Mechanism of the Periodate Oxidation of Ethane-1,2-diamine, *NN'*-Dimethylethane-1,2-diamine, and 2-Aminoethanol

By **László Maros,* Ibolya Molnár-Perl, Enikó Schissel, and Vilmos Szerdahelyi**, Institute of Inorganic and Analytical Chemistry, L. Eötvös University, 1088 Budapest, Hungary

The kinetics of the oxidation by periodate of ethane-1,2-diamine, *NN'*-dimethylethane-1,2-diamine, and 2-aminoethanol have been studied at pH 4—12 and 293.2 K. The reaction rates are highest at pH 9—11. It is assumed that periodate monoanion reacts with the unprotonated amines. The reactions of 1,2-diamines with periodate are catalysed by acids and bases. The oxidation of 2-aminoethanol is catalysed by bases, and at high concentration of catalysts the rate seems to approach a limiting value. The pH dependence of the rate of oxidation of these compounds can be explained in terms of multi-stage reactions similar to those in the oxidation of 1,2-diols by periodate.

THE periodate oxidation of 1,2-diols involves the formation of a cyclic periodate ester of the diol which decomposes to products.[1] The periodate ester is formed by the electrophilic attack of periodate,[2] and the products are formed by the rupture of the cyclic ester monoanion, probably in its dehydrated form.[3] Simple 1,2-diols, *e.g.* ethane-1,2-diol, form a cyclic ester (C_2) with periodate (Per.) rapidly and reversibly, which slowly decomposes to products [3,4] [reaction (1)], and the kinetic form of the reaction [4] is given by equation (2), where the

$$\text{Per.} + \text{diol} \overset{K}{\rightleftharpoons} C_2 \xrightarrow[\text{Slow}]{k} \text{products} \quad (1)$$

$$k' = kK[\text{diol}]/(1 + K[\text{diol}]) \quad (2)$$

diol is in large excess over periodate, and k' is the observed pseudo-first-order rate constant with respect to periodate. Highly substituted 1,2-diols, *e.g.* pinacol, have second-order kinetics in the periodate oxidation over a wide range of reagent concentration. This may be due to the fact that $K[\text{diol}] \ll 1$, and the second-order rate constant k'' equals kK. The kinetics of the oxidation of pinacol indicate the occurrence of general acid–base catalysis.[5,6] It has been shown by Buist, Bunton and his co-workers [6] that the catalysed step is the formation of the cyclic intermediate, and they suggested a mechanism which is probably common to all oxidations of 1,2-diols by periodate, *viz.* the formation of a periodate monoester (C_1), followed by ring-closure to a cyclic ester, then decomposition of the monoanion of the cyclic ester to products [reaction (3)].

$$\text{Per.} + \text{diol} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2 \xrightarrow{k} \text{products} \quad (3)$$

We will show that several features of the kinetics of periodate oxidation of 1,2-diamines and 2-aminoethanol resemble closely those observed for the oxidation of pinacol, and a plausible mechanism can be given by an acylation-type reaction of periodate with the amines forming stepwise a cyclic intermediate which decomposes to products.

Dahlgren and his co-workers [7] have studied the kinetics of periodate oxidation of 2-aminoethanol and 2-(methylamino)ethanol over the pH range 3.6—6.4 and temperature range 273—323 K, and found second-order kinetics for the reactions. The pH-dependence of the rate is in agreement with the assumption that either the periodate monoanion reacts with the unprotonated 2-aminoethanol or the periodate dianion reacts with the protonated compound.[7b] The assumption that the dehydrated periodate monoanion, IO_4^-, is the reactive species leads to a negative enthalpy of activation.[7a] Second-order kinetics and a catalytic effect of buffers were observed in the oxidation of cyclic and substituted α-amino-alcohols by periodate.[8,9]

The oxidation of ethane-1,2-diamine by periodate yields formaldehyde and ammonia.[10,11a] The anomalous decrease of the reaction rate (if periodate is in excess) is due to the reaction of formaldehyde, or the imine-like primary oxidation product, with ethane-1,2-diamine. The oxidation of ethane-1,2-diamine and *NN'*-dimethylethane-1,2-diamine becomes fast and stoicheiometric in the presence of a many-fold excess of propane-1,3-diamine.[11b]

EXPERIMENTAL

Materials.—Ethane-1,2-diamine, *NN'*-dimethylethane-1,2-diamine and 2-aminoethanol (Fluka) were vacuum-distilled and tested for purity. Sodium periodate was recrystallized. All other chemicals were of analytical grade.

Kinetics.—Reaction rates were measured in solution by following the decrease of periodate concentration with time. Titrimetric and spectrophotometric [6] methods were used. For titrimetric measurements (in the pH-range 4—7) aliquot portions of the solutions were added to acidic potassium iodide solution and titrated with 0.02N sodium thiosulphate. A Unicam SP 700 spectrophotometer with water-jacketted cell holders, and 0.1-, 1-, and 4-cm silica cells was used. All reactions were carried out at 293.2 K, and solutions were previously thermostatted overnight. In the kinetic experiments, the comparison cell was filled with amine solution containing all components except periodate. The amine and periodate solutions were mixed in a volumetric flask and a portion was added into the reaction cell. In most cases recording began after 20—25 s.

The lowest ratio of diamine : periodate was 20 : 1 at the beginning of the kinetic runs. For 2-aminoethanol this ratio was 10 : 1. The lowest initial periodate concentration was 1×10^{-5}M for the spectrophotometric measurements.

Perchloric acid and sodium hydroxide were used to make the solutions acidic or alkaline, respectively. The ionic strength was maintained constant by sodium perchlorate. The pH of the solution was measured during the runs and was constant within ±0.02 pH unit.

2—4 parallel runs were carried out. Errors in $k_{obs.}$ for titrimetric measurement were ±5%, but for the fast reactions followed spectrophotometrically errors were ±20%.

RESULTS AND DISCUSSION

The oxidation of 2-aminoethanol by periodate follows second-order kinetics, first-order in each reactant. Self-catalysis by the 1,2-diamine occurs in the oxidation of ethane-1,2-diamine and *NN'*-dimethylethane-1,2-diamine, the reactions being first order in periodate. The reactions are catalysed by buffers.

The observed second-order rate constants, $k_{obs.}$, were extrapolated to zero buffer concentrations, and, in the self-catalysed reactions of the 1,2-diamines, to zero 1,2-diamine concentrations (k_2^o). In equations (4) and (5),

$$\text{Rate} = k_{obs.}[\text{Per.}]_T[\text{Amine}]_T \qquad (4)$$

$$k_{obs.} = k_2^o + k_3^a[\text{Amine}]_T + k_3^b[\text{Buffer}]_T \qquad (5)$$

$[\text{Per.}]_T$, $[\text{Amine}]_T$, and $[\text{Buffer}]_T$ are the corresponding total concentrations.

