Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part 7.† Kinetics of the Oxidation of Propiolic and Phenylpropiolic Acids

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The permanganate oxidation of propiolic acid (PA) and phenylpropiolic acid (PPA) has been studied in aqueous perchloric acid. Short-lived intermediates of the reactions are manganese(III) and the corresponding dioxo-compounds. According to stopped-flow kinetic measurements, the reactions are first order with respect to both MnO_4^- and the acids, and the second-order rate constant is pH dependent, owing to the different reactivities of the acids and anions. The resolved rate constants at 25 °C are ($dm^3 mol^{-1} s^{-1}$) 183 and 43.2 for PA and its anion, and 38.8 and 11.6 for PPA and its anion, respectively. The relative reactivities of several acetylenic species are discussed in terms of a near-concerted nucleophilic attack of MnO_4^- on the triple bond.

PREVIOUS studies concerned with the permanganate oxidation of acetylenedicarboxylic acid and some substituted propynes [1-4] in acidic solutions have revealed that the rapid, multistep processes involve the attack of MnO_4^- on the bridgehead atoms of the triple bond as the rate-determining step. This is a two-electron process, resulting in the formation of a short-lived, cyclic intermediate containing manganese(V), which then either decomposes to manganese(III) and a dioxo-compound [4] or reacts rapidly with MnO_4^- *via* a complex route,[2] to yield manganese(III) and cleavage products. In all cases, manganese(III) can be readily detected before it is consumed in reactions with the organic intermediates. Stopped-flow kinetic measurements have shown that the triple bond is strongly activated by carboxy-groups but less so by carboxylate and CH_2X (X = Cl, Br, or OH) substituents. In order to elucidate further the mechanism of permanganate oxidation of acetylenic systems, we have performed a kinetic analysis of the reactions with propiolic (PA) and phenylpropiolic acid (PPA).

RESULTS AND DISCUSSION

Stoicheiometry and Intermediates.—From the results of direct titration with MnO_4^- in 5% H_2SO_4, PA is oxidised to CO_2 and H_2O, whereas PPA consumes eight oxidation equivalents, yielding benzoic acid and CO_2. Spectrophotometric titration of PPA with MnO_4^- in 0.3M-$HClO_4$ in the presence of excess of pyrophosphate shows that 1 mol MnO_4^- is rapidly converted to manganese(III) identified on the basis of the spectrum of its pyrophosphate complex,[2] following which the reaction becomes rather slow. Pyrophosphatomanganese(III) formed upon the addition of 1 mol MnO_4^- to PPA persists for several minutes, whereas in the case of PA, its disappearance is much faster. However, stopped-flow experiments reveal two readily distinguishable reactions with PA also. In both cases the life-time of pyrophosphatomanganese(III) is sufficiently long to permit quenching of the reaction by rapid injection of sulphite solution, which rapidly reduces Mn^{III} to Mn^{II}. Treatment of the quenched solutions with 2,4-dinitrophenylhydrazine yields yellow precipitates, whose amounts, analyses, and n.m.r. spectra correspond to bis-2,4-dinitrophenylhydrazones formed from dioxo-compounds derived from PA and PPA (Table 1).

According to these results, the first reaction of the overall process with both PA and PPA is oxidation to

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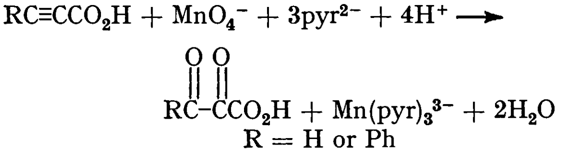
† Part 6, M. Jáky and L. I. Simándi, *J.C.S. Perkin II*, 1976, 939.

[1] L. I. Simándi and M. Jáky, *Tetrahedron Letters*, 1970, 3489.
[2] M. Jáky and L. I. Simándi, *J.C.S. Perkin II*, 1972, 1481.
[3] L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1972, 2326.
[4] L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1973, 1861.

the dioxo-derivative with concomitant formation of manganese(III) as a short-lived intermediate [equation (1)]. This is followed by oxidation of the dioxo-compounds by manganese(III). If MnO_4^- is added in excess of the 1 : 1 mole ratio, oxidation to the final products will occur with participation of the Guyard reaction as shown earlier for some substituted butynes.[4]



$$RC{\equiv}CCO_2H + MnO_4^- + 3pyr^{2-} + 4H^+ \longrightarrow \overset{O}{\overset{\|}{RC}}-\overset{O}{\overset{\|}{C}}CO_2H + Mn(pyr)_3^{3-} + 2H_2O \quad (1)$$

R = H or Ph

Kinetic Measurements.—The object of this work was to study the kinetics and mechanism of reaction (1), in which permanganate attacks the triple bond. Kinetic measurements were performed by the stopped-flow technique, following the disappearance of MnO_4^- at 540 nm.[5] A 10-fold excess of pyrophosphate over MnO_4^- was used to prevent manganese(III) from further reduction on the stopped-flow time scale, thus eliminating possible interference by the Guyard reaction. The ionic strength was maintained at 1.5M with added $NaClO_4$; the required acidity was adjusted by adding $HClO_4$ and/or a suitable buffer with negligible reactivity towards MnO_4^-.

