Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part II.[1] Stopped-flow Kinetic Study of the Oxidation of Acetylenedicarboxylic Acid

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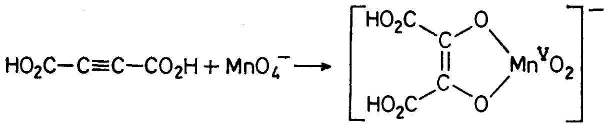
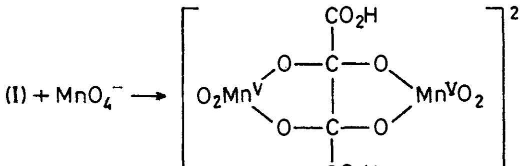
The kinetics of oxidation of acetylenedicarboxylic acid by permanganate have been studied by the stopped-flow technique in aqueous solution between pH 0·25 and 5·3. The reaction is of the first order with respect to both permanganate and the substrate. The apparent second-order rate constant increases with decreasing pH, indicating the reactivity order: undissociated acid > monoanion > dianion. The individual rate constants are in the above order: k_1 = 1420; k_2 = 632; k_3 = 40 l mol^{-1} s^{-1}. The temperature-dependence of k_3 studied in the 13·7—30·3 °C interval yields the activation parameters $\Delta H^\ddagger$ = 25·5 kJ mol^{-1} and $\Delta S^\ddagger$ = −135 J K^{-1} mol^{-1}. The kinetic behaviour is consistent with the rate-determining formation of a short-lived cyclic intermediate containing manganese(V).

THE products and short-lived intermediates of the permanganate oxidation of acetylenedicarboxylic acid (H_2A) in acidic solutions have been reported.[1] Manganese(IV), manganese(III), and oxalic acid were found to occur as intermediates; the last two species were detected directly. Tracer studies carried out in ^{18}O-enriched water provided evidence for oxygen transfer from permanganate to the substrate. The first step of this process is the formation of a cyclic intermediate containing Mn^V. By comparing the predicted results of a variety of possible combinations, the sequence (1)—(5) was found suitable for the interpretation of the experimental results. Here Mn^{IV} represents a soluble species with a very short life-time, whose existence has been inferred from the experimental results.[1] With decreasing H_2A concentration, the reaction of Mn^{IV} with the oxalic acid intermediate (not shown) becomes more and more important; however, under the present conditions this process can be neglected.



(I)

(1)



(2)

$$(\mathrm{II}) \longrightarrow 2Mn^{IV} + 2(CO_2H)_2 \quad (3)$$

$$4Mn^{IV} + (\mathrm{I}) \longrightarrow 5Mn^{III} + (CO_2H)_2 + 2CO_2 \quad (4)$$

$$2Mn^{III} + (CO_2H)_2 \longrightarrow 2Mn^{II} + 2CO_2 + 2H^+ \quad (5)$$

The kinetic study here described was undertaken to obtain more details of this reaction mechanism. The rapidity of the reaction required application of the stopped-flow technique.

RESULTS

The disappearance of permanganate was followed on a stopped-flow device at 540 nm, where the absorbances of all other species present are negligible relative to that of MnO_4^-. Therefore, the kinetic measurements refer to the conversion of MnO_4^- into Mn^{III} represented by the sum of reactions (1)—(4), *i.e.*, (6). Process (6) is rather

$$3H_2A + 5MnO_4^- \longrightarrow 5Mn^{III} + 5(CO_2H)_2 + 2CO_2 \quad (6)$$

sharply separated in time from the subsequent oxidation of oxalic acid by Mn^{III}. This is demonstrated by the stopped-flow traces shown in Figure 1, which refer to identical reacting solutions but to different wavelengths. The 250 nm trace illustrates the accumulation and decay of Mn^{III},[1] whereas the 540 nm curve represents the disappearance of MnO_4^-. It is apparent from the traces that the permanganate is practically fully converted into Mn^{III} before the latter reacts to any significant extent: at t = 0·16 s, the MnO_4^- concentration has dropped to 10% of its initial value, while the decay of Mn^{III} has just about started. According to the kinetic curves, no auto-

