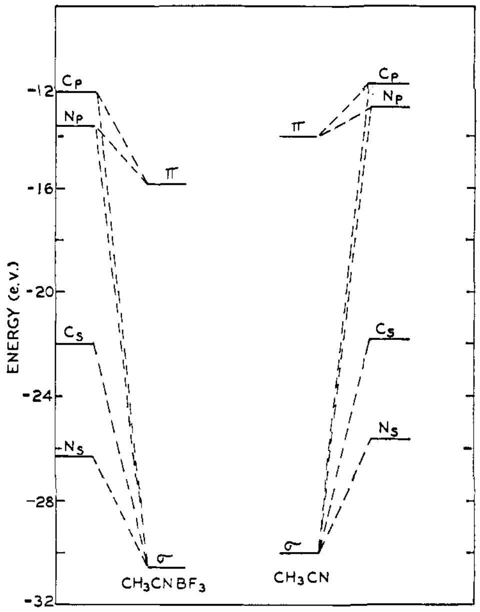

Figure 3. Molecular orbital diagrams for the "CN orbitals" of $CH_3CN \cdot BF_3$ and CH_3CN.

(dipole moment) in the CN link. This rationalization fails to take into account the fact that the *normal mode* referred to as the CN stretching mode actually is different for the adduct and free ligand. The assumption of a greater "CN" dipole is apparently based on charge flow, incurred by coordination, in the CN link. The results of the extended Hückel calculation reported here indicated that the "CN" dipole is smaller in the BF_3 adduct than in CH_3CN. In addition to a slightly shorter bond distance in the adduct, the difference in C and N net charges decreases from slightly greater than 1 in the donor to approximately 0.8 electrostatic unit in the adduct! The vibrational analyses indicate that the cause for the intensity increase may well lie in the fact that the "CN" normal mode changes upon coordination. The eigenvectors for the "CN" normal mode in the adduct show that the NB bond stretching vibration is activated (*cf.* kinematic coupling above) in this normal mode, and the charge on the boron atom, from the molecular orbital calculation, is approximately a full atomic unit. The inclusion of motion of this highly charged atom in the normal mode would cause an increase in the absorption intensity of the normal mode. In keeping with this argument, the intensity of the "NB" stretching vibration at ~600 cm^{-1} is appreciably larger than that of the "CN" vibration, indicating that stretching the "NB" bond will contribute significantly to the intensity of the "CN" vibration.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

Kinetic Study of the Reaction of Peroxydiphosphate with Iodide

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Contribution from the Chemistry Department, University of Ferrara, Ferrara, Italy. *Received September 24, 1965*

Abstract: The rate of the reaction of potassium peroxydiphosphate with potassium iodide has been measured in acid media at different reactant concentrations at 25°. The reaction takes place through at least three main paths, which can be represented as

$$H_3P_2O_8^- + I^- \longrightarrow HPO_4^{2-} + H_2PO_4^- + I^+$$

$$H_3P_2O_8^- + H_2O \longrightarrow H_2PO_4^- + H_2PO_5^- + H^+$$

$$H_2P_2O_8^{2-} + I^- \longrightarrow 2HPO_4^{2-} + I^+$$

followed by very fast reactions which give the final products. The first path is the easiest to verify; the existence of the others has been confirmed with runs performed in the absence of iodide and by means of a study of the salt effects, respectively. The differences in behavior toward the iodide ion of the peroxydiphosphate and of the peroxydisulfate ion are discussed.

The peroxydiphosphate ion reacts readily with the iodide ion in acid media to form phosphoric acid and iodine.[1] The kinetics of this reaction, however, has never been investigated quantitatively, as far as we know, so that its mechanism is unknown. This is in contrast with the reaction of peroxydisulfate with iodide, which takes place in neutral media, and which has been extensively investigated.[2,3] The reaction of peroxydiphosphate with iodide in the absence of acid could have escaped attention because iodate is formed, since a solution of $K_4P_2O_8$ is decidedly alkaline.[1] On the other hand, it is possible that the oxidation of the iodide ions take place mainly through the formation of peroxymonophosphate; the latter, in fact,

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(1) F. Fichter and A. Rius y Miro, *Helv. Chim. Acta*, **2**, 3 (1919).

(2) R. Namias, "La chimica fotografica (Modena)," 1898; *Chem. Zentr.*, *II*, 806 (1900); C. A. Peters and S. E. Moody, *Z. Anorg. Chem.*, **29**, 326 (1902).

(3) D. A. House, *Chem. Rev.*, **62**, 185 (1962).

is formed in acid solution from the peroxydiphosphate, which, on the contrary, is very stable in alkaline solution.[4] We have considered it interesting, therefore, to compare the kinetics and mechanism of this reaction and of the peroxydisulfate–iodide reaction.

