Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part V.† Intermediates and Kinetics of the Oxidation of Substituted Propynes

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The permanganate oxidation of propargyl alcohol (PA), but-2-yne-1,4-diol (BD), and propargyl chloride (PC) and bromide (PB) has been studied in aqueous perchloric acid. The stoicheiometry for PA and BD depends on the substrate:MnO_4^- mole ratio, three limiting cases being observed. Manganese(III) has been detected as a short-lived intermediate by the stopped-flow technique. The organic substrates yield αβ-dioxo-intermediates, which are oxidised by manganese(III) to the corresponding acids. In the presence of pyrophosphate, the dioxo-compounds are stable products. Stopped-flow kinetic measurements under conditions eliminating interference by the Guyard reaction show that the reactions are first order with respect to both MnO_4^- and the substrates, and independent of pH between 0·98 and 4·9. The second-order rate constants at 25 °C are: 10·0 (PA), 11·5 (PC and PB), and 12·5 (BD) $dm^3 mol^{-1} s^{-1}$, with the activation parameters $\Delta H^‡ = 26·4$ (PA) and 22·0 (BD) kJ mol^{-1}; $\Delta S^‡ = -138$ (PA) and -150 (BD) J $mol^{-1} K^{-1}$. The rate-determining step is assumed to be concerted attack of MnO_4^- on the triple bond, resulting in the formation of a short-lived cyclic intermediate containing manganese(V).

It has been shown previously [1-3] that acetylenedicarboxylic acid is rapidly oxidised by acidic permanganate to carbon dioxide. The multistep reaction involves soluble manganese(IV), manganese(III), and oxalic acid as intermediates. A detailed analysis of the kinetic results in combination with other types of mechanistic information has led to the conclusion that the first step is the attack of permanganate on the acetylene bond resulting in the formation of a five-membered ring containing manganese(V). The process involves complete oxygen atom transfer from MnO_4^- to the substrate. In order to obtain additional information about the mechanism of oxidation of acetylenic compounds by permanganate, we have studied the intermediates and the kinetics of the reactions with propargyl alcohol (PA), but-2-yne-1,4-diol (BD), and propargyl chloride (PC) and bromide (PB) in aqueous solutions.

The oxidation of acetylenic compounds by neutral permanganate has been shown to lead to cleavage at the triple bond with the formation of the corresponding acids; in isolated cases the reaction yields diketo-compounds.[4-7] The latter have been proposed as unstable intermediates in the oxidations involving rupture of the acetylenic bond. Of the compounds studied in this work, but-2-yne-1,4-diol diacetate has been reported to yield acetylglycolic acid.[4]

RESULTS AND DISCUSSION

Stoicheiometry and Intermediates.—The products of the reaction of permanganate in 0·3M-$HClO_4$ with PA and BD depend on the substrate:MnO_4^- mole ratio (N). At large excesses of the substrate ($N = 30$—100) MnO_4^- is converted to manganese(II) and no precipitate is formed; the product solution contains glycolic acid (strongly positive test with 2,7-dihydroxynaphthalene [8]), a dioxo-compound [positive tests with 2,4-dinitrophenylhydrazine, hydroxylamine, and nickel(II) or cobalt(II),[8] and with thiophen [9]] and, in the case of PA, formic acid.

Upon decreasing the mole ratio, the reactions yield increasing amounts of MnO_2 and a large decrease in the quantities of the dioxo-compounds. Glycolic acid becomes the predominant product, accompanied by 0·95 mole of formic acid per mole of MnO_4^- in the case of PA at $N = 1·5$. The MnO_2 precipitated contains up to *ca.* 40% of the oxidation equivalent of the MnO_4^- added (*cf.* Table 1).

