Mechanism of the Oxidation of Glyoxylic and Pyruvic Acids by Periodate

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The kinetics of the oxidation of glyoxylic and pyruvic acids by periodate have been studied at pH 0—9 and 273—303 K. The kinetics are second order, first order in each reactant and the rate has a maximum at pH 6. It is suggested that the dehydrated periodate monoanion IO_4^- is the only reactive periodate species and the α-oxo-carboxylic acids and their anions react in their dehydrated forms.

THE main data on the mechanism of the periodate oxidation of organic compounds containing α-hydroxy-, -oxo-, or -amino-groups [1] are as follows. Oxidation of 1,2-diols involves the formation of a cyclic periodate ester of the diol which decomposes to products.[2,3] Many simple 1,2-diols form cyclic esters with periodate rapidly and reversibly and these slowly decompose to products.[2,3a,b] The products are formed by rupture of the cyclic ester monoanion, probably in its dehydrated form.[3a] The kinetics of the periodate oxidation of 1,2-diones are second order, first order in each reactant.[4,5]

Tracer studies with ^{18}O have shown that in the oxidation of 1,2-diols the intermediate is formed by electrophilic attack of periodate, while the mechanism of oxidation of 1,2-diones is nucleophilic attack by periodate upon the carbonyl carbon atoms.[6] Periodate acts simultaneously as an electrophile and a nucleophile in the oxidation of α-hydroxy-ketones. In the oxidation of methylacetoin the oxygen of the acetone comes from the hydroxy-group of the hydroxy-ketone and the additional oxygen atom in the acetic acid produced from the periodate.[6]

Second-order kinetics were found for the oxidation of α-amino-alcohols by periodate.[7-9] Unprotonated amino-alcohol and dehydrated periodate monoanion were suggested as the reactive species in these reactions.[7,9] The

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[1] (*a*) C. A. Bunton, ' Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965, ch. VI; (*b*) B. Sklarz, *Quart. Rev.*, 1967, **21**, 3; (*c*) G. Dryhurst, ' Periodate Oxidation of Diol and Other Functional Groups,' ' Monographs in Organic Functional Group Analysis,' Pergamon, Oxford, 1970, vol. 2; (*d*) G. J. Buist, ' Kinetics of Oxidations by Periodate ' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 6, p. 435.

[2] (*a*) F. R. Duke, *J. Amer. Chem. Soc.*, 1947, **69**, 3054; (*b*) F. R. Duke and V. C. Bulgrin, *ibid.*, 1954, **76**, 3803.

[3] (*a*) G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1954, 1406; 1957, 4580; *J. Chem. Soc.* (*B*), 1971, 2117; (*b*) G. J. Buist, C. A. Bunton, and J. H. Miles, *J. Chem. Soc.*, 1957, 4567, 4575; 1959, 743; (*c*) G. J. Buist, C. A. Bunton, and J. Lomas, *J. Chem. Soc.* (*B*), 1966, 1094, 1099; (*d*) G. J. Buist and J. D. Lewis, *ibid.*, 1968, 90; (*e*) G. J. Buist, C. A. Bunton, and W. C. P. Hipperson, *ibid.*, 1971, 2128.

[4] V. J. Shiner, jun., and C. R. Wasmuth, *J. Amer. Chem. Soc.*, 1959, **81**, 37.

[5] G. Dahlgren and K. L. Reed, *J. Amer. Chem. Soc.*, 1967, **89**, 1380.

[6] C. A. Bunton and V. J. Shiner, jun., *J. Chem. Soc.*, 1960, 1593.

[7] G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5161.

[8] J. Kovar, J. Jary, and J. Blaha, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2199.

[9] G. Dahlgren and J. M. Hodsdon, *J. Phys. Chem.*, 1964, **68**, 416.

negative enthalpy of activation of the oxidation of 2-aminoethanol led to the suggestion that the rate-determining step is preceded by an equilibrium,[9] possibly similar to that demonstrated kinetically for simple 1,2-diols.