Experimental Section

Potassium peroxydiphosphate has been prepared by the method of Fichter and Gutzwiller.[4] The crude product was distinctly yellow because of the presence of chromate, and attempts of purification by recrystallization failed completely. No improvement was obtained by using a quantity of chromate smaller than the one suggested by Fichter and Gutzwiller; the diminution in chromate was only proportional, and the yield was much lower. By metathesis with $NaClO_4$, sodium peroxydiphosphate could be obtained, which, instead, was easily purified by recrystallization. The final product was identical with the one described by Simon and Richter,[5] as judged from the debyeogram (X-ray diffraction pattern) performed on the anhydrous salt. In the same way lithium peroxydiphosphate could be obtained, which could also be purified by recrystallization.[6] From $Li_4P_2O_8 \cdot 4H_2O$ pure potassium peroxydiphosphate could be obtained by metathesis with K_3PO_4.[7] The debyeogram of $K_4P_2O_8$ was also identical with the one published by Simon and Richter.[5] These three salts were analyzed for P, active O, and water with the methods given by Simon and Richter, and for Na and K by flame spectrometry.

Anal. Calcd for $K_4P_2O_8$: P, 17.89; act. O, 4.62; K, 45.15. Found: P, 17.96; act. O, 4.55; K, 45.83. Calcd for $Na_4P_2O_8$: P, 21.98; act. O, 5.68; Na, 32.62. Found: P, 22.21; act. O, 5.50; Na, 33.1. Calcd for $Li_4P_2O_8 \cdot 4H_2O$: P, 21.39; act. O, 5.52; H_2O, 24.85. Found: P, 21.00; act. O, 5.50; H_2O, 25.3.

Other salts were Carlo Erba RP or BDH LR reagents, and usually were not further purified. Some KI was recrystallized from water under nitrogen, since a trace of free iodine was present in the original product. Kinetic runs performed with the original and the purified products gave indistinguishable results.

The reaction rate was followed with the dead-stop microtitration method previously described.[8] The usual precautions were taken to avoid the presence of an excess of $Na_2S_2O_3$, except for the brief period necessary to determine the instant of reappearance of the iodine. A small amount of EDTA (2.5×10^{-5} *M*) was added to the reacting mixture to complex possible traces of heavy metals, which could have a catalytic action. The reaction was followed for a very small fraction of its course (less than 1%) so that the amounts of added $Na_2S_2O_3$ were a linear function of the time, and the initial rate was measured. However, when the peroxydiphosphate was added to the other reactants, an appreciable amount of iodine appeared instantaneously, which was equivalent to about the 0.01% of the total peroxydiphosphate. We attribute this to the presence of a trace of peroxymonophosphate, which we were unable to eliminate. A corresponding amount of thiosulfate was therefore added at the beginning of each run, and the initial time was taken as the instant of reappearance of free iodine. The temperature was in all cases 25.0°; the reaction vessel was made of dark glass, to avoid any possible photochemical reaction.[9]

All the data reported in the present paper have been obtained by using the same sample of $K_4P_2O_8$, and each measurement was repeated at least twice, with differences less than 5%. All measurements were repeated with a different sample of $K_4P_2O_8$, and the differences from the average results reported in the tables were of the order of 10%. This does not modify the conclusions which can be drawn, but indicates the limits of reliability of the results. A certain number of runs has also been performed with the peroxydiphosphates of sodium and lithium, and the results in all cases agreed with the data of the tables within the same limits.

Runs were made to measure the rate of the reaction of peroxydiphosphate with hydrogen ion to give peroxymonophosphate. The relative solutions were brought to temperature and mixed, and 50-ml samples were taken at suitable intervals. The reaction was quenched by neutralizing with $NaHCO_3$, an excess of KI was added, and the iodine liberated instantaneously[10] was titrated by adding an excess of $Na_2S_2O_3$ and backtitrating with 0.00005 *M* iodine. The dead-stop end point was used.

The rates reported in the tables refer to the decrease in the number of moles of peroxydiphosphate per liter and per second.

The debyeograms were obtained with a General Electric XRD-5 equipment, using a copper target.

