuration was determined from the anomalous scattering effects that showed the correct enantiomer to have an R factor of 0.093 while the other was 0.121. This difference was significant at the 0.005 level[43] and was confirmed by careful remeasurement of 13 enantiomorph sensitive reflections. Hydrogens were put in calculated positions and assigned isotropic temperature factors corresponding to their attached atoms. The function $\sum w(|F_0| - |F_c|)^2$ with $1/(\sigma F_0)^2$ was minimized to give an unweighted residual of 0.087. The conformations of the two crystallographically distinct molecules were different primarily in the amide side chain. For instance, the dihedral angle for N12–C13–C15–C16 was −92.4°, while the angle for N12′–C13′–C15′–C16′ was 114.1°. No abnormally short intermolecular contacts were noted. Tables I–III containing the final fractional coordinates, temperature parameters, bond distances, and bond angles are available as supplementary material. Figure 1 is a computer-generated perspective drawing of 28 from the final X-ray coordinates.

Acknowledgment. It is a pleasure to acknowledge the efforts of Drs. P. Reider, A. King, and E. J. J. Grabowski who were instrumental in optimizing the reaction conditions summarized in Scheme III. We are also indebted to Mr. J. P. Moreau (chemical analysis), Ms. J. S. Murphy, Dr. S. L. Varga, Dr. S. M. Pitzenberger (^{1}H NMR), Mr. J. Smith, Dr. H. Ramjit (mass spectrum), and Mr. C. F. Homnick (HPLC analysis). We thank Dr. P. S. Anderson for support and encouragement.

(43) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Kinetics and Mechanism of the Oxidation of Unsaturated Carboxylic Acids by Methyltributylammonium Permanganate in Methylene Chloride Solutions

Joaquin F. Perez-Benito and Donald G. Lee*

Department of Chemistry, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

Received January 20, 1987

The product obtained when permanganate is reduced by unsaturated carboxylic acids under anhydrous conditions is manganese(III). The rate of reaction, which is subject to acid catalysis, exhibits a Hammet ρ value of 1.11 and inverse secondary isotope effects (k_H/k_D = 0.96–0.98) when the hydrogens on the double bond are replaced by deuterium. The involvement of a free-radical process is indicated by the formation of polymer during the oxidation of acrylic and methacrylic acids. The reaction is believed to be initiated by formation of an organometallic complex in which the double bond is a η^2 ligand on manganese. Rearrangement of this complex results in the formation of a reactive manganate(V) cyclic diester, which undergoes a rapid (free-radical) reduction to manganese(III).

The oxidation of unsaturated carboxylic acids (and their salts) by aqueous potassium permanganate has received considerable attention. For example, the oxidations of cinnamic acids,[1–4] cinnamate ion,[5,6] crotonic acid,[7] oleic acid,[9,10] oleate ion,[5,11,12] butenoate ions,[1,5] pentenoate ions,[1] propenoate ions,[1] 3-thienyl-2-propenoate ions,[13] and 2-pyridinyl-2-propenoate ions[13] have been described in the literature. More recently, however, it has become common to carry out permanganate oxidations, with the aid of phase-transfer agents, in nonaqueous solvents.[14] Despite the usefulness of this procedure, practically no kinetic or mechanistic information is available with respect to the oxidation of unsaturated carboxylic acids, although a closely related reaction—the oxidation of cinnamate esters—has been studied.[15]

As the results presented in this paper indicate, the oxidation of unsaturated carboxylic acids in nonaqueous solvents contrasts in several ways, both with the corresponding aqueous phase oxidations and with the oxidation of unsaturated esters.

Experimental Section

The solvent used in all of the experiments, anhydrous methylene chloride, was purified by double distillation over 4-Å molecular sieves. The oxidizing agent, methyltributylammonium permanganate, was obtained by precipitation from an aqueous mixture of methyltributylammonium bromide and potassium permanganate.[16] Because of its instability, it was stored in the dark and at low temperatures. With the exception of the deuteriated derivatives of cinnamic acid, the reducing agents were obtained commercially and purified by either fractional distillation or crystallization. Cinnamic-α-*d* and -β-*d* acids were prepared according to the procedure previously reported.[17] Crotonic acid and all the derivatives of cinnamic acid were used in the trans form.