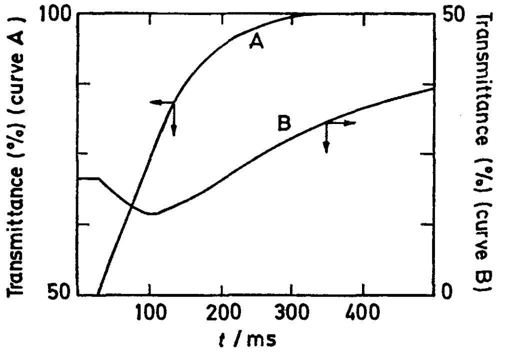


FIGURE 1 Stopped-flow traces illustrating the variation of the concentration of MnO_4^- and the Mn^{III} intermediate during the reaction (the flow stops at t = 30 ms). A, MnO_4^- trace: 540 nm; B, Mn^{III} trace: 250 nm; $[MnO_4^-]_0 = 10^{-3}$M; $[H_2A]_T = 10^{-2}$M; $[HClO_4]$ = 0·25M; I_c = 1·5M; t = 25 °C

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

catalytic behaviour is exhibited by the reaction although this phenomenon is frequently observed with permanganate oxidations.

In the kinetic study of reaction (6), H_2A was used in 10—20-fold excess over permanganate. Under such conditions, the disappearance of MnO_4^- obeys a pseudo-first-order rate law, *i.e.*, excellent straight lines are obtained by plotting the logarithm of the absorbance against time. The slope of these straight lines was found to be proportional to the overall concentration of acetylenedicarboxylic acid.

Kinetic measurements were performed in the temperature range 14—30 °C. The ionic strength of the solutions was maintained at $I_c = 1{\cdot}5$M with $NaClO_4$ or $(NH_4)_2SO_4$. The hydrolysis of the latter was taken into account.

TABLE 1

pH-dependence of the apparent rate constants for the oxidation of acetylenedicarboxylic acid by permanganate in sulphuric acid media; ionic strength $I_c = 1{\cdot}5$M, with $(NH_4)_2SO_4$; wavelength 540 nm; t = 25 °C; $[H_2A]_T/[MnO_4^-]_0 \geqslant 10$

		k_{obs}/s^{-1}						
		$10^2[H_2A]_T$/M				$10^{-2}k$ *	10^2F †	$10^{-2}G$ ‡
No.	pH	0·25	0·50	0·75	1·00	$l\ mol^{-1}\ s^{-1}$	$mol^2\ l^{-2}$	s^{-1}
1	2·36	0·38	0·90	1·40	2·00	1·92	1·64	2·77
2	2·07	0·58	1·43	1·70	2·62	2·52	1·80	2·43
3	1·72	0·87	2·21	2·55	3·87	3·80	2·20	2·28
4	1·63	1·05	2·26	2·80	4·12	4·30	2·38	2·33
5	1·49	1·20	3·08	3·97	5·43	5·30	2·75	2·50
6	1·37	1·81	3·64	4·94	6·86	7·00	3·21	2·98
7	0·82	3·15	7·15	9·30	12·3	12·7	9·27	4·63
8	0·47	4·33	8·70	12·4	18·0	17·5	24·4	7·54
9	0·23	4·90	9·44		18·4	18·4	58·3	10·90

* From the slopes of the straight-line plot of k_{obs} against $[H_2A]$–. † Equation (15). ‡ Equation (17).

