the solvent: if not via Equilibrium (1), then by pulling an oxide ion off a solvent molecule.

We may conclude that Jander's concepts, at least as far as thionyl compounds are concerned, are in need of modification. As has been pointed out,5 for instance, an ionization equilibrium for thionyl chloride intrinsically more likely than Equation (2) would be

$$SOC1_2 \xrightarrow{} SOC1^+ + C1^-$$
 (6)

In general it seems clear that Jander places too great emphasis on strictly ionic mechanisms for his reactions in sulfur dioxide. It seems likely that the concept of mobile oxide ions might be more fruitful for the understanding of chemical reactions in this solvent.

Having rejected the concept of the direct production of thionyl ions from thionyl compounds, we are left with an open question as to the mechanisms by which they react. We are at present planning chloride ion exchange experiments to investigate the possibility of Equilibrium (6). An O<sup>18</sup> tracer study of the thionyl chloride-sulfur dioxide exchange would be of considerable interest as a test of the possible operation of such an equilibrium as

$$SO_2 + SOCl_2 \xrightarrow{\longrightarrow} SO^{++} + SO_2Cl_2^-$$
 (7)

We are also projecting, as mentioned above, a tracer study of the potassium bromide-thionyl chloride reaction (in sulfur dioxide) which may be of considerable interest in this connection. If, as appears to be the case in this reaction, considerable activity finds its way from the thionyl chloride into the solvent, this might come about through the operation of Equilibrium (7) followed by the reaction

$$S^*O_2Cl_2^- \xrightarrow{} S^*O_2 + 2Cl^-$$

The thionyl bromide would then be formed by combination of bromide ions with the thionyl ions produced in Equilibrium (7).

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CORVALLIS, ORE.

# The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium<sup>1</sup>

### By I. M. Kolthoff and I. K. Miller<sup>2</sup>

Evidence is given that potassium persulfate decomposes thermally in aqueous solutions by two reactions, (a) a symmetrical rupture of the O-O bond to form two sulfate free-radicals which disappear by reaction with water to liberate oxygen, and (b) an acid-catalyzed reaction involving the unsymmetrical rupture of the O-O bond of the HS2O8<sup>-</sup> ion to form sulfur tetroxide an actd-catalyzed reaction involving the unsymmetrical rupture of the O-O bond of the  $HS_2O_8^-$  ion to form sulfur tetroxide and bisulfate. In dilute acid solutions sulfur tetroxide decomposes rapidly to form oxygen and sulfuric acid while in solu-tions 2 to 5 *M* in perchloric or sulfuric acid sulfur tetroxide hydrolyzes rapidly to Caro's acid ( $H_2SO_8$ ). The kinetics of the thermal decomposition of the persulfate ion are described by the equation  $-dS_2O_8^-/dt = k_1[S_2O_8^-] + k_2[H^+][S_2O_8^-]$ . The values of  $k_1$  and  $k_2$ , respectively, are  $6.0 \times 10^{-6}$  min.<sup>-1</sup> and  $3.5 \times 10^{-3}$  (min.<sup>-1</sup>)(m./1.)<sup>-1</sup> at an ionic strength of 0.4 at 50°. The activation energy for the uncatalyzed reaction is 33.5 kcal. and for the acid-catalyzed reaction 26.0 kcal. The rate of the uncatalyzed reaction is independent of ionic strength but the rate of the acid-catalyzed reaction decreases with increasing ionic strength. The oxygen liberated by the uncatalyzed reaction comes from the water while the oxygen liber-ated by the acid-catalyzed reaction comes from the persulfate ion.

Since the discovery of persulfuric acid  $(H_2S_2O_3)$ in 1878 by Berthelot,<sup>3</sup> numerous papers have appeared concerning the properties and reactions of persulfuric acid and persulfates. Elbs and Schönherr<sup>4</sup> found that persulfuric acid is unstable in aqueous solutions, decomposing in dilute sulfuric acid solutions with liberation of oxygen while in more concentrated sulfuric acid solutions hydrogen peroxide rather than oxygen is formed. The formation of monopersulfuric acid (H2SO3) by strongly acid persulfate solutions was observed by Caro<sup>5a</sup> while later work by Palme<sup>5b</sup> showed that this acid is an intermediate in the decomposition of persulfuric acid in strongly acid solutions to form hydrogen peroxide.