The kinetic experiments were all carried out in the presence of excess alkene. The reaction rates were followed by use of a Hewlett-Packard 8450A UV–vis spectrophotometer, provided with a thermostated cuvette holder. The permanganate band at 526

---

(1) Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628.
(2) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 3033.
(3) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 5517.
(4) Simandi, L. I.; Jaky, M. *J. Am. Chem. Soc.* **1976**, *98*, 1995.
(5) Wiberg, K. B.; Geer, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 5827.
(6) Lee, D. G.; Nagarajan, K. *Can. J. Chem.* **1985**, *63*, 1018.
(7) Polgar K.; Jaky, M.; Simandi, L. I. *React. Kinet. Catal. Lett.* **1976**, *5*, 489.
(8) Wiberg, K. B.; Deutsch, C. J.; Rocek, J. *J. Am. Chem. Soc.* **1973**, *95*, 3034.
(9) Iwahashi, M.; Toyoki, K.; Watanabe, T.; Muramatsu, M. *J. Colloid Interface Sci.* **1981**, *79*, 21.
(10) Garti, N.; Avui, E. *Colloids Surf.* **1982**, *4*, 33.
(11) Simandi, L. I.; Jaky, M. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 605.
(12) Coleman, J. E.; Ricciuti, C.; Swern, D. *J. Am. Chem. Soc.* **1956**, *78*, 5342.
(13) Freeman, F.; Chang, L. Y. *J. Am. Chem. Soc.* **1986**, *108*, 4504.
(14) Lee, D. G. In *Oxidation in Organic Chemistry, Part D*; Trahanovsky, W. S., Ed.; Academic: New York, 1982; p 147.
(15) Lee, D. G.; Brown, K. C. *J. Am. Chem. Soc.* **1982**, *104*, 5076.
(16) Karaman, H.; Barton, R. J.; Robertson, B. E.; Lee, D. G. *J. Org. Chem.* **1984**, *49*, 4509.
(17) Lee, D. G.; Brownridge, J. R. *Can. J. Chem.* **1973**, *51*, 2102.

0022-3263/87/1952-3239$01.50/0

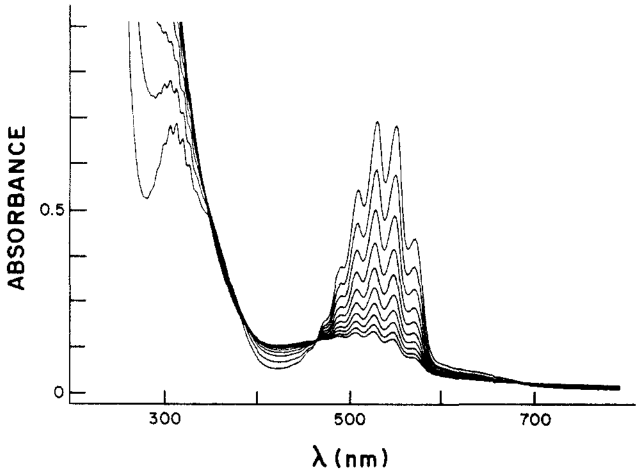


Figure 1. Successive scans at 9-s intervals for the oxidation of crotonic acid (3.09×10^{-3} M) by methyltributylammonium permanganate (3.00×10^{-4} M) in methylene chloride at 25.0 °C (isosbestic point 465 nm).

nm (ϵ 2.63×10^3) was chosen to monitor the rate of reaction. Pseudo-first-order rate constants were obtained from the slopes of $-\ln (A - A_f)$ vs. time plots. A small correction was introduced to account for the slow oxidation of the solvent by permanganate.

In a typical experiment, a 50-mL volumetric flask containing a solutin of 3,3-dimethylacrylic acid (1.20×10^{-2} M) in methylene chloride was held for about 10 min in a thermostated bath at 25.0 °C. Methyltributylammonium permanganate (5×10^{-3} g) was then added and the solution vigorously stirred until homogeneous. About 2 mL of the solution was immediately transferred to a cell (also at 25.0 °C) in the thermostated compartment of the spectrophotometer. Absorbances were periodically recorded until the reaction was complete.