TABLE 1

Yields of MnO_2 and the dioxo-compound at various substrate to MnO_4^- mole ratios (N) in 0·3M aqueous $HClO_4$ (25 °C); $[MnO_4^-]_0 = 0·01$M

Substrate	N	MnO_2 [a]	Dioxo [b]
Propargyl alcohol	100	0·0	51·0
	30	0·0	42·6
	12	4·6	9·5
	2	14·4	4·6
	1·5 [c]	19·3	Trace
	1·0	22·0	0·0
	0·5	38·8	0·0
But-2-yne-1,4-diol	100	0·0	47·3
	30	0·0	41·1
	9	4·4	9·0
	2	12·5	4·9
	1·5	17·9	Trace
	1·0	20·4	0·0
	0·5	36·9	0·0

[a] Oxidation equivalent of the MnO_2 formed (in % of the total added as MnO_4^-). [b] Mole % of MnO_4^- added. [c] The product solution contains 0·95 mole formic acid per mole of MnO_4^- added.

In order to obtain information about the pathway of the formation of MnO_2 and manganese(II), we have made an attempt at identifying short-lived intermediates possibly formed from MnO_4^-. As the reactions under consideration are too fast for conventional kinetic

† Part IV, L. I. Simandi and M. Jáky, preceding paper.

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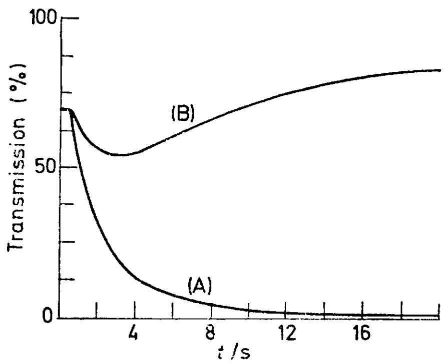
[5] W. N. Krestinsky and M. K. Kelbowskaja, *Ber.*, 1935, **68**, 512.
[6] V. I. Nikitin, S. D. Savranskaya, and I. M. Timofeyeva, *Zhur. obshchei. Khim.*, 1960, **30**, 764.
[7] N. A. Khan and M. S. Newman, *J. Org. Chem.*, 1952, **17**, 1063.
[8] F. Feigl, 'Spot Tests in Organic Analysis,' Elsevier, London and New York, 1956.
[9] L. I. Simándi, *Magyar Kém. Folyóirat*, 1969, **75**, 269.

methods, the stopped-flow technique [9] has been used to examine whether the reduction of MnO_4^- involves the temporary accumulation of manganese in oxidation states between 7 and 2. At mole ratios of $N \geqslant 30$, no MnO_2 is formed in the reaction; therefore, the stopped-flow traces can be recorded without difficulty. The traces obtained in the wavelength range between 200 and 800 nm show that the accumulation and decay of an intermediate can be observed only in the vicinity of 250 nm (Figure). Upon the addition of a five-fold excess of pyrophosphate over MnO_4^-, the minimum disappeared and the transmission steadily increased to a limiting



Stopped-flow traces of the permanganate oxidation of propargyl alcohol at 250 nm: [PA] = 3×10^{-2}M; $[MnO_4]_0 = 10^{-3}$M; $[HClO_4]$ = 0·1M; ionic strength 1·5M; temp. 25 °C. Trace (A), in the presence of 5×10^{-3}M-sodium pyrophosphate; trace (B), in the absence of pyrophosphate

value. Following the procedure described in detail elsewhere,[2] the short-lived species has been identified as manganese(III). The fact that the formation of MnO_2 is eliminated by the presence of pyrophosphate (at mole ratios where it would otherwise have been formed) shows that, when a product, it is derived from manganese(III) *via* disproportionation rather than directly from MnO_4^- in a three-electron process. This has the important consequence that pyrophosphate may alter the course of the reaction by acting as a scavenger for manganese(III). Complex formation with pyrophosphate is known to suppress disproportionation into MnO_2 and manganese(II), as well as to decrease the oxidising vigour of manganese(III).[10] The colour of the tris(dihydrogenpyrophosphato)manganese(III) complex persists for *ca.* 1 h in a typical experiment with $N = 1$, whereas that of the MnO_4^- added disappears within 1 min. This also implies that pyrophosphate strongly suppresses the Guyard reaction [10,11] requiring the presence of manganese(II), which, however, can only be formed from manganese(III).