Thus the decomposition of persulfate in aqueous solutions involves the reactions

(1) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the synthetic rubber program of the United States Government.

(2) From a thesis submitted by I. K. Miller to the Graduate School of the University of Minnesota, 1950.

(3) M. Berthelot, Ann. chim. phys., 14, 345 (1878).

(5) (a) H. Caro, Z. angew. Chem., 845 (1898); (b) H. Palme, Z. anorg. Chem., 112, 97 (1920).

$S_2O_8 + H_2O - $	$\rightarrow 2HSO_4^-$	$+ 1/_{2}O_{2}$	(1)
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- $\begin{array}{l} H_2S_2O_8 \,+\, H_2O \longrightarrow H_2SO_5 \,+\, H_2SO_4 \\ H_2SO_5 \,+\, H_2O \longrightarrow H_2O_2 \,+\, H_2SO_4 \end{array}$ (2)
- (3)

In alkaline, neutral and dilute acid solutions persulfate decomposes according to reaction (1)while in strongly acid solutions reactions (2) and (3) occur.

Studies of the kinetics of the decomposition of the potassium and sodium salts of persulfuric acid in alkaline, neutral and dilute acid solutions were first made by Levi and Migliorini<sup>6</sup> and later by Green and Masson<sup>7</sup> and by Kailan and co-workers.<sup>8</sup> There is general agreement among these workers that persulfate decomposition in aqueous solutions is first order and that the reaction is catalyzed by hydrogen ion. Since the data in the literature are not adequate to make possible a quantitative treatment of the influence of hydrogen ion on the rate of persulfate decomposition in aqueous solutions, the kinetics of the reaction have been reinvestigated in more detail.

(6) M. G. Levi and E. Migliorini, Gazs. chim. ital., 36, II, 599 (1906).

(7) L. Green and O. Masson, J. Chem. Soc., 97, 2083 (1910).

(8) A. Kailan and L. Olbrich, Wien. Akad. Ber., IIb 135, 423 (1926).

<sup>(4)</sup> K. Elbs and O. Schönherr, Z. Elektrochem., 1, 468 (1895).

There is considerable evidence that sulfate free radicals (SO<sub>4</sub> $\overline{\phantom{\cdot}}$ ) are formed by the thermal decomposition of persulfate in neutral and alkaline solutions according to the mechanism proposed by Bartlett.<sup>9</sup> Smith<sup>10</sup> and also Bartlett<sup>11</sup> have shown that sulfate groups are introduced into certain monomers when persulfate is used to initiate vinyl polymerization in emulsion systems.

No mechanism is proposed in the literature for the acid-catalyzed decomposition of persulfate in aqueous solutions.

A detailed investigation of the kinetics of the reaction and also tracer studies using water enriched with  $H_2O^{18}$  to determine the source of the liberated oxygen have been made to provide evidence for the mechanism of the thermal decomposition of the persulfate ion.

#### Experimental

**Materials.**—Merck and Co., Inc. potassium persulfate was recrystallized twice from conductivity water and dried at room temperature in a vacuum desiccator. The salts used in preparation of the various buffer solutions were reagent grade chemicals. Merck and Co., Inc., 60% perchloric and Bakers 85% phosphoric acids were used. The H<sub>2</sub>O<sup>18</sup> enriched water was obtained from the Stuart Oxygen Company and was distilled first from alkaline permanganate



Fig. 1.—The influence of pH on the rate of decomposition of persulfate at 50° (0.01 *M* K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): O, *p*H 13.0;  $\bullet$ , *p*H 10.0; O<sup>-</sup>, *p*H 7.0;  $\ominus$ , *p*H 1.50.