The oxidation state of manganese in the product mixture was determined by means of an iodometric technique. When the spectrum showed that all of the permanganate had been consumed, a 5.0-mL aliquot was withdrawn from the solution and transferred to a 50-mL volumetric flask. An excess of tetrabutylammonium iodide (2×10^{-2} g) was then added, followed by 5 mL of glacial acetic acid. The yellow solution thus obtained was diluted to 50 mL with methylene chloride, and the resultant mixture was stirred to homogeneity. The quaternary ammonium triiodide (QI_3) concentration was determined by measuring its absorbance at 365 nm ($\epsilon = 2.62 \times 10^4$).

In a separate experiment, addition of methyltributylammonium permanganate (0.1 g) to acrylic acid (1 g) in 50 mL of methylene chloride produced an immediate reaction with the formation of a dark red solution. The solvent was removed by a rotatory evaporator, and the remaining solid was treated with glacial acetic acid. After the solvent was evaporated again, a white solid (0.52 g) was obtained and identified by IR spectroscopy as polyacrylic acid. Polymerization of methacrylic acid under similar conditions was also observed.

Results

Sequential scans obtained during the oxidaton of crotonic acid by methyltributylammonium permanganate, shown in Figure 1, indicate an isosbestic point for this reaction at 465 nm. According to the iodometric technique described above, the oxidation state of manganese at the end of the reactions is 2.99 ± 0.11. This average value was obtained from 95 experiments involving the oxidation of 16 different unsaturated acids. The spectra recorded at the end of the reactions display an absorbance maximum at 478 nm, which is very near the maximum reported for Mn^{3+} and $Mn(OH)^{2+}$ in aqueous solutions.[18] Thus, it can be concluded that the final product obtained from the reduction of permanganate by unsaturated acids in methylene chloride solutions is a Mn(III) species. The color exhibited by this product is deep red at high concentrations and pale red-brown at low concentrations.

Table I. Activation Parameters for the Oxidation of Unsaturated Carboxylic Acids by Methyltributylammonium Permanganate in Methylene Chloride[a]

substrate	$\Delta H^{\ddagger}$, kJ mol^{-1}	$-\Delta S^{\ddagger}$,[b] J K^{-1} mol^{-1}
acrylic acid	19.8 ± 1.9	149 ± 7
methacrylic acid	29.3 ± 1.4	124 ± 5
crotonic acid	31.9 ± 2.3	120 ± 9
3,3-dimethylacrylic acid	39.4 ± 0.2	119 ± 1
cinnamic acid	33.6 ± 1.1	118 ± 4
elaidic acid	40.0 ± 2.7	133 ± 10
oleic acid	40.8 ± 0.4	132 ± 1

[a] Temperature range 0.0–25.0 °C. [b] The entropies of activation are referred to the 1 M standard state.

Table II. Isotope Effects on the Oxidation of Cinnamic Acid by Methyltributylammonium Permanganate in Methylene Chloride Solutions

substrate	k_2, M^{-1} s^{-1}	k_H/k_D
cinnamic acid	5.53	
cinnamic-α-*d* acid	5.67	0.98
cinnamic-β-*d* acid	5.79	0.96

Table III. Rate Constants for the Oxidation of Ethyl Cinnamate and 3,3-Dimethylacrylic Acid by Methyltributylammonium Permanganate in Methylene Chloride Solutions Containing Acetic Acid

substrate	[acetic acid], M	k_2, M^{-1} s^{-1}
ethyl cinnamate	0.0	0.882
	0.35	1.52
	0.70	1.90
	1.05	2.19
	1.40	2.56
3,3-dimethylacrylic acid	0.0	0.434
	0.26	0.770
	0.35	0.835
	0.70	0.963
	1.05	1.06
	1.34	1.17
	1.75	1.25
	2.10	1.36

Plots of $-\ln (A - A_f)$ vs. time are linear, thus indicating that the reaction rates are first order with respect to oxidizing agent. This was confirmed by measuring the initial rates of oxidation of 3,3-dimethylacrylic acid at several permanganate concentrations; the initial rates are proportional to the initial permanganate concentrations. (See paragraph at the end of paper concerning supplementary material.)

