Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part 8.† Kinetics of the Oxidation of Halogenomaleic Acids

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A study of the short-lived intermediates of the permanganate oxidation of halogenomaleic acids has revealed that an initial 4-electron process occurs, followed by reactions between manganese(III) and the organic intermediates. According to stopped-flow kinetic measurements, the reaction is of the first order with respect to both reactants. The pH dependence of the second-order rate constant is constant with the reactivity order: monoanion > acid > dianion. The reactivity trends reflected by the individual rate constants indicate the predominance of steric over electronic effects.

THE kinetics and mechanism of the permanganate oxidation of various olefinic and acetylenic derivatives have been the subject of several recent studies, indicating renewed interest in these classical reactions, which, owing to their rapidity and complex mechanism, are still incompletely understood. The main features of olefin oxidation in neutral and alkaline media have been elucidated.[1-4] A study of the oxidation of maleic and fumaric acids as well as their diethyl esters and methyl-

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† Part 7, L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1977, 630.

[1] R. Stewart, ' Oxidation by Permanganate,' in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York and London, 1965.

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

[3] K. B. Wiberg, C. J. Deutsch, and J. Roček, *J. Amer. Chem. Soc.*, 1973, **95**, 3034.

[4] F. Freeman, C. O. Fuselier, and E. M. Karchefski, *Tetrahedron Letters*, 1975, 2133.

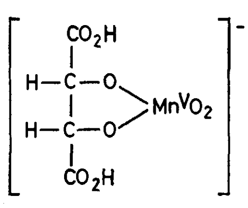
substituted derivatives in acidic solutions[5-7] has revealed that the primary reaction is a 4-electron process leading to manganese(III) as a short-lived intermediate. This is accompanied by cleavage of the organic substrate *via* oxidative decarboxylation of the cyclic manganese(V) ester, an undetectable, short-lived intermediate whose formation is, however, supported by indirect evidence. A different and unique oxidation pattern involving soluble manganese(IV) has been observed in the case of *trans*-cinnamic acid.[8] Kinetic analysis of the permanganate oxidation of the above substrates has shown that the relative reactivities are governed mainly by steric factors and superimposed electronic effects related to conjugative interaction of the double bond with carboxy, carboxylate, and ethoxycarbonyl groups. In order to throw further light on the effect of substituents on the double bond, we have performed a stopped-flow kinetic study of the oxidation of chloromaleic (CM), dichloromaleic (DCM), bromomaleic (BM), and dibromomaleic (DBM) acids.

RESULTS AND DISCUSSION

Stoicheiometry and Intermediates.—Direct titration with permanganate in strong acid shows that the reactions slow down after consumption of 7.8—9.6 oxidation equivalents. The end-points are therefore drawn-out and uninformative. At the end of the titrations, a slight odour of chlorine or bromine was perceptible.

If the permanganate oxidation of CM, DCM, BM, and DBM is carried out in the presence of a ten-fold excess of pyrophosphate with respect to permanganate, then, as shown by successively recorded u.v.–visible spectra, permanganate is converted into pyrophosphatomanganese(III), which persists for considerable periods of time. This is in line with earlier observations which revealed that aquomanganese(III) is a short-lived intermediate in permanganate oxidations in acidic media.[5,6,9] In the absence of pyrophosphate, manganese(III) is not stabilised by complex formation and disappears by rapid reactions with the organic intermediates or by competitive disproportionation into Mn^{II} and manganese dioxide. In fact, with the substrates studied in this paper, transient minima were observed on the stopped-flow traces recorded at 415 nm, which indicates that *ca.* 10% of the manganese(III) formed undergoes disproportionation rather than reaction with the organic intermediates. As shown earlier, such minima are due to a soluble manganese(IV) species, which appears prior to the precipitation of manganese dioxide.[7,8]

Previous studies on the permanganate oxidation of maleic acid have shown that the observed organic intermediates can be readily accounted for by assuming cleavage of the short-lived hypomanganate ester (1) at different C–C bonds,[6,9] accompanied by formation of manganese(III). On the basis of these concepts, we searched for organic intermediates derived from the analogous halogeno-substituted species.