Fig. 2.—The influence of pH on the rate of decomposition of persulfate at 50° (0.01 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>): O, pH 3.0;  $\odot$ , pH 1.95; O-, pH 1.60;  $\ominus$ , pH 1.00.

(10) W. V. Smith and H. N. Campbell, J. Chem. Phys., 15, 338 (1947).
(11) P. D. Bartlett and K. Nozaki, J. Polymer Sci., 3, 216 (1948).

solution, then from a solution containing a trace of phosphoric acid before use. Water not enriched in  $O^{18}$  was distilled from alkaline permanganate, dilute acid and finally without any addition.

Analytical Methods.—Persulfate analyses were made by the polarographic method of Kolthoff, *et al.*,<sup>12</sup> with the slight modification that gelatin was found to be a more effective maximum suppressor than methyl red. In solutions containing persulfate, Caro's acid and hydrogen peroxide, the sum of persulfate and Caro's acid was determined polarographically, Caro's acid was determined by reaction with iodide according to the procedure of Palme<sup>5b</sup> and hydrogen peroxide was determined by titration with standard ceric sulfate.

Determination of the isotopic composition of the oxygen liberated in the tracer experiments was made with a mass spectrograph under the supervision of Professor A. O. C. Nier of the Physics Department of the University of Minnesota.

**Procedure.**—In the kinetics experiments, 100-ml. portions of persulfate and buffer solution were placed in separate vessels and brought to the desired temperature in a thermostat and then mixed. Samples were withdrawn periodically by pipet and were added to a tenfold excess of water at room temperature to practically stop the reaction. Gelatin and supporting electrolyte were then added and the solution was diluted to a known volume for the polarographic analysis.

The tracer experiments were carried out in a vessel composed of a tube of about 20-ml. capacity connected to a bulb of about 100-ml. capacity by a three-way vacuum stopcock. A 10-ml. portion of 0.1 M potassium persulfate solution con-taining the desired buffer in the H<sub>2</sub>O<sup>18</sup> enriched water was placed in the small tube and bubbled for 15 minutes with purified nitrogen to remove oxygen from the solution. The liquid was then frozen in a Dry Ice-ethanol mixture and the tube was evacuated and sealed. The tube was then immersed in a thermostat at the desired temperature for a period of time sufficient to decompose approximately half of the persulfate present, then the mixture was again frozen in the Dry Ice-ethanol mixture to remove most of the water vapor from the liberated oxygen. The large bulb was then evacuated and the dry oxygen allowed to pass into the evacuated bulb. The vessel was then attached to the mass spectrograph by means of the third outlet of the three-way stopcock and the 34/32 mass ratio for the liberated oxygen was determined.

### **Experimental Results**

Kinetics. Order of the Reaction.—The rate of decomposition of potassium persulfate (initially 0.1 M) in solution of various hydrogen ion concentrations was determined at 50°. As shown by Figs. 1 and 2, persulfate decomposition in these solutions is first order in any given experiment and the reaction is catalyzed by hydrogen ion.

The Effect of Ionic Strength.—The rate of decomposition of persulfate in 0.1 M sodium hydroxide solution and in 0.1 M perchloric acid solution in the presence of varying amounts of sodium perchlorate was determined. The first order rate constants obtained in solutions of varying ionic strength, given in Table I, show that the reaction rate in alkaline solution is not influenced by ionic strength but in 0.1 M perchloric acid solu-

#### TABLE I

Effect of Ionic Strength on the Rate of Thermal Decomposition of 0.01 M Potassium Persulfate at 50°

NaClO <sub>4</sub> concentration	k <sub>0</sub> (min. <sup>-1</sup> ) × 10 <sup>5</sup> 0.1 <i>M</i> NaOH	0.1 M HClO4
0	6.05	57.1
0.1	6.02	45.4
.4	6.04	34.1
9	6 05	27.8

(12) I. M. Kolthoff, L. S. Guss, D. R. May and A. I. Medalia, J. Polymer Sci., 1, 340 (1946).