The periodate oxidation of glyoxylic and pyruvic acids involves the cleavage of C–C bonds.[10,11] Because of its similarity to the oxidations mentioned above and because of the various possibilities for reaction between the several different species of both periodate and α-oxocarboxylic acid that can exist in aqueous solution, it seemed that a thorough investigation of the oxidation of α-oxocarboxylic acids would be of interest.

In aqueous periodate solution equilibria (1), (2), and (4)—(6) were detected and the various equilibrium

$$H_5IO_6 \overset{K_1}{\rightleftharpoons} H_4IO_6^- + H^+ \qquad (1)$$

$$H_4IO_6^- \overset{K_D}{\rightleftharpoons} IO_4^- + 2\ H_2O \qquad (2)$$

$$\bar{K}_1 = [H_4IO_6^- + IO_4^-]f^- a_{H^+}/[H_5IO_6] = K_1(K_D + 1) \qquad (3)$$

$$H_4IO_6^- \overset{K_2}{\rightleftharpoons} H_3IO_6^{2-} + H^+ \qquad (4)$$

$$2\ H_3IO_6^{2-} \overset{K_{2'}}{\rightleftharpoons} H_2I_2O_{10}^{4-} + 2\ H_2O \qquad (5)$$

$$H_3IO_6^{2-} \overset{K_3}{\rightleftharpoons} H_2IO_6^{3-} + H^+ \qquad (6)$$

$$\bar{K}_2 = [H_3IO_6^{2-}]f^{2-}\ a_{H^+}/[H_4IO_6^- + IO_4^-]f^- \qquad (7)$$

constants determined.[12-14] The acid dissociation constant of glyoxylic acid [15,16] and pyruvic acid [15-18] and the hydration constant [15,16,19-21] for these acids and their anions are also known [reactions (8) and (9)]. The

$$RCO{\cdot}CO_2H + H_2O \overset{K_{H_1}}{\rightleftharpoons} RC(OH)_2{\cdot}CO_2H \qquad (8)$$

$$RCO{\cdot}CO_2^- + H_2O \overset{K_{H_2}}{\rightleftharpoons} RC(OH)_2{\cdot}CO_2^- \qquad (9)$$

constants used in the treatment of our kinetic data at 293.2 K are shown in Table 1.

TABLE 1

	$\bar{K}_1$/mol l^{-1}	$\bar{K}_2$/mol l^{-1}	K_D
Periodic acid	1.6×10^{-4} [3e]	5.4×10^{-9} [13]	19.0 [14]
	K_a/mol l^{-1}	K_{H_1}	K_{H_2}
Glyoxylic acid	5×10^{-4} [15]	10^3 [19]	16.5 [19]
Pyruvic acid	3.0×10^{-3} [16]	3.1 [20]	4.4×10^{-2} [20,21]

RESULTS AND DISCUSSION

Kinetic studies indicated that no kinetically detectable concentration of an intermediate complex is formed in the oxidation of glyoxylic and pyruvic acid by periodate. A typical example is given in Table 2.

TABLE 2

Second-order rate constants for the oxidation of glyoxylic acid by periodate. [Periodate]$_0$ 2.0×10^{-3}M; 273.2 K; pH 6.0—5.5; I 0.500M

10^2 [Glyoxylic acid]/M	2.00	4.00	6.00	12.00
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	2.66	2.70	2.70	2.69

The rate of oxidation of glyoxylic acid was measured over the pH range 0—9. Pyruvic acid enolises in alkaline solution and the enol form reacts differently with periodate; thus the kinetics of oxidation of this compound were studied in the pH range pH 1—7. Tables 3 and 4 show the pH dependence of the rate of oxidation for glyoxylic and pyruvic acids.

TABLE 3

Rate constants for the oxidation of glyoxylic acid by periodate at various pH values, at 293.2 K and I 0.500M

pH	0.43	0.65	0.73	1.13
10^4 k_{obs}/dm^3 mol^{-1} s^{-1}	1.66	2.67	3.07	8.60
pH	1.30	1.53	1.85	2.06
10^3 k_{obs}/dm^3 mol^{-1} s^{-1}	1.25	2.21	4.82	7.21
pH	2.62	2.70	3.10	3.18
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	2.18	2.77	4.92	5.60
pH	3.40	3.60	5.5—6.0	
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	6.96	8.00	10.7	
pH	7.92	8.47	8.95	
10^2 $(k_{obs})_0$ */dm^3 mol^{-1} s^{-1}	5.10	2.28	0.87	

* Extrapolated to zero dimer periodate concentration. See ref. 3*e*.

