

aqueous solutions. However, it seems reasonable to assume that the implication of "free" is that such molecules are not specifically solvated but are simply subjected to the forces of the general dipolar environment of the medium, water. If "free" has this meaning, then it seems reasonable to assume that the spectral behavior of such "free" ammonia molecules would be very like that of ammonia molecules in diethyl ether solution, where there are the strong general dipolar forces associated with the C-O bonds but no possibility of specific solvation such as is implied in the formula  $\text{NH}_4\text{OH}$ .<sup>12</sup>

Subject to the assumptions indicated in the previous paragraph, one can conclude that the absorption spectrum of *aqua* ammonia, as given by Curve II of Fig. 1, is the sum of two quantities

$$A_{(\text{aq. NH}_3)} = (1 - \alpha) A_{\text{NH}_3} + \alpha A_{\text{NH}_4\text{OH}} \quad (3)$$

where  $\alpha$  is the fraction of the dissolved ammonia in the form of  $\text{NH}_4\text{OH}$ , *i.e.*, specifically solvated,  $A_{\text{NH}_4\text{OH}}$  is the absorptivity of  $\text{NH}_4\text{OH}$  at the wave length  $\lambda$ , and  $A_{\text{NH}_3}$  is the absorptivity of "free" ammonia molecules and is to be taken equal to that of a diethyl ether solution at  $\lambda$ . Since  $\alpha A_{\text{NH}_4\text{OH}}$  is of necessity a positive quantity, we have from (3) for the fraction of free ammonia molecules,  $1 - \alpha$ , the inequality

$$(1 - \alpha) \leq \frac{A_{\lambda(\text{aq. NH}_3)}}{A_{\text{NH}_3}} = 0.005 \quad (2100 \leq \lambda \leq 2200 \text{ \AA.}) \quad (4)$$

and the conclusion that less than 0.5% of the ammonia in water solutions is "free."

Similar reasoning applied to the data on the vapor and water solution spectra of water, phosphine and hydrogen sulfide leads to the conclusion that less than 0.2%  $\text{H}_2\text{O}$ , 50%  $\text{PH}_3$  and 42%  $\text{H}_2\text{S}$  are "free" in water solution at about 25°.

In order to ascertain that the decrease in absorptivities associated with change of solvent from ether to water in the case of ammonia is appropriately attributable to specific complex formation, obser-

(12) By the formula,  $\text{NH}_4\text{OH}$ , we imply an "outer complex" in the sense of Fig. 2 of the definitive paper of R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

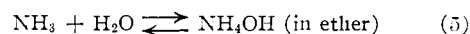
vations were made of the effect on the ammonia spectrum of the addition of water to diethyl ether solutions of ammonia. There were measured the optical densities at 2125, 2150 and 2175 Å. (1.0 cm. cell), of ether solutions of  $\text{NH}_3$  with various concentrations of water. As may be seen in Table II, the presence of 5 to 10 ml. of  $\text{H}_2\text{O}$  per liter of ether causes a large reduction in the effective absorptivity of the ammonia solutions at these wave lengths.

TABLE II

EFFECT OF  $\text{H}_2\text{O}$  ON THE SPECTRUM OF  $\text{NH}_3$  IN DIETHYL ETHER

$C^0$ ( $\text{NH}_3$ ), $M$	0.0139	0.0139	0.139
$C^0$ ( $\text{H}_2\text{O}$ ), $M$	0.0000	.0334	.555
O.D. (1 cm.)	2125	1.460	.686
	2150	0.695	.332
	2175	0.327	.147
$\langle D/D_0 \rangle$		0.455 ± 0.012	0.406 ± 0.005
$K$		3.4 ± 0.1	2.6 ± 0.1

If one assumes the optical density of each of these solutions is proportional to the concentration of "free" ammonia in the solution, one can calculate an apparent association constant for the reaction



from the expression

$$K = \frac{[1 - D/D_0]}{(D/D_0)[\text{H}_2\text{O}]} \quad (6)$$

since the total  $\text{NH}_3$  concentration in the solution is small compared with the water concentration. As may be seen in the last line of Table II, the spectral data give  $\sim 3$  l./mole for the ( $\text{NH}_3\text{—H}_2\text{O}$ ) association constant in the ether solution. Such a value for the association constant would imply that considerably less than 1% of the ammonia in water solution is free, if the association constant were independent of solvent. Clearly the results of the measurements on the effect of water on the spectrum of the ether solution of ammonia are completely compatible with the interpretation given above of the difference between the spectra of the water and the ether solutions of ammonia.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

## The Oxidation of Oxalate Ion by Peroxodisulfate. II. The Kinetics and Mechanism of the Catalysis by Copper(II)<sup>1</sup>

BY EPHRAIM BEN-ZVI<sup>2</sup> AND THOMAS L. ALLEN

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The oxidation of oxalate ion by peroxodisulfate is strongly catalyzed by copper(II), but the catalysis is subject to inhibition by molecular oxygen. An investigation has been made of the kinetics of the catalyzed reaction in the absence of oxygen. The rate law is first-order in peroxodisulfate, zero-order in oxalate, and half-order in the catalyst. A free-radical chain mechanism, involving oxidation of copper to the terpositive state, is postulated for the reaction. It is shown that copper does not take part in the chain-initiating step. Reduction of copper to the unipositive state probably does not occur.