The regular changes with pH and the concentration of 1,2-diamines are in good agreement with the assumption that the periodate monoanion reacts with the unprotonated 1,2-diamines in general acid–base catalysed reactions.

The pseudo-second-order rate constants of the reactions of periodate monoanion and unprotonated 1,2-diamines, $k_{10\psi}$, were calculated according to equation (6),

$$k_{10\psi} = k_{obs.}[1 + \bar{K}_2 f^-/a_{H^+} f^{2-} + \bar{K}_2\bar{K}_3 f^-/(a_{H^+})^2 f^{3-}][1 + a_{H^+}/K_{a2}f^+ + (a_{H^+})^2/K_{a1}K_{a2}f^{2+}] \qquad (6)$$

where $\bar{K}_2$ and $\bar{K}_3$ are the second and third acid dissociation constants of periodic acid, K_{a1} and K_{a2} the first and second acid dissociation constants of the diprotonated 1,2-diamines,† and the *f* values are the activity coefficients of the ions calculated according to the Davies equation.[15]

For the oxidations of 1,2-diamines the rate constants k_2^o show a broad maximum in the pH range 9—11, and the values of the pseudo-second-order rate constant extrapolated to zero buffer and 1,2-diamine concentrations, $k_{10\psi}^o$, have a minimum in the pH range 8—9 (Tables 1 and 2).

We assume that the reactions of periodate monoanion with unprotonated 1,2-diamines are catalysed by water, hydronium, and hydroxide ions [equation (7)].

$$k_{10\psi}^o = k_{10}^{H_2O}[H_2O] + k_{10}^{H_3O^+}[H_3O^+] + k_{10}^{OH^-}[OH^-] \qquad (7)$$

Table 3 shows the pH-dependence of the second-order rate constants k_2^o and $k_{10\psi}^o$ calculated for the periodate oxidation of 2-aminoethanol.*

Acetate, phosphate, ammonia, and borate buffers have been used to maintain the pH constant and to examine the catalytic effect of the buffers. A catalytic effect was not found for borate. In the oxidations of 1,2-diamines the reaction rate increases linearly with increase in buffer concentration.

TABLE 1

Second-order rate constants extrapolated to zero buffer concentrations for the periodate oxidation of ethane-1,2-diamine at *I* 0.300 mol dm^{-3}. (Units for all rate constants are dm^3 mol^{-1} s^{-1})

pH	6.07	6.20	7.28	8.10
$10^2k_2^o$	1.03	1.20	10.7	22
$10^{-2}k_{10\psi}^o$	33.5	21.8	2.8	1.0
pH	8.45	8.60	8.82	9.22
$10^2k_2^o$	31	32	34	67
$10^{-2}k_{10\psi}^o$	1.0	1.0	1.0	1.8
pH	9.84	10.31	10.80	11.35
$10^2k_2^o$	82	82	90	35
$10^{-2}k_{10\psi}^o$	2.7	4.4	11.5	18.7
pH	11.90	12.46	12.82	
$10^2k_2^o$	20	7.0	3.0	
$10^{-2}k_{10\psi}^o$	72	255	540	

The self-catalysis of 1,2-diamines was expressed in terms of the observed overall third-order catalytic constant k_3^a in equation (5). Furthermore we have calculated the pseudo-third-order catalytic constant $k_{10\psi}^{AH^+}$, for the oxidation of unprotonated 1,2-diamine by periodate monoanion catalysed by the monoprotonated 1,2-diamine, AH$^+$, according to equation (8).

TABLE 2

Second-order rate constants extrapolated to zero buffer concentrations for the periodate oxidation of *NN'*-dimethylethane-1,2-diamine. (Units for all rate constants are dm^3 mol^{-1} s^{-1})

pH (*I* 0.300 mol dm^{-3})	4.52	4.72	4.99	5.07	5.42
$10^3k_2^o$	1.00	1.85	3.80	4.20	8.60
$10^{-3}k_{10\psi}^o$	1 010	735	435	355	105
pH (*I* 0.300 mol dm^{-3})	6.13	6.55			
$10^3k_2^o$	44.0	155			
$10^{-3}k_{10\psi}^o$	28	15.4			
pH (*I* 0.100 mol dm^{-3})	8.08	8.86	9.32	9.80	10.00
k_2^o	4.4	8.7	8.7	10.0	10.0
$10^{-3}k_{10\psi}^o$	2.8	3.0	2.8	3.7	3.9
pH (*I* 0.010 mol dm^{-3})	10.26	10.80	11.08	11.66	11.93
k_2^o	15.6	10.2	10.3	9.7	9.5
$10^{-3}k_{10\psi}^o$	4.7	6.9	12.0	51	140
pH	12.20	12.83	13.06		
I/mol dm^{-3}	0.020	0.060	0.100		
k_2^o	6.0	1.0	0.45		
$10^{-3}k_{10\psi}^o$	230	890	1 520		

$$k_{10\psi} = k_{10\psi}^o + k_{10\psi}^{AH^+}[AH^+] \qquad (8)$$

The variation of the rate constants k_3^a and $k_{10\psi}^{AH^+}$

---

† The dissociation constants for periodic acid[12] at 293.2 K are: $\bar{K}_2$ 5.43 × 10^{-9} mol dm^{-3} and $\bar{K}_3$ 6.3 × 10^{-13} mol dm^{-3}; for the diprotonated ethane-1,2-diamine[13] K_{a1} 1.0 × 10^{-7} mol dm^{-3} and K_{a2} 8.2 × 10^{-11} mol dm^{-3}; and for the diprotonated *NN'*-dimethylethane-1,2-diamine[14] K_{a1} 5.97 × 10^{-8} mol dm^{-3} and K_{a2} 5.16 × 10^{-11} mol dm^{-3}.

* The acid dissociation constant of protonated 2-aminoethanol[16] is K_a 2.26 × 10^{-10} mol dm^{-3} at 293.2 K.

with pH for the oxidation of ethane-1,2-diamine is shown in Table 4.

At pH < 7 no measurable self-catalytic effect for ethane-1,2-diamine was found, and the pH-dependence of $k_{10\psi}^{AH^+}$ suggests the monoprotonated and unprotonated ethane-1,2-diamine to be the effective catalysts. Using equation (9), graphical evaluation yielded the values of $k_{10}^{AH^+}$ and $k_{10}^{A^0}$.