The spectrophotometric titration of PA and BD with MnO_4^- in the presence of pyrophosphate reveals that at $N \geqslant 1$, the spectrum of MnO_4^- cannot be observed 1 min after its addition. In the interval $1 > N > 2/3$, the MnO_4^- spectrum disappears within 15—30 min, apparently *via* the Guyard reaction occurring with the slowly formed manganese(II). At $N \leqslant 2/3$, the colour of MnO_4^- persists even after 1—2 h.

The above results are consistent with a rapid, initial four-electron process [equation (1)] yielding an αβ-dioxo compound and manganese(III), followed by a two-electron process [equation (2)] resulting in the formation of the corresponding acids. Thus in the absence of pyrophosphate, for large excesses of the substrates, the overall stoicheiometry is given by equation (3). Under

$$MnO_4^- + RC{\equiv}CCH_2OH + 4\,H^+ \longrightarrow RC(=O){-}C(=O)CH_2OH + Mn^{3+} + 2\,H_2O \quad (1)$$

(R = H or CH_2OH)

$$RC(=O){-}C(=O)CH_2OH + 2\,Mn^{3+} + 2\,H_2O \longrightarrow RCO_2H + HOCH_2CO_2H + 2\,Mn^{2+} + 2\,H^+ \quad (2)$$

$$2\,MnO_4^+ + 2\,RC{\equiv}CCH_2OH + 6\,H^+ \longrightarrow RC(=O){-}C(=O)CH_2OH + RCO_2H + HOCH_2CO_2H + 2\,Mn^{2+} + 2\,H_2O \quad (3)$$

such conditions, reaction (1) is much faster than (2) (*cf.* kinetics); consequently, MnO_4^- and manganese(II) do not coexist at any time during the reaction which eliminates the Guyard reaction. Owing to this, no MnO_2 is formed and one-half of the dioxo-compound is retained as product. It should be noted that MnO_4^- does not directly oxidise the dioxo-compound, as demonstrated experimentally with diacetyl, which reacts only after a long induction period. Manganese(III), however, reacts rapidly with substrates capable of chelate formation *via* oxygen donor atoms.[10]

Upon decreasing the excess of the substrate ($N < 20$), reaction (1) becomes relatively slower, which opens up the possibility of the Guyard reaction [equation (4)]. Thus MnO_2 becomes a product, whereas only small amounts of the dioxo-compound can be detected (Table 1). The Guyard reaction now provides a pathway for recycling manganese(III); thus the dioxo-compound can be completely removed from the system, the excess of manganese(III) being consumed by disproportionation [equation (5)]. In the limiting case when the dioxo-compound ceases to be a product, the stoicheiometric equation (6) is valid [equations (1), (2), (4), and (5)

$$MnO_4^- + 4\,Mn^{2+} + 8\,H^+ \longrightarrow 5\,Mn^{3+} + 4\,H_2O \quad (4)$$

$$2\,Mn^{3+} + 2\,H_2O \longrightarrow MnO_2 + Mn^{2+} + 4\,H^+ \quad (5)$$

$$6\,MnO_4^- + 4\,RC{\equiv}CCH_2OH + 12\,H^+ \longrightarrow 4\,RCO_2H + 4\,HOCH_2CO_2H + 3\,MnO_2 + 3\,Mn^{2+} + 2\,H_2O \quad (6)$$

[10] R. Stewart, 'Oxidation by Permanganate,' and 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.

