Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part IV.[1] Kinetic Investigation of the Oxidation of Maleic and Fumaric Acids

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The kinetics of the permanganate oxidation of maleic and fumaric acids to formyl(hydroxy)acetic acid have been studied by the stopped-flow technique in aqueous solution between pH 0·5 and 5·5. The reactions are first order with respect to both MnO_4^- and the substrates. The second-order rate constant depends strongly on the pH. The rate of interconversion of the acid, the mono-, and the di-anion is much higher than the rate of oxidation. The resolved rate constants are, in the above order (at 25 °C): 1080, 1880, and 1000 $dm^3\ mol^{-1}\ s^{-1}$ (maleic acid and 15,000, 3000, and 1180 $dm^3\ mol^{-1}\ s^{-1}$ (fumaric acid). Low activation enthalpies and high negative activation entropies are observed for both substrates. The rate-determining step is the *cis*-attack of permanganate on the double bond, resulting in the formation of a short-lived cyclic intermediate which contains manganese(V). The 14-fold difference between the reactivities of fumaric and maleic acids points to steric hindrance in the latter against forcing the *cis*-carboxy-groups towards each other.

In Part III,[1] which was concerned with the short-lived intermediates and the products of the permanganate oxidation of maleic and fumaric acids, it was shown that the first stage of the process is the four-electron oxidation of the substrates yielding formyl(hydroxy)acetic acid and manganese(III) [equation (1)]. At later stages, a variety of other intermediates and products can be detected, indicating a complex reaction pattern. As no

$$HO_2C{\cdot}CH{=}CH{\cdot}CO_2H + MnO_4^- \xrightarrow[-2\,H_2O]{+\,4\,H^+} CHO{\cdot}CHOH{\cdot}CO_2H + Mn^{III} + CO_2 \quad (1)$$

kinetic data are available for the permanganate oxidation of olefinic compounds in acidic solution, we have carried out a detailed kinetic study of reaction (1) with the aim of obtaining mechanistic information about the interaction of MnO_4^- and the double bond. The results on fumaric acid have been reported in short form.[2] In agreement with earlier findings,[3] the reactions in question are very fast; therefore the rate measurements have been performed by means of the stopped-flow technique.[4]

RESULTS

Kinetic Measurements.—The disappearance of MnO_4^- has been followed at 540 nm in the presence of a 5—20 fold excess of the substrate over permanganate. Under such conditions the manganese(III) formed in equation (1) remains in solution owing to complex formation with maleic or fumaric acid and, in a slower process, oxidises one half of formyl(hydroxy)acetic acid to hydroxymalonic acid. Although deviations from this simple two-stage process have been observed,[1] these occur mainly in the vicinity of equal reactant concentrations. The stopped-flow traces gave excellent first-order plots up to *ca.* 70—80% conversion with no indication of autocatalytic behaviour. The rate constants reported in this paper refer to those sections of the kinetic curves which reveal no deviation from first-order behaviour.

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[1] Part III, M. Jáky, L. I. Simándi, L. Maros, and I. Molnar-Perl, *J.C.S. Perkin II*, 1973, 1565.

[2] L. I. Simándi and M. Jáky, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 605.

[3] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1953, 435.

[4] L. I. Simándi, *Magyar Kém. Folyóirat*, 1969, **75**, 269.

Throughout the pH range studied (0·5—5·5), the observed pseudo-first-order rate constant (k_0) was found to be proportional to the total concentration ($[H_2A]_T$) of maleic (fumaric) acid. Therefore, the rate law can be written as (2). Table 1 lists the pseudo-first-order rate constants for

$$-\,d[MnO_4^-]/dt = k_0[MnO_4^-] = k[H_2A]_T[MnO_4^-] \qquad (2)$$

maleic acid at various pH values and total maleic acid concentrations in sulphate media together with the experimental conditions. The values of k given in column 6 have been obtained from the slope of the k_0 *vs.* $[H_2A]_T$ straight lines using the data in columns 2—5.