<sup>(9)</sup> P. D. Bartlett and J. D. Cotman, Jr., THIS JOURNAL, 71, 1419 (1949).

Table II	
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The Influence of pH on the Rate of Decomposition of Potassium Persulfate at 50° (Rate Constants Corrected to  $\mu = 0.4$ )

$10 \mu \leftrightarrow 0.1$							
Solu	tion	[H <sup>+</sup> ], M	μ	$(\times 10^4)$	(× 103)	$k_2^c$ (cor.) ( $\times 10^3$ )	$^{k_0^a(\mathrm{cor.})}_{( imes\ 10^4)}$
$0.01 \ M \ K_2 S_2 O_8$	$0.1 \ M$ NaOH	$10^{-13}$	0.13	0.61		• • •	0.61
$.01 \ M \ K_2 S_2 O_3$	Carbonate buffer	$10^{-10^{b}}$	.13	.69	•••		. 69
$.01 \ M \ K_2S_2O_8$	Phosphate buffer	$10^{-7^{b}}$	.13	.87	•••	• • •	.87
$.01 \ M \ K_2S_2O_8$	Phosphate buffer	10 <sup>-36</sup>	.13	1.0		• • •	1.0
.01 $M  \mathrm{K_2S_2O_8}$	Phosphate buffer	0.011	.13	1.4	7.2	(4.6)	1.1
$.01 \ M \ K_2 S_2 O_8$	$0.1 M \text{ KHSO}_4$	$.025^{b}$	.18	1.7	4.3	3.1	1.4
$.01 \ M \ K_2 S_2 O_8$	$.1 M H_{3}PO_{4}$	$.032^{b}$	.13	2.0	4.3	2.8	1.5
$.01 \ M \ K_2 S_2 O_8$	$.1 M HClO_{\bullet}$	.100	. 13	5.7	5.1	3.3	3.9
$.1~M~{ m K_2S_2O_8}$	$.1 M H_3PO_4$	.032	.33	1.9	4.1	3.8	1.8
$.1~M~\mathrm{K_2S_2O_8}$	$.1 M HClO_4$	. 100	.40	4.0	3.4	3.4	4.0
$.1 \ M \ K_2 S_2 O_8$	.2 M HClO4	.200	.50	6.7	3.0	3.5	7.7
$.1 M K_2 S_2 O_8$	.3 $M$ HClO <sub>4</sub>	.300	.60	9.1	2.8	3.5	11.0
$.1 M \text{ K}_2\text{S}_2\text{O}_8$	.4 $M$ HClO <sub>4</sub>	.400	.70	10.6	2.5	3.3	13.8

<sup>a</sup> Min.<sup>-1</sup>. <sup>b</sup> pH measured with the glass electrode. <sup>c</sup> (Min.)<sup>-1</sup>(moles per l.)<sup>-1</sup>.

tion the reaction rate decreases with increasing ionic strength.

Assuming that persulfate decomposes by two simultaneous reactions, one uncatalyzed and the other catalyzed by hydrogen ion, the reaction rate is given by the equation

$$-d[S_2O_8^-]/dt = k_1[S_2O_8^-] + k_2[H^+][S_2O_8^-]$$
(4)

and the over-all rate constant of the reaction is given by

$$k_0 = k_1 + k_2[\mathrm{H}^+] \tag{5}$$

The results in Table I show that the salt effect on the reaction rate must be attributed entirely to an ionic strength effect on the acid-catalyzed reaction. Values of the over-all rate constant,  $k_0$ , for the reaction in solutions of various hydrogen ion concentrations, corrected to an ionic strength of 0.4, are given in Table II. The corrected  $k_0$ values plotted against hydrogen ion concentration yield a straight line in agreement with equation 5.