TABLE 2

pH-dependence of the apparent second-order rate constant in perchlorate media; ionic strength $I_c = 1{\cdot}5$M, with $NaClO_4$; wavelength 540 nm; t = 25 °C; $[H_2A]_T/[MnO_4^-]_0 \geqslant 10$

pH	$10^{-2}k$ / $l\ mol^{-1}\ s^{-1}$	10^2F / $mol^2\ l^{-2}$	$10^{-2}G/s^{-1}$	$k(K_2 + a_H)$ / s^{-1}
0·25	18·1	53·1	10·2	
0·52	16·4	21·5	6·98	
0·65	14·4	14·6	5·60	
0·88	11·0	7·97	3·93	
0·97	11·5	6·48	4·12	
1·18	9·0	4·20	3·34	
1·39	7·3	3·13	3·21	
1·70	3·75	2·39	2·37	23·8
1·76	3·45	2·29	2·35	20·2
1·78	3·22	2·25	2·22	18·6
1·88	2·70	2·10	2·08	14·6
2·20	1·90			9·00
2·70	0·90			3·87
3·06	0·67			
3·29	0·68			
3·60	0·80			
3·72	0·69			
4·09	0·75			
5·27	0·54			

Under pseudo-first-order conditions, the variation of the reaction rate with pH was investigated between pH 0·25 and 5·3, in both perchlorate and sulphate media. The kinetic behaviour was found to be independent of the acid used for adjusting the pH.

The experimental results concerning the kinetics of reaction (6) are listed in Tables 1—3. The rate constants in the Tables are based on the empirical rate law (7), where k_{obs} is given by equation (8) and $[H_2A]_T$ is the total concentration of acetylenedicarboxylic acid.

TABLE 3

The apparent first-order rate constant as a function of $[H_2A]_T$ in perchlorate media; pH = 0·97; ionic strength $I_c = 1{\cdot}5$M, with $NaClO_4$; wavelength 540 nm; t = 25 °C; $[H_2A]_T/[MnO_4^-]_0 = 10$

$10^2[H_2A]_T$/M	k_{obs}/s^{-1}
0·25	2·59
0·50	5·72
0·75	8·44
1·00	11·4
1·50	17·8
2·00	22·9

$$-d[MnO_4^-]/dt = k[H_2A]_T[MnO_4^-] \qquad (7)$$

$$k_{obs} = k[H_2A]_T \qquad (8)$$

Table 1 contains the values of k_{obs} measured in sulphuric acid media as a function of the pH and the total concentration of acetylenedicarboxylic acid. By plotting k_{obs} against $[H_2A]_T$ at constant pH, straight lines passing through the origin are obtained. The corresponding slopes yield the value of k on the basis of equation (8); these are shown in column 7 of Table 1. All values of k_{obs} are the average results of 3—5 individual kinetic runs.

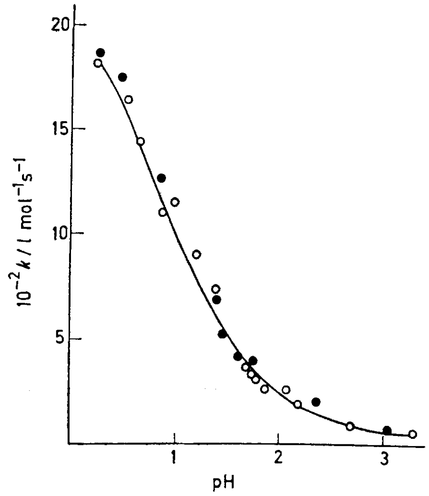

FIGURE 2 Dependence of the rate constant k on pH; ○, perchlorate medium; ●, sulphate medium; solid curve: pH-dependence calculated from k_1, k_2, k_3, and the dissociation constants

The values of k_{obs} obtained in perchlorate media are listed in Table 2 for $[H_2A]_T$ = 0·01M. The data in Table 3 illustrate the validity of equation (8) in perchlorate solutions of pH 0·97.

The pH dependence of k is shown in Figure 2 for 25 °C. Since the reaction is accompanied by a change in the pH, monochloroacetic acid and succinic acid buffers were added in the pH range of 1·7—3·1 and 3·4—5·3, respectively. The buffer concentration did not contribute more than

0·1M to the total ionic strength of 1·5M.[2] The pH–rate profile shows that upon changing the pH from 0·25 to 3, the rate constant drops to 1/20th of its value.