(1)

In the case of DCM, only two possibilities were considered: (i) oxidative decarboxylation with cleavage at C(1)–C(2) yields chlorohydroxymalonic acid monochloride, which is rapidly hydrolysed to chlorohydroxymalonic acid (hydrolysis of the acid halides is assumed to be fast); (ii) oxidative cleavage at C(2)–C(3) leads to oxalic acid monochloride and subsequently to oxalic acid.

In the case of DCM, we have determined the amount of oxalic acid formed at pH 4.0 and a DCM–MnO_4^- molar ratio of 2.0 : 1. After complete disappearance of the colour of MnO_4^-, and subsequently of manganese(III), an average of 0.52 mol of oxalic acid was found for each mol of MnO_4^- added. If the reaction was carried out in the presence of a 5-fold excess of pyrophosphate with respect to MnO_4^- and the pyrophosphatomanganese(III) complex was quenched with sulphite, then, under otherwise identical conditions, the amount of oxalic acid decreased to 0.053 mol per mol MnO_4^-.

These results imply that oxalic acid is formed only if manganese(III) is allowed to react with the organic intermediate. Accordingly, route (ii) cannot be operative, because it would have produced 2.0 mol of oxalic acid per mol of MnO_4^- with quenching and 1.5 mol per mol without quenching.

Product solutions prepared similarly to the above gave yellow precipitates with 2,4-dinitrophenylhydrazine (2,4-DNPH) both in the presence and in the absence of pyrophosphate. However, mass spectrometric analysis has shown that the precipitate is the cyclic *NN'*-hydrazide of the starting DCM: the fragmentation pattern was identical with that of the yellow compound obtained directly from DCM and 2,4-DNPH. Comparison with the mass spectrum of the 2,4-dinitrophenylhydrazone prepared from authentic mesoxalic acid showed that mesoxalic acid is not an intermediate in the reaction under study.

It follows from these data that the organic intermediate is chlorohydroxymalonic acid, which does not undergo further hydrolysis under the experimental conditions. When allowed to react with manganese(III), it produces 0.5 mol of oxalic acid per mol of MnO_4^-.

As the same behaviour is exhibited by DBM, the

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[5] L. I. Simándi, and M. Jáky, *J.C.S. Perkin II*, 1973, 1856.

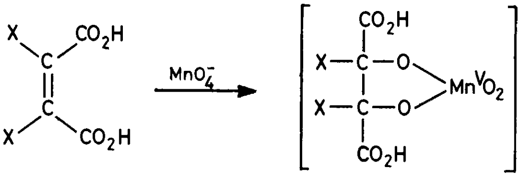
[6] M. Jáky and L. I. Simándi, *J.C.S. Perkin II*, 1976, 939.

[7] M. Jáky and L. I. Simándi, *React. Kinet. Catal. Letters*, 1975, **3**, 397.

[8] L. I. Simándi and M. Jáky, *J. Amer. Chem. Soc.*, 1976, **98**, 1995.

[9] M. Jáky, L. I. Simándi, L. Maros, and I. Molnár-Perl, *J.C.S. Perkin II*, 1973, 1565.

oxidation pattern of the disubstituted maleic acids studied can be described by equations (1)—(3).



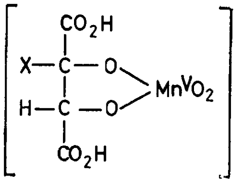
(1)

(1a)

$$(1a) \xrightarrow[-CO_2]{-Mn^{III}} HO_2C\text{—}C(OH)X\text{—}COX \xrightarrow{\text{hydrolysis}} HO_2C\text{—}C(OH)X\text{—}CO_2H \quad (2)$$

$$HO_2\text{—}C(OH)X\text{—}CO_2H + 2Mn^{III} \xrightarrow[-CO_2,\ -2H^+]{+H_2O,\ -HX} (CO_2H)_2 + 2Mn^{II} \quad (3)$$

With monosubstituted maleic acids (CM and BM) and the corresponding cyclic intermediate (1b) three modes of cleavage were considered, with three sets of products. These are (i) oxidative decarboxylation with cleavage at C(1)–C(2), yielding hydroxymalonic acid, (ii) cleavage at C(2)–C(3), leading to oxalic and glyoxylic acid in a 1 : 1 ratio; and (iii) oxidative decarboxylation at C(3)–C(4), affording halogenohydroxymalonaldehydic acid, which may split off HX to produce oxomalonaldehydic acid.