TABLE 4

Rate constants for the oxidation of pyruvic acid by periodate at various pH values, at 293.2K and I 0.500M

pH	0.95	1.13	2.18	2.55	3.20
10^3 k_{obs}/dm^3 mol^{-1} s^{-1}	0.089	0.140	1.10	1.75	2.60
pH	5.00	5.70	7.03		
10^3 k_{obs}/dm^3 mol^{-1} s^{-1}	3.00	3.00	2.60		

The oxidation rates have thus been correlated fairly well with the assumption that the rate can be expressed as $k_{obs}[Per]_T[Oxa]_T = k_{11}[Per^-][Oxa^-] + k_{10}[Per^-][Oxa^0]$ where $[Per]_T$ and $[Oxa]_T$ are the total concentrations of periodate and the α-oxocarboxylic acid, respectively, $[Per^-] = [H_4IO_6^- + IO_4^-]$, $[Oxa^-] = [RC(OH)_2{\cdot}CO_2^- + RCO{\cdot}CO_2^-]$, and $[Oxa^0] = [RC(OH)_2{\cdot}CO_2H + RCO{\cdot}CO_2H]$.

The pH dependence of the oxidation rate of glyoxylic acid by periodate presented in Table 3 can be interpreted as follows. At pH 5.5—6.0 k_{obs} equals k_{11}. In alkaline

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[20] H. Patting and H. Strehlow, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 534.

[21] J. Pocker, J. E. Meany, B. J. Nist, and C. Zadorojny, *J. Phys. Chem.*, 1969, **73**, 2879.

solutions the reaction rate decreases with increasing pH. (Deviations from second-order kinetics occur particularly at high pH, *e.g.* $k_{\rm obs}$ increases with the decrease of initial periodate concentration due to the dimerisation of periodate.)

In the pH range 6—9, the kinetics fit equation (10).

$$\bar{K}_2 = \{[k_{11}/(k_{\rm obs})_0] - 1\}(f^{2-}/f^-)\, a_{\rm H^+} \qquad (10)$$

We calculate the second acid dissociation constant of periodic acid, $\bar{K}_2$, as $5.1 \pm 0.2 \times 10^{-9}$ mol l^{-1}. This indicates that the dimer and the monomeric periodate dianion are unreactive towards glyoxylate ion.

Equation (11) is a good approximation of the rate law in the pH range 3.2—6.0 and equation (12) in the range pH < 1.

$$1/k_{\rm obs} = f^- a_{\rm H^+}/k_{11}K_{\rm a} + 1/k_{11} \qquad (11)$$

$$1/k_{\rm obs} = f^- a_{\rm H^+}/k_{10}\bar{K}_1 + 1/k_{10} \qquad (12)$$

On plotting $1/k_{\rm obs}$ *versus* $f^- a_{\rm H^+}$, graphical evaluation yields $K_{\rm a}$ 5.2×10^{-4} for the acid dissociation constant of glyoxylic acid and 1.7×10^{-2} mol l^{-1} for the first acid dissociation constant $\bar{K}_1$ of periodic acid. Calculated values of k_{11} and k_{10} are fairly constant over the pH range covered experimentally.

The oxidation of pyruvic acid by periodate can be also described by a similar equation including two terms.

The rate constants for the oxidation of glyoxylic acid and pyruvic acid at 293.2 K and I 0.500M are given in Table 5. The rate of oxidation of glyoxylate increases with increasing ionic strength (pH 5.5—6.0, 293.2 K).