In the presence of a 10-fold excess of PA or PPA, the 540 nm stopped-flow traces gave excellent first-order plots of log $(A - A_\infty)$ *versus* time. The pseudo-first-order rate constant k_{obs} was found to be proportional to the substrate concentration (Table 2). Consequently, the kinetic law for both PA and PPA can be given as equation (2), where $k[S]_0 = k_{obs}$. The second-order rate constant k varies with the pH of the solution as shown in Figures 1 and 2. This behaviour can be interpreted in terms of different reactivities of the undissociated acid and the monoanion towards MnO_4^-. If it is assumed that the acid–base equilbria are much faster than the reaction with MnO_4^-, then k can be expressed by equation (3), where k_1 and k_2 are the second-order rate constants for the acid and the anion, respectively, K is the acid dissociation constant and a_H is the hydrogen ion activity. The individual rate constants have been determined by fitting equation (3) to the experimental k *versus* pH curve, using a computer program based on a ' steepest descent ' type gradient method. The resolved rate constants are listed in Table 3. The fitting procedure was run as a three-parameter problem, *i.e.* the acid dissociation constant was also permitted to vary. Its best value was then compared with the value obtained by pH titration in order to check the reliability of the results. The computer calculations yielded K 3.94×10^{-2} (PA) and 9.47×10^{-3} l mol^{-1} (PPA), in good agreement with the pH data: 5.22×10^{-2} (PA) and 1.07×10^{-2} l mol^{-1} (PPA).

$$-d[MnO_4^-]/dt = k[S]_0[MnO_4^-] \qquad (2)$$

$$k = (k_1a_H + k_2K)/(K + a_H) \qquad (3)$$

TABLE 1

Analytical and n.m.r. data for the bis-2,4-dinitrophenylhydrazones of the intermediate dioxo-compounds

Source	M.p. (°C)	Formula	C (%)		H (%)		N (%)		Yield (%)
			Calc.	Found	Calc.	Found	Calc.	Found	
Propiolic acid	350 (decomp.)	$C_{15}H_{10}N_8O_{10}$ [a]	39.0	39.9	2.15	2.15	24.2	24.4	93.4
Phenylpropiolic acid	201—202	$C_{21}H_{14}N_8O_{10}$ [b]	46.8	47.1	2.6	3.2	20.8	20.75	96.6

[a] N.m.r.: δ 8.80 (1 H, s, CH=N), 8.10—8.65 (4 H, m, 5- and 6-H in the 2,4-dinitrophenyl rings), 8.83 (2 H, d, J_m 2.2 Hz, 3-H in the 2,4-dinitrophenyl rings), and 11.70br and 13.66br (2 × 1 H, 2 × s, exchangeable protons). [b] N.m.r.: δ 7.66 (5 H, m, Ph), 7.48 and 8.02 (2 × 1 H, d, J_0 8.5 Hz, 6-H in the 2,4-dinitrophenyl rings), 8.38 and 8.44 (2 × 1 H, dd, J_0 8.5, J_m 2.5 Hz, 5-H in the 2,4-dinitrophenyl rings), 8.85 (2 H, d, J_m 2.5, 3-H in the 2,4-dinitrophenyl rings), and 11.26br and 13.00br (2 × 1 H, 2 × s, exchangeable protons).

TABLE 2

Dependence of the first-order rate constant (k_{obs} [a]) on the substrate concentration (T 25 °C; pH 3.77; ionic strength 1.5M)

Substrate	$10^2[S]_0$/M	$10^3[MnO_4^-]_0$/M	10^2k_{obs}/s^{-1}	k/dm^3 mol^{-1} s^{-1}
Propiolic acid	0.50	0.50	22.4	44.8
	1.0	1.50	43.7	43.7
	2.0	1.50	87.1	43.6
	3.0	1.50	132	44.1
Phenylpropiolic acid	0.25	0.25	2.92	11.7
	0.50	0.50	5.97	11.9
	1.0	0.50	11.9	11.9
	1.5	0.50	17.9	12.0

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

TABLE 3

Resolved rate constants (dm^3 mol^{-1} s^{-1}) and activation parameters [a] for propiolic and phenylpropiolic acid

Substrate	k_1	k_2	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J mol^{-1} K^{-1}
Propiolic acid	183	43.2	25.8	−128
Phenylpropiolic acid	38.8	11.6	30.3	−129

[a] For k_2 at pH = 3.77

As an illustration of the fit achieved, the k *versus* pH curves calculated with the resolved rate constants are shown by solid lines in Figures 1 and 2.

