Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part III.[1] Intermediates in the Oxidation of Maleic and Fumaric Acids

By **Miklós Jáky** and **László I. Simándi,*** Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest, Hungary
László Maros and **Ibolya Molnár-Perl**, Department of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

The intermediates in the permanganate oxidation of maleic and fumaric acids have been studied in acidic solutions. The accumulation and decay of manganese(III) has been demonstrated by the stopped-flow technique. The concomitant four-electron oxidation of the substrates leads to the formation of formyl(hydroxy)acetic acid. The subsequent reactions reveal a complex pattern in which hydroxymalonic, glyoxylic, and oxalic acid are further intermediates. The product distribution has been determined as a function of the pH and the mole ratio of the reactants. A reaction scheme is suggested which rationalises the observed behaviour.

THE literature available on permanganate oxidation [2-4] contains little information on the kinetics and mechanism of the oxidation of olefinic and acetylenic substrates, particularly in acidic solutions. One of the possible reasons for this may be the rapidity of these reactions which, until recently, could not be subjected to kinetic studies permitting mechanistic conclusions. The observations of Drummond and Waters,[5] as well as our earlier work [1,6-8] have revealed that the rates of such oxidations

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[1] Part II, L. I. Simándi and M. Jáky, *J.C.S. Perkin, II*, 1972, 2326.

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

[3] J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, 1958, **58**, 403.

[4] W. A. Waters, *Quart. Rev.*, 1958, **12**, 277.

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

[6] L. I. Simándi and M. Jáky, *Tetrahedron Letters*, 1970, 3489.

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

[8] M. Jáky and L. I. Simándi, *J.C.S. Perkin, II*, 1972, 1481.

are especially high in acidic solutions. In neutral and alkaline media the rates are lower but are still characterised by rate constants well in excess of 100 $dm^3 mol^{-1} s^{-1}$ as shown by Wiberg and Geer [9] for a number of olefins. These authors have performed a detailed kinetic investigation on some permanganate oxidations in alkaline solutions but have not studied the substrates used in this work and the reactions in acidic media.

In neutral and alkaline solutions, information on the mechanism of olefin oxidation has been obtained from product analyses and tracer studies. At higher pH, *cis*-hydroxylation takes place whereas towards pH 7 ketol formation becomes predominant.[10-12] As shown by studies on bicyclo[2.2.1]hept-2-ene, the double bond may also be cleaved to yield aldehydes in neutral solutions.[12] By performing the oxidation with ^{18}O-enriched permanganate, the transfer of oxygen atoms has been demonstrated in the case of oleic acid.[12]

Maleic and fumaric acids are known to react with acidic permanganate according to the stoicheiometric equation (1).[13] On direct titration, the reaction is very fast up to a mole ratio of 1 : 1, then it slows down, and a drawn-out end-point is observed. By means of ^{11}C and ^{3}H tracer studies, Allen and Ruben [14] have shown that the formic acid is derived from one of the methine groups and one C–H bond remains intact during the reaction. Without detecting any intermediates, the above authors assume that the reaction occurs *via* the sequence fumaric ⟶ monohydroxyfumaric ⟶ hydroxymalonic ⟶ glyoxylic acid.

$$HO_2C{\cdot}CH{=}CH{\cdot}CO_2H + 2\,MnO_4^- + 6\,H^+ \longrightarrow 3\,CO_2 + HCO_2H + 2\,Mn^{2+} + 4\,H_2O \qquad (1)$$

In this paper we report on the intermediates and products of the permanganate oxidation of maleic and fumaric acids in aqueous acidic solutions. The measurements have been carried out by the stopped-flow technique [15] and by conventional analytical procedures.

RESULTS AND DISCUSSION

Intermediates from Permanganate.—The question whether any manganese species between the oxidation states +7 and +2 temporarily accumulate during the oxidation can be investigated [8] by the stopped-flow technique. If the life time of an intermediate is sufficiently long (at least 10—100 ms), the transmission *vs.* time curves should reveal a minimum at a suitably selected wavelength.