The pseudo-first-order rate constants were observed to be proportional to the alkene concentrations. Thus, it may be concluded that the reactions are also first order with respect to the reductants.

Plots of $-\ln (k_2/T)$ vs. $1/T$ were linear in all cases (see supplementary material), and the activation parameters for the oxidation of several typical unsaturated acids are summarized in Table I. The maximum possible error corresponding to each activation parameter, calculated according to the method proposed by Petersen,[19] is also given in Table I.

The rate of oxidation of cinnamic acid exhibits inverse secondary deuterium isotope effects at both the α- and β-positions. The data are in Table II.

---

(18) Wells, C. F.; Davies, G. *J. Chem. Soc. A* **1967**, 1858.

(19) Petersen, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819.

Table IV. Dependence of the Initial Rate for the Catalytic Reaction on the Methyltributylammonium Permanganate Concentration[a]

$[QMnO_4]_i$,[b] M × 10^4	r',[c] M s^{-1} × 10^6	k_1',[d] s^{-1} × 10^3	$[QMnO_4]_i$,[b] M × 10^4	r',[c] M s^{-1} × 10^6	k_1',[d] s^{-1} × 10^3
0.75	0.73	9.73	3.75	3.67	9.79
1.50	1.55	10.33	4.50	4.29	9.53
2.25	2.23	9.91	5.25	5.13	9.77
3.00	2.93	9.77	6.00	5.83	9.72

[a] [3,3-Dimethylacrylic acid] = 1.20 × 10^{-2} M; [acetic acid] = 1.75 M; temperature 25 °C. [b] Initial permanganate concentration. [c] Initial rates of the catalytic portion of the reaction. [d] $k_1' = r'/[QMnO_4]_i$.

Table V. Dependence of the Rate Constants for the Catalytic Reaction on the Concentration of 3,3-Dimethylacrylic Acid[a]

[3,3-dimethylacrylic acid], M × 10^2	k_1',[b] s^{-1} × 10^3	k_2',[c] M^{-1} s^{-1}	[3,3-dimethylacrylic acid], M × 10^2	k_1',[b] s^{-1} × 10^3	k_2',[c] M^{-1} s^{-1}
0.60	4.79	0.798	1.41	11.2	0.794
0.80	6.43	0.804	1.60	12.4	0.775
1.00	7.77	0.777	1.80	14.4	0.800
1.20	9.73	0.811			

[a] $[QMnO_4]$ = 3.00 × 10^{-4} M; [acetic acid] = 1.75 M; temperature 25.0 °C. [b] Pseudo-first-order rate constants for the catalytic portion of the reaction. [c] $k_2' = k_1'/$[3,3-dimethylacrylic acid].

The second-order rate constants for the oxidation of a series of meta- and para-substituted cinnamic acids exhibit a linear Hammet correlation (see supplementary material) with a positive slope (ρ = 1.11 at 0.0 °C), which indicates an electron-rich transition state.

The rate of oxidation of these compounds is catalyzed by the presence of carboxylic acids. For example, it can be seen from the data in Table III that the rates of oxidation of both ethyl cinnamate and 3,3-dimethylacrylic acid are accelerated by the presence of acetic acid. Consequently, it must be assumed that during the oxidation of unsaturated carboxylic acids the substrate serves as both the reductant and the catalyst. Under pseudo-first-order conditions where the substrate is present in a large excess, there would, however, be no concern about a significant reduction in the concentration of catalyst as the reaction proceeds.

A study of the oxidation of 3,3-dimethylacrylic acid in the presence of excess acetic acid (1.75 M) confirmed that the acid-catalyzed reaction is also first order in both oxidant and reductant. See Tables IV and V. In these tables, the rate of the catalytic portion of the reaction was obtained by subtracting the known rate in the absence of catalyst (acetic acid) from that observed when catalyst is present.