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should be multiplied by the factors 4,4,2, and 3, respectively]. This corresponds to 20% residual oxidation power in the form of MnO_2, reached in the absence of pyrophosphate at *N ca.* 1. The reason why this occurs earlier than at $N = 2/3$ to be expected from equation (6) should be sought in the competition between reactions (2) and (5); equation (6) is based on the assumption that manganese(III) undergoes disproportionation only after the dioxo-compound is removed from the system. This is obviously not quite true; earlier disproportionation and recycling *via* the Guyard reaction leads to the formation of larger amounts of MnO_2 already before $N = 2/3$ is reached. The results of spectrophotometric titrations in the presence of pyrophosphate lend support to this view: this additive completely eliminates reaction (5), which is the source of the excess of MnO_2 over the amount required by equation (6). Reactions (2) and (4) may still occur though more slowly than in the absence of pyrophosphate; therefore, the validity of the assumption underlying equation (6) is ensured as witnessed by the two equivalence points observed at $N = 1$ and 2/3, corresponding to equations (1) and (7), respectively. With added pyrophosphate, the product of reaction (1) is $Mn(pyr)_3^{3-}$, ($pyr^{2-} = H_2P_2O_7^{2-}$), whereas equation (7) is obtained from equations (1), (2), and (4), using the factors 4,4, and 2, respectively, and replacing Mn^{3+} by $Mn(pyr)_3^{3-}$.

$$6\,MnO_4^- + 4\,RC{\equiv}CCH_2OH \xrightarrow[-8\,H_2O]{+18\,pyr^{2-}\,+\,24\,H^+} 4\,RCO_2H + 4\,HOCH_2CO_2H + 6\,Mn(pyr)_3^{3-} \quad (7)$$

If the amount of MnO_4^- is increased further so that N reaches the value of 0·5, then the manganese(II) produced according to equation (6) is eventually converted into MnO_2 *via* repeated cycles of the Guyard reaction with the MnO_4^- still present, followed by disproportionation. This occurs because the reactions of the product acids with MnO_4^- are very slow (verified experimentally) and reaction (5) is faster than the oxidation of the organic acids by manganese(III). The stoicheiometric equation (9) valid under these conditions is obtained by adding equation (6) and the Guyard reaction written as in (8). As shown by the results in Table 1, at $N = 0{\cdot}5$ the amount of MnO_2 actually corresponds to nearly 40% of the total oxidation equivalent added as MnO_4^-.

$$2\,MnO_4^- + 3\,Mn^{2+} + 2\,H_2O \longrightarrow 5\,MnO_2 + 4\,H^+ \quad (8)$$

$$8\,MnO_4^- + 4\,RC{\equiv}CCH_2OH + 8\,H^+ \longrightarrow 4\,RCO_2H + 4\,HOCH_2CO_2H + 8\,MnO_2 \quad (9)$$

The reaction scheme outlined above also receives support from the amount of dioxo-compounds formed at various mole ratios (*cf.* Table 1). The yields have been determined by precipitating the corresponding bis-2,4-dinitrophenylhydrazones whose identities have been proved by elemental analyses, molecular weight determinations, and comparison of the m.p.s with literature data where available. In the absence of pyrophosphate, at large excesses of the substrates, the yield is *ca.* 50 mole % of the MnO_4^- added [equation (3)], but decreases to zero as N tends to unity. Upon the addition of pyrophosphate [$Mn(pyr)_3^{3-}$ quenched with sodium sulphite before precipitation], the yield approaches 100 mole % of MnO_4^- in agreement with equation (1) (Table 2). These results clearly demonstrate that the oxidation of PA and BD involves αβ-dioxo-compounds as short-lived intermediates.

TABLE 2

Yield of the dioxo-compound in the presence of pyrophosphate {$[MnO_4^-]_0 = 0{\cdot}01$M; $[H_2P_2O_7^{2-}] = 0{\cdot}05$M; the $Mn(pyr)_3^{3-}$ complex was quenched with sulphite after 98% MnO_4^- had reacted}

Substrate	pH	N [a]	Dioxo [b]
Propargyl alcohol	1·0	1·0	95·7
		5	95·7
		2	92·5
		1	78·9
	3·8	10	99·1
		5	98·6
		2	95·0
		1	83·6
But-2-yne-1,4-diol	1·0	10	97·4
		5	96·2
		2	93·6
		1	80·5
	3·8	10	99·1
		5	97·8
		2	95·6
		1	86·8

[a] Substrate : MnO_4^- mole ratio. [b] Mol % of MnO_4^- added.