We have studied the effect of a number of metal ions on the rate of oxidation: Mn^{2+}, Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ni^{2+} were found to have no effect in the $HClO_4$ concentration range of 0·5—1·5M. The absence of an acceleration in the presence of Mn^{2+} is consistent with the fact that the kinetic curves in other runs have revealed no autocatalysis.

The rate constant is rather insensitive to changes in the ionic strength. For example, at pH 3 the increase of the ionic strength from 0·1 to 1·5M merely increases k by 30%. At pH 0·3 a change of I_c from 1·5 to 3·0 results in an acceleration of 10%.

In order to resolve the pH-dependence of the rate constant, it was necessary to determine the dissociation constants of acetylenedicarboxylic acid at the given ionic strength. The values reported[3] are rather diverse and there are no data for the ionic strength of 1·5M.

The acid dissociation constants are defined by the equations (9) and (10) where a_H is the hydrogen-ion activity. K_1 and K_2 are mixed constants inasmuch as they

$$K_1 = [HA^-]a_H/[H_2A] \quad (9)$$

$$K_2 = [A^{2-}]a_H/[HA^-] \quad (10)$$

are expressed partly in terms of activities and partly of concentrations. The constants so defined are convenient for our purposes since the activity coefficients of the anions can be regarded as constant and a_H is directly obtained from the pH.

The acid dissociation constants were determined by pH-metric titration. The curves were evaluated by a standard method recommended for dibasic acids with overlapping ionisation equilibria.[4,5] The following values were obtained at 25 °C ($I_c = 1{\cdot}5$ M): $K_1 = 0{\cdot}40 \pm 0{\cdot}04$ mol l^{-1}; $pK_1 = 0{\cdot}40$ and $K_2 = (3{\cdot}90 \pm 0{\cdot}10) \times 10^{-2}$ mol l^{-1}; $pK_2 = 1{\cdot}41$.

DISCUSSION

The results of kinetic measurements showed that the rate of disappearance of MnO_4^- is of the first order with respect to both permanganate and acetylenedicarboxylic acid. The apparent second-order rate constant (k) was found to vary strongly with pH. This can be interpreted in terms of the different reactivities of the acid, monoanion, and dianion, whose relative amounts are determined by the pH and the acidity constants only. This assumption implies that the dissociation equilibria are established much more rapidly than the oxidation of the substrate. The character of the pH–rate profile indicates the reactivity order $H_2A > HA^- > A^{2-}$. In the vicinity of pH 3, a limiting value is attained owing to practically complete dissociation of H_2A.

The reaction mechanism (1)—(5) inferred from extrakinetic information in our previous paper[1] is consistent with the observed kinetic behaviour if step (1) is rate-determining and (2), (3), and (4) are fast. The rate of the disappearance of MnO_4^- can be written as the sum (11) of 3 terms. The factor of 3/5

$$-3d[MnO_4^-]/5dt = (k_1[H_2A] + k_2[HA^-] + k_3[A^{2-}])[MnO_4^-] \quad (11)$$

is required because the rate-determining step is followed by the rapid reaction of a second permanganate but one out of every 3 rate-determining steps is followed by step (4) instead [*cf.* equation (6)]. The mass-balance equation for acetylenedicarboxylic acid, combined with equations (9) and (10), yields expressions (12)—(14) for the concentrations of the individual acetylenedicarboxylic species, where F is defined by equation (15). Substituting the species concentrations from

$$[H_2A] = [H_2A]_T a_H^2/F \quad (12)$$

$$[HA^-] = [H_2A]_T K_1 a_H/F \quad (13)$$

$$[A^{2-}] = [H_2A]_T K_1 K_2/F \quad (14)$$

$$F = K_1K_2 + K_1a_H + a_H^2 \quad (15)$$

equations (12)—(14) into equation (11), and comparing the result with equation (7), one obtains equation (16) for the apparent second-order rate constant.