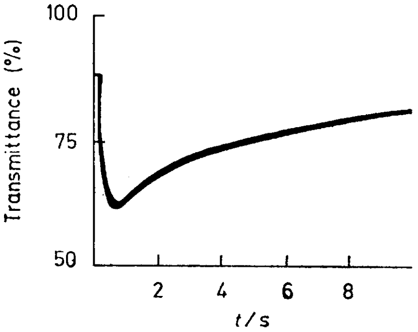
The stopped-flow traces for the oxidation of both maleic and fumaric acid have been recorded at 20 nm intervals between 200 and 800 nm in the pH range 1—4. In some experiments a five-fold excess of pyrophosphate was added to the solution as scavenger for Mn^{III} and/or Mn^{IV}. The pyrophosphate complex of Mn^{III} is a weaker oxidising agent than the aquomanganese(III) ion.[16]

In the absence of pyrophosphate, the stopped-flow traces show the following behaviour. (a) Between 240 and 270 nm, the transmission *vs.* time curves reveal a minimum (Figure). (b) Between 325 and 410 nm, as well as between 490 and 800 nm, the transmission increases with time, corresponding to the disappearance of MnO_4^-. (c) At 300 and 420 nm, the transmission practically does not change with time, *i.e.* horizontal traces are obtained.

Since Mn^{VI} and Mn^{V} have strong absorption maxima at *ca.* 600 and 700 nm, respectively, and the molar absorptivities greatly exceed those of MnO_4^- at these wavelengths,[2] the lack of transmission minima in these regions [*cf.* observation (b)] indicates the absence of Mn^{VI} and Mn^{V} as detectable intermediates.

In the presence of pyrophosphate (d) no minimum is observed in the stopped-flow traces between 240 and 270 nm; instead, the transmission decreases to a limiting value; (e) practically horizontal traces are obtained in the immediate vicinity of 320 and 430 nm; (f) the transmission increases to a limiting value between 320 and 420 nm, and above 500 nm.

Observations (a)—(f) can be interpreted by means of the spectra of MnO_4^-, Mn^{IV}, and Mn^{III}, which have been described previously.[8] Points (c) and (e) eliminate Mn^{IV} as the accumulating intermediate because the spectra of MnO_4^- and Mn^{III} intersect at these wavelengths, whereas the molar absorptivity of Mn^{IV} is greater than that of either species. Consequently, the observed minimum on the transmission *vs.* time curves corresponds to the accumulation and decay of manganese-



Stopped-flow trace at 250 nm illustrating the accumulation and decay of the manganese(III) intermediate: [Fumaric acid] = 10^{-2}M; $[MnO_4^-]_0 = 10^{-3}$M; pH 4 (succinic acid buffer); t = 25 °C

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

[10] G. King, *J. Chem. Soc.*, 1936, 1788.

[11] J. E. Coleman, C. Ricciuti, and D. Swern, *J. Amer. Chem. Soc.*, 1956, **78**, 5342.

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

[13] L. Perdrix, *Bull. Soc. chim. France*, 1897, 100.

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

[15] L. I. Simándi, *Magyar Kém, Folyoirat*, 1969, **75**, 269.

[16] W. A. Waters and J. S. Littler, ' Oxidation by Vanadium(V), Cobalt(III), and Manganese(III),' in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York and London, 1965.

(III). In the presence of pyrophosphate, Mn^{III} can be regarded as a stable product on the time scale of the stopped-flow measurements, which is in line with the absence of the minimum [point (d)]. The above conclusion is supported also by observations (b) and (f), since the molar absorptivities of the aquo- and the pyrophosphato-manganese(III) complexes are lower than that of MnO_4^- at the wavelengths in question.