The temperature dependence of k_2 has been determined between 12 and 36 °C at pH 3.77; the activation parameters are given in Table 3.

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

The kinetic measurements performed at a substrate : MnO_4^- mole ratio of 1 : 1 are consistent with a consumption ratio of 1 : 1 in line with equation (1).

The kinetic behaviour reported is consistent with the rate-determining attack of MnO_4^- on the triple bond, resulting in the formation of a five-membered cyclic intermediate, which rapidly collapses to a dioxo-derivative and manganese(III), the first detectable intermediates. A mechanism accounting for the observed facts is given in equation (4). In view of previous results,[1-4] this mechanistic pattern seems to be quite general for the permanganate oxidation of acetylenes.

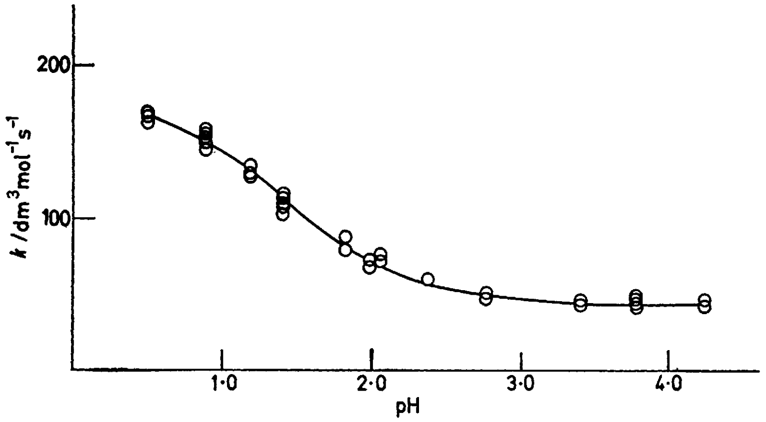


FIGURE 1 pH Dependence of the second-order rate constant for propiolic acid (solid curve calculated from the resolved rate constants)

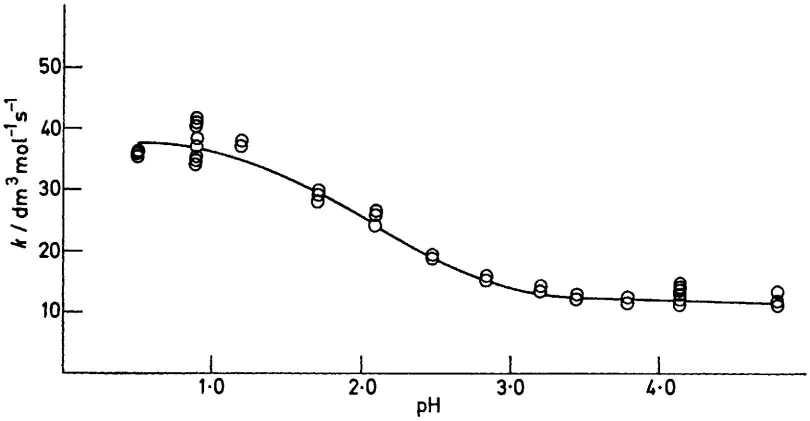
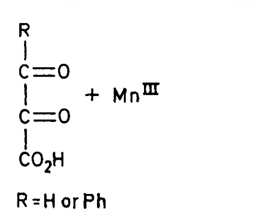


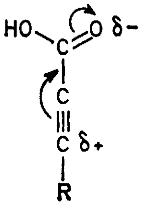
FIGURE 2 pH Dependence of the second-order rate constant for phenylpropiolic acid (solid curve calculated from the resolved rate constants)



(4)

The reactions are primarily entropy controlled, the activation energies being very small. The formation of the cyclic hypomanganate ester is energetically favourable, requiring only insignificant bond breaking.