The existence of general-acid catalysis for these reactions was confirmed by a systematic study of the catalytic effect of different carboxylic acids on the rate of oxidation of 3,3-dimethylacrylic acid by methyltributylammonium permanganate in methylene chloride solutions. Plots of log k_1 vs. log [catalyst] were linear in all cases. The intercepts and the slopes obtained for each acid catalyst are compiled in Table VI. It can be seen that the kinetic order with respect to the catalytic agent covers the range 0.5–1.0, with most of the values being fractional. This nonintegral order appears to be due to the tendency of weak organic acids to dimerize in nonpolar solvents such as methylene chloride. The weakest acids, such as acetic and benzoic, which are most likely to dimerize, exhibit orders of approximately 0.5, while the stronger acids such as dichloroacetic and trichloroacetic, which are less susceptible to dimerization, show orders close to unity.

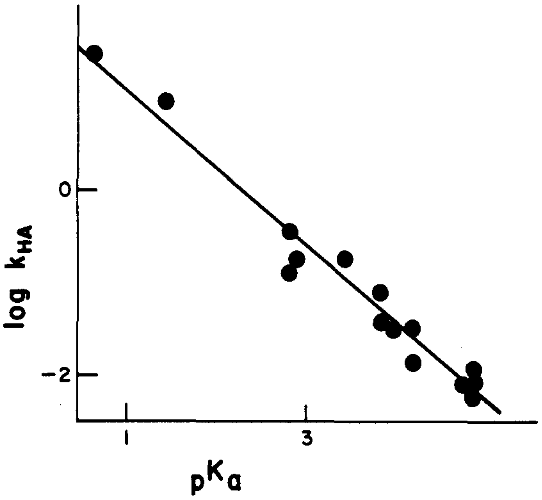


Figure 2. Brønsted plot for general-acid catalysis in the oxidation of 3,3-dimethylacrylic acid (1.20 × 10^{-2} M) by methyltributylammonium permanganate (3.00 × 10^{-4} M) in methylene chloride at 25.0 °C.

The intercepts of these plots, which are the logarithms of the rate constants when the concentration of catalyst is equal to 1.0 M, are linearly related to the pK_a's of the catalyst. The resulting Brønsted plot is shown in Figure 2.

The effect of added quaternary ammonium salts on the rates of reaction was also studied. The results have been summarized in Table VII.

Discussion

The effect of substituents on the rate of oxidation of cinnamic acid clearly indicates that the transition state is electron rich as compared with the ground state. A similar result was previously reported for the oxidation of the corresponding methyl esters under comparable conditions.[15]

Reports from other laboratories presented convincing evidence that these and related reactions are initiated by

Table VI. Kinetic Data for the Oxidation of 3,3-Dimethylacrylic Acid in Methylene Chloride Solutions Containing Various Carboxylic Acids[a]

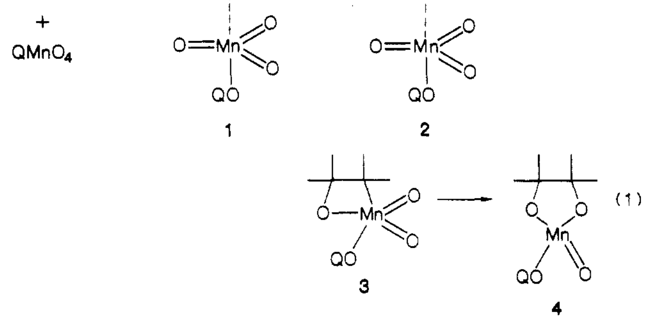
acid	log k_{HA}[b]	order[c]	acid	log k_{HA}[b]	order[c]
propionic	−2.06	0.80	*m*-bromobenzoic	−1.42	0.54
caproic	−1.95	0.82	*p*-nitrophenylacetic	−1.09	0.70
valeric	−1.95	0.86	*m*-nitrobenzoic	−0.72	0.80
isobutyric	−2.23	0.66	*o*-chlorobenzoic	−0.74	0.76
butyric	−2.14	0.68	chloroacetic	−0.45	0.81
acetic	−2.12	0.47	2-chloropropionic	−0.90	0.65
benzoic	−1.86	0.47	dichloroacetic	0.96	1.03
p-chlorophenylacetic	−1.48	0.64	trichloroacetic	1.48	0.99
3-chloropropionic	−1.49	0.54			

[a] $[QMnO_4]$ = 3.00 × 10^{-4} M; [3,3-dimethylacrylic acid] = 1.20 × 10^{-2} M; temperature 25.0 °C. [b] Intercept from the log k_1' vs. log [catalyst]. [c] Slope from the log k_1' vs. log [catalyst].