(1b)

The solution obtained at a BM–MnO_4^- molar ratio of 1 : 1 in an excess of pyrophosphate (1M-$HClO_4$), after quenching with iron(II), gave a yellow precipitate with 2,4-DNPH. The mass spectrum of the precipitate showed the presence of the bis-(2,4-dinitrophenylhydrazone) of mesoxaldehydic acid [*m/e* 462, 444 ($M - H_2O$), and 418 ($M - CO_2$)]. The precipitate also contained some cyclic *NN'*-hydrazide of BM, but no other components were detected in significant amounts.

As the 2,4-dinitrophenylhydrazone of glyoxylic acid was not detected by mass spectrometry, route (ii) can be ruled out. The lack of glyoxylic acid in product solutions prepared in the absence of pyrophosphate eliminates path (i), because the manganese(III) oxidation of the hydroxymalonic intermediate should lead to glyoxylic acid. Consequently, the results strongly indicate route (iii), with HBr elimination as the predominant reaction.

When the manganese(III) was quenched, the BM solution was found to contain 0.2 mol of oxalic acid per mol of MnO_4^-. Without quenching, the amount of oxalic acid was increased to 0.32 mol per mol of MnO_4^-. As route (ii) is not involved, oxalic acid must be a secondary intermediate formed *via* oxidation of the hemialdehyde by manganese(III). Apparently this reaction cannot be fully suppressed by added pyrophosphate.

Essentially the same behaviour was observed for the oxidation of CM.

In view of the above results, the oxidation of BM and CM can be depicted by equations (4)—(6).

Kinetic Measurements.—The primary aim of this work was to obtain kinetic information on the attack of MnO_4^- on the double bond; therefore all rate measurements were performed in an excess of pyrophosphate to suppress manganese(III) oxidations. The stopped-flow traces recorded at 540 nm in the presence of an at least ten-fold excess of the substrate gave excellect first-order plots. At constant pH, the slope was proportional to the overall substrate concentration as illustrated by the results for DCM and BM (Tables 1 and 2). Thus the rate law is given by equation (7), where $[S]_T$ is the overall substrate concentration, and $k_{obs.} = k[S]_T$. The second-

$$HO_2C\text{—}CX\text{=}CH\text{—}CO_2H + MnO_4^- \longrightarrow (1b) \quad (4)$$

$$(1b) \xrightarrow[-CO_2]{-Mn^{III}} HO_2C\text{—}C(OH)X\text{—}CHO \xrightarrow{-HX} HO_2C\text{—}CO\text{—}CHO \quad (5)$$

$$HO_2C\text{—}CO\text{—}CHO + 2Mn^{III} \xrightarrow[-2H^+]{+2H_2O} (CO_2H)_2 + HCO_2H + 2Mn^{II} \quad (6)$$

$$-d[MnO_4^-]/dt = k[S]_T[MnO_4^-] \quad (7)$$

order rate constant (k) depends on the pH as shown by the points in the Figure. In line with earlier findings,[5,6] this is due to the different reactivities of the undissociated acid and its mono- and di-anion, as depicted

TABLE 1

Dependence of the first-order rate constant $k_{obs.}$ on the concentrations of DCM[a] {t 25 °C; aqueous solutions; ionic strength 1.5M ($NaClO_4$), succinic acid buffer, $[DCM]_T/[MnO_4^-]_0 = 10$, [pyrophosphate] = $10[MnO_4^-]_0$}

	k_{obs}/s^{-1}	
10^2 $[DCM]_T$/M	pH 0.88	pH 3.80
0.25	0.536	
0.50	0.927	0.543
1.00	1.80	1.16
1.50	2.87	1.88
2.00	3.55	2.46

[a] Each value is the average result of 3 runs reproducible to within ±5%.