TABLE 5

	k_{11}/dm^3 mol^{-1} s^{-1}		k_{10}/dm^3 mol^{-1} s^{-1}		
Glyoxylic acid	1.07×10^{-1}		2.76×10^{-3}		
Pyruvic acid	3.00×10^{-3}		4.90×10^{-4}		
I/M	0.020	0.050	0.100	0.150	0.500
$k_{11} = k_{\rm obs}$/dm^3 mol^{-1} s^{-1}	0.074	0.084	0.092	0.097	0.107

Plotting log $k_{\rm obs}$ *versus* $I^{1/2}$ gives a straight line with slope +1. The calculation was carried out by using the ionic strength term of the Davies equation.[22]

The basis of our interpretation of the reaction mechanism is that the initial step of oxidation is nucleophilic attack of the periodate monoanion on the oxo-group. Studies of the oxidation of 1,2-dioxo-compounds by periodate [4-6] show a regular increase of the reaction rate with the charge of the hydrated periodate species H_5IO_6, $H_4IO_6^-$, and $H_3IO_6^{2-}$.

It is important in arriving at an interpretation of the mechanism that the periodate dianion does not react with the anions of the α-oxocarboxylic acids. Another important observation is that undissociated periodic acid does not react with undissociated α-oxocarboxylic acids. Since it can be proved that these reactions do not take place, it may be supposed that undissociated periodic acid does not react with the anions of the α-oxocarboxylic acids either, or the probability of this reaction is much lower than that of periodate monoanion with undissociated α-oxocarboxylic acids. Thus, only the reaction of periodate monoanion among the various forms of periodate leads to products, whereas both α-oxocarboxylic acid and its anion are reactive.

Given this interpretation it seems a contradiction that k_{11} is much higher than k_{10} for both α-oxocarboxylic acids. This can be resolved, if one assumes that both the α-oxocarboxylic acid and its anion are able to react with periodate only in their dehydrated forms. The rate constants of the reaction of periodate monoanion with dehydrated α-oxocarboxylic acid and its dehydrated anion, $k_{\rm 10d}$ and $k_{\rm 11d}$, can be calculated from the values of k_{11} and k_{10} and from the corresponding equilibrium constants of hydration given by correlations (13) and (14) where $k^0{}_{\rm 11d}$ and $k^0{}_{11}$ are the values corrected to zero ionic strength.

$$k_{\rm 10d} = k_{10}(K_{\rm H1} + 1) \qquad (13)$$

$$k^0{}_{\rm 11d} = k^0{}_{11}(K_{\rm H2} + 1) \qquad (14)$$

In the oxidation of pyruvic acid at 293.2 K $k_{\rm 10d}$ is 2.0×10^{-3} and $k^0{}_{\rm 11d}$ 1.7×10^{-3} dm^3 mol^{-1} s^{-1}.

Glyoxylic acid and glyoxylate ion are considerably hydrated. Only an estimated value is available for the equilibrium constant of hydration of glyoxylic acid. Under the same conditions the rate constant of the reaction of periodate ion with dehydrated glyoxylate ion, $k^0{}_{\rm 11d}$, is 1.02 dm^3 mol^{-1} s^{-1}. Provided the ratio of $k^0{}_{\rm 11d}$ and $k_{\rm 10d}$ is approximately the same as that for pyruvic acid, and $k_{\rm 10d}$ is 1.1 dm^3 mol^{-1} s^{-1}, the hydration constant of glyoxylic acid, $K_{\rm H_1}$, is 4.0×10^2 on the basis of the kinetic data.

According to the measurements the calculated energies of activation for both k_{11} and k_{10} decrease with increasing temperature. As calculations show, this observation can be attributed to the fact that the hydration equilibria of species Per$^-$, Oxa$^-$, and Oxa^0 play a role in pre-equilibria in the activation process. It can be supposed that only dehydrated forms participate directly in the reaction. The rate constants of the reactions of the dehydrated forms, $k_{\rm 1d1d}$ and $k_{\rm 1d0d}$ can be calculated by equations (15) and (16).

$$k_{\rm 1d1d} = k_{11}\,(1 + 1/K_{\rm D})(1 + K_{\rm H2}) \qquad (15)$$

$$k_{\rm 1d0d} = k_{10}\,(1 + 1/K_{\rm D})\,(1 + K_{\rm H1}) \qquad (16)$$

The values of the energy of activation caculated from the rate constants measured and from those corrected [*] are shown in Table 6.