Results

Table I reports the results obtained at ionic strength 0.1, $KClO_4$ being the added salt. The concentrations of the various ionic species and the ionic strength have been calculated by using the dissociation constants of $H_4P_2O_8$ given by Crutchfield and Edwards.[7] These constants have been corrected for the effect of the ionic strength *I* by means of a Güntelberg[11] equation

$$\log f_z = -Az^2I^{1/2}/(1 + I^{1/2}) \qquad (1)$$

where f_z is the activity coefficient of an ion of charge *z*, and *A* is the Debye–Hückel constant (for water, at 25.0°, $A = 0.5085$). The peroxydiphosphate is largely in form of $H_2P_2O_8^{2-}$, and only minor quantities of $HP_2O_8^{3-}$ and of $H_3P_2O_8^{-}$ are present. At first sight the rate appears to be approximately proportional to the concentration of peroxydiphosphate (see runs 4, 6, 7, 24, 27, 28), of iodide (see runs 13–16; 19 and 20; 23 and 24), and of hydrogen ion (see runs 1–3). This relationship, however, is very rough, and a more careful examination reveals that the rate does not extrapolate to zero for zero concentration of hydrogen ion or of iodide. Figure 1 reports plots of the rates corresponding to the runs from 8 to 14, from 17 to 20, and from 21 to 24, against the iodide concentration. The intercepts of the straight lines correspond to the rates in the absence of iodide. Figure 2 reports the rates cor-

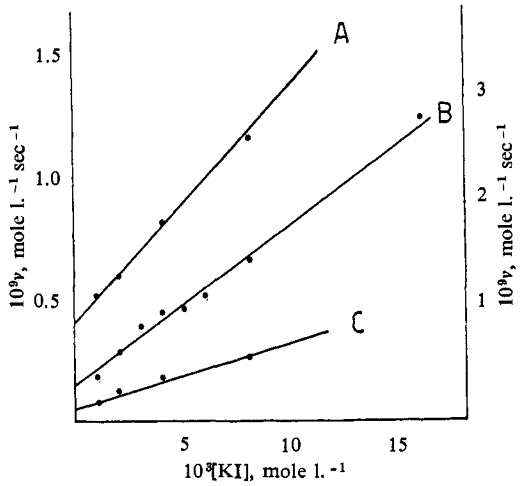

Figure 1. Reaction rates as a function of the iodide concentration for different peroxydiphosphate and hydrogen ion concentrations: (A) $10^3[H_2P_2O_8^{2-}] = 0.489$, $10^3[H^+] = 18.99$; (B) $10^3[H_2P_2O_8^{2-}] = 0.985$, $10^3[H^+] = 3.01$; (C) $10^3[H_2P_2O_8^{2-}] = 0.488$, $10^3[H^+] = 1.511$ (left scale, lines B and C; right scale, line A).

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(4) F. Fichter and E. Gutzwiller, *Helv. Chim. Acta*, **11**, 323 (1928).

(5) A. Simon and H. Richter, *Z. Anorg. Allgem. Chem.*, **302**, 165 (1959).

(6) Interplanar spacings of anhydrous $Li_4P_2O_8$ can be obtained from the authors on request.

(7) M. M. Crutchfield and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 3532 (1960).

(8) A. Indelli and J. E. Prue, *J. Chem. Soc.*, 107 (1959); A. Indelli, G. Nolan, and E. S. Amis, *J. Am. Chem. Soc.*, **82**, 3233 (1960).

(9) F. G. Soper and E. Williams, *Proc. Roy. Soc.* (London), **A140**, 59 (1933).

(10) J. Schmidlin and P. Massini, *Ber.*, **43**, 1162 (1910).

(11) E. Güntelberg, *Z. Physik. Chem.*, **123**, 199 (1926); E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

Table I. Initial Rates, ν (mole l.$^{-1}$ sec^{-1}), of the Reaction between Peroxydiphosphate and Iodide, at 25.0° and Ionic Strength 0.1

N	$10^3C_{HClO_4}{}^a$	$10^3C_{KI}{}^a$	$10^3C_{K_4P_2O_8}{}^a$	$10^3[H_2P_2O_8{}^{2-}]^a$	$10^3[H^+]^a$	$10^9\nu$
1	2.5	8	1	0.940	0.559	0.25
2	10	8	1	0.987	8.00	1.71
3	20	8	1	0.979	17.98	4.7
4	22	8	1	0.977	19.98	4.9
5	40	8	1	0.960	38.0	13.4
6	24	8	2	1.954	19.96	9.2
7	26	8	3	2.93	19.95	13.2
8	5	1	1	0.985	3.01	0.18
9	5	2	1	0.985	3.01	0.27
10	5	3	1	0.985	3.01	0.39
11	5	4	1	0.985	3.01	0.43
12	5	5	1	0.985	3.01	0.45
13	5	6	1	0.985	3.01	0.50
14	5	8	1	0.985	3.01	0.65
15	5	16	1	0.985	3.01	1.22
16	5	32	1	0.985	3.01	2.5
17	2.5	1	0.5	0.488	1.511	0.073
18	2.5	2	0.5	0.488	1.511	0.120
19	2.5	4	0.5	0.488	1.511	0.170
20	2.5	8	0.5	0.488	1.511	0.25
21	20	1	0.5	0.489	18.99	1.16
22	20	2	0.5	0.489	18.99	1.33
23	20	4	0.5	0.489	18.99	1.84
24	20	8	0.5	0.489	18.99	2.63
25	5	8	0.5	0.493	4.00	0.50
26	11	8	0.5	0.498	10.00	1.09
27	20	8	0.125	0.1222	19.75	0.78
28	20	8	0.25	0.244	19.50	1.42
29	8	16	4	3.64	0.360	1.14
30	4	16	2	1.749	0.250	0.45
31	5	8	0.25	0.247	4.50	0.39
32	5	8	2	1.933	1.062	0.65
33	3.5	16	2	1.414	0.086	0.37