$$k = 5(k_1a_H^2 + k_2K_1a_H + k_3K_1K_2)/3F \quad (16)$$

To demonstrate the consistency between the experimental values of k and expression (16) we used the following procedure. Upon decreasing the hydrogen-ion activity, k apparently tends to $(5/3)k_3$. Thus from the limiting value above pH 3, $k_3 = 42$ l mol^{-1} s^{-1}. The remaining two rate constants can be determined from the linearised form (17) of equation (16). If

$$G = \left(\frac{3kF}{5} - k_3K_1K_2\right)\frac{1}{a_H} = k_1a_H + k_2K_1 \quad (17)$$

equation (16) is valid, G must be a linear function of the hydrogen-ion activity. Next to the k values at pH $\leqslant$ 2·36, we have listed the calculated G and F values in Tables 1 and 2. As shown in Figure 3, the plot corresponding to equation (17) gives a straight line. The rate constants obtained by a least-squares procedure from the slope and the intercept are $k_1 = 1420$ and $k_2 = 625$ l mol^{-1} s^{-1}. The validity of equation (16) can also be demonstrated by a different plot by use of the data at pH $\geqslant$ 1·7. In this range we obtain equations

$$F \approx K_1(a_H + K_2) \quad (18)$$

$$k_1a_H^2 \ll k_2K_1a_H + k_3K_1K_2 \quad (19)$$

(18) and (19). Therefore, after rearrangement, equation

$$k(K_2 + a_H) = 5(k_2a_H + k_3K_2)/3 \quad (20)$$

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[2] D. D. Perrin, *Austral. J. Chem.*, 1963, **16**, 572.

[3] (*a*) H. W. Ashton and J. R. Partington, *Trans. Faraday Soc.*, 1934, **30**, 598; (*b*) J. Radell, B. W. Brodman, A. Hirshfeld, and E. D. Bergmann, *J. Phys. Chem.*, 1965, **69**, 928; (*c*) M. L. Dondon, *J. Chim. phys.*, 1957, 304; (*d*) R. S. Bottei and W. A. Joern, *J. Chem. Eng. Data*, 1968, **13**, 522.

[4] H. T. S. Britton, ' Hydrogen Ions,' vol. 1, p. 218, Chapman and Hall, London, 1955.

[5] A. Albert and E. P. Serjeant, ' Ionisation Constants of Acids and Bases ', Methuen, London, 1962, p. 51.

(16) becomes (20). The plot of the left-hand side of equation (20) against a_H yields a straight line as illustrated by Figure 4. The data used are listed in Tables 1 and 2. From the slope obtained by a least-squares fit $k_2 = 640$ l mol^{-1} s^{-1} and from the intercept, in combination with the known value of K_2, $k_3 = 38$ l mol^{-1} s^{-1}, in excellent agreement with the constants obtained from equation (17) and the limiting value above pH 3.

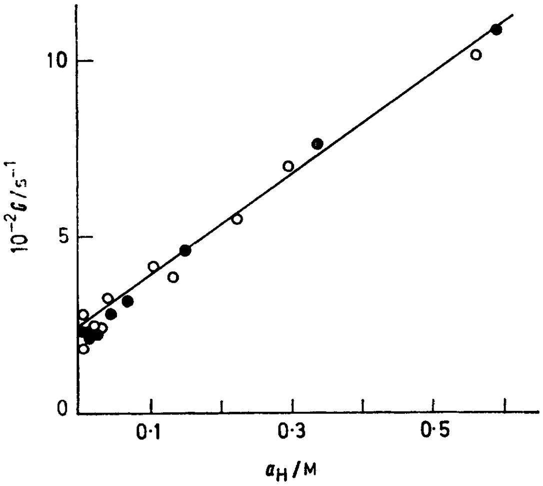

FIGURE 3 Plot of the experimental results according to equation (17); ○, perchlorate medium; ●, sulphate medium