In the first part of this series<sup>3</sup> it was shown that copper(II) is a very effective catalyst for the oxida-

tion of oxalate ion by the  $\text{S}_2\text{O}_8^{2-}$  ion,<sup>4</sup> and a brief study of the kinetics of the copper-catalyzed re-

(1) This work was assisted by a research grant from the National Science Foundation.

(2) Abstracted in part from the Ph.D. Dissertation of Ephraim Ben-Zvi, University of California, Davis, 1960.

(3) T. L. Allen, *J. Am. Chem. Soc.*, **73**, 3589 (1951).

(4) In common usage  $\text{S}_2\text{O}_8^{2-}$  is persulfate. Under the "1940 Rules" [W. P. Jorissen, H. Bassett, A. Damiens, F. Fichter and H. Rémy, *ibid.*, **63**, 889 (1941)] and in *Chemical Abstracts* it is designated peroxydisulfate. In the "Definitive Rules for Nomenclature of Inorganic Chemistry," *ibid.*, **82**, 5523 (1960)] it is peroxodisulfate.

action was included. A detailed investigation now has been made and the results are reported below.

### Experimental

**Materials.**—Redistilled water was used in all of the kinetic experiments. It was prepared from ordinary distilled water by successive distillation from dilute alkaline  $\text{KMnO}_4$  solution, dilute  $\text{KHSO}_4$  solution and finally, without addition of any reagent, through a 36-inch Vigreux column. The connection between the column and the condenser was heated with a heating tape to break the liquid film on the inner wall of the distillation system, thus preventing diffusion of impurities into the distillate.<sup>5</sup>

Potassium peroxodisulfate was recrystallized from redistilled water and dried under vacuum at 50°. The purified reagent contained an acidic substance (probably  $\text{KHSO}_4$ ) which lowered the  $\text{pH}$  of the reaction solution, containing five times as much  $\text{Na}_2\text{C}_2\text{O}_4$  as  $\text{K}_2\text{S}_2\text{O}_8$ , to  $6.0 \pm 0.2$ . (A slightly acidic solution was desirable to avoid precipitation of the catalyst.) To provide an inert atmosphere Matheson prepurified  $\text{N}_2$  and "bone-dry"  $\text{CO}_2$  were used. All other substances were reagent grade. So that reproducible results might be obtained standard solutions were used.<sup>3</sup> All solutions were filtered through sintered-glass filters.

**Apparatus.**—The reaction vessels were 250-ml. Pyrex gas-washing bottles with fritted discs, modified to permit withdrawal of samples by pipet through the gas-outlet tube. A separate bottle of the same type was used to remove  $\text{O}_2$  from the  $\text{K}_2\text{S}_2\text{O}_8$  solution prior to mixing.  $\text{N}_2$  (or  $\text{CO}_2$  in a few experiments) saturated with water vapor was passed through flowmeters to the gas-washing bottles. Tygon tubing was used for connections. The reaction vessels were maintained at a constant temperature in a water thermostat. Light was not excluded, as preliminary expts. showed that the results were not significantly different when the expts. were conducted in the dark. Measurements of  $\text{pH}$  were made with a Beckman model G  $\text{pH}$  meter on samples at room temperature. The absorption spectra were measured at 25° with a Beckman model DU spectrophotometer using 10-cm. cells.

The reaction rate and the reproducibility of the results depended to some extent upon the method used to clean the reaction vessels. In each case the vessels were dried after washing with one of these sequences of reagents:

(1) Soap, concentrated  $\text{HCl}$ , distilled water (7 times) and redistilled water.

(2) Hot concentrated aqua regia, distilled water (12–15 times) and redistilled water (3 times).

(3) Redistilled water (3 times).

(4) A 10% solution of  $\text{NaOH}$  in redistilled water and redistilled water (6–8 times). (After about 5 washings the wash water was colorless to phenolphthalein indicator.) The effect of coating the glass surface with Beckman Desicote also was tested.

**Procedures.**—Appropriate volumes of the standard solutions, except  $\text{K}_2\text{S}_2\text{O}_8$ , were pipetted into the reaction vessel, which was then placed in the thermostat. The  $\text{K}_2\text{S}_2\text{O}_8$  solution was kept at room temperature, and  $\text{N}_2$  was bubbled through each solution at 350 ml./min. After 40 min. the  $\text{K}_2\text{S}_2\text{O}_8$  bottle was placed in the thermostat without disrupting the flow of  $\text{N}_2$ , and 20 min. later the  $\text{K}_2\text{S}_2\text{O}_8$  solution having reached the thermostat temperature, 25 ml. were pipetted into the reaction vessel. The flow of  $\text{N}_2$  was maintained throughout the experiment.