The transient formation of Mn^{III} in the oxidation of maleic and fumaric acids supports the conclusion made by Drummond and Waters [5] based on visual observation. The rapid formation of manganese(III) indicates that the first reaction of the oxidation is a four-electron process. This is at variance with the assumption of Allen and Ruben who suggest a two-electron first step followed by a four-electron process.[14]

Intermediates from Maleic and Fumaric Acid.—If the oxidation is carried out in acidic solutions in the presence of a 10-fold excess of maleic (fumaric) acid, then after the disappearance of the colour of MnO_4^- and manganese(III), the solution exhibits the characteristic reactions of aldehydes: the addition of bisulphite is observed and yellow precipitates are formed with 2,4-dinitrophenylhydrazine. In solutions buffered with sodium hydrogen carbonate, iodine is consumed indicating the presence of a HC(O)C(OH)=C(OH)H function. The oxidation is accompanied by the evolution of 1·5 moles of CO_2 per mole of permanganate consumed. Depending on the pH and on the substrate: permanganate mole ratio, various amounts of glyoxylic acid can be detected by the specific test with pyrogallocarboxylic acid.[17] The oxidised solutions were found to contain hydroxymalonic acid as demonstrated by the colour reaction with β,β′-dinaphthol,[1] and some oxalic acid was detected by the formation of Aniline Blue.[17] Upon standing or brief heating, considerable amounts of glycolaldehyde were detected (bright green colour with diphenylamine [18]).

TABLE 1

Product distribution in the permanganate oxidation of maleic acid (MA)

			Amount of product (mol % of MnO_4^-)			Sum
pH	$[MA]_T$/M	$[MA]_T$: $[MnO_4^-]_0$	GD	GA	HM	[equation (9)]
0·3	0·2	50	39	1	67	113
	0·08	20	34	1	74	117
	0·04	10	30	0	67	104
	0·004	1	0·5	22	53	99
0·4	0·6	150	26	7	58	96
	0·2	50	24	5	60	99
	0·08	20	23	6	69	111
	0·04	10	18	8	65	105
	0·004	1	1	9	20	39
1·1	0·16	40	20	14	51	100
	0·08	20	14	18	55	106
	0·04	10	10	19	52	101
	0·004	1	0	12	33	59
1·3—2·2	0·4	100	3	24	58	110
	0·2	50	15	8	66	104
	0·1	25	5	26	65	124
	0·08	20	3	17	59	100
	0·04	10	1	35	65	135
	0·004	1	1	30	58	118
3·4	0·2	50	14	27	59	125
	0·1	25	6	35	52	123
	0·04	10	3	42	41	119
	0·004	1	4	31	7	61
4·5 *	0·2	50	0	30	13	88
	0·08	20	0	30	16	91
	0·04	10	0	31	15	92
	0·004	1	0	18	0	53

* Unchanged manganese(III) reduced with sulphite; yield of oxalic acid is 15 mol %.

In order to obtain more detailed information about the distribution of the products mentioned, we determined the amount of glycolaldehyde (GD), glyoxylic acid (GA) and hydroxymalonic acid (HM) as well as that of oxalic acid in some cases. The analyses based on the spectrophotometric determination of the condensation products with diphenylamine (GD and GA), and that of the Molybdenum Blue formed from ammonium molybdate (GD and HM) (see Experimental section) were performed after the complete disappearance of the colour of MnO_4^- and manganese(III). The results are shown in Table 1 for maleic and in Table 2 for fumaric acid. The amount of oxalic acid formed is 2—4 mol %, except at pH 4·3 where it is 15 mol % for both substrates (these data are not included in the Tables).

TABLE 2

Product distribution in the permanganate oxidation of fumaric acid (FA)

			Amount of product (mol % of MnO_4^-)			Sum
pH	$[FA]_T$/M	$[FA]_T$: $[MnO_4^-]_0$	GD	GA	HM	[equation (9)]
0·3	0·02	10	55	0	45	98
	0·01	5	51	0	53	104
	0·002	1	1	11	52	81
0·4	0·03	7·5	28	2	58	95
	0·02	5	25	3	62	99
	0·008	2	25	1	57	90
	0·004	1	15	2	57	84
1·0	0·04	10	39	0	56	98
	0·02	5	27	4	62	102
	0·004	1	16	0	36	56
2·3	0·02	10	29	13	33	84
	0·01	5	30	17	33	91
	0·002	1	23	26	24	89
4·5 *	0·2	50	15	15	10	72
	0·04	10	8	26	8	82
	0·004	1	1	14	0	55

* Unchanged manganese(III) reduced with sulphite; yield of oxalic acid is 15 mol %.