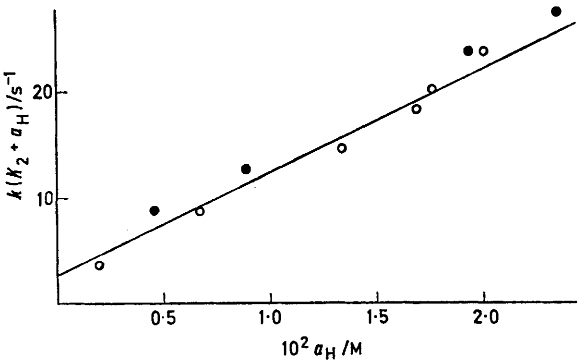

FIGURE 4 Plot of the experimental results according to equation (20); ○, perchlorate medium; ●, sulphate medium

Thus the kinetic results are consistent with the mechanism (1)—(4), which served as the basis for deriving expression (16).

Kinetic equation (11) was also checked in the case when the solution did not contain a large excess of H_2A. Under these conditions we can investigate whether or not the factor 5/3 deduced from non-kinetic results is consistent with the kinetics as well. If the consumption of neither reactant is negligible, the integrated rate equation corresponding to (7) will depend on the ratio in which the two reactants (MnO_4^- and H_2A) disappear. Let x and a be the concentration of permanganate and acetylenedicarboxylic acid, respectively, at time t, and x_0 and a_0 the initial values. Then, if the two reactants are consumed in a 5 : 3 ratio, we have equation (21). With this condition, equation (7)

$$x_0 - x = 5(a_0 - a)/3 \qquad (21)$$

integrates to (22). The kinetic curves obtained in the

$$kt = \frac{5}{2a_0} \ln \frac{2a_0 + 3x}{5x} \qquad (22)$$

case of $x_0 = a_0$ gave excellent straight lines when plotted according to equation (22), and the rate constant agreed very well with the value calculated from the pseudo-first-order measurements at the same pH and ionic strength. On the other hand, integrated rate equations corresponding to other consumption ratios either gave curves on plotting or, if the curvature was small enough to permit drawing a straight line, the rate constant differed strongly from the one obtained under pseudo-first-order conditions. Thus the kinetic results referring to equal initial concentrations are also in agreement with the proposed reaction mechanism.

The temperature-dependence of the rate constant k has been studied beteeen 13·7 and 30·3 °C at pH 3·8, where it reaches its limiting value (*cf.* Figure 2). Thus the activation parameters obtained can be unequivocally assigned to k_3. At lower pH values this would not have been possible owing to the temperature-dependence of the acid dissociation constants and the presence of more than one reacting species. The pertinent data are in Table 4; each rate constant is the average of 3 measurements. The Arrhenius parameters are $\Delta H^\ddagger = 25{\cdot}5$ kJ mol^{-1} and $\Delta S^\ddagger = -135$ J K^{-1} mol^{-1}. The results presented indicate that the rate-determining step of process (6) is the reaction of a permanganate ion with H_2A, HA^-, or A^{2-}, which are in rapid equilibrium with each other. Thus the relative amount of these species is solely determined by K_1, K_2, and the pH and their mutual conversion does not influence the overall rate.

TABLE 4

Temperature-dependence of k at pH = 3·8; succinic acid buffer; $[H_2A]_T = 10^{-2}$M; $[MnO_4^-]_0 = 10^{-3}$M; ionic strength I_c = 1·5M, with $NaClO_4$

t/°C	k/l mol^{-1} s^{-1}
13·7	39
19·2	51
21·2	54
24·4	60
30·3	72

The undissociated acid is 2·2 times more reactive than the monoanion which, in turn, reacts about 16 times more rapidly than the dianion. This reactivity order cannot be attributed solely to electrostatic factors, owing to the rather low value of $k_1/k_2 = 2{\cdot}2$. Also, changes in the ionic strength influence the rate rather weakly: at pH 3 k is 67 l mol^{-1} s^{-1} at ionic strength

1·5M and 54 l mol^{-1} s^{-1} at 0·1M. This also points to only minor contributions from electrostatic effects to the relative reactivities.

