It is to be concluded that the photochemical stability possessed by an unsaturated carbonyl compound extends to both type I and type II processes. The determination of the exact role of the double bond in the photochemistry of these compounds must await further experimental work.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Kinetics of the Oxidation of Halide Ions by Monosubstituted Peroxides

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The kinetics of some halide ion oxidations by peroxyacids have been investigated. The reaction of bromide ion with peroxymonosulfate has the rate law $R = k[Br^-][HSO_5^-]$ with a rate constant of 1.04 l. mole^{-1}-sec.$^{-1}$ at 25° and $\mu = 0.2$. The activation energy and entropy were found to be 10.6 kcal. mole^{-1} and -24.8 cal. mole^{-1}-deg.$^{-1}$, respectively. The oxidation of chloride ion by peroxymonosulfate has an analogous rate law and a rate constant of 1.4×10^{-3} l. mole^{-1}-sec.$^{-1}$. The activation energy and entropy were found to be 14.6 kcal. mole^{-1} and -24.1 cal. mole^{-1}-deg.$^{-1}$, respectively. The oxidation of bromide ion by peroxyacetic acid has the rate law $R = k[CH_3CO_3H][Br^-]$ with a rate constant of 0.258 l. mole^{-1}-sec.$^{-1}$ at 25° and $\mu = 0.2$; the activation energy and entropy are 13.7 kcal. mole^{-1} and -17.4 cal. mole^{-1}-deg.$^{-1}$, respectively. Peroxymonophosphoric acid oxidizes bromide ion with a rate which is first order each in peroxide concentration and in bromide ion concentration. The reaction was found to have an unusual pH dependence which has been interpreted in terms of the rate law $R = k_1[H_2PO_5^-][Br^-] + k_2[H_2PO_5^-][Br^-][H^+]$ and of the second ionization equilibrium constant K_2 of peroxymonophosphoric acid. Values of k_1, k_2, K_2 were found to be 3.2×10^{-2} l. mole^{-1}-sec.$^{-1}$, 9 l.^{2} moles^{-2}-sec.$^{-1}$ and 1.4×10^{-5}, respectively at $\mu = 1.5$ and 25°. Mechanistic conclusions are drawn.

Introduction

Caro's acid (peroxymonosulfuric acid) and the phosphorus analog have been long known, but until recently there have been few studies made of their chemistries, especially of the kinetics and mechanisms of reactions. Preliminary observations made in this Laboratory indicated that Caro's acid oxidizes halide ions to free halogens at markedly different rates. The reaction is "instantaneous" with iodide ion, rapid with bromide ion and slow with chloride ion.[1] The present study was undertaken to elucidate the kinetics and mechanism of the reaction of Caro's acid with halide ions and also to find out about the related reactions of peroxymonophosphoric acid and peroxyacetic acid with halide ions.

Experimental

Equipment. Bromide Oxidations.—Because the half-lives of these three oxidation reactions were less than a minute in the dilute solution ranges used here, the reaction was followed colorimetrically by measuring the absorption of bromine produced. A modified Bausch and Lomb "Spectronic 20" spectrophotometer equipped with a manual shutter and a special thermostated absorption cell was used. The absorption cell was a piece of 13 mm. outside diameter Pyrex glass tubing with a 25 mm. outside diameter Pyrex glass water jacket. Two brass endplates centered the inner tube in the jacket and provided an inlet and outlet for the filtered water, which was circulated to maintain constant temperature. The inner tube extended beyond the outer tube in both directions. The top was open to receive the sample and the bottom was connected to a short piece of Tygon tubing closed with a pinch clamp. The exposed portions of the jacket were painted black to eliminate stray light.

A 400-ml. beaker equipped with a Teflon plug stopcock at the bottom and surrounded by copper cooling coils to maintain constant temperature was used as the mixing vessel. The reactants were thoroughly mixed with a glass stirrer as the peroxyacid solution was added from a 1.5-ml. syringe held above the beaker by a holder constructed so that ejection of peroxide occurred simultaneously with starting of a stopwatch.

Caro's Acid-chloride.—This reaction was followed by determining the concentration of Caro's acid iodometrically in acid solution with standard sodium thiosulfate solution. A glass reaction vessel was assembled and immersed in a constant temperature bath. Nitrogen saturated with water vapor at the reaction temperature was continuously bubbled through the vessel in order to flush the liberated chlorine from the system.