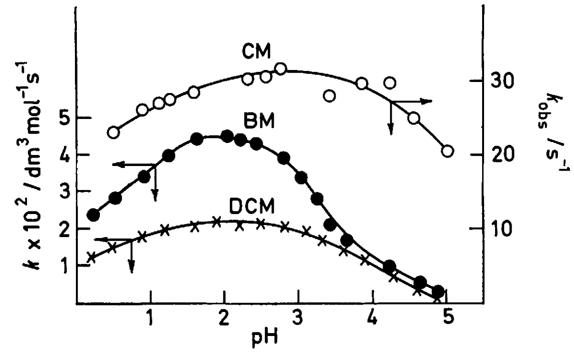
TABLE 2

Dependence of the first-order rate constant $k_{obs.}$ on the concentration of BM[a] {t 25 °C; aqueous solutions; ionic strength 1.5M ($NaClO_4$), succinic acid buffer, $[BM]_T/[MnO_4^-]_0 = 10$, [pyrophosphate] = $10[MnO_4^-]_0$}

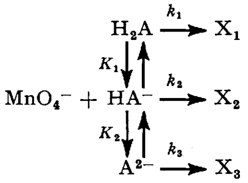
	$k_{obs.}$/s^{-1}	
10^2 $[BM]_T$/M	pH 0.88	pH 4.10
0.75	2.66	0.62
1.12	3.73	0.88
1.50	4.97	1.32
1.87	6.66	1.73

[a] Each value is the average result of 3 runs reproducible to within ±5%.

by the Scheme, where X_i are intermediates of the type shown in equation (1).



Dependence of the apparent second-order rate constant (k) on the pH (for BM and DCM). For CM (containing 8.6 mol % maleic acid), first-order rate constants are shown (t 25 °C; ionic strength 1.5M)



SCHEME

If the acid–base equilibria are established fast in comparison with the rate of oxidation, the Scheme leads to equation (8), where a_H is the hydrogen ion activity.[5,6] The individual rate constants and acid dissociation constants for BM and DCM have been evaluated by fitting equation (8) to the experimental k *vs.* pH function, using a gradient method. The procedure yielded the parameters listed in Tables 3 and 4. The k *vs.* pH curves corresponding to the best rate and acidity constants are shown by solid lines in the Figure.

$$k = \frac{k_1 a_H{}^2 + k_2 K_1 a_H + k_3 K_1 K_2}{K_1 K_2 + K_1 a_H + a_H{}^2} \qquad (8)$$

TABLE 3

Resolved rate constants (dm^3 mol^{-1} s^{-1}) of the substrates studied [t 25 °C; aqueous solutions; ionic strength 1.5M (NaClO$_4$); estimated accuracy ±8%]

Substrate	k_1	k_2	k_3	Ref.
Chloromaleic acid	141	509	4.0	This work
Dichloromaleic acid	101	214	3.7	
Bromomaleic acid	102	457	2.7	
Dibromomaleic acid	3.3 [a]	7.10×10^{-2}	3.7×10^{-2}	
Maleic acid	1 080	1 880	1 000	5
Methylmaleic acid	150	660	310	6
Dimethylmaleic acid	25	90	54	6, 10
Dimethylmaleic anhydride	270			10

[a] Rate constant for dibromomaleic anhydride.