In the experiments with allyl acetate the solutions were deaerated by bubbling  $\text{N}_2$  through them for 30 min. at 61.8°. They were then transferred to glass-stoppered Erlenmeyer flasks to prevent evaporation.

**Analyses.**—Aliquot portions were withdrawn at suitable intervals and analyzed for  $\text{S}_2\text{O}_8^{2-}$  by a slight modification of the method adopted previously.<sup>3</sup> It should be noted that quenching of the oxalate reaction was accomplished by the much faster reaction of  $\text{S}_2\text{O}_8^{2-}$  with iodide ion and not by precipitation of  $\text{CuI}$  as reported earlier.<sup>3</sup> (Copper(II), when complexed with oxalate, does not react with iodide.) Calculations based on the results of King and co-workers<sup>6</sup>

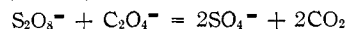
(5) R. Ballentine, *Anal. Chem.*, **26**, 549 (1954).

(6) E. Jette and C. V. King, *J. Am. Chem. Soc.*, **51**, 1034 (1929); C. V. King and E. Jette, *ibid.*, **51**, 1048 (1929); C. V. King and M. B. Jacobs, *ibid.*, **53**, 1704 (1931).

have shown that, under the conditions employed, the peroxodisulfate-iodide reaction was at least one hundred times faster than the reaction under investigation.

### Results

**Stoichiometry.**—To verify the stoichiometry of the reaction, a solution containing 0.00830  $M$   $\text{K}_2\text{S}_2\text{O}_8$ , 0.01000  $M$   $\text{Na}_2\text{C}_2\text{O}_4$  and  $2.0 \times 10^{-4}$   $M$   $\text{CuSO}_4$  was allowed to react for 41 hr. at 40.2° under  $\text{N}_2$ . It was then analyzed, and the final concentrations were  $1 \times 10^{-5}$   $M$   $\text{S}_2\text{O}_8^{2-}$  and  $1.74 \times 10^{-3}$   $M$   $\text{C}_2\text{O}_4^{2-}$ . The decrease in  $\text{C}_2\text{O}_4^{2-}$  concentration (0.00826  $M$ ) was essentially identical with the decrease in  $\text{S}_2\text{O}_8^{2-}$  concentration (0.00829  $M$ ), in accordance with the equation for the same reaction catalyzed by silver ion<sup>3,7</sup>



**Peroxodisulfate Dependence.**—During an experiment the logarithm of the  $\text{S}_2\text{O}_8^{2-}$  concentration decreased linearly with time, showing that the rate law for the reaction is first-order in peroxodisulfate concentration

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k'(\text{S}_2\text{O}_8^{2-})$$

Values of  $k'$  were obtained from graphs of the logarithm of the volume of thiosulfate solution (which is proportional to the concentration of  $\text{S}_2\text{O}_8^{2-}$ ) versus time. As the graphs were quite straight it was possible to obtain an accurate value of  $k'$  for each experiment. However, the slopes for different experiments under the same conditions varied somewhat. (Reproducibility is discussed in detail in the section on surface effects.) The first-order dependence was also verified by changing the initial concentration of peroxodisulfate. The results are shown in Table I.

TABLE I

PEROXODISULFATE DEPENDENCE <sup>a</sup>	
( $\text{K}_2\text{S}_2\text{O}_8$ ), $M$	$10^4 k'$ , sec. <sup>-1</sup>
0.0058 <sup>b</sup>	3.07
.0083 <sup>b</sup>	3.42
.0116 <sup>b</sup>	3.43
.0046 <sup>c</sup>	3.03
.0083 <sup>c</sup>	3.73
.0332 <sup>c</sup>	3.77

<sup>a</sup> 40.47°, 0.040  $M$   $\text{Na}_2\text{C}_2\text{O}_4$  and  $4.0 \times 10^{-4}$   $M$   $\text{CuSO}_4$ .  
<sup>b</sup> Reaction vessel cleaned by method 2. <sup>c</sup> Method 4.

**Oxalate Dependence.**—The rate is essentially independent of oxalate concentration (Table II). When  $\text{Na}_2\text{SO}_4$  was added to maintain constant ionic strength, variation of the oxalate concentration over a four-fold range did not produce any significant change in rate. When the ionic strength was allowed to vary, the rate tended to increase slightly with increasing oxalate concentration. Similar results were obtained in other experiments with ( $\text{Na}_2\text{C}_2\text{O}_4$ ) from 0.008 to 0.16  $M$ ,  $\mu$  from 0.05 to 0.51 and cleaning by method 2. (The  $\text{pH}$  of the experiments of this section varied from 5.1 to 6.5. It will be shown that this had no significant effect on the rate.)

**Copper Dependence.**—To determine the order of the reaction with respect to the catalyst, ( $\text{CuSO}_4$ ) was varied from  $1.6 \times 10^{-5}$  to  $40.0 \times 10^{-5}$   $M$  using  $\text{N}_2$  and from  $0.8 \times 10^{-5}$  to  $50.0 \times 10^{-5}$   $M$

(7) C. V. King, *ibid.*, **50**, 2089 (1928).