Materials.—Laboratory distilled water and reagent grade chemicals were used except where otherwise specified. Caro's acid was prepared by treating BECCO 98% hydrogen peroxide with freshly distilled practical grade chlorosulfonic acid. With some modification in technique this is the method used by Ball.[2] The Caro's acid was diluted with cold water in a special ground glass stoppered mixing flask. When tested with silver nitrate the Caro's acid was found to be essentially free from chloride ion. Potassium dihydrogen phosphate-sulfuric acid buffers were used in the pH range 1 to 3 and potassium monohydrogen phosphate-potassium dihydrogen phosphate buffers at pH 5 to 6 for the Caro's acid oxidations.

The buffers employed in the peroxymonophosphoric acid reaction are listed in the table of rate data for this reaction. The peroxymonophosphoric acid solutions were made by acid hydrolysis of lithium peroxydiphosphate, $Li_4P_2O_8{\cdot}4H_2O$; the hydrolysis was stopped by dilution at the time calibrated for maximum yield of the monosubstituted peroxide. For the chloride oxidation, solutions of potassium chloride (2.00 M) and potassium nitrate (2.00 M) were prepared by diluting weighed samples of salt with the appropriate buffer solutions.

Peroxyacetic acid solutions were prepared by diluting BECCO 40% peroxyacetic acid with appropriate buffers. Solutions of sodium bromide (0.100 M) and sodium nitrate (0.100 M) were prepared in the same manner as before.

Procedure. Bromide Oxidations.—Preliminary studies were made to determine a procedure and concentrations of reactants that would give optimum results with the equipment. If the concentration of either reactant was too high the reaction proceeded too fast ($t_{1/2} < 15$ seconds). If the concentration of bromide ion was too low or if the concentration of peroxyacid was high, an appreciable fraction of the bromide ion was consumed. A very low concentra-

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[1] J. Girard and R. Carlson, unpublished experiments, Brown University.

[2] (a) D. L. Ball and J. O. Edwards, THIS JOURNAL, **78**, 1125 (1956); *J. Phys. Chem.*, **62**, 343 (1958); (b) D. H. Fortnum, Ph.D. Thesis, Brown University, 1958, p. 47.

tion of peroxide produced too little bromine for accurate measurement of the change in optical density. It was found that satisfactory runs could be made with bromide ion concentrations between 0.0049 and 0.0595 *M*, and initial Caro's acid concentrations between 0.000128 and 0.00231 *M*. Similar concentration ranges were chosen for the peroxymonophosphoric acid and peroxyacetic acid oxidations.

A known volume containing buffer solution and bromide solution at the desired temperature was placed in the mixing beaker. The glass syringe was filled with dilute peroxyacid solution. The acid was ejected from the syringe into the bromide and buffer solution which was being stirred rapidly. Check experiments showed that mixing was achieved within one second. Some of this reaction mixture then was admitted to the absorption cell, the first few ml. being used to rinse the cell. Readings of transmittance were taken at regular intervals, usually ten seconds. However, the first reading was not taken until twenty seconds after the start of the reaction because of the time consumed in admitting the sample and rinsing the cell.

Optical densities were measured at 400 mμ because extinction coefficients for both Br_3^- and Br_2 are known at this wave length.[3] Calculations of total bromine concentration were made using these values and the equilibrium constant[3] for the dissociation of tribromide ion. For all measurements made with the same absorption cell at constant bromide ion concentration, the total bromide concentration is given by

$$[Br_2]_{total} = ZD$$

where D is the optical density and Z is a constant depending upon cell length and bromide ion concentration. At any time, the peroxyacid concentration is proportional to the difference between the final optical density D_∞ and the optical density at the specified time D_t

$$[\text{Peroxyacid}]_t = Z(D_\infty - D_t)$$

In any one run, the *p*H remained constant and bromide ion was in large excess.

Chloride Oxidations.—A Caro's acid solution of known concentration (*ca.* 0.1 *M*) was prepared by diluting concentrated Caro's acid with buffer solution. This solution was allowed to stand at room temperature until a constant titer was obtained (usually 2 hr.). Varying volumes of potassium chloride and potassium nitrate totalling ten ml. in all were mixed and added to exactly 50 ml. of dilute Caro's acid solution. The KNO_3 was used so that the concentration of chloride ion could be varied at constant ionic strength. Five-ml. aliquots were withdrawn from the reaction vessel at appropriate intervals and diluted with an excess of 1.0 *M* potassium iodide solution. The aliquots were titrated with sodium thiosulfate solution.