The above approach is not applicable in the case of DBM as the corresponding anhydride does not undergo hydrolysis. This is supported by the fact that, in contrast with other substituted maleic acids, the k value of DBM decreases steadily upon increasing the pH from *ca.* 0.5 to 3.5. In the case of ' normal ' behaviour, *i.e.* when no anhydride is present in the solution, k_2 is greater than k_1, because MnO_4^- attacks the H-bonded planar monoanion more easily then it does the undissociated acid with freely rotating carboxy-groups. The pH dependence of k for DBM implies that the species present at low pH is more reactive than the monoanion; thus the former cannot be the undissociated acid. The planar structure of dibromomaleic anhydride would impose no steric hindrance on the approach of MnO_4^-; thus a relatively high reactivity is expected for this species. Therefore, the rate constant obtained from the low pH end of the k *vs.* pH dependence should be ascribed to dibromomaleic anhydride (*cf.* Table 3). We determined the rate constants for the anhydride and A^{2-} from the limiting k values attained below pH 0.5 and above pH 2.8, respectively. Subsequently, the acid dissociation constants (from pH-metric measurements) were used to evaluate k_2 for HA^- from the rising section of the curve immediately below the pH 2.8 limit, thus minimising the importance of anhydride formation. No rate constant value can be obtained for the undissociated acid but the trend[10] observed with other maleic acid derivatives suggests that it should be less than k_2, *i.e.* <0.07 dm^3 mol^{-1} s^{-1}.

TABLE 4

Acid dissociation constants of the substrates studied [t 25 °C; aqueous solutions; ionic strength 1.5M (NaClO$_4$); estimated accuracy ±10%]

Substrate	K_1/mol dm^{-3}	K_2/mol dm^{-3}
Chloromaleic acid	6.7×10^{-1}	9.7×10^{-6}
Dichloromaleic acid	2.3×10^{-1}	1.4×10^{-4}
Bromomaleic acid	4.2×10^{-1}	3.9×10^{-4}
Dibromomaleic anhydride	5.1×10^{-2} [a]	4.2×10^{-5}

[a] $K_1/(1 + K)$, where K is the hydrolysis constant.

As the available CM sample contained 8.6 mol % of maleic acid (azeotropic mixture), the kinetic measurements were performed at a 100-fold excess of this substrate with respect to MnO_4^- to ensure first-order conditions for both components. The composition was determined by pH-metric titration of a sample of known weight. In contrast to the other substrates, in the case of CM computer fitting was based on the first-order rate constants ($k^*_{obs.}$) obtained at various pH values, in combination with the known constant for maleic acid.[5]

The activation parameters have been determined for the three substrates available in pure form (Table 5).

Relative Reactivities.—The effect of substituents on the rate of alkene oxidation by MnO_4^- has been studied for *para*-substituted *trans*-cinnamic acids;[11] the changes in reactivity are extremely small, indicating that no charge is developed in the transition state. A comparison of the behaviour of acrylate and crotonate ions[2] has shown that methyl substitution slightly hinders the reaction of the conjugated double bond with MnO_4^-.

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[10] Z. Szeverényi, M. Jaky, and L. I. Simandi, *Inorg. Chim. Acta*, 1977, **23**, L31.

[11] D. G. Lee and J. R. Brownridge, *J. Amer. Chem. Soc.*, 1974, **96**, 5517.

The results reported and quoted in this paper draw attention to the considerable decrease in reactivity upon going from maleic acid to its substituted derivatives, a trend valid for all three reacting species of each substrate (H_2A, HA^-, and A^{2-}). The 21 rate constants listed in Table 3 for maleic acid and its various mono- and di-substituted derivatives reveal a number of remarkable trends, which merit more detailed consideration.

TABLE 5

Activation parameters corresponding to the individual rate constants (temperature interval 12—40 °C; estimated accuracy ±15%)

Rate constant	pH[a]	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J mol^{-1} K^{-1}
Bromomaleic acid			
k_1	0.10	18.1	−140
k_2	2.50	20.6	−127
k_3	4.96	17.4	−164
Dibromomaleic ahydride	0.10	14.2	−187
Dichloromaleic acid			
k_1	0.88	21.0	−134
k_2	2.50	22.1	−127
k_3	4.90	15.2	−169

[a] pH chosen to ensure predominance of the desired species.