TABLE 3

Second-order rate constants extrapolated to zero buffer concentration for the oxidation of 2-aminoethanol by periodate at I 0.300 mol dm^{-3}. (Units for all rate constants are dm^3 mol^{-1} s^{-1})

pH	4.92	5.23	5.65	6.27	6.93	7.65
k_2^o	0.066	0.098	0.23	0.60	3.5	13.7
$10^{-3}k_{10\psi}^o$	3.9	3.3	2.8	2.0	2.7	3.0

pH	8.15	8.53	9.38	10.34	10.53	10.84
k_2^o	33	48	51	27	15	8.3
$10^{-3}k_{10\psi}^o$	4.2	5.0	6.0	11.0	9.0	10.2

pH	11.30	11.58	11.90	11.93	11.95
k_2^o	3.4	1.6	0.59	0.54	0.52
$10^{-3}k_{10\psi}^o$	15	18	21	21	22

$$k_{10\psi}^{AH^+} = k_{10}^{AH^+} + k_{10}^{A^0}[A^0]/[AH^+] \qquad (9)$$

The pH-dependence of the pseudo-third-order catalytic constant for ammonium, $k_{10\psi}^{NH_4^+}$, is shown in Table 5 for the oxidation of ethane-1,2-diamine. The values of $k_{10}^{NH_3}$ and $k_{10}^{NH_4^+}$ were evaluated graphically.

TABLE 4

Third-order self-catalytic constants for the oxidation of ethane-1,2-diamine by periodate at I 0.300 mol dm^{-3} (Units for all rate constants are dm^6 mol^{-2} s^{-1})

pH	7.28	8.10	8.45	8.60	8.82
$[AH_2^{2+}]/[AH^+]$	2.1	0.2	0.09		
k_3^a	4	58	70	81	111
$10^{-4}k_{10\psi}^{AH^+}$	3	3.0	2.5	3.0	3.3

pH	9.48	9.84	10.34	10.80
$[A^0]/[AH^+]$	0.177	0.415	1.22	3.79
k_3^a	111	113	62	23
$10^{-4}k_{10\psi}^{AH^+}$	3.7	5.3	7.3	13.8

For the oxidation of *NN'*-dimethylethane-1,2-diamine the values of the catalytic constants $k_{10}^{A^0}$, $k_{10}^{AH^+}$, $k_{10}^{NH_3}$, and $k_{10}^{NH_4^+}$ were evaluated from the data in Table 6.

Self-catalysis was not detectable for the oxidation of 2-aminoethanol, probably owing to the very low concentrations needed for the rate measurements. Plots of $k_{10\psi}^o$ against acetate concentration are linear, but plots against hydrogenphosphate (Figure 1), ammonia (Figure 2), and hydroxide concentration show marked curvatures. The slopes of the linear regions of the curves are independent of buffer ratio; *i.e.*, only the bases are effective catalysts in the oxidation of 2-aminoethanol. However, the small increase in $k_{10\psi}^o$ with decrease in pH in the pH range 4.92—6.27 (see Table 3) may be due to catalysis by hydronium ion. The catalytic constants for the oxidation of 2-aminoethanol were evaluated according to the treatment used by Buist, Bunton, and their co-workers[6] for 1,2-diol oxidations.

TABLE 5

Pseudo-third-order catalytic constants (in dm^6 mol^{-2} s^{-1}) for ammonium in the oxidation of ethane-1,2-diamine by periodate; I 0.300 mol dm^{-3}

pH	8.64	9.02	9.30	9.45	9.65	10.00
$[NH_4^+]/[NH_3]$	12.9	3.4	1.8	1.26	0.79	0.35
$10^{-4}k_{10\psi}^{NH_4^+}$	0.75	1.15	1.43	2.0	3.4	8.8

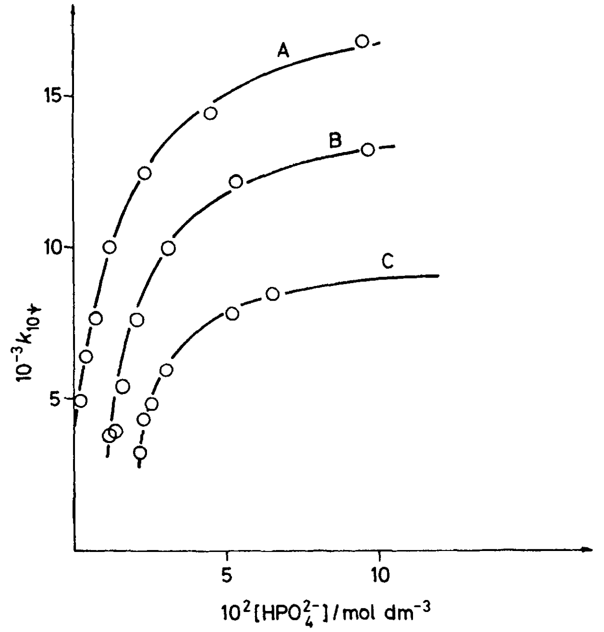


FIGURE 1 Hydrogenphosphatecatalysis in the oxidation of 2-aminoethanol by periodate: (A) pH 8.15, (B) pH 7.65, (C) pH 6.93. The zeros of successive curves are displaced by one unit on the concentration axis

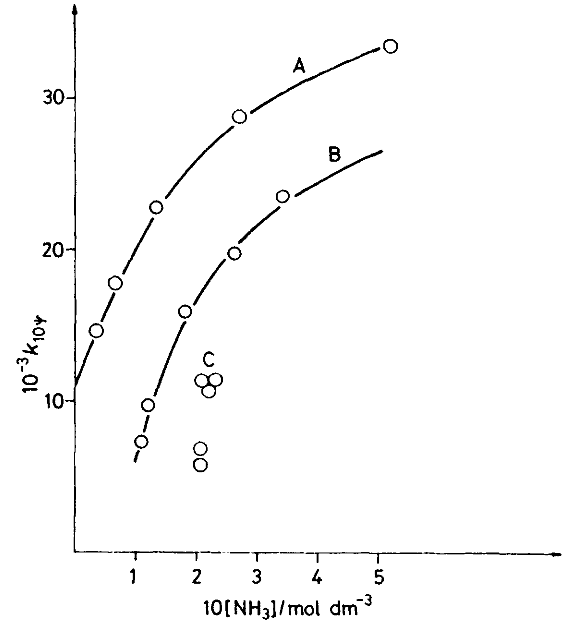


FIGURE 2 Ammonia catalysis in the oxidation of 2-aminoethanol by periodate: (A) pH 10.34, (B) pH 9.38, (C) pH 8.53. The zeros of successive curves are displaced by one unit on the concentration axis

The catalytic constants for the reactions are summarized in Table 7.