[a] C_{XX}'s indicate the stoichiometrical concentrations of the added substances, whereas the [X]'s indicate the concentrations of the various species, taking into account the equilibria. $C_{KI} = [I^-]$.

responding to runs 1–4, 14, and to runs 20, 24–26 against the hydrogen ion concentration, and, in this case too, an intercept definitely positive is observed.

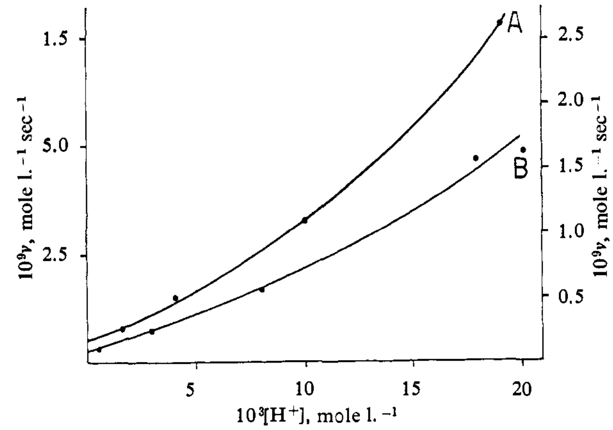

Figure 2. Reaction rates as a function of the hydrogen ion concentration for different peroxydiphosphate concentrations, $10^3C_{KI} = 8$: (A) $10^3[H_2P_2O_8{}^{2-}] \cong 0.49$; (B) $10^3[H_2P_2O_8{}^{2-}] = 0.98$ (left scale, curve B; right scale, curve A).

The reaction between peroxydiphosphate and iodide takes place, therefore, through at least three different paths, which, as a first approximation, can all be considered dependent upon the first power of the $H_2P_2O_8{}^{2-}$ concentration. Accordingly we have made a statistical analysis of the data of Table I, by minimizing the function

$$\Sigma\left(1 - k_1\frac{[H^+][H_2P_2O_8{}^{2-}][I^-]}{\nu} - k_2\frac{[H^+][H_2P_2O_8{}^{2-}]}{\nu} - k_3\frac{[H_2P_2O_8{}^{2-}][I^-]}{\nu}\right)^2 \quad (2)$$

This treatment corresponds to the assumption that the rate is given by the equation

$$\nu = k_1[H^+][H_2P_2O_8{}^{2-}][I^-] + k_2[H^+][H_2P_2O_8{}^{2-}] + k_3[H_2P_2O_8{}^{2-}][I^-] \quad (3)$$

and to the assumption that the relative error in the determination of the reaction rates is almost independent upon the reactants concentrations and upon the reaction rate.[12] For k_1, k_2, and k_3 the following values are obtained: $k_1 = 0.021$ l.^{2} mole^{-2} sec^{-1}; $10^3k_2 = 0.06$ l. mole^{-1} sec^{-1}; $10^3k_3 = 0.01$ l. mole^{-1} sec^{-1}. Introducing these constants and the relevant concentrations in eq 3, the experimental reaction rates are approximately reproduced, with a mean-square deviation of about 20%. This result is considered satisfactory in view of the large changes in the concentrations of the

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(12) Neither of these assumptions is rigorously correct. The orders with respect to $H_2P_2O_8{}^{-2}$ (see below) and to H^+ are not exactly 1.0. In fact, the points of Figure 2 are not on straight lines but on curves, and the addition of the point corresponding to run 5 (omitted for space reasons) would emphasize this fact. Moreover, the difficulties in measuring reaction rates very high and very low are much greater than for intermediate ones. The accuracy of the data does not seem to warrant the remarkable amount of work that a more correct statistical treatment would involve. Anyway, the results obtained from eq 2 can be considered as significant, even though a perfect agreement of eq 3 with the experimental data cannot be expected.