Table VII. Rate Constants for the Oxidation of Cinnamic Acid by Tetrabutylammonium Permanganate in Methylene Chloride Solutions Containing Other Quaternary Ammonium Salts

quaternary ammonium salt	[QX], M × 10^2	k_2, M^{-1} s^{-1}
tetrabutylammonium perchlorate	0	4.03
	0.39	4.01
	0.77	4.06
	1.15	3.96
	1.53	3.92
	1.91	3.88
tetrabutylammonium hydrogen sulfate	0.19	4.00
	0.96	3.72
	1.73	4.07
tetrabutylammonium acetate	0.38	2.38
	0.77	1.46
	1.15	1.09
	1.53	0.89
	1.91	0.77

the formation of a complex in which the double bond becomes a η^2 ligand on manganese, as in eq 1.[20,1] Products



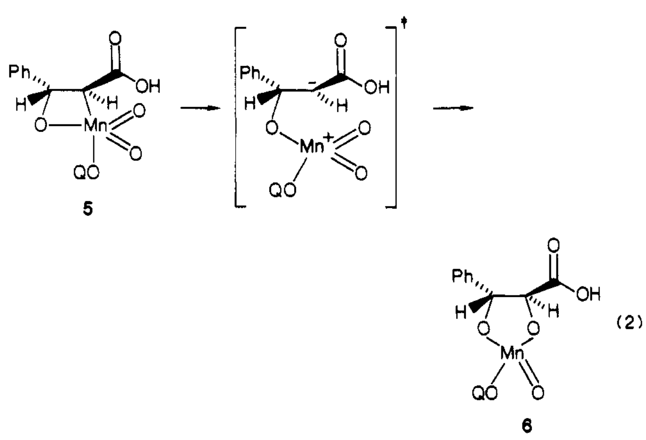
(1)

develop when the manganese slips toward one end of the double bond (as in structure **2**) and a cyclic organometallic compound **3** forms.[20,21] Rearrangement of **3** into **4** by migration of the carbon from manganese to oxygen results in the formation of a cyclic manganese(V) diester, which is known to be an important intermediate in these reactions.[22]

The first three steps depicted in eq 1 all involve bond formation, whereas the last step requires cleavage of a C–Mn bond. Consequently, it seems reasonable to consider this last step to be rate limiting, a suggestion that is consistent with the observed isotope effects in this and other analogous reactions.[23] A highly structured transition state is also consistent with the large negative entropies of activation reported in Table I.

Since the Hammett ρ value is positive, it is apparent that the rate-limiting step must proceed with the development of negative charge on the α-carbon, as in eq 2.

The results presented in Table III indicate that the reaction is subject to acid catalysis, a good Brønsted plot being obtained when carboxylic acids of various structures are used as the source of protons (Figure 2). It is instructive to consider possible points in the reaction sequence where acid catalysis could logically occur. It is known, for example, that protonation of permanganate ion



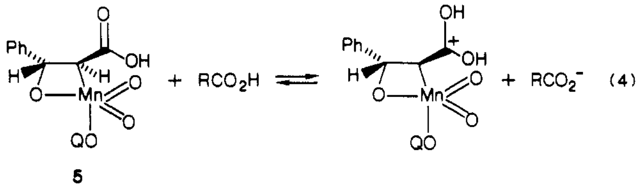
(2)

produces a powerful oxidant, $HMnO_4$.[24] Proton exchange, as depicted in eq 3, could therefore account for the observed catalysis.

$$Q^+MnO_4^- + RCO_2H \rightleftharpoons HMnO_4 + RCO_2^-Q^+ \quad (3)$$

However, a comparison of the pK_a's of $HMnO_4$ with those of the carboxylic acids indicates that the equilibrium shown in eq 3 would lie well to the left; i.e., the pK_a's of permanganate acid and acetic acid are −2.25 and 4.8, respectively.[25,26] Consequently, if the acidities measured in aqueous solutions are applicable to methylene chloride solutions, the concentration of $HMnO_4$ in the experiments described herein would be less than 1×10^{-10} M.