The exponents of the Brönsted equation, β and α, were calculated with the statistical corrections *p* and *q* used by Bell and Evans.[17] The β-values calculated for the OH^- and H_2O catalysis are: for ethane-1,2-diamine oxidation, 0.33; for *NN*′-dimethylethane-1,2-diamine oxidation, 0.31; and for 2-aminoethanol oxidation, 0.32.

TABLE 6

Pseudo-third-order catalytic constants (in $dm^6\ mol^{-2}\ s^{-1}$) for the oxidation of *NN*′-dimethylethane-1,2-diamine by periodate (I 0.100 mol dm^{-3})

pH	8.08—9.32	9.80	10.80 *
$10^{-5}k_{10\psi}^{AH^+}$	6 ± 2	9	42
pH	9.00	9.45	10.00
$10^{-5}k_{10\psi}^{NH_4^+}$	1.0	4.2	12.5

* $I = 0.010$ mol dm^{-3}.

The α-values calculated for the H_3O^+ and H_2O catalysis are: for ethane-1,2-diamine oxidation, 0.51; and for *NN*′-dimethylethane-1,2-diamine oxidation, 0.49.

The acid–base catalysis can be explained in terms of a reaction in which the periodate and diamine react reversibly to form a monoamide, C_1, which cyclises to a diamide, C_2, which in turn decomposes rapidly to products, according to reaction (3).

The general acid-base catalysis can be attributed to the catalysis of the cyclization of the monoanion, C_1^-, formed rapidly and reversibly by the electrophilic attack of periodate monoanion on the unprotonated amino-group. Cyclization is rate-determining in the oxidation of 1,2-diamines over the whole range of concentration of reactants and catalysts used in the kinetic study.

TABLE 7

Catalytic constants for the periodate oxidations of 1,2-diamines and 2-aminoethanol. (Units for all constants are $dm^6\ mol^{-2}\ s^{-1}$)

	Ethane-1,2-diamine	*NN*′-Dimethyl-ethane-1,2-diamine	2-Amino-ethanol
$k_{10}^{H_2O}$	1.8	50	108 [a]
$k_{10}^{OH^-}$	1.0 × 10^6	1.5 × 10^7	1.6 × 10^7 [a]
$k_{10}^{H_3O^+}$	2.7 × 10^9	2.7 × 10^{10}	1.0 × 10^8
$k_{10}^{NH_3}$	2.8 × 10^4	4 × 10^5	2.6 × 10^5 [a]
$k_{10}^{NH_4^+}$	6 × 10^3	5 × 10^4	
$k_{10}^{A^0}$	2.6 × 10^4	1.2 × 10^6	
$k_{10}^{AH^+}$	3.0 × 10^4	6 × 10^5	
$k_{10}^{AcO^-}$			1.5 × 10^4
k_{10}^{AcOH}		5 × 10^6	
$k_{10}^{HPO_4^{2-}}$			1.4 × 10^6 [a]

[a] Catalytic constants were calculated from equations (13)—(15).

Buffer Catalysis in the Oxidation of 2-*Aminoethanol.*—In the oxidation of 2-aminoethanol, when strong bases are used as catalysts, cyclization is accelerated so much that another step of the reaction becomes partly or wholly rate-limiting. We have only observed second-order kinetics for the oxidations, and therefore we assume that the concentrations of the intermediates C_1 and C_2 are low, and for reactions (10)—(12) the steady-state approximation is applicable (AE = 2-aminoethanol; A and B = conjugated acid–base pair.)

This leads to equation (13a) for the pseudo-second-order rate constant $k_{10\psi}$, where $K_1 = k_1/k_{-1}$, $K_2^B = k_2^B/k_{-2}^A$, and $K_3^A = k_3^A/k_{-3}^B$.

$$\text{Per.}^- + \text{AE} \xrightleftharpoons[k_{-1}]{k_1} C_1^- \tag{10}$$

$$C_1^- + B \xrightleftharpoons[k_{-2}^A]{k_2^B} C_2^{2-} + A;\quad C_2^{2-} \xrightarrow{k^{2-}} \text{products} \tag{11}$$

$$C_2^{2-} + A \xrightleftharpoons[k_{-3}^B]{k_3^A} C_2^- + B;\ C_2^- \xrightarrow{k^-} \text{products} \tag{12}$$

$$1/k_{10\psi} = 1k/_1 + 1/K_1k_2^B\,[B] + 1/\{(K_1K_2^Bk^{2-}[B]/[A]) + K_1K_2^Bk_3^Ak^-\,[B]/(k_{-3}^B[B] + k^-)\} \tag{13a}$$

If $k_{-3}^B[B] \gg k^-$, equation (13a) can be simplified into equation (13b) for $k_{10\psi}$, and equation (14) is obtained for the limiting pseudo-second-order rate constant, $k_{10\psi(\text{lim.})}$.

$$1/k_{10\psi} = 1/K_1k_2^B[B] + 1/k_{10\psi(\text{lim.})} \tag{13b}$$

$$1/k_{10\psi(\text{lim.})} = 1/k_1 + 1/\{(K_1K_2^Bk^{2-}[B]/[A]) + K_1K_2^BK_3^Ak^-\} \tag{14}$$

The following treatment was used to evaluate the catalytic constants for bases[6] in the oxidation of 2-aminoethanol: at constant pH, when base-catalysed cyclization predominates, the catalytic effect of water and hydroxide ion cannot be neglected at low concentrations of B; the kinetic results can be described by equation (15), where $k_{10\psi}^o$ is the pseudo-second-order rate constant at zero buffer concentrations.

$$1/k_{10\psi} = 1/(K_1k_2^B[B] + k_{10\psi}^o) + 1/k_{10\psi(\text{lim.})} \tag{15}$$

Results were obtained by successive approximations: at high base concentrations equation (13b) was used to obtain values for $k_{10\psi(\text{lim.})}$ by extrapolating a plot of $1/k_{10\psi}$ against $1/[B]$ to $1/[B] = 0$. The results at low buffer concentrations were treated according to equation (16), a transformation of equation (15), to give the first

$$1/[(1/k_{10\psi}) - (1/k_{10\psi(\text{lim.})})] = k_{10\psi}^o + K_1k_2^B[B] \tag{16}$$

approximation to values of $K_{10\psi}^o$ and $K_1k_2^B$. The second approximation to $k_{10\psi(\text{lim.})}$ was found by plotting $1/k_{10\psi}$ against $1/(K_1k_2^B[B] + k_{10\psi}^o)$.