Results

Caro's Acid and Bromide Ion.—The data for a typical kinetic run are given in Table I. The time and transmittance values are from the experiment, and the optical density was obtained from the logarithm of the transmittance. It is possible using the known extinction coefficients of bromine and tribromide ion to calculate the concentration of Caro's acid present at each point; such was done for several of the runs; however, the usual method (plots of log $(D_\infty - D_t)$ against time) for determination of the rate constant was quicker while giving the same result.

The initial experiments at 25° and μ = 0.2 showed that the rate was first order in Caro's acid concentration when bromide ion was in large excess; first-order plots gave good straight lines over as many as four half-lives. The first-order rate slopes m were found to be independent of Caro's acid concentration as may be seen in the data of Table II. A number of runs were made at different bromide ion concentrations (always in excess) and it was found that the plot of log m against log bromide concentration had a slope of 1.03, from which it was concluded that the order is one.

TABLE I

SAMPLE OF DATA COLLECTED DURING A TYPICAL KINETICS RUN

*p*H 2.67, μ = 0.20, 25.0°, and average $[Br^-]$ = 0.0232. Calculated values are m = 0.0104 sec.$^{-1}$ and k = 1.03 l. mole^{-1} sec.$^{-1}$

Time, sec.	T[a]	$[Br_2]$[b]	$[HSO_5^-]$[b]
0	100.0	0.00000	0.00101
20	77.2	.00040	.00061
30	71.3	.00053	.00048
40	66.7	.00063	.00038
50	63.4	.00071	.00030
60	60.6	.00078	.00023
70	58.8	.00083	.00018
80	57.3	.00087	.00014
90	56.3	.00090	.00011
100	55.5	.00092	.00009
110	54.6	.00094	.00007
120	54.3	.00095	.00006
150	53.5	.00097	.00004
180	53.3	.00098	.00003
210	52.7	.00100	.00001
600	52.3	.00101	.00000
N.S.[c]	53.9	.00096[d]	....

[a] Per cent. transmittance. [b] Moles/liter. [c] New sample admitted from the beaker. [d] Value from thiosulfate titration.

Most of the runs were carried out at *p*H 2.67. It was found that variation of the *p*H to 2.30 and to 5.70 did not significantly change the rate. Thus the rate constant does not depend on hydrogen ion concentration. The overwhelmingly predominant form of Caro's acid in this *p*H range is known[2a] to be HSO_5^- The rate law for the reaction is therefore

$$-\frac{d[HSO_5^-]}{dt} = k[HSO_5^-][Br^-].$$

To determine the temperature dependence, rate data were obtained at 12.9 and 1.1° as well as 25.0°. Several values for these temperatures are also given in Table II. By least squares, the Arrhenius activation energy E_a was found to be 10.6 kcal. mole^{-1}. The enthalpy of activation ΔH^* and the entropy of activation ΔS^* were found to be 10.0 kcal. mole^{-1} and -24.8 cal. mole^{-1}-deg.$^{-1}$.

Caro's Acid and Chloride Ion.—The method of following this reaction was quite different from that used for the bromide oxidation by Caro's acid and the rate is much slower; however, the rate behavior is entirely analogous. With an excess of chloride ion, first-order plots for Caro's acid gave good straight lines and the first-order constant so obtained did not depend on the concentration of peroxide. When the chloride ion concentration was varied, the first-order rate changed to the same extent thus indicating a first-order dependence on chloride ion concentration too. Variation of *p*H (in the weakly acid range) caused no change in rate; some erratic behavior was noted, however, in acetate buffers near *p*H 5 although the rate was roughly the same.

Data for kinetic runs at various conditions of concentration, ionic strength and temperature are presented in Table III. For the reaction at ionic

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(3) H. A. Young, THIS JOURNAL, **72**, 3310 (1950).