TABLE 1

Rate constants for the oxidation of maleic acid (H_2A) in sulphate medium $\{[H_2A]_T/[MnO_4^-]_0 = 10;\ t = 25\ °C;$ ionic strength 1·5M, with $(NH_4)_2SO_4$; buffers: monochloroacetic or succinic acid$\}$

	k_0/s^{-1} [a]				
	$10^2[H_2A]_T$/M				
pH	0·25	0·50	0·75	1·0	$10^{-2}k$/dm^3 mol^{-1} s^{-1} [b]
0·80	2·9	5·9	9·1	12·0	12·0
1·35	4·3	7·5	11·0	14·6	14·6
1·35 [c]	2·7	5·3	8·0	10·1	10·2
1·50	4·4	7·9	11·2	15·6	15·6
1·67	4·6	8·7	12·2	16·5	16·4
1·74	4·7	9·1	12·4	15·0	17·2
2·08	5·1	9·8	13·1	17·2	17·5
2·34	5·0	9·4	13·8	17·2	18·0

[a] Each value is the average result of 4—6 individual kinetic runs, reproducible to within ±5%. [b] Determined from the slope of the k_0 *vs.* $[H_2A]_T$ plot. [c] Ionic strength 0·37M.

The pH dependence of k for maleic acid in perchlorate media is shown by the data in Table 2. In this series the value of $[H_2A]_T$ was kept constant (0·01M). There is no difference between the rate constants in sulphate and perchlorate media, the value of k being determined solely by the pH at fixed ionic strength and constant temperature.

TABLE 2

Rate constants for the oxidation of maleic acid (H_2A) in perchlorate media ($[H_2A]_T = 10^{-2}$M; $[MnO_4^-]_0 = 10^{-3}$M; $t = 25$ °C; ionic strength 1·5M with $NaClO_4$; buffers: monochloroacetic or succinic acid)

pH	$10^{-2}k$/dm^3 mol^{-1} s^{-1} [a]	pH	$10^{-2}k$/dm^3 mol^{-1} s^{-1} [a]
0·22 [b]	10·6	2·95 [c]	12·9
0·25	10·5	3·12	18·1
0·52	11·6	3·45	17·7
0·65	12·0	3·83	17·7
0·88	12·8	4·07	18·4
1·18	15·0	4·31	17·2
1·39	15·1	4·35	17·3
1·70	15·9	4·76	16·6
1·84	16·8	4·79	15·7
2·24	18·2	4·83	14·7
2·25	18·1	5·24	14·5
2·27	19·5	5·27	15·1
2·61	17·8	5·28	14·8
2·70	20·0	5·73	12·8
2·72	18·3	5·75	11·0
2·73	19·1		

[a] Each value is the average result of 4—6 individual kinetic runs, reproducible to within ±5%. [b] Ionic strength 3·0M. [c] Ionic strength 0·1M.

The effect of ionic strength is illustrated by k values at pH 0·22 (I 3·0M), 1·35 (I 0·37M), and 2·95 (I 0·1M) (see Tables 1 and 2). At high acidities the ionic strength does not affect the rate, whereas at pH 1·35 and 2·95 its change produces an effect consistent with the reaction of identically charged species in the rate-determining step.

The observed rate constants for the oxidation of fumaric acid are listed in Table 3 at various pH values. Table 4 gives the results at a fixed pH as a function of the overall fumaric acid concentration.

TABLE 3

Rate constants for the oxidation of fumaric acid (H_2A) in perchlorate medium ($[H_2A]_T/[MnO_4^-]_0 = 10$; ionic strength 1·5M with $NaClO_4$; buffers: monochloroacetic or succinic acid; $t = 25$ °C)

pH	$10\ [H_2A]_T$/M	$10^{-3}k$/dm^3 mol^{-1} s^{-1} [a]
0·68	1·0	14·3
0·97	1·0	14·8
1·22	2·5	14·6
1·27	1·0	14·5
1·42	2·5	13·7
2·20	1·0	11·0
2·37	2·0	9·5
2·70	2·0	8·0
2·95	2·0	7·1
3·06		6·5 [b]
3·39	4·0	3·4
3·45	5·0	4·0
4·09	2·0	1·8
4·45	4·0	1·5
4·83	4·0	1·3
5·28	5·0	1·3

[a] Each value is the average result of 4—6 individual kinetic runs, reproducible to within ±5%. [b] From the plot of k_0 against $(H_2A)_T$; *cf.* Table 4.