For hydrogenphosphate catalysis (Figure 1) the broken lines are fitted by equation (15) with $K_1k_2^{HPO_4^{2-}}$ 1.4 × 10^6 $dm^6\ mol^{-2}\ s^{-1}$, and at pH 6.93, 7.65, and 8.15 with $k_{10\psi}^o$ 2.7 × 10^3, 3.0 × 10^3, and 4.2 × 10^3 $dm^3\ mol^{-1}\ s^{-1}$, and with $k_{10\psi(\text{lim.})}$ 9.6 × 10^3, 1.5 × 10^4, and 1.9 × 10^4 $dm^3\ mol^{-1}\ s^{-1}$, respectively.

For ammonia catalysis (Figure 2) the broken lines are fitted by equation (15) with $K_1k_2^{NH_3}$ 2.6 × 10^5 $dm^6\ mol^{-2}\ s^{-1}$ and at pH 9.38 and 10.34 with $k_{10\psi}^o$ 6.0 × 10^3 and 1.1 × 10^4 $dm^3\ mol^{-1}\ s^{-1}$ and with $k_{10\psi(\text{lim.})}$ 3.4 × 10^4 and 4.3 × 10^4 $dm^3\ mol^{-1}\ s^{-1}$, respectively. At pH 8.53 $k_{10\psi}^o$ is 5.1 × 10^3 $dm^3\ mol^{-1}\ s^{-1}$, and $k_{10\psi(\text{lim.})}$ is *ca.* 1.4 × 10^4 $dm^3\ mol^{-1}\ s^{-1}$.

The change of $1/k_{10\psi(\text{lim.})}$ with the buffer ratio [A]/[B] according to equation (14) can be fitted by successive approximation. This yields, for hydrogenphosphate catalysis, $k^{2-}K_1K_2^{\mathrm{HPO_4{}^{2-}}}$ 5.0×10^3 dm^3 mol^{-1} s^{-1}, $k^{-}K_1K_2^{\mathrm{HPO_4{}^{2-}}}K^{\mathrm{H_2PO_4{}^{-}}}$ 1.0×10^4 dm^3 mol^{-1} s^{-1}, and k_1 2.2×10^4 dm^3 mol^{-1} s^{-1}; and for ammonia catalysis, $k^{2-}K_1K_2^{\mathrm{NH_3}}$ 2×10^5 dm^3 mol^{-1} s^{-1}, $k^{-}K_1K_2^{\mathrm{NH_3}}K_3^{\mathrm{NH_4{}^+}}$ *ca.* 1×10^3 dm^3 mol^{-1} s^{-1} and k_1 4.3×10^4 dm^3 mol^{-1} s^{-1}.

From these data we obtain, for $k^{2-}/k^{-}K_3^{\mathrm{H_2PO_4{}^{-}}}$ 0.5, and for $k^{2-}/k^{-}K_3^{\mathrm{NH_4{}^+}}$ *ca.* 200.

The equilibrium constant K_3^{A} of equation (12) can be expressed as $K_3^{\mathrm{A}} = K_{\mathrm{a}}/K_{\mathrm{a2}}^{\mathrm{C_2}}$, where $K_{\mathrm{a2}}^{\mathrm{C_2}}$ is the second acid dissociation constant of the cyclic intermediate $\mathrm{C_2}$, and K_{a} the acid dissociation constant of the conjugate acid of the base catalyst.[18] Therefore,[18] a value for $K_{\mathrm{a2}}^{\mathrm{C_2}}k^{2-}/k^{-}$ which can be calculated, from the hydrogenphosphate catalysis data, is 3.0×10^{-8} mol dm^{-3} and from the ammonia catalysis data is *ca.* 2×10^{-8} mol dm^{-3}.*

Hydroxide, Water, and Hydronium Catalysis in the Oxidation of 2-*Aminoethanol*.—To evaluate the catalytic constants for hydroxide and water we used equation (17) for $k_{10\psi}^{\mathrm{o}}$ (see Table 3) which was fitted by successive approximations where the terms $K^{\mathrm{OH^-}}$ and K' are defined

$$1/k_{10\psi}^{\mathrm{o}} = 1/(K^{\mathrm{OH^-}}[\mathrm{OH^-}] + K'] + 1/k_{10\psi(\mathrm{lim.})}^{\mathrm{o}} \quad (17)$$

as shown below. In the pH range 10.5—12 we obtain for $k_{10\psi(\mathrm{lim.})}^{\mathrm{o}}$ 2.5×10^4 dm^3 mol^{-1} s^{-1}; for K' 6×10^3 dm^3 mol^{-1} s^{-1}; and for $K^{\mathrm{OH^-}}$ 1.6×10^7 dm^6 mol^{-2} s^{-1}. In comparing these constants with the constants for hydrogenphosphate catalysis we assume $k_{10\psi(\mathrm{lim.})}^{\mathrm{o}} = k_1$, $K^{\mathrm{OH^-}} = K_1k_2^{\mathrm{OH^-}}$, and $K' = K_1k_2^{\mathrm{H_2O}}[\mathrm{H_2O}]$; *i.e.*, equation (17) becomes equation (17a).

$$1/k_{10\psi}^{\mathrm{o}} = \\ 1/(K_1k_2^{\mathrm{OH^-}}[\mathrm{OH^-}] + K_1k_2^{\mathrm{H_2O}}[\mathrm{H_2O}]) + 1/k_1 \quad (17a)$$

In the pH range 7—9.5 the best fit of equation (17) was found with $k_{10\psi(\mathrm{lim.})}^{\mathrm{o}}$ 6×10^3 dm^3 mol^{-1} s^{-1}, with K' 2.3×10^3 dm^3 mol^{-1} s^{-1}, and with $K^{\mathrm{OH^-}}$ 9×10^9 dm^6 mol^{-2} s^{-1}. In this pH range hydroxide catalysis is negligible and we assume that water-catalysed cyclization and hydronium ion-catalysed ring-opening is the partly rate-determining step. In this case the $1/k_1$ term of equation (13a) can be neglected, the ' limiting ' rate constant $k_{10\psi(\mathrm{lim.})}^{\mathrm{o}}$ is $K_1k_2^{\mathrm{H_2O}}[\mathrm{H_2O}]$ and the transformation of $K^{\mathrm{OH^-}}$ yields for $k^{2-}K_1K_2^{\mathrm{H_2O}}$ a value of 2.0×10^{-6} dm^3 mol^{-1} s^{-1}, *i.e.*, equation (17) becomes equation (17b), where $1/[\mathrm{H_3O^+}] = [\mathrm{OH^-}]/K_{\mathrm{w}}$, K_{w} being the ionic product of water.