The oxidation of propargyl chloride and bromide reveals essentially the same behaviour. Manganese(III) is a detectable intermediate and in the presence of pyrophosphate, the corresponding dioxo-compounds can be precipitated as bis-2,4-diphenylhydrazones in high yields, whereas only traces are found if this scavenger has not been added.

Kinetic Measurements.—We intended to obtain kinetic information on reaction (1), *i.e.* the attack of MnO_4^- on the acetylenic bond. Therefore, it was necessary to examine the possible disturbing effect of those reactions which may still occur in spite of the presence of the pyrophosphate scavenger added in the kinetic measurements concerning reaction (1). The reaction between the dioxo-compound and MnO_4^- is autocatalytic (*cf.* previous section) and does not occur on the stopped-flow time scale, as demonstrated with diacetyl. $Mn(pyr)_3^{3-}$ shows no appreciable reaction with either substrate in 30 min.

The stopped-flow traces obtained at 540 nm show that after the rapid disappearance of MnO_4^-, the concentration of $Mn(pyr)_3^{3-}$ changes but very slowly.

This indicates that, although the dioxo-compound is oxidised by $Mn(pyr)_3^{3-}$, this reaction does not influence the rate of disappearance of MnO_4^- [*via* the Guyard reaction occurring with the product manganese(II)]. For quantitative comparison, we have examined the kinetics of the dioxo–$Mn(pyr)_3^{3-}$ reaction, which is slow enough to be followed on a recording spectrophotometer. MnO_4^- was added to a 10-fold excess of PA or BD in the presence of pyr^{2-} at pH 0·9 ($HClO_4$; ionic strength 1·5 with $NaClO_4$) and the absorbance *vs.* time curve was recorded at 540 nm. After a few seconds required for MnO_4^- to disappear [reaction (1)], a slower process was observed for *ca.* 15 min, corresponding to reaction (2) involving $Mn(pyr)_3^{3-}$. The rate equation for the oxidation of the dioxo-compound was assumed to be of the form (10). If $Mn(pyr)_3^{3-}$ and the dioxo-compound are initially present at equal concentrations, which is also equal to $[MnO_4^-]_0$, but are consumed in a 2 : 1 ratio as given by equation (11), then rate equation (10) integrates to (12) conveniently written in terms of absorbances. The plots of $\log(A + A_0)/A$ *vs.* time were linear, indicating the validity of equation (10). The rate constants obtained from the slope are 1·79 and 1·55 dm³ mol⁻¹ s⁻¹

$$-\frac{1}{2}\frac{d[Mn(pyr)_3^{3-}]}{dt} = k[Mn(pyr)_3^{3-}][dioxo] \quad (10)$$

$$\frac{1}{2}([Mn(pyr)_3^{3-}]_0 - [Mn(pyr)_3^{3-}]) = [dioxo]_0 - [dioxo] \quad (11)$$

$$\frac{2\cdot3}{[Mn(pyr)_3^{3-}]_0}\log\frac{A + A_0}{2A} = kt \quad (12)$$

for hydroxymethylglyoxal (from PA) and bis(hydroxyacetyl) (from BD), respectively. Using the rate constants for reaction (1) (see later), for a typical rate measurement with $[MnO_4^-]_0 = 1\cdot5 \times 10^{-3}$M and a 10-fold excess of the substrate, one obtains half-lives of 4·6 and 3·5 s for PA and BD, respectively. For the same kinetic run, the half-lives of dioxo-compound oxidation are equal to 154 and 178 s, respectively, which clearly shows that the Guyard reaction is negligible when pyrophosphate is present in the system. [At pH >0·9, the oxidation of the dioxo-compounds becomes slower, whereas the rate constants for (1) remain unchanged.]

In view of the slow oxidation of the dioxo-compounds, interference by the oxidation of the product acids by either permanganate or tris(dihydrogenpyrophosphato)-manganese(III) is negligible, too, in the kinetic study of reaction (1).