TABLE II

CARO'S ACID AND BROMIDE ION EXPERIMENTS

$[HSO_5^-]$	$[Br^-]$	k
Group I; at 25.0° and $\mu = 0.2$		
0.00231	0.0448	1.14
.00209	.0452	1.03
.00213	.0450	1.05
.000568	.0469	1.10
.000583	.0469	1.24
.000540	.0469	1.10
.000337	.0472	1.08
.000350	.0472	1.05
.000594	.0093	1.04
.000591	.0093	0.97
.001011	.0232	1.03
.001105	.0231	1.01
.000553	.0331	1.11
.001044	.0326	1.01
.000425	.0143	0.91
.000675	.0143	.96
.000671	.0143	.99
.000679	.0093	.97
.000128	.0049	1.10
.000718	.0188	0.97
.000639	.0168	1.02
.000387	.0070	1.01
.000259	.0071	1.00
Av. $k = 1.04 \pm 0.04$ l. mole^{-1}-sec.$^{-1}$		
Group II; at 12.9° and $\mu = 0.2$		
0.000541	0.0195	0.47
.000663	.0073	.52
.000539	.0395	.47
.000483	.0595	.47
Av. $k = 0.48 \pm 0.02$ l. mole^{-1}-sec.$^{-1}$		
Group III; at 1.1° and $\mu = 0.2$		
0.000445	0.0195	0.20
.000322	.0077	.20
.000279	.0397	.24
.000472	.0396	.23
Av. $k = 0.22 \pm 0.02$ l. mole^{-1}-sec.$^{-1}$		

TABLE III

CARO'S ACID AND CHLORIDE EXPERIMENTS

$[Cl^-]$	$[HSO_5^-]$	$k \times 10^3$	*p*H
Group I; at 25.0° and $\mu = 0.5$			
0.0615	0.0064	1.80	1.23 ± 0.03
.0945	.0067	1.80	
.161	.0066	1.85	
.260	.0066	1.87	
.332	.0015	1.68	
.0604	.0079	1.62	2.86
.0606	.0073	1.77	2.44
.1595	.0081	1.73	2.92
.160	.0072	1.90	2.56
.193	.0076	1.78	2.98
.225	.0076	1.75	2.97
.253	.0072	1.97	2.55
Av. $k = (1.80 \pm 0.07) \times 10^{-3}$ l. mole^{-1}-sec.$^{-1}$			
Group II; at 25.0° and $\mu = 0.2$			
0.0172	0.0087	1.43	
.0192	.00094	1.48	
.0193	.00079	1.13	
Av. $k = (1.35 \pm 0.14) \times 10^{-3}$ l. mole^{-1}-sec.$^{-1}$			
Group III; at 35.0° and $\mu = 0.5$			
0.0590	0.0077	3.93	
.0921	.0080	4.00	
.0953	.0049	4.03	
.159	.0078	4.18	
.160	.0070	3.90	
Av. $k = (4.02 \pm 0.08) \times 10^{-3}$ l. mole^{-1}-sec.$^{-1}$			
Group IV; at 0.0° and $\mu = 0.5$			
0.327	0.0083	0.185	
.327	.0082	.187	
.328	.0081	.192	
.330	.0082	.180	
Av. $k = (0.187 \pm 0.003) \times 10^{-3}$ l. mole^{-1}-sec.$^{-1}$			

TABLE IV

VARIATION OF RATE WITH IONIC STRENGTH[a]

$[Cl^-]$	$[HSO_5^-] \times 10^3$	μ	$k \times 10^3$
0.172	8.7	0.20	1.43
.119	4.1	.25	1.47
.176	6.9	.32	1.58
.244	1.6	.38	1.68
.327	6.1	.47	1.85
.062	6.4	.52	1.80

[a] At 25°; units of k are l. mole^{-1}-sec.$^{-1}$.

strength 0.5, the values of activation enthalpy and activation entropy were found to be 14.0 kcal. mole^{-1} and -24.1 cal. mole^{-1}-deg.$^{-1}$, respectively. As expected the rate constant decreased as the ionic strength decreased; some data illustrating this point are presented in Table IV.