It is seen in Table II that the over-all rate constant  $k_0$  is appreciably greater in a carbonate buffer of pH 10 and a phosphate buffer of pH 7 than in 0.1 M sodium hydroxide solution, even though the concentration of hydrogen ion at pH 10 and at pH 7 is negligibly small. It is possible that this increase in the rate constant may be attributed to an acid catalysis by the acid constituents of the buffers. The catalytic effect of acids other than  $H_3O^+$  on the rate of persulfate decomposition has not been investigated.

The Activation Energy.—Rate constants, determined at several temperatures, for the decomposition of 0.01 M potassium persulfate in 0.1 Msodium hydroxide and in 0.1 M perchloric acid

#### TABLE III

INFLUENCE OF TEMPERATURE ON THE RATE OF DECOMPOSI-TION OF POTASSIUM PERSULFATE

		0.1 M HCIO4		
Temp., °C.	0.1 M NaOH ko (min. <sup>-1</sup> )	k0 (min1)	$k_2$ (min. $^{-1}$ ) (moles/l.) $^{-1}$	
50	$6.0 imes10^{-5}$	$5.7  imes 10^{-4}$	$5.1  imes 10^{-3}$	
60	$3.0  imes 10^{-4}$	$1.9 imes10^{-3}$	$1.6 imes10^{-2}$	
70	$1.4  imes 10^{-3}$	$6.4 imes10^{-3}$	$5.0 imes10^{-2}$	
80	$5.5 imes10^{-3}$	$2.1  imes 10^{-2}$	$1.6 \times 0^{-1}$	
90	$2.1 imes10^{-2}$	$6.8  imes 10^{-2}$	$4.7  imes 10^{-1}$	
Activation energy	33.5 kcal.		26.0 kcal.	

solutions, together with activation energies for the catalyzed and uncatalyzed reactions are given in Table III.

Persulfate Decomposition in Strongly Acid Solutions.-In agreement with Palme<sup>5b</sup> it was found that oxygen is liberated by the decomposition of persulfate in alkaline, neutral and dilute acid solutions ([H<sup>+</sup>] < 0.5 M) but in strongly acid solutions (2 to 5 M HClO<sub>4</sub>) Caro's acid is formed which hydrolyzes further to hydrogen peroxide. As shown in Table IV, both oxygen and Caro's acid are formed in solutions of perchloric acid between 0.5 M and 2 M at  $50^{\circ}$ . The first order rate constants for the decomposition of persulfate are also given in Table IV. The plot of persulfate disappearance, Caro's acid and hydrogen peroxide formation in 5 M perchloric acid solution given in Fig. 3 reveals that in this solution persulfate first decomposes quantitatively to Caro's acid which hydrolyzes further to hydrogen peroxide. At any point the sum of the persulfate, Caro's acid and hydrogen peroxide concentrations is equal to the initial persulfate concentration. As seen from Fig. 4 this is no longer true in 2 M perchloric acid solution in which a small fraction of the persulfate decomposes with formation of oxygen (see also Table IV).

#### TABLE IV

RATIO OF OXYGEN TO CARO'S ACID FORMED BY DECOMPOSI-TION OF POTASSIUM PERSULFATE IN 0.5 TO 5.0 M HClO<sub>4</sub> Solutions at 50°

HClO <sub>4</sub> , M	$k_0 \ (\min.^{-1})$	$\frac{O}{H_2SO_5}$
0.5	$1.5 imes10^{-3}$	8
<b>i</b> .0	$2.8  imes 10^{-3}$	0.51
1.5	$4.5  imes 10^{-3}$	.19
2.0	$6.9  imes 10^{-3}$	.03
5.0	$(1,5)^{a}$	.00

<sup>a</sup> Estimated from initial slope of log  $[S_2O_3^-]$  vs. time plot which was not linear in the later stages of the reaction.

Source of Oxygen Liberated by Persulfate Decomposition.—The possibility of exchange of oxygen between water enriched with  $H_2O^{18}$  and persulfate was investigated by heating solutions of 0.1 *M* potassium persulfate in the enriched water at 50 and 90° for a time sufficient to decompose



Fig. 3.—The decomposition of persulfate in 5 M HClO<sub>4</sub> at 50°: O, S<sub>2</sub>O<sub>8</sub>-; O-, H<sub>2</sub>SO<sub>6</sub>;  $\bullet$ , H<sub>2</sub>O<sub>2</sub>.