The permanganate oxidations of all four substrates are too fast for conventional kinetic methods; therefore, the stopped-flow technique was used throughout. The disappearance of permanganate was followed at 540 nm. In order to avoid the formation of MnO_2, a five-fold excess of pyrophosphate was added, which also eliminated the complicating factors mentioned in the previous section. Except when stated otherwise, the ionic strength of the aqueous solutions was 1·5M, adjusted with $NaClO_4$. 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 BD, the disappearance of MnO_4^- was found to obey a first-order rate law, *i.e.* the plot of $\log(A - A_\infty)$ against time gave excellent straight lines. The pseudo-first-order rate constant was found to be proportional to the substrate concentration (Table 3). The kinetic law for reaction

TABLE 3

Pseudo-first-order rate constants (k_{obs}) for the oxidation of propargyl alcohol and but-2-yne-1,4-diol at various substrate concentrations (pH 2·4; five-fold excess of pyrophosphate, substrate : MnO_4^- mole ratio 10; ionic strength 1·5M; temp. 25 °C; each rate constant is the average of three measurements)

	k_{obs}/s⁻¹	
$10^2[S]_0$/M [a]	Propargyl alcohol	But-2-yne-1,4-diol
0·5	0·0517	0·0631
1·0	0·108	0·121
1·5		0·170
2·0	0·198	0·229
3·0	0·302	0·361
3·5	0·333	
4·0	0·410	0·507
5·0		0·614

[a] S = Substrate.

(1) is thus given by equation (13), where $k[S]_0 = k_{obs}$. The value of k is independent of the pH for both substrates in the interval between 0·98 and 4·9 (Table 4), and remains unchanged upon decreasing the ionic

$$-d[MnO_4^-]/dt = k\,[S]_0\,[MnO_4^-] \quad (13)$$

TABLE 4

Second-order rate constants (k) for the oxidation of propargyl alcohol and but-2-yne-1,4-diol at various pH values ($N = 10$; $[MnO_4^-]_0 = 1\cdot5 \times 10^{-3}$M; ionic strength 1·5M with $NaClO_4$; five-fold excess of pyrophosphate; temp. 25 °C; each rate constant is the average of six measurements)

	k/dm³ mol⁻¹ s⁻¹	
pH	Propargyl alcohol	But-2-yne-1,4-diol
0·98	9·8	12·5
0·98 [a]	10·2	13·0
2·40 [b]	10·2	12·4
3·80	10·0	11·9
4·90	10·1	13·3

[a] Measurements with equal concentrations ($N = 1$). [b] From the k_{obs} *vs.* $[S]_0$ plot (Table 3).

strength to 0·1M. The average values of k (25 °C) are 10·0 ± 0·2 and 12·5 ± 0·8 dm³ mol⁻¹ s⁻¹ for PA and BD, respectively. The temperature dependence of k given in Table 5 yields the following Arrhenius parameters:

TABLE 5

Temperature dependence of the second-order rate constants (k) for the oxidation of propargyl alcohol and but-2-yne-1,4-diol (each rate constant is an average of three measurements; pH 0·98)

	k/dm³ mol⁻¹ s⁻¹	
Temp. (°C)	Propargyl alcohol	But-2-yne-1,4-diol
15	7·0	9·0
19	8·1	9·9
25	9·9	12·7
31	12·3	14·5
37	15·2	17·9

$\Delta H^\ddagger = 26\cdot4$ (PA) and $22\cdot0$ (BD) kJ mol⁻¹; $\Delta S^\ddagger = -138$ (PA) and -150 (BD) J mol⁻¹ K⁻¹.

The validity of kinetic equation (13) was also examined at a substrate : permanganate mole ratio (N) of 1. As the substrate and MnO_4^- are consumed in a 1 : 1

ratio, for this case, one obtains equation (14). The plots of $1/(A - A_\infty)$ against time were found to be linear,

$$\frac{1}{[\mathrm{MnO_4^-}]} - \frac{1}{[\mathrm{MnO_4^-}]_0} = kt \qquad (14)$$

the slopes yielding k values identical to those obtained under pseudo-first-order conditions.