TABLE II  
 OXALATE DEPENDENCE<sup>a</sup>

(Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ), M	$\mu^b$	$10^4 k'$ , sec. <sup>-1</sup>
0.04	0.55	3.08
.08	.55	3.72
.16	.55	3.13
.02	.09	3.63
.04	.15	3.73
.08	.27	3.87
.12	.39	4.75
.17	.54	4.30

<sup>a</sup> 40.47°, 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub> and cleaning by method 4. <sup>b</sup> Ionic strength adjusted with Na<sub>2</sub>SO<sub>4</sub> in first 3 experiments.

using CO<sub>2</sub>. (The other concentrations were 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, the temperature was 40.4° and the reaction vessels were cleaned by method 1.) In Fig. 1  $k'$  is plotted *versus* the

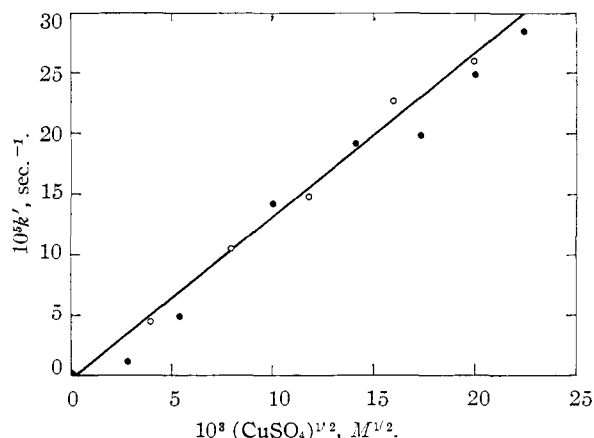


Fig. 1.—The effect of catalyst concentration on the first-order rate constant: O, under N<sub>2</sub>; ●, under CO<sub>2</sub>.

square root of the CuSO<sub>4</sub> concentration. Each point represents the least-squares method average of duplicate or triplicate experiments. The best straight line determined by least squares for the experiments under N<sub>2</sub> is shown; it fits the results with CO<sub>2</sub> almost equally well. Therefore the rate is independent of the concentration of CO<sub>2</sub> (a reaction product), and it is proportional to the square root of the catalyst concentration

$$k' = k(\text{Cu})_T^{1/2}$$

where (Cu)<sub>T</sub> designates the total concentration of the various species of copper in solution.

**Surface Effects.**—Table III summarizes the results of experiments designed to test the effect of

 TABLE III  
 SURFACE EFFECTS<sup>a</sup>

Added substance	$10^4 k'$ , sec. <sup>-1</sup>
.....	2.17
Pyrex glass	2.18
0.025 g. BaSO <sub>4</sub>	2.38
.227 g. BaSO <sub>4</sub>	2.37
.737 g. BaSO <sub>4</sub>	2.27

<sup>a</sup> 40.2°, 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub> and cleaning by method 1.

surface area. In the second experiment small Pyrex glass tubes were placed in the reaction vessel, doubling the surface-to-volume ratio. In the last

three experiments powdered BaSO<sub>4</sub> was added to the reaction solution.

Although these experiments indicate that the extent of the surface has no appreciable effect, the method of treating the reaction vessel surface did affect the rate and its reproducibility (Table IV). The highest rate and most reproducible results were obtained using method 4. It was adopted after the experiments with Desicote, and the values of  $10^4 k'$  (sec.<sup>-1</sup>) in the first five consecutive experiments were 2.28, 2.40, 2.83, 3.42 and 3.77, respectively. Following this period of conditioning the surface and/or removing the last traces of Desicote the results were fairly consistent, as indicated in Table IV.

 TABLE IV  
 EFFECT OF SURFACE TREATMENT<sup>a</sup>

Surface treatment	No. of expts.	$10^4 k'$ (ave.), sec. <sup>-1</sup>	Ave. dev., %
Method 1	13	2.58	16
Method 2	14	3.42	7
Method 3	15	2.97	8
Method 4	10	3.73	6
Desicote	4	1.80	26

<sup>a</sup> 40.47°, 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub>.

**Ionic Strength Dependence.**—The effect of changing ionic strength was studied using NaClO<sub>4</sub> (Table V). In the range 0.15–0.39, ionic strength has no significant effect on the rate; at higher ionic strength  $k'$  is somewhat smaller. Similar results were obtained in other experiments using from 0.04 to 0.32 M Na<sub>2</sub>SO<sub>4</sub>. The experiments in which (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) was varied (see above) provide evidence that the rate is essentially independent of ionic strength in the range 0.05–0.54.

 TABLE V  
 IONIC STRENGTH DEPENDENCE<sup>a</sup>

(NaClO <sub>4</sub> ), M	$\mu$	$10^4 k'$ (sec. <sup>-1</sup> )
...	0.15	3.42 <sup>b</sup>
0.021	.17	3.40
.061	.21	3.10
.12	.27	3.13
.24	.39	3.25
.60	.75	2.75
1.20	1.35	2.10

<sup>a</sup> 40.47°, 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub> and cleaning by method 2. <sup>b</sup> ±0.25, av. of 14 experiments.