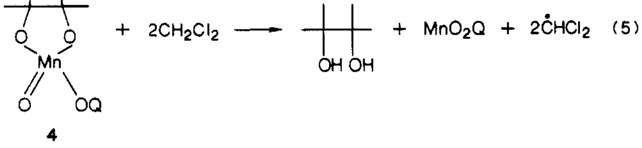
A more likely possibility is that protonation of the metallacyclobutane **5** decreases the activation energy of the rate-limiting step, **5** → **6**. Protonation of **5** as in eq 4 would greatly reduce the energy required to achieve the enolate-like transition state depicted in eq 2.



(4)

The involvement of eq 4 in the reaction sequence also accounts for the decrease in rate observed when tetrabutylammonium acetate is added to the reaction mixture (Table VII). The presence of the basic acetate ion would tend to shift this equilibrium to the left. It should be noted that addition of other quaternary ammonium salts, such as tetrabutylammonium perchlorate, does not affect the rate, thus eliminating the possibility of ascribing the suppression in rate caused by the quaternary ammonium acetate to a salt effect.

The fact that acrylic and methacrylic acids polymerized during the course of these reactions indicates the presence of free radicals. It is quite likely that these radicals are formed during the reduction of the reactive manganese(V) diester **4** to manganese(III) as in eq 5.



(5)

---

[20] Sharpless, K. B.; Teranishi, A. Y.; Blackvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

[21] Rappe', A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 3287.

[22] Stewart, R. In *Oxidation in Organic Chemistry*, Part A; Academic: New York, 1965; p 42. Freeman, F. *Rev. React. Species Chem. React.* **1976**, *1*, 179.

[23] Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

[24] Frigerio, N. A. *J. Am. Chem. Soc.* **1969**, *91*, 6200.

[25] Bailey, N.; Carrington, A.; Lott, K. A. K.; Symons, M. C. R. *J. Chem. Soc.* **1960**, 290.

[26] Bordwell, F. G. *Organic Chemistry*; Macmillan: New York, 1963, p 869.

Although this step has previously been proposed for comparable reactions,[27] experimental evidence for the occurrence of free radicals has previously been lacking.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada is acknowledged. J.F.P.-B. is also thankful to the Spanish Ministry of Education and Science for the grant that made possible his participation in this project.

Registry No. Acrylic acid, 79-10-7; methacrylic acid, 79-41-4; crotonic acid, 3724-65-0; 3,3-dimethylacrylic acid, 541-47-9; cinnamic acid, 621-82-9; elaidic acid, 112-79-8; oleic acid, 112-80-1; methyltributylammonium permanganate, 82444-42-6; deuterium, 7782-39-0; propionic acid, 79-09-4; caproic acid, 142-62-1; valeric acid, 109-52-4; isobutyric acid, 79-31-2; butyric acid, 107-92-6; acetic acid, 64-19-7; benzoic acid, 65-85-0; *p*-chlorophenylacetic acid, 1878-66-6; 3-chloropropionic acid, 107-94-8; *m*-bromobenzoic acid, 585-76-2; *p*-nitrophenylacetic acid, 104-03-0; *m*-nitrobenzoic acid, 121-92-6; *o*-chlorobenzoic acid, 118-91-2; chloroacetic acid, 79-11-8; 2-chloropropionic acid, 598-78-7; dichloroacetic acid, 79-43-6; trichloroacetic acid, 76-03-9.

Supplementary Material Available: Spectrum of the product (Mn^{3+}), typical first-order plot for the oxidation of oleic acid by methyltributylammonium permanganate, Arrhenius plot for the oxidation of cinnamic acid by methyltributylammonium permanganate, Hammett plot for the oxidation of meta- and para-substituted cinnamic acids by methyltributylammonium permanganate, and tables of rate constants for the oxidation of 3,3-dimethylacrylic acid and crotonic acid by methyltributylammonium permanganate (6 pages). Ordering information is given on any current masthead page.

---

[27] Lee, D. G.; Perez-Benito, J. F. *Can. J. Chem.* **1985**, *63*, 1275.