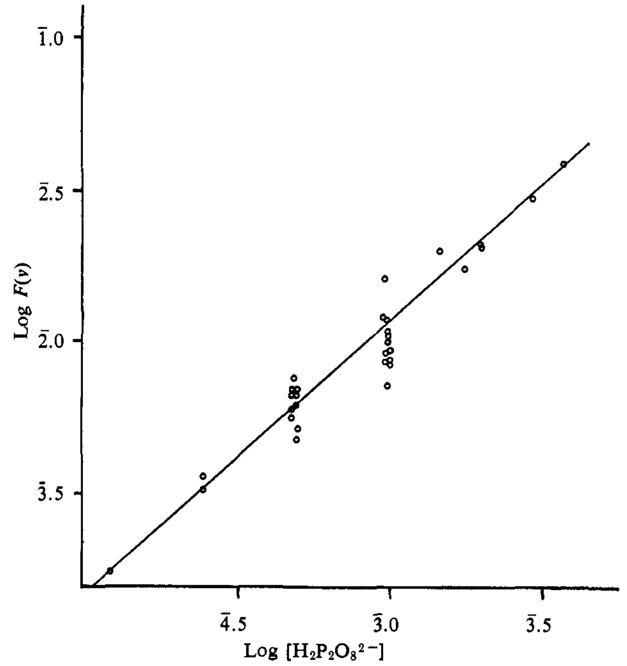

Figure 3. Reaction order with respect to $H_2P_2O_8^{2-}$.

reactants. It indicates, however, that eq 3 is not exact, and this is confirmed by the systematic character of the deviations.

Figure 3 reports a plot of log $F(v)$, defined as

$$F(v) = v/(2[I^-][H^+] + 6 \times 10^{-3}[H^+] + 10^{-3}[I^-]) \quad (4)$$

against log $[H_2P_2O_8^{2-}]$. All the points lie around a straight line, whose slope, however, indicates an order with respect to the peroxydiphosphate ion of 0.88 instead of 1.0.

An analogous statistical treatment of the results based on the equation

$$v = k_1' [H^+][H_2P_2O_8^{2-}][I^-] + k_2[H^+][H_2P_2O_8^{2-}] \quad (5)$$

gives not very different parameters; that is, $k_1' = 0.025$ l.^{2} mole^{-2} sec^{-1}; $10^3k_2' = 0.058$ l. mole^{-1} sec^{-1}. These values, introduced in eq 5, give a mean-square deviation larger than that obtained from eq 3. Moreover, when the hydrogen ion concentration is very low (runs 1, 29, 30, 33), the differences from the experimental results become very large.

We have confirmed in other ways the existence of reaction paths independent of the concentrations of I^- and H^+, respectively. We have measured the rate of the reaction of peroxydiphosphate to give peroxymonophosphate in acid media. The latter oxidizes instantaneously the iodide ion.[1,3] The results are reported in Figure 4 as amounts of liberated iodine against time, and in Table II. The rate constants k_2 are calculated on the assumption that the rate is first order with respect to the peroxydiphosphate and first order with respect to the hydrogen ion. At the lowest acid concentrations, which are not far from the ones prevailing in Table I, k_2 is in agreement with the value obtained in the presence of iodide. There is, however, a clear drift that indicates that the order with respect to the hydrogen ion is almost two, rather than one. A comparison is also possible with the results obtained by Crutchfield in a wide range of pH in buffered solutions.[13] By interpolation it can be seen that the two sets of data agree to better than a factor of 2. This agreement can be considered satisfactory, in view of the differences in conditions.

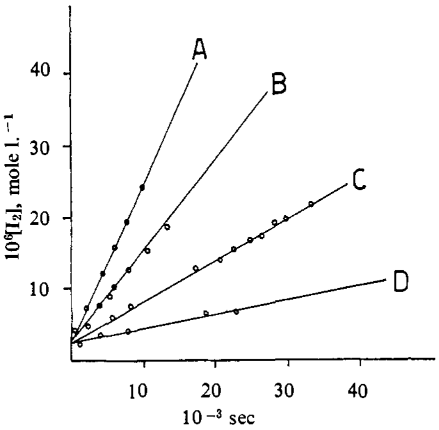

Figure 4. Reaction rates of peroxydiphosphate in acid media in the absence of iodide, $10^3C_{HClO_4}$: (A) 40; (B) 30; (C) 20; (D) 10 mole l.$^{-1}$.