TABLE 4

Dependence of the observed first-order rate constant on the fumaric acid concentration (pH = 3·06; ionic strength 1·5M with $NaClO_4$; $t = 25$ °C; monochloroacetic acid buffer; $[MnO_4^-]_0 = 10^{-4}$M)

$10^3[H_2A]_T$/M	k_0/s^{-1}
0·50	3·7
1·00	6·8
1·50	9·0
2·00	12·9

Acid Dissociation Constants.—The interpretation of the pH dependence of the rate constants requires knowledge of the stepwise acid dissociation constants for both substrates. As these are not available at an ionic strength of 1·5, we have determined them by pH-metric titration. This technique yields so-called mixed values[5] defined by equations (3) in terms of hydrogen ion activity (a_H) and the concentration of maleic (fumaric) species; H_2A stands for the undissociated acid. The results are listed in Table 5.

TABLE 5

Dissociation constants of maleic and fumaric acids ($t = 25$ °C; ionic strength 1·5M with $NaClO_4$)

	K_1/mol dm^{-3}	K_2/mol dm^{-3}
Maleic acid	$(3·5 \pm 0·2) \times 10^{-2}$	$(6·0 \pm 0·4) \times 10^{-6}$
Fumaric acid	$(2·3 \pm 0·2) \times 10^{-3}$	$(1·4 \pm 0·1) \times 10^{-4}$

Clearly, the acidity constants obtained are considerably larger than those referring to infinite dilution or lower ionic strengths.[5]

$$K_1 = a_H \frac{[HA^-]}{[H_2A]};\quad K_2 = a_H \frac{[A^{2-}]}{[HA^-]} \qquad (3)$$

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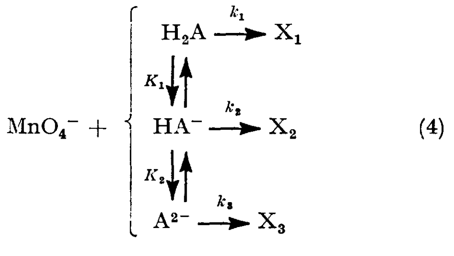
[5] A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases,' Wiley, New York, 1962.

Interpretation of the pH *Dependence*.—The rate law (2) and the variation of the second-order rate constant k with the pH are consistent with a common mechanism for maleic and fumaric acids in which the rate-determining step of process (1) is a bimolecular reaction between MnO_4^- and any of the three possible maleic (fumaric) species [equation (4)]. If one assumes that the dissociation equilibria are



(4)

attained much faster than the rate of reaction with permanganate, the rate law can be written as equation (5).

$$-d[MnO_4^-]/dt = (k_1[H_2A] + k_2[HA^-] + k_3[A^{2-}])[MnO_4^-] \quad (5)$$

The concentrations of the maleic (fumaric) species can be expressed from the material balance for the substrate and from the acid dissociation constants. Upon inserting the expressions obtained into equation (5) one obtains equation (6). If $[H_2A]_T \gg [MnO_4^-]_0$, equation (6) integrates to (7).

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_1a_H^2 + k_2K_1a_H + k_3K_1K_2}{K_1K_2 + K_1a_H + a_H^2}[H_2A]_T[MnO_4^-] \quad (6)$$

$$2{\cdot}303 \log\frac{[MnO_4^-]_0}{[MnO_4^-]} = \frac{k_1a_H^2 + k_2K_1a_H + k_3K_1K_2}{K_1K_2 + K_1a_H + a_H^2}[H_2A]_Tt = k[H_2A]_Tt \quad (7)$$

Equation (7) can be linearised using the known values of K_1 and K_2 to obtain the individual rate constants k_1, k_2, and k_3. At sufficiently high pH value the approximations (8) and (9) are valid, which means that the reaction occurs

$$a_H^2 \ll K_1K_2 + K_1a_H \quad (8)$$

$$k_1a_H^2 \ll k_2K_1a_H + k_3K_1K_2 \quad (9)$$

predominantly *via* the mono- and di-anions of the substrate. With these, equation (7) can be rearranged to (10). If

$$k(K_2 + a_H) = k_3K_2 + k_2a_H \quad (10)$$

the left-hand side containing the experimental second-order rate constant k is plotted against a_H, a straight line should be obtained, provided that the starting assumptions are correct. The corresponding plots based on data in Tables 1—3 are shown in Figures 1 and 2 for maleic and fumaric acid, respectively.

Once the value of k_3 is accurately determined from equation (10), the linearised form of equation (7), given by (11), can be used throughout the pH range studied. This procedure has been used in the case of fumaric acid,

$$G \equiv [k(K_1K_2 + K_1a_H + a_H^2) - k_3K_1K_2]\frac{1}{a_H} = k_1a_H + k_2K_1 \quad (11)$$

the plot of G against a_H being shown in Figure 2 for two different pH intervals.