**Sulfate Dependence.**—As sulfate ion is a reaction product its concentration increases during an experiment. The lack of any significant deviation from first-order kinetics therefore indicates that the reaction rate is independent of sulfate concentration. (However, this is not true of the experiments at low pH discussed below.) Further evidence is provided by the first three experiments of Table II and by the experiments on ionic strength dependence with Na<sub>2</sub>SO<sub>4</sub> mentioned above. In these experiments anhydrous Na<sub>2</sub>SO<sub>4</sub> was used. With the decahydrate the rate decreased with increasing sulfate concentration. Although the effect was not large, the presence of an inhibitor in the analytical reagent grade decahydrate is indicated.

**pH Dependence.**—The effect of pH has been investigated by the addition of NaOH or KHSO<sub>4</sub> and by replacing part or all of the Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with NaHC<sub>2</sub>O<sub>4</sub>. During each experiment the pH of the solution remained constant. The results in Table VI show that the rate is essentially independent of pH in the range 3.85–6.32. At higher pH the rate decreases, probably because of precipitation of the catalyst. At low pH (2.52–3.60) the semi-logarithmic graphs are non-linear. Although the effect on the initial rate is not very pronounced, the rate decreases rather markedly as the reaction proceeds.

TABLE VI  
pH DEPENDENCE<sup>a</sup>

pH	10 <sup>4</sup> k', sec. <sup>-1</sup>
7.08	2.68
6.60	2.92
6.32	4.07
6.00	3.73 <sup>b</sup>
5.43	3.30
4.32	3.72
3.85	3.75

<sup>a</sup> 40.47°, 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub>, 0.040 M (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + NaHC<sub>2</sub>O<sub>4</sub>) and cleaning by method 4. <sup>b</sup> ± 0.22, av. of 10 expts.; pH ± 0.20.

**Temperature Dependence.**—The variation of rate constant with temperature is shown in Table VII. When log k' was plotted versus 1/T the experimental points fell along a straight line. From the slope of the line the activation energy was found to be 32.2 kcal./mole.

TABLE VII  
TEMPERATURE DEPENDENCE<sup>a</sup>

Temp., °C.	10 <sup>4</sup> k', sec. <sup>-1</sup>
25.64	0.322
32.70	1.02
40.47	3.73
44.30	6.83

<sup>a</sup> 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub> and cleaning by method 4.

**Oxygen Inhibition.**—In some preliminary experiments it was found that the rate increased when: (a) air was removed with oil-pumped nitrogen; (b) prepurified nitrogen was used instead; (c) the reaction vessels were modified so that samples could be obtained without removing the stoppers. However, the presence of air did not change the form of the rate law. In experiments using 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub>, 10<sup>4</sup>k' was 0.65 sec.<sup>-1</sup> at 40.47° when O<sub>2</sub> was bubbled through the solution, compared to 3.73 sec.<sup>-1</sup> under N<sub>2</sub> and otherwise similar conditions. Tests of the reaction solutions with titanium sulfate showed that the presence of oxygen did not lead to the formation of hydrogen peroxide.

**Allyl Acetate Inhibition.**—Allyl acetate is an extremely effective inhibitor for this reaction. Two expts. were carried out at 61.8° and a pH of 4.7, using 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 0.230 M allyl acetate and 0.005 M KHSO<sub>4</sub>. (The KHSO<sub>4</sub> was added to prevent hydrolysis of the allyl acetate.<sup>8</sup>) One solution contained 4.0 ×

(8) I. M. Kolthoff, E. J. Meehan and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953).

10<sup>-4</sup> M CuSO<sub>4</sub>; the other contained no catalyst. In both expts. the first-order rate constant was 9.0 × 10<sup>-6</sup> sec.<sup>-1</sup>. For comparison, the rate constant for the thermal decomposition of peroxodisulfate in 0.1 M NaOH at this temperature, calculated from the data of Kolthoff and Miller,<sup>9</sup> is 6.7 × 10<sup>-6</sup> sec.<sup>-1</sup>.

**Influence of Other Substances.**—Various other substances were added to the reaction solution, usually at a concentration of 1.0 × 10<sup>-4</sup> M. (The temperature was 40.2°, and the other concentrations were 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and usually 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub>.) Silver nitrate increased the rate markedly. Substances which inhibited the catalyzed reaction to varying degrees included Mn<sup>++</sup>, MnO<sub>4</sub><sup>-</sup>, NH<sub>4</sub>OH, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and Cl<sup>-</sup>. Dust was also found to be an effective inhibitor. Substances with no appreciable effect on the rate included NH<sub>4</sub><sup>+</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Sn<sup>++</sup>, Pb<sup>++</sup>, Fe<sup>++</sup>, Fe<sup>+++</sup>, Al<sup>+++</sup>, H<sub>2</sub>O<sub>2</sub>, SO<sub>3</sub><sup>2-</sup>, OAc<sup>-</sup>, methanol, 1-propanol, 1-butanol and *tert*-butyl alcohol. Variation of the N<sub>2</sub> flow rate over an eight-fold range also had no effect.