Table II. Initial Reaction Rates, v (mole l.$^{-1}$ sec^{-1}), and Second-Order Rate Constants, k_2 (l. mole^{-1} sec^{-1}), for the Reaction of Peroxydiphosphate in Acid Media, at 25° and at Ionic Strength 0.1

N	$10^3 C_{HClO_4}$	$10^3 C_{K_4P_2O_8}$	$10^3[H_2P_2O_8^{2-}]$	$10^3[H^+]$	10^9v	10^3k_2
34	10	0.5	0.493	9.00	0.20	0.046
35	20	0.5	0.489	18.99	0.58	0.063
36	30	0.5	0.484	28.98	1.25	0.09
37	40	0.5	0.479	38.98	2.2	0.12

We have tested the existence of a reaction path independent of the hydrogen ion concentration by using the salt effects. According to the Brønsted theory,[14] the rate constants k_1, k_2, and k_3 should depend upon the activity coefficients, f_i, of species of charge i according to the equations

$$\log k_1 = \log k_1^0 + \log \frac{f_1 f_1 f_2}{f_2} = \log k_1^0 + 2 \log f_1 \quad (6)$$

$$\log k_2 = \log k_2^0 + \log \frac{f_1 f_2}{f_1} = \log k_2^0 + \log f_2 \quad (7)$$

$$\log k_3 = \log k_3^0 + \log \frac{f_1 f_2}{f_3} \quad (8)$$

We should expect, therefore, that k_1 and k_2 decrease when increasing the ionic strength of the solution, whereas k_3 should increase. Since k_3 corresponds to a reaction between two anions, it should increase strongly in the presence of multivalent cations.[15] These predictions could be verified by making runs

[13] M. M. Crutchfield in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience, John Wiley and Sons, Inc., New York, N. Y., 1962, p 41. Thanks are due to one of the referees for having called our attention to this important book.

[14] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p 124.

[15] G. Scatchard, National Bureau of Standards Circular No. 134, U. S. Government Printing Office, Washington, D. C., 1953, p 185; V. K. LaMer and R. W. Fessenden, *J. Am. Chem. Soc.*, 54, 2351 (1932).

under such conditions that the terms in k_1 and k_2, or, respectively, the term in k_3, are predominant.

Most of the runs reported in Table I correspond to a strong preponderance of the terms in k_1 and k_2, with the exception of runs 29, 30, and 33, where the hydrogen ion concentration is small enough for the term in k_3 to predominate. We have made runs, therefore, with the same reactant concentrations as in run 30, but with no $KClO_4$, in the presence and in the absence of $Ca(NO_3)_2$ and of $Ba(NO_3)_2$. The results, together with others corresponding to a predominance of the terms in k_1 and k_2, are reported in Table III. The addition of $KClO_4$ has little influence if the acidity is low (compare run 38 of Table III with run 30 of Table I), whereas it produces a remarkable decrease if the acidity is high (compare run 39 of Table III with run 24 of Table I). The effect of the barium and calcium nitrate is also in the predicted direction, but with much greater evidence (compare run 38 with runs 40–43, and run 39 with runs 44–47).

Table III. Initial Rates, ν (mole l.$^{-1}$ sec^{-1}), of the Reaction between Peroxydiphosphate and Iodide at 25.0° at Variable Ionic Strength

N	10^3 C_{HClO_4}	10^3 C_{KI}	10^3 $C_{K_4P_2O_8}$	$C_{Ca(NO_3)_2}$	$C_{Ba(NO_3)_2}$	$10^9\nu$
38	4	16	2	...	...	0.46
39	20	8	0.5	...	...	3.2
40	4	16	2	0.05	...	0.98
41	4	16	2	...	0.05	1.06
42	4	16	2	0.10	...	1.23
43	4	16	2	...	0.10	1.34
44	20	8	0.5	0.05	...	2.17
45	20	8	0.5	...	0.05	2.15
46	20	8	0.5	0.10	...	2.15
47	20	8	0.5	...	0.10	2.19

Discussion

The composition of the main activated complexes of the reaction of peroxydiphosphate with iodide in acid media, is, therefore, neglecting the molecules of water, $H_3P_2O_8I^{2-}$, $H_3P_2O_8^-$ and $H_4P_2O_8$, and $H_2P_2O_8I^{3-}$. The latter corresponds almost exactly to the only activated complex which can be observed in the reaction of peroxydisulfate with iodide ions. For this reaction the following mechanism has been proposed.[16]

$$S_2O_8^{2-} + I^- \longrightarrow S_2O_8I^{3-} \longrightarrow I^+ + 2SO_4^{2-} \qquad (9)$$

$$I^+ + I^- \longrightarrow I_2 \quad \text{very fast} \qquad (10)$$

Analogous mechanisms can be assumed for the reaction of peroxydiphosphate, namely

$$H^+ + H_2P_2O_8^{2-} \rightleftharpoons H_3P_2O_8^- \qquad (11)$$

$$H_3P_2O_8^- + I^- \longrightarrow H_3P_2O_8I^{2-} \longrightarrow HPO_4^{2-} + H_2PO_4^- + I^+ \qquad (12)$$

and

$$H_2P_2O_8^{2-} + I^- \longrightarrow H_2P_2O_8I^{3-} \longrightarrow 2HPO_4^{2-} + I^+ \qquad (13)$$

Moreover, there are the reactions

$$H_3P_2O_8^- + H_2O \longrightarrow H_2PO_4^- + H_2PO_5^- + H^+ \qquad (14)$$

$$H_2PO_5^- + I^- + 2H^+ \longrightarrow H_2PO_4^- + I^+ + H_2O \quad \text{very fast} \qquad (15)$$

and analogous ones starting from $H_4P_2O_8$. The equilibrium constant of reaction 11 is about 1.0 at ionic strength 0.1, so that the rate constant of reaction 12 is about 2000 times greater than that of reaction 13.