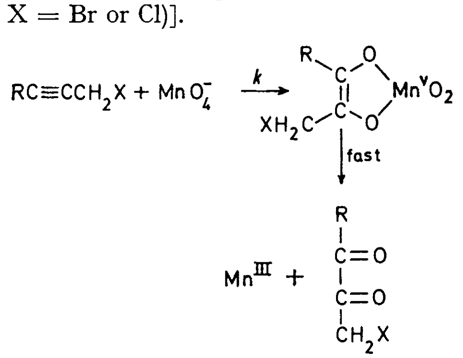
In the case of propargyl bromide and chloride, the kinetic measurements have been performed in both water and 30 vol % methanol, under pseudo-first-order conditions (25 °C). The reactions are first order with respect to both reactants; thus kinetic equation (13) is valid in this case, too. The results are listed in Table 6. The second-order rate constant is independent of the pH between 1 and 4, and of the ionic strength.

TABLE 6

Second-order rate constants for propargyl bromide and chloride in water and 30% (v/v) ethanol ($N = 10$; $[\mathrm{MnO_4^-}]_0 = 1{\cdot}5 \times 10^{-3}$M; $[\mathrm{HClO_4}] = 0{\cdot}1$M; ionic strength 0·1M; five-fold excess of pyrophosphate; temp. 25 °C). For comparison, the rate constants of PA are shown for the same conditions

	$k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$		
Medium	Propargyl bromide	Propargyl chloride	Propargyl alcohol
Water	11·3	11·2	10·2
	11·6	11·6	9·7
	11·5	11·6	9·9
Average	11·5	11·5	9·9
30% Ethanol–water(v/v)	8·7	9·0	7·3
	8·5	8·8	7·5
	8·4	8·7	7·3
	8·9	8·5	7·7
	8·9	8·7	7·2
Average	8·7	8·7	7·4

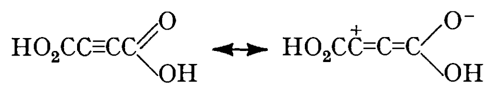
The kinetic behaviour of the substrates studied is consistent with the following reaction mechanism. The rate-determining step is the attack of $\mathrm{MnO_4^-}$ on the acetylenic bond, resulting in the formation of a short-lived cyclic intermediate containing manganese(V); the intramolecular transfer of two electrons leads to manganese(III) and the corresponding dioxo-compound [equation (15; R = H or CH_2OH with X = OH; and R = H with X = Br or Cl)].



(15)

The existence of the cyclic intermediate receives support from the large negative entropies of activation, which imply a cyclic transition state with a structure closely resembling that of the intermediate. This resemblance is also reflected by the low enthalpy of activation, indicating little bond breaking but extensive bond making in the rate determining step. A similar cyclic intermediate has been shown to be involved in the permanganate oxidation of acetylenedicarboxylic acid [1-3] and in the related case of *cis*-hydroxylation of olefins by alkaline permanganate.[12] According to the proposed mechanism (15), the oxidation takes place by oxygen atom transfer from $\mathrm{MnO_4^-}$, a fact proved in the case of acetylenedicarboxylic acid by ^{18}O tracer experiments.[2]

The rate constant for oxidation varies very little with the solvent composition and the ionic strength, which points to a concerted process with negligible charge separation upon going from reactants to the transition state. The same conclusion can be drawn from the lack of a pronounced substituent effect. The reactivity order observed is BD > PB = PC > PA but the largest rate constant exceeds the lowest one only by 25%. Acetylenedicarboxylic acid, and its mono- and di-anion, have been found to react with rate constants of 1420, 632 and 40 dm^3 mol^{-1} s^{-1}, respectively,[3] indicating the strong activating effect of the carboxy-group; this may be related to the appreciable contribution of resonance hybrid (A) [equation (16)], facilitating a near-concerted



(16)

(A)

cis-attack. The absence of the carboxy-group in the substrates studied in this work precludes this type of resonance and the process, therefore, must take place *via* concerted *cis*-attack, which is insensitive to solvent and substituent effects. It should be noted that the cyclic intermediate shown in equation (15) is unreactive towards $\mathrm{MnO_4^-}$. In the case of acetylenedicarboxylic acid, the rapid attack of a second $\mathrm{MnO_4^-}$ on this intermediate has been demonstrated; this again points to the importance of carboxy-conjugation in determining the reactivity of unsaturated compounds towards permanganate.