**Absorption Spectra.**—The absorption spectra of solutions containing 0.040 M Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 4.0 × 10<sup>-4</sup> M CuSO<sub>4</sub> and either with or without 0.0083 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were measured over the range 600–850 mμ. The presence of peroxodisulfate had no effect on the spectrum. There was a broad maximum at 710–720 mμ with a molar absorptivity (based on copper concentration) of 35.

**Cuprous Oxalate.**—To determine whether copper(I) could exist in an oxalate solution, a sample of cuprous chloride was dissolved in a sodium oxalate solution. As it dissolved, it disproportionated, forming dioxalatocuprate(II) ion and metallic copper.

**Comparison with Earlier Results.**—In the first article of this series<sup>3</sup> the copper-catalyzed reaction was studied at 69.7° using very low concentrations of catalyst. Oxygen was not excluded. To about 50% reaction the rate was zero-order in both S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. Dependence on CuSO<sub>4</sub> concentration was linear with a relatively large constant term. Concentrations were not varied over a very wide range, and reconsideration of the data shows that they fit the rate law established in the present work fairly well. The large constant term had been interpreted as being due to a copper impurity of 1 × 10<sup>-7</sup> M, but this hypothesis conflicted with analyses showing that the impurity was only about 2 × 10<sup>-8</sup> M. When the data are reinterpreted using the new rate law, this paradox disappears. A comparison of the reaction rates obtained in the earlier work with values calculated using the results of the present investigation shows that the two sets of data are in fairly good agreement.

## Discussion

There are several reasons for believing that the copper-catalyzed reaction of peroxodisulfate and oxalate is a free-radical chain reaction:

(1) The very marked inhibition by allyl acetate is indicative of a chain reaction involving SO<sub>4</sub><sup>-</sup> free radicals. It has been shown by Kolthoff,

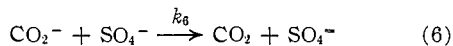
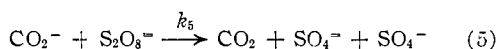
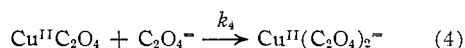
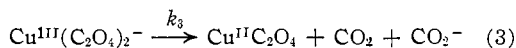
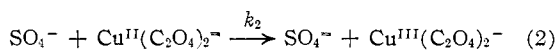
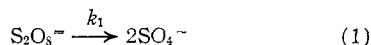
(9) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

Meehan and Carr that allyl acetate is a highly efficient captor of sulfate radicals.<sup>8</sup> Furthermore, the first-order rate constant in the experiments with allyl acetate was essentially the same as that of the thermal decomposition of  $S_2O_8^{2-}$  in 0.1 M NaOH, where the reaction  $S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$  is the rate-determining step.<sup>9</sup> Therefore neither oxalate nor copper participates in the chain-initiating reaction, which is the homolytic cleavage of  $S_2O_8^{2-}$ .

(2) Inhibition by oxygen indicates that this is a chain reaction in which  $CO_2^{\cdot -}$  (or  $C_2O_4^{\cdot -}$ ) radicals participate. Oxygen is known to inhibit certain chain reactions involving  $CO_2^{\cdot -}$  radicals, such as the oxidation of oxalate by permanganate<sup>10-12</sup> or mercuric chloride.<sup>13-15</sup>

(3) The difficulty of obtaining reproducible results and the sensitivity of the rate to the treatment of the reaction vessel surface indicate that this is a chain reaction with very long chains. Other studies of free-radical chain reactions in aqueous solution in which similar problems have been encountered include the gamma-ray induced decomposition of hydrogen peroxide<sup>16</sup> and the peroxodisulfate induced exchange of oxygen atoms between water and molecular oxygen.<sup>17,18</sup>

A reasonable mechanism of this type which leads to the experimental rate law is



Using the usual steady-state approximation and the assumption that  $4k_2k_5(Cu^{II}(C_2O_4)_2^{2-}) > k_1k_6$ , it may be shown that

$$-d(S_2O_8^{2-})/dt = (k_1k_2k_5/k_6)^{1/2}(S_2O_8^{2-})(Cu^{II}(C_2O_4)_2^{2-})^{1/2}$$

This rate law has the same form as the experimental rate law, provided that the concentrations of other species of copper in solution are negligible with respect to that of dioxalato-cuprate(II) ion. Calculations based on the equilibrium constants determined by Watters<sup>19</sup> have shown that in a typical experiment dioxalato-cuprate(II) ion comprised about 99.7% of the total copper(II) in solution, assuming equilibrium between the various copper(II) species. Since the absorption spectrum of a solution containing dioxalato-cuprate(II) was found to be unaffected by the presence of  $S_2O_8^{2-}$ , it is likely that the steady-state concentration of

(10) H. F. Launer, *J. Am. Chem. Soc.*, **54**, 2597 (1932); **55**, 865 (1933).