One reason of this difference in rate is certainly the smaller electrostatic repulsion[17] that there is between two ions both of charge -1, in comparison with the repulsion between an ion of charge -2 and an ion of charge -1. A more careful examination, however, shows that this cannot be the only reason and not even the most important one. The effect of the electrostatic repulsion on the reaction rate is expressed by a factor

$$\exp(-z_1z_2\epsilon^2/DrKT) \qquad (16)$$

where z_1 and z_2 are the charges of the ions, ϵ is the charge of the electron, D is the dielectric constant, r is the reaction distance between the two ions, K is the Boltzmann constant, and T is the absolute temperature. The difference between the logarithms of the rate constants of reactions 12 and 13 should, therefore, be given by[18]

$$\log k_1 - \log k_3 = \frac{0.4343\epsilon^2}{DKT}\left(\frac{2}{r_3} - \frac{1}{r_1}\right) \qquad (17)$$

where r_1 and r_3 correspond to reactions 12 and 13. If the r values are expressed in Å, and the numerical values for the various constants are introduced, one obtains

$$\log k_1/k_3 = 3.11(2/r_3 - 1/r_1) \qquad (18)$$

To account for a ratio k_1/k_3 of 2000, the r values should be less than 1 Å, if they are about equal. Even assuming that r_1 is much larger than r_3, the latter cannot be larger than 1.88 Å. This appears unreasonable, because the ionic radius of I^- is 2.19 Å,[19] and the ionic radii of PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ are all approximately 2.9 Å.[20] Assuming a value of about 5 Å for the r values, the diminution of electrostatic repulsion accounts for a ratio k_1/k_3 of about 4.[21]

A nonelectrostatic effect[22] is clearly involved in this case too. The change in hydration of the reactants and of the activated complex[23] between reactions 12 and 13 is probably important, and its effect is expected to produce a more negative activation entropy in reaction 13, because of the greater charge concentration. The polarizing effect of the proton[24] on the peroxydiphosphate anion should also favor the electron transfer from the iodide ion. We think, however, that another factor of primary importance is the tendency of all phosphorus oxyacids to liberate only one proton for each phosphorus atom. In fact HPO_4^{2-}, $HP_2O_7^{3-}$, $HP_2O_8^{3-}$, $HP_3O_{10}^{4-}$, and $HP_4O_{13}^{5-}$ are all rather strong bases, whereas $H_2PO_4^-$, $H_2P_2O_7^{2-}$, $H_2P_2O_8^{2-}$, $H_2P_3O_{10}^{3-}$, $H_2P_4O_{13}^{4-}$, $P_3O_9^{3-}$, and $P_4O_{12}^{4-}$ are all very weak bases.[25]

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[16] H. Galiba, L. J. Csanyi, and Z. G. Szabò, *Z. Anorg. Allgem. Chem.*, **287**, 169 (1956); for a review see also ref 3.

[17] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd ed, Clarendon Press, Oxford, 1947, p 83.

[18] A. Indelli, *Ann. Chim.* (Rome), **46**, 717 (1956).

[19] J. A. A. Ketelaar, "Chemical Constitution," 2nd ed, Elsevier Publishing Co., Amsterdam, 1958, p 28.

[20] J. R. Van Wazer, "Phosphorus and its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, p 58.

[21] Equations 16, 17, and 18 are strictly valid only at the limit of zero ionic strength. However, the change, if any, in k_1/k_3 in passing from ionic strength 0.00 to 0.10, should be in the sense of a decrease, because the kinetic salt effect is greater for k_3 than for k_1.

[22] A. Indelli and E. S. Amis, *J. Am. Chem. Soc.*, **82**, 332 (1960).

[23] B. Perlmutter-Hayman and G. Stein, *J. Chem. Phys.*, 40, 848 (1964).

[24] A. Indelli and G. C. Guaraldi, *J. Chem. Soc.*, 36 (1964).

[25] See ref 20, p 459.