Fig. 4.—The decomposition of persulfate in 2 M HClO<sub>4</sub> at  $50^{\circ}$ : O, S<sub>2</sub>O<sub>8</sub><sup>-</sup>; O<sup>-</sup>, H<sub>2</sub>SO<sub>5</sub>; O<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>.

half of the persulfate, after which the unreacted persulfate was crystallized from the solution by cooling to 0°. The dried salt was then heated in the reaction vessel and the isotopic composition of the liberated oxygen was determined. In alkaline solution no exchange was found at 50 or 90°. In 0.5 M sulfuric acid solution 2% exchange was found at 90° and 0.4% at 50°.

The effect of pH on the source of the oxygen liberated from 0.1 M potassium persultate solutions at 90° and 50° is given in Table V.

The oxygen liberated from dilute acid solutions of persulfate contained ozone as evidenced by the odor of the gas and by the action of the gas on starch iodide paper.

#### Discussion

The following mechanism is proposed for the thermal decomposition of persulfate in aqueous solutions.

A: Uncatalyzed reaction 
$$S_2O_8 \longrightarrow 2SO_4 \overline{\cdot}$$
 (6)

$$O_4 = + 2H_2O \longrightarrow 2HSO_4 = + 2HO \cdot (7)$$

$$2HO \cdot \longrightarrow H_2O + \frac{1}{2}O_2 \tag{8}$$

$$\begin{array}{ccc} \text{atalyzed reaction} & \text{SO}_4 + \text{HSO}_4^- & (9) \end{array}$$

2S

D. Und.

$$SO_4 \longrightarrow SO_3 + 1/_2O_2$$
 (10)

C: In strong acid 
$$SO_4 + H_2O \longrightarrow H_2SO_5$$
 (11)

With two assumptions, (1) that the uncatalyzed and catalyzed decompositions are independent

Table V Source of Oxygen Liberated by Persulfate in Water Enriched with  $H_2O^{18}$ 

Solution	¢Н	la.	% O2 from H2O	$\frac{\mathrm{O}_2(\mathrm{H}_2\mathrm{O})}{\mathrm{O}_2(\mathrm{S}_2\mathrm{O}_8\text{-})}$	$\frac{k_1b}{k_2[\mathrm{H}^+]}$
		90°			
0.1 <i>M</i> NaOH	13	60	100	8	
Carbonate buffer	10	60	98	49	
Phosphate buffer	7.2	60	96	24	
Phosphate buffer	2.1	60	77	3.3	5.5
0.1 M H3PO4	1.5	30	67	2.0	1.4
0.1 M HClO <sub>4</sub>	1.0	<b>30</b>	33	0.51	0.4
0.5 M HC104	0.3	10	6	0.06	0.09
		50°			
0.1 <i>M</i> NaOH	13	24	100	æ	
Phosphate buffer	2.6	22	<b>94</b>	16	7
Phosphate buffer	2.2	22	85	5.7	2.8
0.1 <i>M</i> H <sub>3</sub> PO <sub>4</sub>	1.5	20	63	1.7	0.6
0.1 M HC.O <sub>4</sub>	1.0	20	<b>29</b>	0.41	0.2
0.5 M HClO <sub>4</sub>	0.3	3	0	0.0	

<sup>a</sup> Time in minutes of heating reaction mixture. <sup>b</sup> If the oxygen liberated by the uncatalyzed reaction comes from the water but oxygen liberated by the catalyzed reaction comes from the persulfate ion, the following relation should hold:  $\frac{O_2(H_2O)}{O_2(S_2O_8^-)} = \frac{k_1[S_2O_8^-]}{k_2[H^+][S_2O_8^-]} = \frac{k_1}{k_2[H^+]}$ .

reactions which occur simultaneously in persulfate solutions and (2) that reactions (6) and (9) are the rate-determining steps of these reactions, this mechanism is consistent with the kinetics data given in the experimental part.