Free Radicals in Organic Synthesis. A Novel Synthesis of Ethylene Glycol Based on Formaldehyde

John R. Sanderson,* Ernest L. Yeakey, Jiang J. Lin, Roger Duranleau, and Edward T. Marquis

Texaco Chemical Company, Austin, Texas 78752

Received February 13, 1987

1,3-Dioxolane reacted with formaldehyde in the presence of free radical initiators to produce 2-(hydroxymethyl)-1,3-dioxolane in moderate yield. 2-(Hydroxymethyl)-1,3-dioxolane was catalytically hydrogenated to ethylene glycol.

Introduction

The use of free radical reactions for the formation of carbon–carbon bonds has been known for years[1–4] but has not been used extensively in organic synthesis except for special reactions such as free radical cyclizations.[5] Free radical reactions have, however, been used increasingly in recent years for the synthesis of organic molecules.[6–10]

Kollar reported in 1984 on the development of a novel route to ethylene glycol based on the free radical addition of methanol to formaldehyde.[11–15] Radicals are generated by the thermal decomposition of di-*tert*-butyl peroxide. *tert*-Butyl alcohol and acetone are produced as important byproducts.[16] The process is summarized in eq 1–4.

$$(CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_3CO^{\bullet} \qquad (1)$$

$$(CH_3)_3CO^{\bullet} + CH_3OH \rightarrow (CH_3)_3COH + \dot{C}H_2OH \qquad (2)$$

$$\dot{C}H_2OH + CH_2{=}O \rightarrow HOCH_2CH_2O^{\bullet} \qquad (3)$$

$$CH_3OH + HOCH_2CH_2O^{\bullet} \rightarrow HOCH_2CH_2OH + \dot{C}H_2OH \qquad (4)$$

Because of the ease of reaction of formals under free radical generating conditions,[17–20] we investigated the reaction of 1,3-dioxolane (1) with formaldehyde under various conditions. This paper reports our initial work on the reaction of 1,3-dioxolane (1) with formaldehyde under free radical conditions. The major product, 2-(hydroxymethyl)-1,3-dioxolane (2), can be hydrogenated to ethylene glycol—an industrially important product.[21]

---

[1] Urry, W. H.; Stacey, F. W.; Juveland, O. O.; McDonnell, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 250.

[2] Urry, W. H.; Stacey, F. W.; Huyser, E. S.; Juveland, O. O. *J. Am. Chem. Soc.* **1954**, *76*, 450.

[3] Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957.

[4] Kharasch, M. S.; Rowe, J. L.; Urry, W. H. *J. Org. Chem.* **1951**, *16*, 905.

[5] Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.

[6] Vogel, H. H. *Synthesis* **1970**, 99.

[7] Hart, D. J. **Science** (*Washington, D.C.*) **1984**, *223*, 883.

[8] Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

[9] Stark, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303.

[10] Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787.

[11] Kollar, J. *CHEMTECH* **1984**, 504.

[12] Kollar, J. (Redox Technologies) U.S. Patent 4393252, 1983.

[13] Kollar, J. (Celanese) U.S. Patent 4337371, 1982.

[14] Kollar, J. (Redox Technologies) U.S. Patent 4412085, 1983.

[15] This reaction had been previously reported by Oyama: Oyama, M. *J. Org. Chem.* **1965**, *30*, 2429.

[16] *Chem. Week* **1984** (March 7), 35.

[17] Watanabe, Y.; Tsuji, Y.; Takeuchi, R.; *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1428.

[18] LaLande, R.; Maillard, B.; Cazaux, M. *Tetrahedron Lett.* **1969**, *9*, 745.

[19] Kalashnikov, S. M.; Glukhova, S. S.; Imashev, U. B.; Zlot-skii, S. S.; Rakhmankulov, D. L. *Zh. Org. Khim.* **1979**, *15*, 2462.

[20] Rakhmankulov, D. L.; Zlotskii, S. S.; Zorin, V. V.; Imashev, V. B.; Karakhanov, R. A. *Russ. Chem. Rev.* (*Engl. Transl.*) 1981, *50*, 762.

0022-3263/87/1952-3243$01.50/0