Each tetrahedral unit PO_4, therefore, has the tendency to have only one negative charge in aqueous solution, each additional charge being easily neutralized by a proton. During reaction 12 the iodide ion must lose two electrons, and in the activated complex, which is about in the middle of the reaction path,[26] about one electron must have been transferred to the peroxydiphosphate ion. The two negative charges of the complex $H_3P_2O_8I^{2-}$ will belong almost entirely to the two PO_4 units, conferring to the activated complex a relative stability, which corresponds to a high reaction rate.

In the case of peroxydisulfate, on the contrary, the tendency to have only one negative charge for each sulfur atom is not remarkable. In fact SO_4^{2-} is almost as weak a base as $P_3O_9^{3-}$ or $P_4O_{12}^{4-}$,[27] and much weaker than HPO_4^{2-}. Accordingly, the effect of the hydrogen ions in the reaction peroxydisulfate–iodide is merely a salt effect, and is even smaller than the effect of the alkali metal ions.[28]

On the other hand, acid catalysis is operating in many reactions of the peroxides, which Edwards considers as nucleophilic substitutions.[29] Edwards attributes the effect of the protonation to the lesser basicity of the leaving group, and this also is a nonelectrostatic effect. The reasons given by Edwards are difficult to compare directly with the ones presented above, because of the difference in the ways to look at the mechanism of the reactions of the peroxides, but they do not seem to be totally different.

The salt effects on reaction 13 are remarkably small. Despite the fact that under the conditions of run 30 over 60% of the reaction takes place through reaction 13, no decrease in rate is observed when the same run is performed in the absence of $KClO_4$ (run 38). Apparently the negative salt effect on equilibrium 11 is sufficient to compensate for the positive salt effect on reaction 13. According to the Brønsted–Debye limiting law it should not be. Only in the presence of calcium and barium ions is the positive salt effect clearly visible, although it is not as great as in other cases reported in the literature.[15] Examples of rather small salt effects in reactions between anions have already been studied, usually when large ions are involved.[30] The accelerating effect of the barium ions is slightly superior to that of the calcium ions. Barium ions are often more effective than calcium ion,[31] but there are instances in which the reverse is true.[30a,32]

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(26) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 10.

(27) C. W. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952); C. W. Davies and C. B. Monk, *J. Chem. Soc.*, 413 (1949); A. Indelli and G. Mantovani, *Trans. Faraday Soc.*, **61**, 909 (1965).

(28) W. J. Howells, *J. Chem. Soc.*, 463 (1939).

(29) J. O. Edwards, see ref 13, p 67.

(30) (a) J. I. Hoppé and J. E. Prue, *J. Chem. Soc.*, 1775 (1957); (b) A. Indelli and G. Saglietto, *Trans. Faraday Soc.*, **58**, 1033 (1962); (c) A. Indelli, *ibid.*, **59**, 1827 (1963).

(31) See, for instance, V. Carassiti and C. Dejak, *Boll. Sci. Fac. Chim. Ind. Bologna*, **15**, 63 (1957).

(32) B. Holmberg, *Z. Physik. Chem.*, **79**, 147 (1912); A. Indelli and A. Giacomelli, *Ann. Chim.* (Rome), **55**, 170 (1965).

Mass Spectrometric Investigation of the Pyrolysis of Boranes. Tetraborane(10)[1]

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Abstract: The intermediates produced in the pyrolysis of $^{n}B_4H_{10}$ were studied with an "integral furnace" mass spectrometer with reactor temperatures between 10 and 285°. The reactor pressure of B_4H_{10} was *ca.* $10^{-5.2}$ atm. B_4H_8 was identified as an intermediate produced in the pyrolysis. Diborane as well as a combination of pentaboranes (B_5H_9 and B_5H_{11}), hexaborane, a combination of heptaboranes, octaborane, decaborane, and possibly nonaborane also were observed. Monoborane and triborane were not observed, but quantities small compared to B_4H_8 could not be excluded.

There have been many studies to elucidate the pyrolysis mechanism of diborane and, in particular, the steps involving tetraborane(10).[2-4] The copyrolysis of B_4H_{10} and B_2H_6 was studied by Pearson and Edwards[5] who suggested that B_4H_{10} decomposes by two simultaneous first-order reactions which yield B_3H_7 and B_4H_8, respectively. The triborane(7) was postulated to react with hydrogen to give diborane.

Dupont and Schaeffer[6] proposed the following two-step reaction for the formation of pentaborane(11)

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(3) R. M. Adams, in "Boron, Metallo-Boron Compounds and Boranes," Interscience Publishers, Inc., New York, N. Y., 1964, p 507 ff.

(4) Reference 3, p 576, in reference to an article by T. W. Clapper, AFN, Inc., Los Angeles, Calif., Technical Report NR ASD-TDR-62-1025, Vol. II, June 1962.

(5) R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p 15N.

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