Equations ( $\hat{6}$ ), (7) and (8) constitute the mechanism proposed by Bartlett<sup>9</sup> for the thermal decomposition of persulfate in aqueous solutions. Bartlett pointed out that a chain mechanism, consistent with the kinetics, can be written but no evidence has been found that a chain reaction is involved.

The proposed mechanism predicts the absence of any influence of ionic strength on the rate of the uncatalyzed reaction but a decrease in the rate of the acid-catalyzed reaction with increasing ionic strength. These predictions are in agreement with the observations reported in the experimental part.

The critical complex for the uncatalyzed decomposition is believed to be the thermally activated persulfate ion which dissociates symmetrically into two sulfate free-radicals, while the critical complex for the acid-catalyzed reaction is believed to be the  $HS_2O_8^-$  ion which, due to the influence of the associated hydrogen ion, decomposes unsymmetrically giving both electrons of the C-O bond to one fragment to form sulfur tetroxide and a This principle of a symmetric bisulfate ion. dissociation of a peroxy bond, caused by an associated hydrogen ion, has been proposed by Leffler<sup>13</sup> to explain the acid-catalyzed decomposition of pmethoxy-p'-nitrobenzoyl peroxide in benzene solutions.

According to the proposed mechanism the sulfur tetroxide formed by reaction (9) rapidly loses oxygen in dilute acid solutions but hydrolyzes to form Caro's acid in strongly acid solutions (equation 11). No exhaustive study of the behavior of sulfur tetroxide has been made but (13) J. E. Leffler, THIS JOURNAL, **72**, 67 (1950). qualitatively the properties of the compound were found to be in agreement with reactions (10) and (11). A solution of an oxidizing agent reported to be composed of sulfur tetroxide was prepared by the action of fluorine on bisulfate according to the method of Fichter and Humpert.<sup>14</sup> The alleged sulfur tetroxide liberated oxygen containing ozone very rapidly at  $50^{\circ}$  in solutions of pH greater than 0, but in 3 M perchloric acid solution it formed Caro's acid quantitatively.

It should be pointed out that the proposed mechanism predicts the kinetics given by equation (4) only if the  $HS_2O_8^-$  ion is a strong acid. Measurement of the pH of solutions of potassium persulfate in 0.01  $\hat{M}$  HCl has shown that  $K_a$  for the  $\mathrm{HS}_2\mathrm{O}_8^-$  ion has a value of 1 or greater. Therefore,  $HS_2O_8^-$  is a much stronger acid than  $HSO_4^-$ .

(14) F. Fichter and K. Humpert, Helv. Chim. Acta, 9, 602 (1926).

The proposed mechanism also accounts for the fact that the oxygen formed by the acid-catalyzed decomposition of persulfate is derived from the persulfate while the oxygen liberated by the uncatalyzed reaction comes from the water.

According to reaction (6) the rate-determining step of the uncatalyzed reaction involves the thermal rupture of the O-O bond. The activation energy for this reaction was found to be 33.5 kcal. per mole. Although Palmer<sup>15</sup> has reported a value of 57 kcal. for the energy of the O-O bond in persulfate it is believed that the energy of the O-O bond in the solvated persulfate ion cannot be much different from the activation energy for the uncatalyzed thermal decomposition of the persulfate ion, namely, 33.5 kcal. per mole.

(15) W. G. Palmer, "Valency," London, 1945.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

# The Cryoscopic Behavior of Organic Compounds in Sulfuric Acid. I. Organosilicon Compounds<sup>1</sup>

## By H. HARRY SZMANT, ORA MAE DEVLIN AND GENE A. BROST

Tetraphenyl- and tetrabenzylsilane are cleaved in sulfuric acid to the corresponding sulfonic acid and partially sulfated polysilicic acid. While tributylsilicon fluoride ionized only to the tributylsilicyl sulfate and protonated hydrogen fluoride, the triphenyl- and tribenzylsilicon fluorides ionize with cleavage of the carbon-silicon bonds. Evidence is presented that the fluorine on cleavage is converted in sulfuric acid to protonated hydrogen fluoride rather than fluosulfonic acid.