In the rate-determining step (15), the hybridisation of the bridgehead carbon atoms changes from sp to sp^2, however, the concomitant mutual approach of the substituents imposes no steric hindrance on the reaction; BD reacts somewhat faster than the $HC{\equiv}CCH_2X$ type substrates.

EXPERIMENTAL

Materials.—Propargyl alcohol, but-2-yne-1,4-diol, and propargyl bromide and chloride were Fluka purum products. All other chemicals were of reagent grade.

Determination of MnO_2.—Immediately after the reaction, the solution containing precipitated MnO_2 was transferred onto a glass filter under suction. After washing, the MnO_2 was dissolved in a known amount of standard oxalic acid solution (in the presence of H_2SO_4), whose excess was determined by permanganate titration.

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

Precipitation of Bis-2,4-dinitrophenylhydrazones.—A six-fold excess of 2,4-dinitrophenylhydrazine over the substrate oxidised was added in 30% (w/w) $HClO_4$ so that the final acid concentration were *ca.* 2M. After being kept overnight in a refrigerator, the precipitate was filtered off and washed with water.

Spectrophotometric Titrations.—To a series of solutions containing the same amount of substrate, were added increasing volumes of 0·02M-$KMnO_4$. The substrate solution also contained $HClO_4$ and a five-fold excess of sodium pyrophosphate. The spectra in the 370—600 nm range were taken at 2 min intervals, using a Hitachi–Perkin-Elmer 124 instrument. Unless the colour of MnO_4^- disappeared instantaneously, the times for which the MnO_4^- spectrum persisted were measured.

TABLE 7

Analytical data for the dioxo-derivatives

Source	M.p. (°C)	Formula	Molecular weight		C(%)		H(%)		N(%)		Cl/Br(%)	
			Calc.	Found [a]	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Propargyl alcohol	266 (decomp.)	$C_{15}H_{12}N_8O_9$	448·0	432·0	40·20	40·25	2·68	2·91	25·00	25·06		
But-2-yne-1,4-diol	274—277 (decomp.)	$C_{16}H_{14}N_8O_{10}$			40·20	39·80	2·93	2·82	23·40	22·20		
Propargyl bromide	214—215	$C_{15}H_{11}BrN_8O_8$	511·0	506·0	35·20	35·00	2·15	2·47	21·90	21·94	15·60	14·00
Propargyl chloride	216—217	$C_{15}H_{11}ClN_8O_8$	466·5	478·0	38·60	38·20	2·36	2·62	24·00	24·30	7·62	7·65

[a] By isothermal distillation of tetrahydrofuran solutions (J. Szilágyi and J. Szilagyi, *Magyar Kém. Lapja*, 1969, **24**, 180).

In the presence of pyrophosphate, the $Mn(pyr)_3^{3-}$ formed was quenched with sodium sulphite, which was added after 98% of the MnO_4^- had been consumed. The corresponding times were calculated from the known rate constants. Under these conditions, 2—5% of the dioxo-compound formed is oxidised by $Mn(pyr)_3^{3-}$. The bis-2,4-dinitrophenylhydrazones are precipitated more slowly in these cases, because the disulphite adducts should first decompose in the acidic solution. The precipitates were filtered after the odour of SO_2 had disappeared, and recrystallised from ethyl acetate (PA, PC, and PB) or dioxan (BD). The analyses, molecular weights, and m.p. data are listed in Table 7.

Kinetic Measurements.—The stopped-flow instrument described earlier [9] was used; the kinetic curves were displayed on a Tektronix 564 storage oscilloscope and photographed with a Polaroid camera.

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