The activation parameters are summarised in Table 7. We assume that the activated complex of the oxidation

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[*] The enthalpy of the dehydration equilibria of periodate ion,[14] 61.9, of pyruvate ion,[16] 18.8 kJ mol^{-1}, and of pyruvic acid,[20] 29.7 kJ mol^{-1}, were used in the calculation. The enthalpy of the acid dissociation of pyruvic acid, 12.1, and that of glyoxylic acid, 2.2 kJ mol^{-1}, are available in the literature.[16] The first apparent acid dissociation constants, $\bar{K}_1$, at various temperatures was calculated from data given in refs. 3*e* and 14.

[22] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, 41.

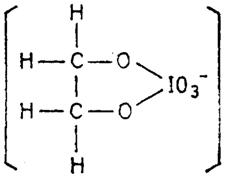
TABLE 6

Corrections of the energy of activation of the oxidation of glyoxylic and pyruvic acids by periodate

T/K	273.2		283.2		293.2		303.2
Pyruvic acid							
$10^3\ k_{11}$/dm^3 mol^{-1} s^{-1}	0.82		1.70		3.00		4.90
E_0/kJ mol^{-1}		51.0		39.3		36.4	
E_a/kJ mol^{-1}		34.3		33.4		33.4	
$10^3\ k_{10}$/dm^3 mol^{-1} s^{-1}			0.170		0.490		1.20
E_0/kJ mol^{-1}				73.2		66.1	
E_1*/kJ mol^{-1}				68.2		64.0	
E_a/kJ mol^{-1}				44.3		43.1	
Glyoxylic acid							
$10\ k_{11}$/dm^3 mol^{-1} s^{-1}	0.269		0.580		1.07		1.87
E_0/kJ mol^{-1}		49.4		42.3		40.2	
E_1†/kJ mol^{-1}		38.1		37.2		38.1	
E_a‡/kJ mol^{-1}				(18.8)			
$10^3\ k_{10}$/dm^3 mol^{-1} s^{-1}					2.76		6.18
E_0/kJ mol^{-1}						59.4	
E_a‡/kJ mol^{-1}						(27.6)	

* Energy of activation calculated from $k_{1d0} = k_{10}(1 + 1/K_D)$. † Energy of activation calculated from $k_{1d1} = k_{11}(1 + 1K_D)$. ‡ Owing to the high hydration equilibrium constant of glyoxylate ion and glyoxylic acid one can use the approximation $E_a = E_1 - \Delta H_D$, where ΔH_D is the enthalpy of dehydration. We assume the value of ΔH_D of glyoxylate ion and glyoxylic acid to be identical with that of pyruvate ion and pyruvic acid, and the hydration constant of glyoxylic acid, K_{H_1}, at 293.2 K is 4.0×10^2.

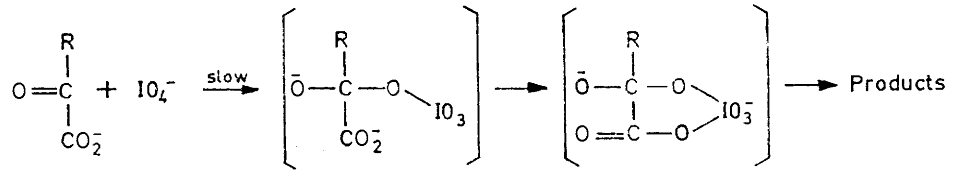
of glyoxylic and pyruvic acid by periodate is cyclic as in the case of 1,2-diol oxidations.*

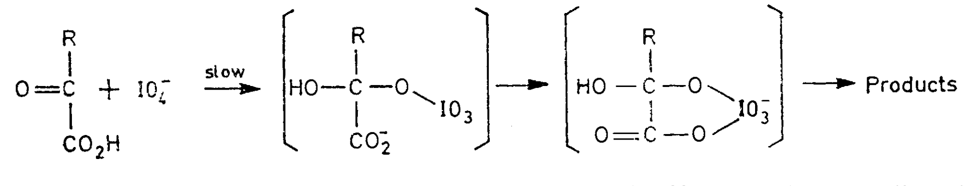


(A)

This assumption is supported by the observation that the periodate dianion, $H_3IO_6^{2-}$ is unreactive towards glyoxylate ion, though its higher nucleophilicity towards the oxo-group compared with the periodate monoanion is established. The lack of reaction between periodate dianion and α-oxocarboxylic acid anions can be interpreted by the inability of the dianion to form a cyclic intermediate.