Peroxyacetic Acid and Bromide Ion.—In view of the similarity in rate of this reaction and that of the Caro's acid and bromide ion, the same techniques were employed. The results of the kinetic runs are presented in Table V. As indicated by the linearity of first-order plots and by the lack of dependence of rate constant on peroxide concentration, this reaction was found to be first order in peroxyacetic acid concentration. Variation in bromide ion concentration showed that the rate is first order in bromide. Thus the rate law is

$$-\frac{d[CH_3CO_3H]}{dt} = k[CH_3CO_3H][Br^-]$$

There is no evidence in Table V for any true dependence, in the sense of an order, of rate on *p*H. The kinetic data near *p*H 4.5 are, however, less reliable than at lower *p*H. In the lower section of Table V, data illustrating the fact that rate constants at higher *p*H and lower bromide ion concentration appear to be low. Further mention of this difficulty and its cause will be found in the Discussion section.

Using the k values of 0.258 and 0.0402 at 25.0 and 2.8°, respectively, it was calculated that E_a = 13.7 kcal. mole^{-1}, ΔH^* = 13.1 kcal. mole^{-1}, and ΔS^* = -17.4 cal. mole^{-1}-deg.$^{-1}$.

Peroxymonophosphoric Acid and Bromide Ion.—The kinetic data obtained for this reaction were found to depend markedly on the *p*H of the reaction mixture. Also, the presence of such materials as hydrogen peroxide and peroxydiphosphoric acid influenced the results although to a lesser extent than the *p*H. We feel therefore that the results on this reaction, while interesting and reasonable, are not as quantitatively definitive as those for the other three reactions. All of the data were obtained at 25° and an ionic strength of 1.5.

TABLE V

PEROXYACETIC ACID AND BROMIDE EXPERIMENTS

$[CH_3CO_3H] \times 10^3$	$[Br^-] \times 10^2$	pH	k
Group I; at 25.0°, $\mu = 0.2$ and low pH			
2.16	2.28	2.00	0.246
2.15	2.28	2.01	.264
2.40	2.25	(~1.7)	.271
2.50	5.72	2.07	.266
1.95	4.79	2.05	.256
2.36	4.74	0.93	.247
Av. $k = 0.258 \pm 0.011$ l. mole^{-1}-sec.$^{-1}$			
Group II; at 2.8°, $\mu = 0.2$ and low pH			
2.52	4.73	0.9	0.0400
2.52	9.70	0.9	0.0404
Av. $k = 0.0402 \pm 0.0002$ l. mole^{-1}-sec.$^{-1}$			
Group III; at 25°, $\mu = 0.2$ and high pH			
2.04	2.52	4.58	0.153
2.33	2.75	4.58	.165
2.21	3.51	4.52	.154
2.11	4.77	4.52	.168
2.33	5.74	4.57	.204
2.32	9.95	4.45	.231
0.216	10.9	4.59	.240

With bromide ion in excess, the plots of log peroxymonophosphate concentration against time were linear through a fair degree of reaction completion. Thus this reaction like the others is first order in peroxyacid concentration. The rate is also first order in bromide ion concentration as may be seen in the data of Table VI. The rate law is therefore

$$\frac{d[Br_2]}{dt} = k_{obs}[PO_5]_T[Br^-]$$

where $[PO_5]_T$ represented peroxymonophosphate in its various ionized forms and $k_{obsd.}$ is a second-order rate constant which is dependent on the pH of the solution. If log $k_{obsd.}$ is plotted against pH a sigmoid type curve is obtained. Curves of this type are found in cases where two (or more) forms of the reactants are present as a result of equilibria and where two (or more) different activated complexes contribute to the over-all rate of reaction.[4] From the knowledge that the second ionization constant for peroxymonophosphoric acid should be somewhat greater than the corresponding constant for phosphoric acid,[5] the curvature near pH 5 is expected. Above this pH, the amount of $H_2PO_5^-$ is negligible and so the rate would be expected to be first order (as observed) in hydrogen ion if $H_2PO_5^-$ is the reactive species. The fact that the rate also is first order in hydrogen ion concentration between pH 1 and 2 indicates that H_3PO_5 though not present in large percentage does contribute significantly to the rate of reaction. Using the value 1.4×10^{-5} for the second ionization constant of peroxymonophosphoric acid, the value 3.2×10^{-2} l. mole^{-1}-sec.$^{-1}$ for the constant in the rate law $R = k_1[H_2PO_5^-][Br^-]$ and the value 9 l.^{2}-mole^{-2}-sec.$^{-1}$ for the constant in the rate law $R = k_2[H_2PO_5^-][Br^-][H^+]$, the line of k_{obsd} against pH was calculated. Although the experimental error leaves something to be desired, the calculated curve follows the same general pattern as the experimental data and reasonable values for the three constants were obtained. It is thus indicated that the over-all basis for the calculation is justifiable.