The product distribution indicates a complex reaction pattern. The formation of manganese(III) as an intermediate shows that the process consists of an initial, rapid four-electron step in which the corresponding organic product is formyl(hydroxy)acetic acid (I) [equation (2)]. This conclusion is based on the presence

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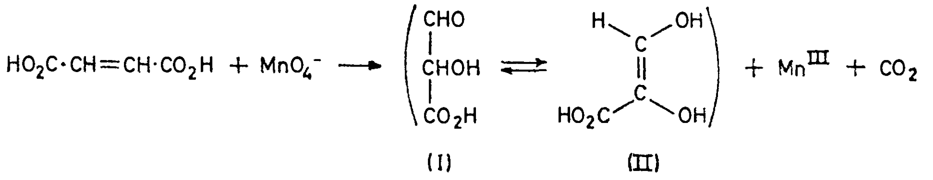
[17] F. Feigl, 'Spot Tests in Organic Analysis,' Elsevier, Amsterdam, 1956.

[18] Z. Diche and E. Borenfreund, *J. Biol. Chem.*, 1949, **180**, 1297.

of up to *ca.* 0·5 mole GD per mole MnO_4^-, because compound (I) is known to yield GD upon standing or heating.[19] The formation of HM in *ca.* 0·5 mole per mole MnO_4^- indicates that this product is due to the two-electron oxidation of compound (I) by the available manganese(III) [equation (3)]. (Only the type of redox transformation is shown in the equations.) Apparently, if reaction (3) were the only route for formation of HM, its amount could never exceed 0·5 mole per mole MnO_4^-. The data in Tables 1 and 2 clearly show that higher values are in fact observed; therefore, an additional route to formation of HM [equation (4)] must be included. This should involve MnO_4^-, too, as the source of the oxidation equivalents required in excess of the total manganese(III). The amount of HM does not vary strongly with either the mole ratio or the pH except that low values are observed at mole ratios of 1 : 1 with both substrates. The apparent absence of competition with (2) indicates that in (4) MnO_4^- is consumed very rapidly, probably by reacting with the free radical derived from (I) by hydrogen atom abstraction.

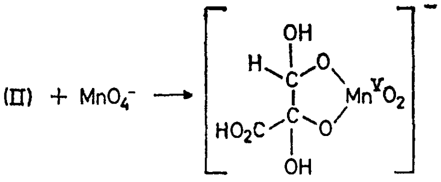


$$\mathrm{HO_2C{\cdot}CH{=}CH{\cdot}CO_2H} + \mathrm{MnO_4^-} \longrightarrow \left(\underset{(\mathrm{I})}{\mathrm{CHO{-}CHOH{-}CO_2H}} \rightleftharpoons \underset{(\mathrm{II})}{\mathrm{(H)(OH)C{=}C(OH)(CO_2H)}} \right) + \mathrm{Mn^{III}} + \mathrm{CO_2} \qquad (2)$$

$$(\mathrm{I}) + 2\,\mathrm{Mn^{III}} \longrightarrow \underset{(\mathrm{HM})}{\mathrm{HO_2C{\cdot}CHOH{\cdot}CO_2H}} + 2\,\mathrm{Mn^{II}} \qquad (3)$$

$$4(\mathrm{I}) + 2\,\mathrm{MnO_4^-} + 2\,\mathrm{Mn^{III}} \longrightarrow 4\,\mathrm{HM} + 4\,\mathrm{Mn^{II}} \qquad (4)$$