We suggest that the reaction between α-oxocarboxylic acid or its anion and periodate monoanion leads to a cyclic intermediate, and the disproportion of the latter yields the products.†





In acidic solutions neither phosphate nor acetate buffer catalysis occurs. The catalytic effect of phosphate buffer at pH 6—8 is shown in Table 8.

The ionic strength is rather high and we cannot ascertain whether the phosphate buffer effect is a specific ionic effect when HPO_4^{2-} is replaced with ClO_4^- to maintain constant ionic strength or if it is acid catalysis. If the latter, the reaction of glyoxylate ion with $H_3IO_6^{2-}$ catalysed by $H_2PO_4^-$ can be assumed. The effect is not large so the suggestion of a mechanism *via* such a reaction can only be tentative. It can be assumed that the

$$\text{Per}^{2-} + \text{HCO}\cdot\text{CO}_2^- \xrightleftharpoons{k_{21}} \text{C}^{3-} \qquad (17)$$

$$\text{C}^{3-} + \text{H}_2\text{PO}_4^- \xrightleftharpoons{k_3} \text{C}^{2-} + \text{HPO}_4^{2-} \qquad (18)$$

$$\text{C}^{2-} \xrightarrow{k} \text{Products} \qquad (19)$$

concentration of the intermediates C^{3-} and C^{2-} is low, and the steady-state approximation may be applied to reactions (17)—(19). This leads to equation (20) for the

$$1/k_{\psi 21} = 1/k_{21} + 1/K_{21}k_3[\text{H}_2\text{PO}_4^-] + 1/kK_{21}K_3[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}] \qquad (20)$$

pseudo-second-order rate constant $k_{\psi 21}$ (*cf.* ref. 3*e*) and (21) for the limiting pseudo-second-order rate constant $k_{\psi 21(\text{lim})}$.

$$1/k_{\psi 21(\text{lim})} = 1/k_{21} + 1/kK_{21}K_3[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}] \qquad (21)$$

Slight inhibition of the reaction by borate buffer can be observed. The rate decreases linearly on increasing the buffer concentration. To explain this inhibition it

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* The activation parameters for the periodate oxidation of ethanediol and pinacol recalculated from the data of Duke and Bulgrin [2] at 293.2 K are $\Delta H^\ddagger$ 23.4 and 30.1 kJ mol^{-1}, $\Delta S^\ddagger$ −167.8 and −195.4 J mol^{-1} K^{-1}, $\Delta G^\ddagger$ 72.4 and 87.4 kJ mol^{-1}, respectively, assuming that IO_4^- is a reactive periodate species and the second-order rate constant for ethanediol, $k_{11} = kK$.

† Buist and Bunton [3a] have proved, for the periodate oxidation of 1,2-diols, that only the cyclic ester monoanion can give the products. This can be explained by the fact that this intermediate is able to dehydrate, whereas the cyclic ester dianion is not. They proposed structure (A) for the intermediate leading to products in the case of ethanediol.

has been assumed that a 1 : 1 complex is formed between the glyoxylate ion and boric acid (borate) in a rapid equilibrium and that this is unreactive towards periodate. From the kinetic data we calculated the value of the stability constant of the complex as $K_s = 1.5 \pm 0.2$ l mol^{-1} at 293.2 K and I 0.500M.

Measurements at pH 7.8 in sodium hydrogen carbonate solution show no effect of hydrogen carbonate on the reaction rate. In ammonia buffer at pH 9.0—9.2 the rate of the reaction is *ca.* 3 times higher than that in unbuffered solution. A 30% overoxidation of glyoxylate is also observed. No overoxidation was found in any other buffers used including unbuffered solutions.