TABLE VI

PEROXYMONOPHOSPHATE AND BROMIDE EXPERIMENTS

At 25.0° and $\mu = 1.5$

pH	$[Br^-]^a$	$k_{obs}{}^b$	Buffer^c	pH	$[Br^-]^a$	$k_{obs}{}^b$	Buffer^c
1.37	0.10	0.527	P	3.62	0.25	0.0419	A
1.37	.05	.508	P	3.63	.10	.0426	A
1.38	.10	.406	S	3.64	.25	.0437	A
1.38	.01	.344	P	3.64	.25	.0409	A
1.39	.35	.511	P	3.65	.50	.0448	A
1.40	.02	.512	P	3.69	.25	.0344	A
1.40	.25	.397	P	3.69	.50	.0365	A
1.66	.05	.212	S	3.69	.75	.0378	A
1.70	.25	.195	S	3.71	.35	.0339	A
1.70	.05	.175	C	3.71	.50	.0417	A
1.70	.10	.181	C	3.86	.50	.0307	A
2.08	.20	.104	P	3.89	.25	.0317	A
2.18	.10	.100	P	3.91	.35	.0285	A
2.19	.25	.0995	C	3.97	.75	.0289	A
2.19	.50	.1035	C	4.07	.25	.0262	A
2.21	.05	.0929	C	4.08	.10	.0244	A
2.24	.10	.0679	P	4.16	.35	.0250	A
2.29	.05	.0488	P	4.20	.50	.0240	A
2.31	.05	.0553	P	4.38	.01	.0240	A
2.31	.25	.0958	P	4.38	.02	.0204	A
2.31	.10	.0553	C	4.38	.05	.0215	A
2.32	.25	.0601	C	4.38	.10	.0212	A
2.37	.05	.0513	C	4.38	.25	.0228	A
2.38	.50	.0981	P	4.38	.35	.0225	A
2.38	.02	.0727	C	4.38	.60	.0233	A
2.39	.05	.0736	C	4.38	.75	.0229	A
2.52	.25	.0656	P	4.38	1.00	.0237	A
2.67	.25	.0569	C	4.39	0.50	.0228	A
2.83	.20	.0450	C	4.69	.50	.0163	A
2.83	.10	.0428	C	4.71	.35	.0165	A
2.94	.10	.0375	C	5.00	.50	.0126	A
2.99	.30	.0375	C	5.00	.60	.0132	A
3.00	.50	.0385	C	5.22	.60	.00937	A
3.04	.20	.0390	C	5.38	.50	.00772	A
3.18	.25	.0375	C	5.53	.75	.00629	A
3.19	.50	.0318	C	5.55	.50	.00580	A
3.61	.50	.0472	A	5.78	.35	.00253	A
3.62	.10	.0395	A	5.78	.50	.00244	A
				5.79	.25	.00292	A
				5.83	.60	.00231	A

[a] Moles/liter. [b] Liter mole^{-1}-sec.$^{-1}$. [c] A = acetic acid, C = chloroacetic acid, P = phosphoric acid and S = sulfuric acid.

Discussion

General Mechanism.—The observed rate laws are all of the type

$$\text{Rate} = k[\text{ROOH}][X^-]$$

wherein R may be SO_3^-, CH_3CO, PO_3H^- or PO_3H_2, and X^- may be Cl^- or Br^-. These results can be explained by the mechanism

$$\text{ROOH} + X^- \longrightarrow \text{RO}^- + \text{HOX} \quad \text{(slow)}$$

$$\text{HOX} + H^+ + X^- \longrightarrow X_2 + H_2O \quad \text{(fast)}$$

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[4] *Cf.* (a) F. S. Williamson and E. L. King, THIS JOURNAL, **79**, 5397 (1957); (b) R. K. Osterheld, *J. Phys. Chem.*, **62**, 1133 (1958).

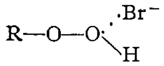
[5] Peroxyboric acid and peroxytelluric acid are stronger acids than boric acid and telluric acid, respectively. These are conclusions from thermodynamic arguments employing acid ionization constants and complexing constants for peroxide with the corresponding anions.

with the first step being rate determining. The fast second step is consistent with the observation that hypohalous acids react rapidly with halide ions in acidic solution to give halogen molecules.