The results referring to maleic acid at low pH values

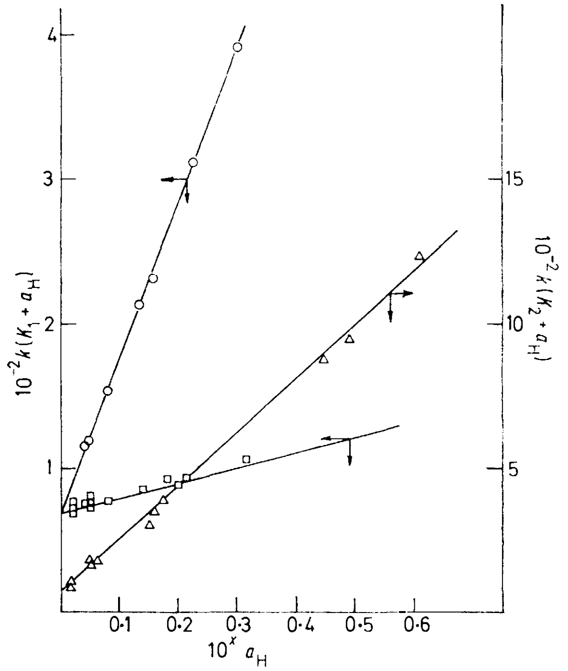


FIGURE 1 Plot of the experimental results for maleic acid according to equations (10) and (14): △ 10^4a_H; □ a_H; ○ $10a_H$

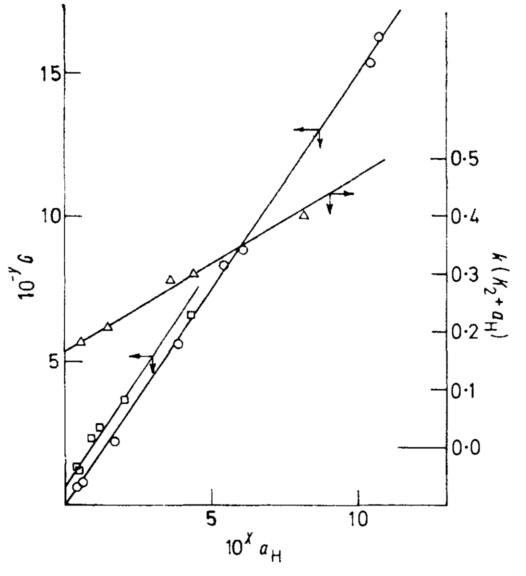


FIGURE 2 Plot of the experimental results for fumaric acid according to equations (10) and (11): ○ $10^{-2}G$, 10^2a_H; □ $10^{-1}G$, 10^3a_H; △ 10^5a_H

have been evaluated on the basis of approximations (12) and (13), which convert equation (7) to the form (14).

$$k_3K_1K_2 \ll k_1a_H^2 + k_2K_1a_H \quad (12)$$

$$K_1K_2 \ll K_1a_H + a_H^2 \quad (13)$$

$$k(K_1 + a_H) = k_2K_1 + k_1a_H \quad (14)$$

The plots corresponding to equation (14) are shown in Figure 1 for two different intervals of a_H.

The plots in Figures 1 and 2 reveal good linearity in all cases, indicating that the observed kinetic behaviour is consistent with the proposed reaction mechanism [equation (4)].

The slopes and intercepts of the straight lines obtained yield the six rate constants listed in Table 6 (25 °C). The pH–rate profiles calculated for the two substrates from these rate constants and the acidity constants are in excellent agreement with the observed results.

TABLE 6

Resolved second-order rate constants [a] ($dm^3\ mol^{-1}\ s^{-1}$) (t = 25 °C; ionic strength 1·5M)

	k_1	k_2	k_3
Maleic acid	1080	1880	1000
Fumaric acid	15,000	3000	1180

[a] Estimated accuracy ±6%.

The activation parameters have been determined in the temperature range 11—40 °C at such pH values that unequivocal assignment to a given rate constant should be possible without determining the temperature dependence of the dissociation constants. The activation parameters obtained by a least-squares fit of the data are listed in Table 7.