Other aldehydes have been found to give the corresponding acids upon oxidation with MnO_4^-.[2] The enol forms react differently, usually with carbon–carbon bond cleavage. In the present case, the enediol (II) is assumed to be the source of glyoxylic and oxalic acid [equation (5)], depending on the way intermediate (III) undergoes cleavage: oxidative decarboxylation [equation (6)] leads to GA, whereas bond rupture between C(2) and C(3) leads to oxalic acid [equation (7)]. The intermediate (III) is of the type assumed in the *cis*-hydroxylation of olefins in alkaline media.[10,11]



(5)

(III)

$$(\mathrm{III}) \longrightarrow \underset{(\mathrm{GA})}{\mathrm{CHO{\cdot}CO_2H}} + \mathrm{CO_2} + \mathrm{Mn^{III}} \qquad (6)$$

$$(\mathrm{III}) \longrightarrow \mathrm{(CO_2H)_2} + \mathrm{HCO_2H} + \mathrm{Mn^{III}} \qquad (7)$$

In most cases the amount of glycolaldehyde remains below the 50 mol % expected from reactions (2) and (3) alone, which again points to the existence of (5).

If MnO_4^- is converted to manganese(II), the oxidation equivalents added should obey the stoicheiometric equation (8) involving the four products detected. In Tables 1 and 2 are listed the sums corresponding to the right-hand side of equation (8) after dividing both sides by 5 $[MnO_4^-]_0$ to obtain the results in mol %.

$$5[\mathrm{MnO_4^-}]_0 = 4[\mathrm{GD}] + 8[\mathrm{GA}] + 6[\mathrm{HM}] + 8[\mathrm{OX}] \qquad (8)$$

As the amount of GA from maleic acid at pH 1·3—3·4 is too high if viewed in the light of reactions (5) and (6), to account for the positive deviations from the material balance, an additional route of GA formation must be assumed [equation (9)]. This path produces 2 moles of GA for each mole of MnO_4^-, as opposed to the 0·5 moles of GA corresponding to equations (5) and (6). The relative contribution of the two routes to glyoxylic acid formation cannot be assessed from the results.

$$\mathrm{HO_2C{\cdot}CH{=}CH{\cdot}CO_2H} + \mathrm{MnO_4^-} \longrightarrow 2\,\mathrm{CHO{\cdot}CO_2H} + \mathrm{Mn^{III}} \qquad (9)$$

The intermediates of reactions (2) and (9) are apparently identical and resemble (III), including the possibility of decomposing in two ways.

The amount of GA increases with increasing pH; its yield becomes significant at pH 1·1 for maleic, but only at pH 2·3 for fumaric acid. Below these pH values, the formation of GA is significant only if the mole ratio is 1 : 1. These trends indicate that reactions (5) and (6), involving a second molecule of MnO_4^-, take place if the rate of (2) is low enough to permit competition. Kinetic results to be reported later show that at higher acidities fumaric acid reacts with MnO_4^- much faster than does maleic acid. Therefore, in the case of fumaric acid the competition of (5) and (6) with (2) is successful only at a mole ratio of 1 : 1. Also, the overall amount of the enolic form [equation (4)] increases with increasing pH since both components have a carboxy-group with apparently different pK values. The pK of (II) may be taken as approximately equal to pK_1 of dihydroxyfumaric acid (1·58 [19]) whereas that of (I) should be close

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[19] M. B. Fleury, *Ann. Chim.*, 1966, **1**, 55; P. Souchay, D. Fleury, and M. Fleury, *Compt. rend.*, 1967, **264c**, 2130.

to the pK of glycolic acid (3·83 [20]). This again favours (5) and (6). Since at pH values where glyoxylic acid is already formed in significant amounts the mole ratio has no effect on its yield, one may assume that the rate of enolisation is low compared with the oxidation of the enediol by MnO_4^-.

At pH 4·5 MnO_4^- is rapidly converted to manganese(III) which is stabilised by complex formation with the anions of the organic acids present. In these experiments manganese(III) was reduced with sulphite before analysis. This of course leads to considerable negative deviations from the material balance.