(1) *Monosubstitution*. The rate constant for the oxidation of monosubstituted maleic acids, regardless of the charge type of the reacting species, decreases in the order H > Me ⩾ Cl > Br. Within this order, the ratios of the rate constants show considerable variation characteristic of the charge type. The quotient k_H/k_{Br} in the above series can be regarded as an indicator of the sensitivity to substitution, its value being 10, 4, and 400 for H_2A, HA^-, and A^{2-}, respectively. We propose that the low sensitivity of the monoanion to substitution is due to its planar structure imposed by strong hydrogen bonding. As MnO_4^- attacks the double bond in a near-concerted fashion from a direction perpendicular to its plane [6] the angle of its access will be the greatest for the monoanion. Mutual repulsion between the carboxylate groups of the dianion will force the former out of the plane, thus decreasing the angle of access for MnO_4^-. In such a situation, the presence of substituents on C(2) will exert a stronger effect, further reducing an already smaller angle. Weak hydrogen bonding in H_2A creates an intermediate situation.

The above order of reactivity seems to be due to the combined effect of the size of substituent and the repulsive interaction between MnO_4^- and the substituent. The van der Waals radii are 1.2, 2.0, 1.8, and 1.95 for H, Me, Cl, and Br, respectively.[12] If this were the only factor, the Me derivative should react slower than either the Cl or the Br species. The order of the two monohalogeno-compounds is in line with their sizes, but the methyl-substituted derivatives are too reactive for the given radius of the Me group. Apparently, the halogen atoms repel the attacking MnO_4^- more strongly than does the Me group, whose bonding electrons are mainly localised between the C and H nuclei.

(2) *Disubstitution*. Introduction of a second substituent of the same kind further reduces the reactivity for all charge types: H > mono > di. This again emphasises the importance of steric factors. The sensitivity to the second substituent, however, depends primarily on the nature of the substituent rather than on the charge type of the reacting species. The quotient of rate constants k_{mono}/k_{di} is 5.7—7.3 for the three Me species, 1.08—2.4 for the Cl, and 67—1 460 for the Br derivatives. The large decrease in the case of Br seems to be in accord with steric effects and repulsion between the reactants. The reason for the observed difference in the sensitivity factors for Cl and Me is not clear.

(3) *Charge type*. For a given maleic acid derivative, the reactivity decreases in the order monoanion > acid > dianion. This trend is due to increasing deviations from the planar structure as mentioned under (1). If the apparent second-order rate constant increases monotonically with decreasing pH (instead of passing through a maximum), the presence of the corresponding anhydride is strongly indicated. The unhydrolysed anhydride, owing to its strictly planar structure, will react considerably faster than the monoanion and the diacid. Resolution of the rate constants requires special experiments and data evaluation. This procedure has been performed for dimethylmaleic acid,[10] yielding the correct rate constants for H_2A and the anhydride, listed in Table 3.

EXPERIMENTAL

Analytical grade chemicals were used throughout.

Details of the stopped-flow kinetic measurements have been described.[5]

Mass spectra were recorded with an A.E.I. MS-902 double-focusing instrument operated at an ionisation energy of 70 eV (trap current 100 μA; source temperature 150—200 °C). Samples were introduced *via* the direct insertion probe. Exact mass measurements (±3 p.p.m.) were carried out at a resolving power of 10 000. The cyclic *NN'*-(2,4-dinitrophenyl)hydrazide of DCM showed *m/e* 350(10%), 348(64), 345.949 7(100, *M*), 302(11), 300(16), 256(28), 254(42), 183(3.8), 181(16), 180(7.0), 169(16), 167(22), 124(20), 122(50), 79(54), 78(40), 75(58), and 30(76). The 2,4-dinitrophenylhydrazone of mesoxalic acid showed *m/e* 298(75%, *M*), 280(50), 254(6.0), 252(18), 208(50), 192(13), 183(40), 180(25), 179(17), 153(20), 131(18), 113(25), 107(12), 91(30), 77(100), 62(60), 44(65), and 30(85).

[7/332 *Received*, 24*th February*, 1977]

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[12] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, The Chemical Rubber Co., Cleveland, 1970—1971.