$$1/k_{10\psi}^{\mathrm{o}} = 1/\{(k^{2-}K_1K_2^{\mathrm{H_2O}}[\mathrm{H_2O}]/[\mathrm{H_3O^+}]) + K'\} + \\ 1/K_1k_2^{\mathrm{H_2O}}[\mathrm{H_2O}] \quad (17b)$$

From the values of $K_1k_2^{\mathrm{B}}$ and $k^{2-}K_1K_2^{\mathrm{B}}$ for the hydrogen phosphate, ammonia, and water catalysis we calculate for the acid-catalysed ring-opening $k_{-2}^{\mathrm{NH_4{}^+}}/k^{2-} = 1.3$, $k_{-2}^{\mathrm{H_2PO_4{}^-}}/k^{2-} = 2.7 + 10^2$, and $k_{-2}^{\mathrm{H_3O^+}}/k^{2-} = 5.5 \times 10^7$ dm^3 mol^{-1}, respectively. The Brönsted plot for ring-opening is necessarily related to the corresponding plot for cyclization. The slope, α', equals $1 - \beta$, *i.e.* 0.68.

The term K' in equation (17b) is equal to $k^{-}K_1K_2^{\mathrm{H_2O}}$-$K_3^{\mathrm{H_3O^+}}$ if $k_{-3}^{\mathrm{H_2O}}[\mathrm{H_2O}] \gg k^{-}$ [see equation (13a)], and leads to $K_{\mathrm{a2}}^{\mathrm{C_2}}k^{2-}/k^{-}$ 1.4×10^{-8} mol dm^{-3}, which is in good agreement with the values calculated for the hydrogenphosphate catalysis. $K' = K_2K_2^{\mathrm{H_2O}}k_3^{\mathrm{HO}}$ $[\mathrm{H_2O}]$ if $k_{-3}^{\mathrm{H_2O}}$-$[\mathrm{H_2O}] \ll k^{-}$, but this assumption need not be necessary (see later).

In the pH range 6.0—4.9 $k_{10\psi}^{\mathrm{o}}$ increases linearly with increasing hydronium ion concentration (see Table 4). We assume for a hydronium ion-catalysed reaction the sequence in reactions (18).

$$\mathrm{Per.^- + AE} \overset{K_1}{\rightleftharpoons} \mathrm{C_1^-}$$

$$\mathrm{C_1^- + H_3O^+} \underset{k_{-2}^{\mathrm{H_2O}}}{\overset{k_2^{\mathrm{H_3O^+}}}{\rightleftharpoons}} \mathrm{C_1^o + H_2O} \underset{k_{-3}^{\mathrm{H_3O^+}}}{\overset{k_3^{\mathrm{H_2O}}}{\rightleftharpoons}} \\ \mathrm{C_2^- + H_3O^+};\ \mathrm{C_2^-} \xrightarrow{k^-} \text{products} \quad (18)$$

We assume that the constant for hydronium ion catalysis, $k_{10}^{\mathrm{H_3O^+}} = K_1k_2^{\mathrm{H_3O^+}}$.

In order to estimate the order of magnitude of the rate constants, we assume all second-order rate constants for protonation by $\mathrm{H_3O^+}$ to be at the diffusion-controlled limit,[18] *viz. ca.* 5×10^{10} dm^3 mol^{-1} s^{-1}. This can be done for $k_3^{\mathrm{H_3O^+}}$ (the rate constant for protonation of $\mathrm{C_2^{2-}}$ to $\mathrm{C_2^-}$ by $\mathrm{H_3O^+}$) and for $k_2^{\mathrm{H_3O^+}}$ (the rate constant for protonation of $\mathrm{C_1^-}$ to $\mathrm{C_1^o}$ by $\mathrm{H_3O^+}$) because they are ' normal ' acid–base reactions: simple proton transfers.[18]

This leads (from $K_1k_2^{\mathrm{H_3O^+}} = 1.0 \times 10^8$ dm^6 mol^{-2} s^{-1}) to a value of 2×10^{-3} dm^3 mol^{-1} for K_1.

In the water-catalysed reaction K' cannot be equal to $K_1K_2^{\mathrm{H_2O}}k_3^{\mathrm{H_3O^+}}[\mathrm{H_2O}]$ $(k_{-3}^{\mathrm{H_2O}}[\mathrm{H_2O}] \ll k^{-})$ because this leads to $(k_3^{\mathrm{H_3O^+}}/k_{-2}^{\mathrm{H_3O^+}}) = 0.4$, and $k_{-2}^{\mathrm{H_3O^+}}$ (the rate constant for ring-opening of $\mathrm{C_2^{2-}}$ to $\mathrm{C_1^-}$ by $\mathrm{H_3O^+}$) cannot exceed $k_3^{\mathrm{H_3O^+}}$, *i.e.*, the diffusion controlled limit. The assumption $K' = k^{-}K_1K_2^{\mathrm{H_2O}}K_3^{\mathrm{H_3O^+}}$ seems to be valid, and we obtain $k_{-3}^{\mathrm{H_2O}}[\mathrm{H_2O}]/k^{-} = 2.5$, as a lower limit, if $k_{+3}^{\mathrm{H_3O^+}} = k_{-2}^{\mathrm{H_3O^+}}$. The latter assumption seems reasonable, and we will use this to provide estimates for other constants.

The third-order catalytic constant for hydroxide ion, $K_1k_2^{\mathrm{OH^-}}$, is 1.6×10^7 dm^6 mol^{-2} s^{-1}, and the estimated value of $k_2^{\mathrm{OH^-}}$ becomes 8×10^9 dm^3 mol^{-1} s^{-1}, which is near the diffusion-controlled limit reported for simple proton-transfer reactions of hydroxide with a negative ion (6×10^9 dm^3 mol^{-1} s^{-1}).[19] This fact is surprising, and makes it possible to assume that the intermediate $\mathrm{C_1^-}$ is not an open intermediate monoanion, but a cyclic intermediate zwitterion. If so, the assumption $k_3^{\mathrm{H_3O^+}} = k_{-2}^{\mathrm{H_3O^+}}$ must be valid, and the equilibrium constant K_2^{B} must represent an equilibrium of simple proton-transfer reactions.

According to this, the estimated rate constant for the decomposition of the intermediate $\mathrm{C_2^{2-}}$ to products, k^{2-}, becomes 9×10^2 s^{-1} from the value of $(k_{-2}^{\mathrm{H_3O^+}}/k^{2-}) = 5.5 \times 10^7$ dm^3 mol^{-1}.