TABLE 7

Arrhenius parameters for the permanganate oxidation of maleic and fumaric acids [a]

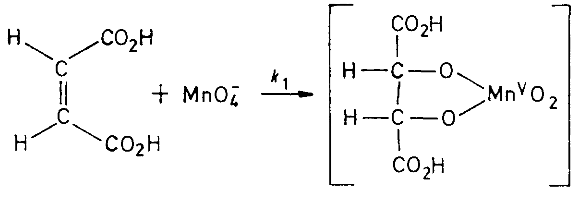
	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}
Maleic acid (pH = 0·50)	14	−140
Maleate(1−) (pH = 3·15)	12	−140
Fumaric acid (pH = 1·0)	0·0	−170
Fumarate(2−) (pH = 5·0)	13	−140

[a] Estimated accuracy ±10%.

DISCUSSION

Since the kinetic results have been found to be consistent with mechanism (4), no acid catalysis or autocatalysis is involved in the oxidation process. The variation of the second-order rate constant with the pH is solely due to the shifts occurring in the dissociation equilibria of maleic and fumaric acids. This is in agreement with the lack of a pH dependence for the oxidation of diethyl maleate and fumarate [6] in the acidity range used in the present work.

As the disappearance of MnO_4^- is first order with respect to both reactants, it is reasonable to assume that the rate-determining step is the *cis*-attack of permanganate on the double bond [equation (15)], resulting in the formation of a cyclic intermediate containing manganese(V). This mode of attack is analogous to the mechanism proposed for the *cis*-hydroxylation of oleic acid by alkaline MnO_4^-.[7] In view of the low activation enthalpies and the high negative activation entropies (Table 7), the transition state for step (15) must closely resemble the structure of the intermediate. Apparently, there is little bond breaking and considerable bond making in the rate-determining step in combination with substantial ordering of the reactants. The rate-determining step is assumed to be of the type (15) for the corresponding mono- and di-anions, too. In the case of maleic acid, the cyclic species has a mesoid configuration as opposed to fumaric acid, which leads to a racemic-type intermediate.



(15)

X_1

As manganese(V) is not detectable by the technique used,[1] step (15) must be followed by the fast step (16), which leads to the first detectable intermediates, manganese(III) and formyl(hydroxy)acetic acid. It should be pointed out that although the cyclic intermediate seems to be similar for permanganate oxidations in alkaline and acidic media, its subsequent fate is totally different in the two cases. The relative stability of manganese(III) in acidic solutions apparently favours further intramolecular reaction over ketol formation involving a second molecule of MnO_4^-.

$$X_1 + 3H^+ \xrightarrow{\text{fast}} HO_2C{\cdot}CHOH{\cdot}CHO + MnOH^{2+} + CO_2 + H_2O \quad (16)$$

According to the product distribution reported previously for maleic and fumaric acids,[1] glyoxylic acid is formed in amounts increasing with decreasing acidity. This implies that, instead of oxidative decarboxylation (16), the cyclic intermediate may also split at the C(2)–C(3) bond. Such cleavage was observed in the alkaline reaction, too, in the case of bicyclo[2.2.1]hept-2-ene.[7] Apparently, ionisation of the carboxy-groups of maleic and fumaric acids favours the cleavage of X_1 and X_2 into two molecules of glyoxylic acid. This branching in the decomposition of the cyclic intermediate has no effect on the kinetics since it is preceded by the rate-determining step.

On the basis of tritium and ^{13}C tracer studies Allen and Ruben [8] suggested that the permanganate oxidation of fumaric acid occurs *via* a two-equivalent step giving monohydroxyfumaric acid, followed by a four-equivalent process affording hydroxymalonic acid and CO_2. These conclusions are at variance with the present results which favour an initial four-equivalent process followed by a two-equivalent reaction. In addition to the fact that

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[6] L. I. Simándi and M. Jáky, unpublished results.

[7] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 2822.

[8] M. B. Allen and S. Ruben, *J. Amer. Chem. Soc.*, 1942, **64**, 948.

formyl(hydroxy)acetic acid is the first detectable intermediate, the main objection to the scheme of Allen and Ruben is that the very high reactivity of maleic and fumaric acid towards MnO_4^- is primarily due to the presence of the double bond, which, therefore, cannot remain intact after the first oxidation step.

The rate constants reported in this work are the highest known values for organic reactions other than of the proton transfer type. The permanganate oxidation of unsaturated compounds is in most cases characterised by rate constants[9] in excess of 100 dm^3 mol^{-1} s^{-1} which is in agreement with the predictions based on Littler's qualitative treatment,[10] using orbital symmetry rules.