TABLE 7

Rate constants and activation parameters for the oxidation of the dehydrated forms of glyoxylic and pyruvic acids by the dehydrated periodate monoanion (293.2 K)

Reaction	Rate constant (dm^3 mol^{-1} s^{-1})	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}	$\Delta G^‡$/ kJ mol^{-1}
$IO_4^- + CHO{\cdot}CO_2^-$	$k^\circ_{1d1d} = 1.07$ *	16.3	−196.6	74.1
$IO_4^- + CHO{\cdot}CO_2H$	$k_{1d0d} = 1.2$	25.1	−166.1	73.6
$IO_4^- + CH_3CHO{\cdot}CO_2^-$	$k^\circ_{1d1d} = 1.8 \times 10^{-3}$ *	31.0	−200.0	89.5
$IO_4^- + CH_3CHO{\cdot}CO_2H$	$k_{1d0d} = 2.1 \times 10^{-3}$	41.0	−164.4	89.1

* Extrapolated to zero ionic strength.

TABLE 8

Second-order rate constants for the oxidation of glyoxylate ion by periodate in phosphate buffers, 293.2 K, I 0.500M. Initial $[\text{Per}]_T = 1.5 \times 10^{-3}$ M; $[HCO{\cdot}CO_2^-]_T = 7.5 \times 10^{-3}$ M

$[\text{Phosphate}]_T$/M	0.00	0.05	0.10	0.15
pH 6.00, k_{obs}/dm^3 mol^{-1} s^{-1}	0.107	0.113	0.113	0.113
pH 6.88, k_{obs}/dm^3 mol^{-1} s^{-1}	0.097	0.122	0.125	0.125
pH 7.80, $(k_{obs})_0$*/dm^3 mol^{-1} s^{-1}	0.059	0.087	0.095	0.098

* Rate constants extrapolated to zero periodate dimer concentration.

EXPERIMENTAL

Materials.—Glyoxylic acid hydrate, sodium pyruvate (Merck), periodic acid, and sodium periodate (recrystallized and tested for purity) were the purest available products. All other chemicals were of analytical grade.

Kinetics.—Reaction rates were measured in solution by following the decrease of periodate concentration with time. After quenching reactions in slightly acidic (pH > 2), neutral, or basic solutions, portions of the reaction mixture were added to sodium arsenite solutions containing potassium iodide and sodium hydrogen carbonate; the excess of arsenite was then titrated with a 0.02N-iodine solution in the presence of starch as indicator. For more acidic solutions (pH < 2), aliquot portions of the solution were added to potassium iodide solution and the iodine content was determined by titration with 0.02N-sodium thiosulphate. In alkaline solution the reaction was followed polarographically [23] and rate constants free of any buffer catalysis could be obtained by maintaining the pH at a constant value by automatic control (addition of alkaline solution by a Radiometer titrigraph, type SBR 2c equipped with a titrator type TTT 1c, a syringe burette type SBU 1a, and a Radelkis polarograph type OH-102). The solutions were deaerated by nitrogen bubbling. The initial periodate and glyoxylic and pyruvic acid concentrations were 2×10^{-3}—4×10^{-2} and 2×10^{-3}—4×10^{-1}M, respectively.

Perchloric acid and sodium hydroxide were used to make the solutions acidic or alkaline, respectively. The ionic strength was maintained constant (normally 0.500M) by sodium perchlorate. The activity coefficient of the ions was calculated by the Davies equation.[22]

Reactions were generally followed to *ca.* 80—90% conversion. In most cases 2—3 runs were carried out; errors in k_{obs} are within 1%.

Dimerisation of Periodate.—Buist *et al.*[3e] stated that the increase of the second-order rate constant k_{obs} with a decrease in periodate concentration observed in the oxidation of pinacol by periodate in alkaline solutions is due to dimerisation of periodate since the dimeric ion is unreactive towards pinacol. A procedure was proposed to obtain $(k_{obs})_0$, the second-order rate constant at zero periodate dimer concentration. According to equation (22) where K_x

$$k_{obs} = (k_{obs})_0 - 2K_x(k_{obs})^2[\overline{\text{Per}}]/(k_{obs})_0 \qquad (22)$$

is the equilibrium constant of dimerisation and $[\overline{\text{Per}}]$ is the total concentration of periodate at 50% conversion, a plot of k_{obs} *versus* $(k_{obs})^2[\overline{\text{Per}}]$ is linear.