The reported studies of the cryoscopic behavior of organosilicon compounds in the solvent sulfuric acid were limited in the past to relatively simple alkyl siloxanes,<sup>2,3</sup> alkoxy silanes and silanols.<sup>3</sup> In view of the interest in cleavage reactions of more complex organosilicon compounds brought about by hydrogen chloride<sup>4</sup> or sulfuric acid,<sup>5</sup> the results of cryoscopic studies using aryl and benzylsilanes, as well as several substituted fluorosilanes, are reported in this paper.

#### Procedure and Data

The apparatus and experimental procedure employed were similar to those described by Newman, et al.6 The temperatures were measured by a platinum resistance thermometer (Leeds and Northrup No. 709,899) which was calibrated by the National Bureau of Standards. All the compounds studied were prepared according to procedures described in the literature and purified with care by several crystalliza-tions and/or distillations. Several series of measurements were made with each of the compounds under study, and each series consisted of at least two determinations using different portions of solute. The reliability of the apparatus and technique was periodically checked by determining the freezing point depression caused by addition of pure benzoic acid. Table I lists representative experimental results obtained in this study and the calculated van't Hoff factor i. In view of the slow dissolution of most of the compounds in

sulfuric acid, and since slow secondary changes in the initially formed products were suspected, the variation of the freezing point depression with time was also observed.

Isolation of Benzene- and Benzylsulfonic Acids.-Benzenesulfonic acid was isolated from the reaction mixture of tetraphenylsilane (or triphenylfluorosilane) by pouring the sulfuric acid solution on ice and neutralizing by the addition of sodium carbonate. Sodium chloride was also added to ensure the precipitation of the sodium benzenesulfonate. The solid was separated by filtration, dried, and extracted in a Soxhlet apparatus with absolute ethanol. On removal of the alcohol, the residue was dissolved in a small amount of water and treated with benzylthiuronium hydrochloride. The resulting product was recrystallized from 50% ethanol to a constant m.p. 144-145°. The melting point of this product was not depressed by admixture with an authentic sample of the S-benzylthiuronium salt of benzenesulfonic acid.

Benzylsulfonic acid was isolated from the reaction mixture of tetrabenzylsilane by pouring the sulfuric acid solution on ice. On standing for 24 hours there were obtained the crystals of benzylsulfonic acid, m.p. 110–111°, the melting point of which was not depressed by an authentic sample of benzylsulfonic acid.

Attempted Isolation of Fluosulfonic Acid.-First we convinced ourselves that fluosulfonic acid could be separated by distillation from a synthetic mixture of 100% sulfuric acid and fluosulfonic acid in essentially quantitative amounts. Then the equivalent distillation experiments were performed on solutions obtained from the interaction of sulfuric acid with sodium fluoride, or benzotrifluoride. No fluosulfonic acid was detected in either one of the two reaction mixtures. The reaction mixture of benzotrifluoride and the sulfuric acid also did not produce any distillate boiling in the range expected of benzoyl fluoride, and the behavior of benzotrifluoride in the presence of sulfuric acid was rather unexpected. The first portion of benzotrifluoride did not react with cold sulfuric acid and formed a clear layer which slowly disappeared only when the sulfuric acid was heated. However, the second portion of the benzotrifluoride reacted progressively more vigorously with the sulfuric acid and it was accompanied by the liberation of hydrogen fluoride and etching of the glassware. Thus, it appears that the initial

<sup>(1)</sup> Presented in part before the Organic Division, American Chemical Society, Philadelphia, April, 1950.

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<sup>(6)</sup> M. S. Newman, et al., ibid., 67, 704 (1945).