According to Carrington and Symons,[6] permanganate cannot be regarded either as an electrophile or a nucleophile in the traditional sense. In its reactions with alcohols, amines, and fluoral hydrate[7] MnO_4^- behaves as an electrophile. However, in the case of carbon monoxide,[8] cyclohexane-, and cyclopentane-nitronate anions[9] oxidation by permanganate is assumed to involve nucleophilic attack.

The reactivity order observed in the case of acetylenedicarboxylic acid and its anions is consistent with the trend expected for nucleophilic attack by permanganate. The large negative entropy of activation lends further support to the conclusion drawn from tracer experiments[1] according to which the first intermediate must be a cyclic species [*cf.* step (1)] containing manganese(V). The activated complex leading to this intermediate seems to involve some charge separation corresponding to a near-concerted *cis*-attack.

An alternative interpretation is a two-step process involving nucleophilic attack and subsequent rapid ring closure. This implies that the activation entropy can be accounted for without ring formation in the transition state. In our opinion the former concept is slightly preferable.

As pointed out by Huisgen[10] and Wiberg and Geer,[11] there appears to be a similarity between 1,3-dipolar additions and the permanganate oxidation of alkenes. This analogy might probably be extended to the oxidation of acetylenedicarboxylic acid: 1,3-dipolar additions are accelerated by carboxy-conjugation, a behaviour observed also in the present case. The ionisation (removal) of the last carboxy-group produces a much larger decrease in reactivity (*cf.* k_2/k_3) than that of the first carboxy (k_1/k_2).

Nucleophilic attack has been observed in the 1,3-dipolar cycloadditions between benzyl azide and *para*-substituted phenylacetylenes.[12] Littler's treatment[13] of alkene oxidations by MnO_4^-, applying orbital symmetry rules, can be readily extended to acetylenic systems, too. In the present case there are two consecutive, allowed electrocyclic reactions with MnO_4^- of which the second is much faster than the first [*cf.* equations (1) and (2)], as it does not affect the kinetic order with respect to MnO_4^-. This is in line with the observation that dihydroxyfumaric acid reacts with permanganate *ca.* 30 times more rapidly than H_2A.[14]

Work is in progress on the permanganate oxidation of other unsaturated systems.

EXPERIMENTAL

Acetylenedicarboxylic acid (Fluka) was purified by repeated dissolution in ether and precipitation by light petroleum. Potassium permanganate and all the other chemicals were of reagent grade.

The acid dissociation constants of acetylenedicarboxylic acid were determined by pH-metric titration with CO_2-free 1·000M-sodium hydroxide. The titration curves were evaluated by the method described by Britton.[4]

The kinetic measurements were carried out on a stopped-flow spectrophotometer described elsewhere.[15] The instrument is suitable for following reactions with half-lives greater than about 15 ms. Thermostatted solutions of the two reagents were rapidly mixed in a 4-jet Teflon mixing chamber and after the flow had been stopped the transmission of the reacting solution was followed spectrophotometrically. The transmission–time curves were displayed on a Tektronix 564 storage oscilloscope and photographed with a Polaroid camera. Typical traces are shown in Figure 1.

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[6] A. Carrington and M. C. R. Symons, *Chem. Rev.*, 1963, **63**, 443.

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

[8] J. Halpern and A. C. Harkness, as quoted in ref. 7.

[9] F. Freeman and A. Yeramyan, *Tetrahedron Letters*, 1968, 4783; F. Freeman, A. Yeramyan, and F. Young, *J. Org. Chem.*, 1969, **34**, 2438.

[10] R. Huisgen, *Angew. Chem.*, 1963, **75**, 604, 742.

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

[12] I. Pintér and A. Messmer, *MTA KKKI Közl.*, 1963, **9**, 35.

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

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

[15] L. I. Simándi, *Magyar Kem. Folyóirat*, 1969, **75**, 269.