The amount of oxalic acid is 2—4 mol % in most cases, except at pH 4·3 where it reaches 15 mol %. If a sodium hydroxide solution is injected into the reaction mixture before the disappearance of the colour of manganese(III), and oxalic acid is determined after filtering off manganese dioxide, yields of 40—60 mol % are found. This is, however, due to the oxidation of compound (I) to oxalic acid while the solution is in contact with manganese dioxide. This has been confirmed by mixing a solution of compound (I) obtained by the decarboxylation of dihydroxyfumaric acid [19] with freshly precipitated manganese dioxide. This also supports the presence of compound (I) as an intermediate, because similar treatment of maleic acid, fumaric acid, glycolaldehyde, and glyoxylic acid gave no oxalic acid. Hydroxymalonic acid gave *ca.* 10% of this product.

In the reaction scheme suggested, step (3) is mainly responsible for the disappearance of manganese(III) from the system. In separate stopped-flow experiments, we have demonstrated that among the intermediates and reactants present, compound (I) is the fastest to react with manganese(III). An aqueous solution of compound (I) at pH 0·5 was found to react with manganese(III) in a pseudo-first-order process giving a rate constant of 1100 $dm^3 mol^{-1} s^{-1}$.

The results refer to substrate : MnO_4^- mole ratios equal or greater than unity. If the mole ratio is between 1 and the 0·5 required by equation (1), about one half of the MnO_4^- is consumed rapidly, but the remainder reacts only slowly. The slow reaction corresponds to the oxidation of the intermediates to carbon dioxide and formic acid.

The sequence of intermediates suggested by Allen and Ruben [14] for fumaric acid also includes hydroxymalonic and glyoxylic acid; however, the first step is assumed to be a two-electron process leading to monohydroxyfumaric acid. The present work demonstrates that the attack on the double bond in fumaric and maleic acids is a four-electron process. In fact, the high reactivity of these compounds towards MnO_4^- is due to the presence of the double bond. It is therefore incorrect to assume that this bond remains intact after attack by permanganate. The formation of a short-lived intermediate of the type (III), containing manganese(V) is much more likely. Further evidence in favour of this concept will be presented in a forthcoming paper.

EXPERIMENTAL

Analytical grade chemicals were used throughout. Absorbance measurements were performed on Hitachi–Perkin-Elmer 124 and Unicam SP 800 instruments.

Product Analysis.—Formyl(hydroxy)acetic acid was determined as glycolaldehyde, the product of its decarboxylation.[21] According to Diche,[18] in strongly acidic media (0·5M-$HClO_4$) GD gives a bright green condensation product with diphenylamine. After suitable calibration, this reaction can be used for the spectrophotometric determination of GD. Under the conditions applied, glyoxylic acid was also found to react with diphenylamine but the spectrum of the condensation product differed significantly from that observed in the case of GD. By measuring the absorbance at 640 and 770 nm, the GD and GA concentrations can be calculated on the basis of the corresponding curves. Maleic, fumaric, hydroxymalonic, formic, and oxalic acids do not react with diphenylamine under these conditions.

Hydroxymalonic acid was determined according to Veitch and Briesley.[22] In the presence of sulphuric and phosphoric acid, HM reduces ammonium molybdate to Molybdenum Blue, which can be measured spectrophotometrically. Of the other compounds present, only GD reacts with ammonium molybdate, but this can be corrected for on the basis of independent analyses. Oxalic acid was determined gravimetrically as calcium oxalate.

[3/188 *Received, 26th January,* 1973]

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[20] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, The Chemical Rubber Co., Cleveland, 51st edn., 1970—1971.

[21] R. W. Hay and S. J. Harvie, *Austral. J. Chem.*, 1965, **18**, 1197.

[22] F. P. Veitch and G. P. Briesley, *Biochem. Biophys. Acta*, 1962, **58**, 467.