The rate step appears to be a nucleophilic attack on oxygen. In addition to being the simplest mechanism that is consistent with the present experimental evidence, nucleophilic attack on peroxidic oxygens have been postulated before for similar rate laws.[6]

Orders of Reactivity.—Experiments, both qualitative and quantitative, have shown that the order of reactivity of halide ions with many peroxides is $I^- > Br^- > Cl^-$. This is the order of nucleophilic power for these anions. It is worth noting that iodide ion is about a million times more reactive in attack on oxygen than is chloride ion; when a carbon compound is the substrate, the relative kinetic reactivity is only about 250.

The rates of bromide oxidations increase in the order $H_2O_2 < H_2PO_5^- < CH_3CO_3H < HSO_5^- < H_3PO_5$. This is just about what one would expect if the activated complex has the general configuration



and if the polar influence of R plus the leaving group influence of RO^- are taken into account. If the oxygen–oxygen bond is breaking in the transition state and the anion RO^- is leaving, then the rate should decrease as the basicity of the anion increases. Such is certainly the general order of reactivity found. It is not demanded, however, because the polar effects of the groups R are not always in the same order as the basicities of RO^-. For example, peroxyacetic acid ($pK_a = 8.2$) is stronger than Caro's acid (peroxide proton $pK_a = 9.4$) even though acetic acid is about a thousandfold weaker than sulfuric acid (second ionization). On the basis of this polar influence of R, peroxyacetic acid should oxidize a nucleophile more rapidly than Caro's acid; such is not the case, thus the stability of the leaving anion is a dominant factor here. The ionization constants of H_3PO_4 and HSO_4^- are closely similar, thus the leaving group effect should be the same for H_3PO_5 and HSO_5^-; the large rate difference presumably can be attributed to the larger positive polar effect of an H_2PO_3 group as compared to a SO_3^- group. We conclude that both bond formation (between the outer peroxide oxygen and the nucleophile) and oxygen–oxygen bond breaking are taking place simultaneously in the transition state.

Influences of Impurities.—The reproducibilities of the analytical methods were such as to cause less than 5% error in rate constants for all cases here. However, larger amounts of divergence were found under some conditions, particularly in the range of *p*H from 4 to 5. The oxidations of the halide ions by hydrogen peroxide are too slow[6c] to cause any significant interference; slow rates also seem to be the case with the disubstituted peroxides and halide ions.

One side reaction did appear to be quite troublesome and hard to correct for. This is the oxidation of hydrogen peroxide (some of which is always present in peroxyacid solutions) by bromine

$$Br_2 + H_2O_2 \longrightarrow 2H^+ + 2Br^- + O_2$$

This reaction has been reported[3] to proceed by the rate law

$$R = k[H_2O_2][HOBr]$$

with a rate constant of 3.5×10^6 l. mole^{-1}-sec.$^{-1}$ at 25°. In our solutions bromine molecule is the predominant form of oxidized bromine, thus the amount of hypobromite is governed by the equilibrium reaction

$$Br_2 + H_2O \rightleftarrows HOBr + H^+ + Br^-$$

It is pertinent to note here that the hypobromous acid concentration will be inversely proportional to the bromide ion concentration and to the hydrogen ion concentration. Therefore loss of bromine by oxidation of impurity hydrogen peroxide should be more serious as the *p*H increases and the bromide ion decreases, and such a loss would result in a low rate constant. Indeed just such a situation has been observed; data exemplifying this are presented in Table V. One rate experiment on the reaction of bromine with hydrogen peroxide was carried out under conditions (*p*H 4.5, $[Br^-] = 2 \times 10^{-2}$, $[Br_2] = 5 \times 10^{-4}$, $[H_2O_2] = 5 \times 10^{-4}$ and 25°) akin to those of the halide ion oxidations by peroxyacids. The reaction was found to be too fast to measure under these conditions. At lower values of *p*H and higher bromide concentrations the hydrogen peroxide did not appear to influence the rate constants for the peroxyacid oxidations of bromide ion, but it is obvious that much of the difficulty in getting good rate data at *p*H 4 is because of the hydrogen peroxide present.

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