(11) H. F. Launer and D. M. Yost, *ibid.*, **56**, 2571 (1934).

(12) S. J. Adler and R. M. Noyes, *ibid.*, **77**, 2036 (1955).

(13) W. E. Roseveare and A. R. Olson, *ibid.*, **51**, 1716 (1929).

(14) W. E. Roseveare, *ibid.*, **52**, 2612 (1930).

(15) E. A. Hausman and T. W. Davis, *ibid.*, **76**, 5341 (1954).

(16) E. J. Hart and M. S. Matheson, *Discussions Faraday Soc.*, **12**, 169 (1952).

(17) H. Taube, *Ann. Rev. Nuclear Sci.*, **6**, 294 (1956).

(18) C. R. Giuliano, N. Schwartz and W. K. Wilmarth, *J. Phys. Chem.*, **63**, 353 (1959).

(19) J. I. Watters, *J. Am. Chem. Soc.*, **81**, 1560 (1959).

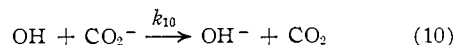
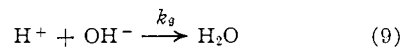
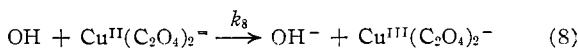
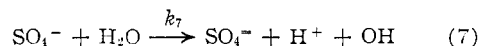
terpositive copper or other copper-containing reaction intermediate is relatively small. Therefore to a good approximation  $(Cu)_T = (Cu^{II}(C_2O_4)_2^{2-})$ , and the experimental rate constant  $k = (k_1k_2k_5/k_6)^{1/2}$ .

At 40.47°  $k_1$  is  $2.0 \times 10^{-7}$  sec.<sup>-1</sup> as calculated from the data of Kolthoff and Miller.<sup>9</sup> In this investigation  $k' = (k_1k_2k_5/k_6)^{1/2}(Cu^{II}(C_2O_4)_2^{2-})^{1/2}$  varied from about 50 to over 2000 times as large as  $k_1$  at the same temperature, depending on the catalyst concentration and other conditions. Therefore the average chain length varied from about 50 to over 2000. Also, it follows that  $(2k'/k_1)^2 = 4k_2k_5(Cu^{II}(C_2O_4)_2^{2-})/k_1k_6 \geq 10^4$ , showing that the results are consistent with the inequality assumed in the derivation.

Oxidation of copper to the +3 state is postulated in the mechanism. Compounds of terpositive copper have been prepared using several powerful oxidizing agents, including peroxodisulfate, in alkaline solution.<sup>20,21</sup> In several investigations it has been postulated that  $Cu^{+++}$  is a reaction intermediate, formed by the reaction of  $Cu^{++}$  with atomic chlorine.<sup>22,23</sup>

Alternatively, reactions 2 and 3 may be combined in a single concerted step without affecting the form of the derived rate law. This change avoids the copper(III) complex, but the function of copper in the mechanism is then less distinctive. Another alternative mechanism may be obtained by combining reactions 3 and 4. As in several other oxalate reactions, substitution of  $C_2O_4^{\cdot -}$  for  $CO_2^{\cdot -}$  has no effect on the rate law. Evidence concerning the relative merits of the two species is summarized by Adler and Noyes.<sup>12</sup>

The reactions between anions should be hindered by coulomb repulsions. A mechanism involving OH radicals avoids all but one of these reactions. In this alternative mechanism  $SO_4^{\cdot -}$  radicals generate OH radicals, which then substitute for  $SO_4^{\cdot -}$ . Besides reactions 1, 3, 4 and 5, it includes



The derived rate law is the same as the one obtained previously, except that  $k_2$  and  $k_6$  are replaced by  $k_8$  and  $k_{10}$ , respectively.

A more complex mechanism involving dioxalato-cuprate(I) ion also leads to the experimental rate law. However, when cuprous chloride is dissolved in a sodium oxalate solution it disproportionates, as described above. The stabilization of the +2 oxidation state of copper with respect to the +1 state occurs with other chelating agents, such as ethylenediamine.<sup>20,24</sup> Oxalate

(20) J. Kleinberg, "Unfamiliar Oxidation States and Their Stabilization," University of Kansas Press, Lawrence, Kansas, 1950.

(21) R. Scholder and U. Voelskow, *Z. anorg. u. allgem. Chem.*, **266**, 256 (1951).

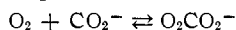
(22) H. Taube and W. C. Bray, *J. Am. Chem. Soc.*, **62**, 3357 (1940).

(23) H. Taube, *ibid.*, **65**, 1876 (1943); **68**, 611 (1946).

(24) W. B. Schaap, A. E. Messner and F. C. Schmidt, *ibid.*, **77**, 2683 (1955).

ion does not complex  $\text{Ag}^+$ , which is similar in many respects to  $\text{Cu}^+$ . Therefore it is unlikely that  $\text{Cu}^+(\text{C}_2\text{O}_4)_2^{\ominus}$  is an important intermediate.