The relative reactivities of the various maleic and fumaric species merit consideration. The most striking difference is observed between fumaric and maleic acid, the former reacting *ca.* 14 times faster. A possible explanation might be the presence of a hydrogen bond in maleic acid, which has to be broken when the cyclic intermediate is formed. However, as shown by preliminary kinetic results on diethyl fumarate and maleate[6] in aqueous ethanol (1 : 1) (25 °C), fumarate is favoured by a factor of *ca.* 10 over maleate. Therefore, the observed difference cannot be due to hydrogen bonding as this is not operative in the esters.

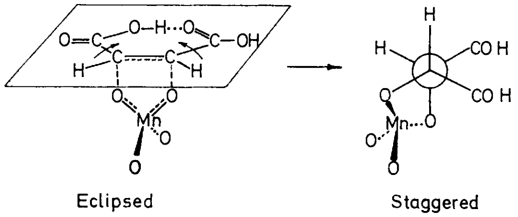

Figure 3 Steric hindrance in the attack of MnO_4^- on maleic acid owing to the mutual repulsion of the carboxy-groups

An explanation that seems to be consistent with all kinetic data is based on steric considerations. The formation of the cyclic intermediate by *cis*-attack of two permanganate oxygen atoms should be accompanied by rehybridisation at C(2) and C(3). These carbon atoms are trigonal (bond angle *ca.* 120°) in the initial state but become tetrahedral (bond angle *ca.* 109°) in the intermediate. The *cis*-approach of MnO_4^- would first impose an eclipsed conformation on the maleic species, *i.e.* upon going to the transition state the carboxy (methoxycarbonyl) groups are forced closer to each other before the staggered conformation in the cyclic intermediate is reached (Figure 3). The steric hindrance due to this repulsion between the *cis*-carboxy (methoxycarbonyl) groups causes the maleic species to react at a lower rate than their fumaric counterparts.

In view of these considerations, the reactivity order of the fumaric species ($H_2A > HA^- > A^{2-}$) is apparently free of steric effects and reflects the trend expected from the electrostatic repulsion between the reactants. An alternative explanation is that the double bond is activated by conjugation with the carboxy-group and ionisation eliminates this effect. The latter interpretation implies nucleophilic attack of MnO_4^- on the double bond, probably in a near-concerted manner.

Interestingly, the dianions react practically at the same rate in spite of the possibility of steric hindrance as shown in Figure 3. Apparently, electrostatic repulsion is the decisive factor in determining the reactivities of these species.

The most reactive maleic species is the monoanion, which also has a planar structure owing to strong hydrogen bonding. This makes carboxy-conjugation relatively more efficient, raising the reactivity of the monoanion above those of the other two species.

Thus the reactivity pattern observed with maleic and fumaric acids reflects the influence of three factors: steric, electrostatic, and conjugative. Work is in progress to elucidate the effects of substituents on the reactivity of both substrates.

EXPERIMENTAL

Analytical grade chemicals were used throughout.

The acid dissociation constants were determined by pH-metric titration with CO_2-free 1·000M-sodium hydroxide, using a Radelkis type OP-205 precision pH-meter and a Radiometer (Copenhagen) GK 2302 B combination electrode (with NaCl solution in the reference compartment). The titration curves were evaluated by the method recommended by Albert and Serjeant.[5] The p*K* values were reproducible to within 0·03 log units.

The kinetic measurements have been performed with a stopped-flow spectrophotometer[4] suitable for following reactions with half-lives greater than *ca.* 15 ms. The reactant solutions were thermostatted both in the storage vessels and in the instrument. The ionic strengths of the solutions to be mixed were equal (1·5M in most cases) to facilitate rapid mixing and to avoid bubble formation. The pH was measured as described above, after the reaction had gone to completion. These values were identical to within 0·01 pH units with the readings obtained in solutions containing all components except permanganate. Monochloroacetic or succinic acid buffers were used where necessary. No reaction was found to occur between the buffers and MnO_4^- on the time scale of the stopped-flow experiments. The transmission *vs.* time curves were displayed on a Tektronix 564 storage oscilloscope and photographed with a Polaroid camera.

[3/688 *Received, 2nd April,* 1973]

[9] K. B. Wiberg and R. D. Geer, *J. Amer. Chem. Soc.*, 1966, **88**, 5827.

[10] J. S. Littler, *Tetrahedron*, 1971, **27**, 81.