When interpreting the reactivity of MnO_4^- toward different unsaturated compounds, it is necessary to emphasise that, as a strong oxidant, permanganate should be regarded as a powerful electrophile. However, this feature refers to the *overall reaction* and is essentially thermodynamic in nature, reflecting the fact that oxidation by MnO_4^- is energetically favourable. As for the relative rates with the individual substrates, factors operative in the rate-determining step [*cf.* equation (4)] are of decisive importance. In order that the electrophilic strength of MnO_4^- could manifest itself, the two reactants should first come into intimate contact *via* chemical bonding. In the transition state thus formed, electrons will readily flow toward the Mn^{VII} centre. The fact that the mono- and/or di-anions of the unsaturated carboxylic acids studied thus far are less reactive than the undissociated acids strongly indicates that the initial attack of MnO_4^- in the rate-determining step is nucleophilic, rather than electrophilic, in nature. This also receives support from the pronounced activating effect of carboxy-group(s) α to the triple bond. Consequently, the ease of attack will depend on the possibility of the formation of an electrophilic centre in the substrate to accommodate an unshared electron pair from a permanganate oxygen. The structure of a reactive acetylene can be depicted as (A), in which an electrophilic centre is created at a bridgehead atom of the triple bond owing to the mesomeric shift caused by carboxy-conjugation.



(A)

The manganese(v) intermediate shown in equation (4) forms in a near-concerted manner but a pre-equilibrium step cannot be excluded. The ionisation of the carboxy-group should decrease the reactivity toward MnO_4^- as the net negative charge interferes with the required mesomeric shift. This is fully consistent with the observed reactivity pattern.

In the case of acetylenedicarboxylic acid (I) (Table 4), the triple bond is activated by the cumulative effect of two carboxy groups, leading to the highest reactivity in the series. It is noteworthy that k_2 for (I) is larger than k_1 for (II), implying that the carboxylate group also has an activating effect although weaker than that of the CO_2H group. This is in line with the relative $-M$ effects of the CO_2R and CO_2^- groups.[6] However, two CO_2^- groups do not seem to have a cumulative effect [*cf.* k_3 for (I) and k_2 for (II)], which may be due to increased electrostatic repulsion between MnO_4^- and the dianion.

TABLE 4

Second-order rate constants ($dm^3\ mol^{-1}\ s^{-1}$) for the reactions of acetylenic derivatives with permanganate in acidic solution (T 25 °C, ionic strength 1.5M)

Reactant	k_1	k_2	k_3	Ref.
Acetylenedicarboxylic acid (I)	1 420	632	40	2
Propiolic acid (II)	183	43.2		This work
Phenylpropiolic acid (III)	38.8	11.6		This work
Propargyl alcohol (IV)	10			4
Propargyl chloride (V)	11.5			4
Propargyl bromide (VI)	11.5			4
But-2-yne-1,4-diol (VII)	12.5			4

The low reactivity of phenylpropiolic acid is apparently the consequence of propagation of the mesomeric shift beyond the triple bond, owing to conjugation with the phenyl group. This effectively removes the electron deficiency from the reaction centre, deactivating it toward nucleophilic attack. Also, the phenyl group may sterically hinder the attack of MnO_4^-.

The reactivities of compounds (IV)—(VII) are essentially identical, indicating insensitivity to inductive effects.

It is generally recognised that alkynes are more susceptible to nucleophilic attack than alkenes. However, fumaric acid[7] and its diethyl ester[8] react *ca.* 10 times faster than acetylenedicarboxylic acid, which, in turn, is *ca.* 1.4 times more reactive than maleic acid,[7] which indicates that the permanganate oxidation of unsaturated compounds cannot be readily interpreted in terms of this broad pattern. The factors governing the rates of these processes are multifarious, involving electrostatic, electronic, and steric effects and it seems that no single factor plays a predominant role for a wide range of substrates. Of necessity, initial nucleophilic attack by an oxidant (electrophile) should display a complicated trend in reactivity not subject to simple interpretation.

EXPERIMENTAL

Propiolic acid and phenylpropiolic acid were Fluka purum products. All other chemicals were of analytical grade. The precipitation of 2,4-dinitrophenylhydrazones, the details of the pH titrations, and the stopped-flow kinetic measurements have been described.[2-4] N.m.r. spectra were recorded at 60 °C in hexadeuteriodimethyl sulphoxide, using a Varian XL-100 pulsed Fourier transform spectrometer operating at 100 MHz.

We are indebted to Mrs. E. Baitz-Gács for recording and interpreting the n.m.r. spectra.

[6/820 *Received, 27th April,* 1976]

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[6] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca and London, 1969, 2nd edn., p. 91.

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

[8] M. Jáky and L. I. Simándi, *Reaction Kinetics Catalysis Letters*, 1975, **3**, 397.