Inhibition by oxygen probably occurs through reaction with  $\text{CO}_2^-$  radicals to form a molecular complex or carbon peroxide<sup>10,12</sup>



followed by chain termination



Reversibility of the first of these reactions is necessary for the rate law to have the same order with respect to peroxodisulfate and catalyst when oxygen is present.

The strong inhibition by  $\text{Mn}^{++}$  and  $\text{MnO}_4^-$  indicates that one or more manganese species derived from them is effective in terminating the reaction chains in this system. A related observation is the failure of manganic ion to catalyze the reaction of peroxodisulfate and oxalic acid.<sup>25</sup> Inhibition by  $\text{S}_2\text{O}_8^{\ominus}$  and  $\text{Cl}^-$  probably also occurs through chain termination, while inhibition by  $\text{NH}_4\text{OH}$  is caused by transformation of the catalyst to the ammonia complex ion.

The proposed mechanism is consistent with the fact that the rate is independent of  $p\text{H}$  over a wide range. It is not known why deviations from first-order kinetics occur at a  $p\text{H}$  of  $\leq 3.60$ , but they may result from "bisulfate inhibition."<sup>26</sup> At sufficiently high values of the product  $(\text{H}^+)(\text{SO}_4^{\ominus})$ , the reverse of reaction 7 becomes important. If the chain-propagating steps are slower and the chain-terminating steps are faster for  $\text{SO}_4^-$  than for  $\text{OH}$ , then the result is inhibition of the over-all rate. In their study of the photolytic decomposition of peroxodisulfate, Tsao and

(25) H. Taube, *J. Am. Chem. Soc.*, **70**, 3928 (1948).

(26) M.-S. Tsao and W. K. Wilmarth, *J. Phys. Chem.*, **63**, 346 (1959).

Wilmarth observed inhibition only at much larger values of  $(\text{H}^+)(\text{SO}_4^{\ominus})$ . However, as the particular reactions involving  $\text{SO}_4^-$  and  $\text{OH}$  vary from one system to another, the region where bisulfate inhibition becomes important may also vary.

Application of the Brønsted equation to the rate law derived from the proposed mechanism shows that at low ionic strength, where the equation is valid,  $k$  should increase with increasing ionic strength. A graph of  $\log k$  versus the square root of the ionic strength should be linear with a slope of 1.5. (For the alternative mechanism involving  $\text{OH}$  radicals, the slope should be 1.0.) Experimentally it was found that the rate constant was essentially independent of ionic strength over the range 0.05–0.54. However, the ionic strength in this range is too high for the Brønsted equation to be applicable. Another ionic reaction which behaves in this way is the reaction  $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{HIO}$ . The rate is approximately independent of ionic strength over the range 0.05–1.2, but at very low ionic strength the behavior expected from the Brønsted equation is approached.<sup>27</sup>

From the relation between the experimental rate constant  $k$  and the rate constants for the separate steps in the mechanism, it follows that the experimental activation energy  $E$  is a composite of the individual activation energies:  $E = \frac{1}{2}(E_1 + E_2 + E_5 - E_6)$ .  $E$  is 32.2 kcal./mole, and  $E_1$  is 33.5 kcal./mole.<sup>9</sup> Therefore  $E_2 + E_5 - E_6 = 30.9$  kcal./mole. It is estimated that  $E_5$  is similar in magnitude to  $E_1$ , while  $E_2$  and  $E_6$  are fairly small.

**Acknowledgment.**—We wish to express our appreciation to Professor R. M. Keefer for many helpful discussions.

(27) F. Bell, R. Gill, D. Holden and W. F. K. Wynne-Jones, *ibid.*, **55**, 874 (1951).

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

## The Activation Energy of Inversion in Substituted 1,2-Dithiane and 1,2-Dioxane Measured by the Nuclear Magnetic Resonance Technique<sup>1</sup>

BY GORAN CLAESON,<sup>2</sup> GAYLORD ANDROES AND MELVIN CALVIN<sup>3</sup>

RECEIVED MAY 29, 1961

The activation energy,  $\Delta E^\ddagger$ , and frequency factor,  $\nu_0$ , for inversion in 3,3,6,6-tetramethyl-1,2-dithiane (IV) and 3,3,6,6-tetramethyl-1,2-dioxane (V) have been measured by high resolution proton magnetic resonance methods. The results are  $\Delta E^\ddagger = 16.1$  kcal./mole and  $\nu_0 = 2 \times 10^{14}$  sec.<sup>-1</sup> for IV and  $\Delta E^\ddagger = 18.5$  kcal./mole and  $\nu_0 = 4.0 \times 10^{18}$  sec.<sup>-1</sup> for V. The difference in the values between the two compounds has been explained by means of a hypothesis of different pathways in the inversion of compounds IV and V.

An organic disulfide,  $\text{R-S-S-R}$ , or the corresponding oxygen or selenium analogs, consists of an equimolar mixture of I and II. These are optical antipodes, and their stability depends on the

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