Furthermore from the estimated value of $K_2^{\mathrm{H_2O}} = 1 \times 10^{-6}$, the second acid dissociation constant of the

---

* The error in this value can be large. This is largely due to the error in $k^{-}K_1K^{\mathrm{NH_3}}K_3^{\mathrm{NH_4{}^+}}$, which depends strongly upon the $k_{10\psi(\mathrm{lim.})}$ value calculated from the values measured at pH 8.53. We have calculated the value of $k_{10\psi(\mathrm{lim.})}$ from 4 measured values (shown by C in Figure 2) and we use this only as an estimated value.

intermediate, $K_{a2}^{C_{12}} = 1.6 \times 10^{-5}$ mol dm^{-3}, can be calculated ($K_2^{H_2O}[H_2O]f^{2-} = K_{a2}^{C_{12}}$).

We assume that in the equilibria (19) $K_2^{H_2O}$ does not

$$C_1^- + H_2O \overset{K_2^{H_2O}}{\rightleftharpoons} C_2^{2-} + H_3O^+ \overset{K_3^{H_3O^+}}{\rightleftharpoons} C_2^- + H_2O \quad (19)$$

differ from $1/K_3^{H_3O^+}$, and so we obtain an estimated value for k^- of 1×10^6 s^{-1} ($K_{a2}^{C_2}k^{2-}/k^- = 1.4 \times 10^{-8}$ mol dm^{-3}).

The estimated rate constants are summarized in Table 8.

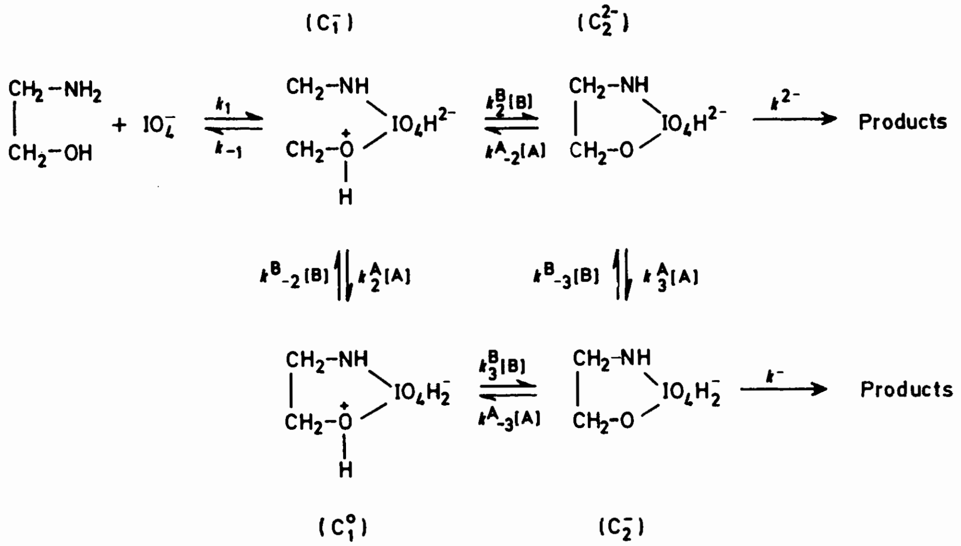
TABLE 8

Estimated rate constants for reactions involving the intermediates C_1^-, C_1^0, C_2^{2-}, and C_2^- in the oxidation by periodate of 2-aminoethanol

Reaction	Rate constant
$Per.^- + AE \longrightarrow C_1^-$	$k_1 = 2.5 \times 10^4$ dm^3 mol^{-1} s^{-1} (obs.)
$C_1^- \longrightarrow Per^- + AE$	$k_{-1} = 1.2 \times 10^7$ s^{-1}
$C_1^- + H_2O \longrightarrow C_2^{2-} + H_3O^+$	$k_2^{H_2O} = 5.4 \times 10^4$ dm^3 mol^{-1} s^{-1}
$C_1^- + OH^- \longrightarrow C_2^{2-} + H_2O$	$k_2^{OH^-} = 8 \times 10^9$ dm^3 mol^{-1} s^{-1}
$C_2^{2-} \longrightarrow$ Products	$k^{2-} = 9 \times 10^2$ s^{-1}
$C_1^- + H_3O^+ \longrightarrow C_1^0 + H_2O$	$k_2^{H_3O^+}$ = 5×10^{10} dm^3 mol^{-1} s^{-1}
$C_2^{2-} + H_3O^+ \longrightarrow C_2^- + H_2O$	$k_3^{H_3O^+}$
$C_2^- + H_3O^+ \longrightarrow C_1^0 + H_2O$	$k_{-3}^{H_3O^+}$
$C_2^{2-} + H_3O^+ \longrightarrow C_1^- + H_2O$	$k_{-2}^{H_3O^+}$
$C_2^- + H_2O \longrightarrow C_2^{2-} + H_3O^+$	$k_{-3}^{H_2O} = 5.4 \times 10^4$ dm^3 mol^{-1} s^{-1}
$C_2^- \longrightarrow$ Products	$k^- = 1 \times 10^6$ s^{-1}

We note that in the periodate oxidation of propane-1,2-diol [6c] k_1 is 5.2×10^2 dm^3 mol^{-1} s^{-1}, while in the oxidation of 2-aminoethanol k_1 is 2.5×10^4 dm^3 mol^{-1} s^{-1}. The catalytic constant for hydroxide ($K_1k_2^{OH^-}$) is 1.1×10^7 dm^6 mol^{-2} s^{-1} and this value is almost the same as that for the oxidation of 2-aminoethanol ($K_1k_2^{OH^-}$ 1.6×10^7 dm^6 mol^{-2} s^{-1}).

Mechanism.—The mechanism in Scheme 1 is one which is in harmony with the experimental facts already discussed for the oxidation by periodate of 2-aminoethanol.