TABLE 9

Dependence of the second-order rate constant on periodate concentration in alkaline solution at various pH values and temperatures and I 0.500M in the oxidation of glyoxylate ion. Values of $(k_{obs})_0$ and K_x are evaluated graphically

283.1 K, pH 8.65, $(k_{obs})_0$ 7.00×10^{-3} dm^3 mol^{-1} s^{-1}, K_x 714 l mol^{-1}

$10^3[\overline{\text{Per}}]$/M	1.82	1.27	0.517	0.497
10^3 k_{obs}/dm^3 mol^{-1} s^{-1}	3.22	3.61	4.71	4.69

293.2 K, pH 7.92, $(k_{obs})_0$ 5.10×10^{-2} dm^3 mol^{-1} s^{-1}, K_x 97.5 l mol^{-1}

$10^3[\overline{\text{Per}}]$/M	2.07	1.89	1.61	1.12	0.996	0.652
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	3.91	3.95	4.07	4.17	4.38	4.57

293.2 K, pH 8.47, $(k_{obs})_0$ 2.28×10^{-2} dm^3 mol^{-1} s^{-1}, K_x 222 l mol^{-1}

$10^3[\overline{\text{Per}}]$/M	1.97	1.60	0.947	0.299
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	1.46	1.54	1.73	2.04

293.2 K, pH 8.95, $(k_{obs})_0$ 8.70×10^{-3} dm^3 mol^{-1} s^{-1}, K_x 326 l mol^{-1}

$10^3[\overline{\text{Per}}]$/M	1.07	0.632	0.383	0.304
10^3 k_{obs}/dm^3 mol^{-1} s^{-1}	5.89	6.59	7.25	7.47

303.2 *K*, pH 8.40, $(k_{obs})_0$ 5.14×10^{-2} dm^3 mol^{-1} s^{-1}, K_x 72.5 l mol^{-1}

$10^3[\overline{\text{Per}}]$/M	1.71	1.49	1.42	0.871	0.583
10^2 k_{obs}/dm^3 mol^{-1} s^{-1}	4.25	4.36	4.36	4.63	4.75

An increase of k_{obs} with decrease of $[\overline{\text{Per}}]$ occurs in the

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[23] P. Zuman and J. Krupicka, *Coll. Czech. Chem. Comm.* 1958, **23**, 589.

oxidation of glyoxylate by periodate in alkaline solutions. Data given in Table 9 prove that this is due to dimerisation of periodate and equation (22) is valid.

From the values of $(k_{\text{obs}})_0$ the thermodynamic second dissociation constants of periodate acid, $\bar{K}_2$, and from K_x the dimerisation constants of periodic dianion, K_2' were calculated. From the values given in Table 9 for 293.2 K and

$$K_{2'} = K_x[(f_2^{2-}a_{H^+}/f^-\bar{K}_2) + 1]^2 \qquad (23)$$

pH 7.92, 8.47 and 8.95 the following values were calculated for $10^9\ \bar{K}_2$, 5.3, 5.0, 5.1 mol l^{-1}, and for K_2', 356, 356, 387 l mol^{-1}, respectively. At 283.1, 293.2, and 303.2 K, the values of $10^9\ \bar{K}_2$ are 6.6, 5.1, and 4.1 mol l^{-1} respectively. A plot of $\mathrm{p}\bar{K}_2$ *versus* $1/T$ gives ΔH -16.7 ± 0.8, kJ mol^{-1}. At these temperatures K_2' is 920, 360, and 140 l mol^{-1}, respectively, and a plot of log K_2' *versus* $1/T$ gives ΔH -67 ± 3 kJ mol^{-1} for the heat of dimerisation. These ΔH values are in good agreement with the values given by Buist *et al.*[13]

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