SCHEME 1

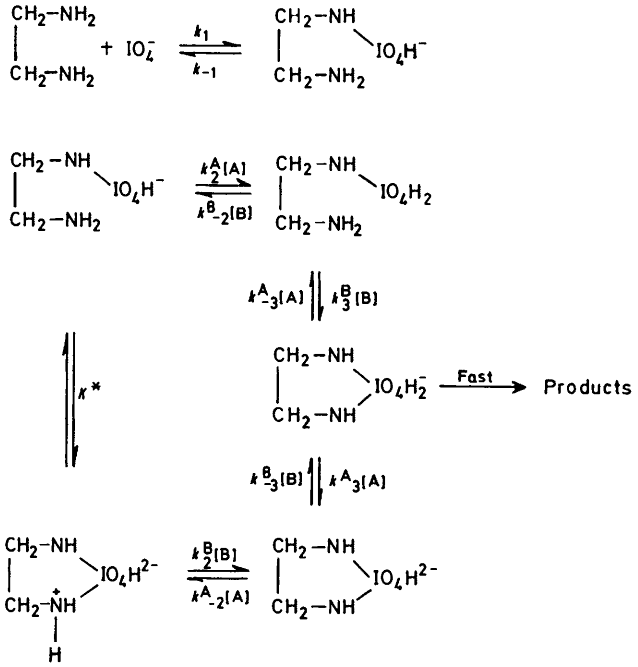
According to the estimated acid dissociation constant, the amide–ester intermediate is an acid about 1 000-fold stronger than periodic acid. Probably this is why the catalytic effect of weak acids was not detectable. The estimated second-order catalytic constants for ammonia, hydrogenphosphate and acetate are $k_2^{NH_3}$ 1.3×10^8, $k_2^{HPO_4^{2-}}$ 7×10^8, and $k_2^{AcO^-}$ 7.5×10^6 dm^3 mol^{-1} s^{-1}, respectively. The second-order catalytic constant for ammonia and hydrogen phosphate is only about one order of magnitude lower than $k_2^{OH^-}$, and it has been shown [20] that for strong bases such catalytic constants can approach the diffusion-controlled limit. In this case the two proton transfers follow a stepwise mechanism. The catalytic constants for water, acetate, ammonia, and hydroxide lie on the Brönsted plot, but the hydrogenphosphate catalytic constant is higher than expected by about an order of magnitude. This can be due either to bifunctional catalysis for the two proton transfers for the conversion of C_1^- into C_2^-, or to the fact that the stepwise proton transfers are involved, in which case β must change from zero to one in the sequence NH_3, HPO_4^{2-}, and AcO^-, and the catalytic constant for water must be abnormally high.[20,21]

For the general acid–base catalysed periodate oxidation of 1,2-diamines we suggest the mechanism in Scheme 2.

We have made a detailed kinetic analysis on the basis of the mechanism in Scheme 2 as follows. The third-order catalytic constant for acid, $k_{10}^A = K_1K_2^Ak_3^B$ and $k_3^B/k_{-2}^B = 1$. The third-order catalytic constant for base, $k_{10}^B = K_1K^*$-$K_2^Bk_3^A$ and $k_3^A/k_{-2}^A = 1$. We assume that all second-order catalytic constants for hydronium ion are 5×10^{10} dm^3 mol^{-1} s^{-1}, the second-order catalytic constant for hydroxide, $k_2^{OH^-}$, is 6×10^9, and $k_3^{OH^-}$ is 1×10^{10} dm^3 mol^{-1} s^{-1}, and water can act both as an acid and a base. In the oxidation of ethane-1,2-diamine this leads to estimated acid dissociation constants for the acid C_1^0, $K_{a1}^{C_1}$, of 3.7×10^{-8} mol dm^{-3} and for the acid C_2^-*,

$K_{a2}^{C_2*}$, of 3.5×10^{-6} mol dm^{-3}, with K_1 5.4×10^{-2} dm^3 mol^{-1} and K^* 3.1×10^{-3}. In the oxidation of *NN'*-dimethylethane-1,2-diamine all these constants have similar orders of magnitude except K_1 which is estimated to be 0.54 dm^3 mol^{-1}.

In the oxidation of 1,2-diamines the third-order catalytic constants for ammonia, 1,2-diamine, and monoprotonated 1,2-diamine are of the same order of magnitude and only 20—30 times lower than the hydroxide catalytic constant. The order of magnitude of the estimated acid dissociation constant $K_{a2}^{C_2*}$ (10^{-6} mol dm^{-3}) makes it possible to assume that the monoprotonated 1,2-diamines act as bases, and the second-order rate constant k_2^B can assume the value of the diffusion controlled limit.



SCHEME 2

[8/2001 *Received*, 17*th November*, 1978]

REFERENCES

[1] C. A. Bunton, in ' Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965, ch. 6; G. J. Buist, ' Kinetics of Oxidations by Periodate,' in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Amsterdam, 1972, vol. 6, p. 435.

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

[3] G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1954, 1406; 1957, 4580.

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

[5] P. Zuman, J. Sicher, J. Krupicka, and M. Svoboda, *Nature*, 1956, **178**, 1407.

[6] (*a*) G. J. Buist, C. A. Bunton, and J. Lomas, *J. Chem. Soc.* (*B*), 1966, 1094, 1099; (*b*) G. J. Buist, C. A. Bunton, and W. C. P. Hipperson, *ibid.*, 1971, 2218; (*c*) G. J. Buist and C. A. Bunton, *ibid*, 1971, 2117.

[7] (*a*) G. Dahlgren and J. M. Hodsdon, *J. Phys. Chem.*, 1964, **68**, 416; (*b*) G. Dahlgren and E. M. Rand, *ibid.*, 1967, **71**, 1955.

[8] G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5164.

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

[10] P. Fleury, J. Courtois, and M. Grandchamp, *Bull. Soc. chim. France*, 1949, 88.

[11] (*a*) L. Maros, I. Molnár-Perl, and E. Schulek, *Acta Chim. Hung.*, 1962, **30**, 119; (*b*) L. Maros, I. Molnár-Perl, and M. Molnar, *ibid.*, in the press.

[12] G. J. Buist, W. C. P. Hipperson, and J. D. Lewis, *J. Chem. Soc.* (*A*), 1969, 307.

[13] C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, 1958, **62**, 444; (*b*) G. H. McIntyre, jun., B. P. Block, and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1959, **81**, 529.

[14] F. Basolo, R. K. Murmann, and Y. T. Chen, *J. Amer. Chem. Soc.*, 1953, **75**, 1478; F. Basolo and R. K. Murmann, *ibid.*, 1954, **76**, 211.

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

[16] R. G. Bates and G. D. Pinching, *J. Res. Nat. Bur. Stand.*, 1951, **56**, No. 5.

[17] R. P. Bell and P. G. Evans, *Proc. Roy. Soc.*, 1966, **A291**, 297.

[18] R. P. Bell, ' The Proton in Chemistry,' 2nd edn., Chapmann and Hall, London, 1973.

[19] M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, 1964, **2**, 308.

[20] W. P. Jencks and M. Sayer, *Faraday Symp. Chem. Soc.*, 1975, **10**, 41, and references therein.

[21] R. E. Barnett, *Accounts Chem. Res.*, 1973, **6**, 41.