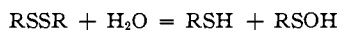


[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Oxidation of Ethyl Disulfide by Hypobromite Ion. The Rate of the Reaction

BY H. A. YOUNG AND M. B. YOUNG

The reaction between ethyl disulfide and hypobromite ion is more complicated than the corresponding one between the disulfide and bromine.¹ Whereas a dilute solution of bromine oxidizes the disulfide quantitatively to ethyl sulfonate, a dilute solution of sodium hypobromite produces some sulfate ion in addition to the sulfonate. In the present investigation, as in the previous ones, the oxidation system consisted of two phases, the solvents being carbon tetrachloride and water. Also, as previously, the primary object of the investigation was the study of the initial reaction between the sulfur compound and the oxidizing agent, particularly with reference to evidence for or against the formation of a "sulfenic" acid according to the reaction



Consequently, all of the organic products of the oxidation were not traced, although the principal one, ethyl sulfonic acid, was identified in the manner previously described.^{1a}

The possibility of a hydrolytic cleavage of the sulfur-sulfur linkage of disulfides, as described in the above equation, has been the subject of many investigations, the most recent of which have been those of Schöberl and his co-workers.²

Stoichiometry

The experiments were carried out as follows. The disulfide was weighed in a weighing ampoule and added to a known volume of carbon tetrachloride in a 1-liter bottle with a tightly fitting ground-glass stopper. The analyzed hypobromite solution, freshly prepared by adding bromine to a solution of sodium hydroxide of known concentration, was then pipetted into the bottle and the mixture shaken violently in a mechanical shaker until samples of the hypobromite layer taken at suitable time intervals showed no appreciable further loss of oxidizing power. A blank experiment containing the same volumes of carbon tetrachloride and hypobromite solutions was run with each experiment, and the results corrected accordingly. The blank corrections were small in

(1) (a) Young, *THIS JOURNAL*, **59**, 811 (1937); (b) Young and Young, *ibid.*, **59**, 812 (1937).

(2) Schöberl, *Ber.*, **70**, 1186 (1937). This is the latest of a series of four papers pertaining to the subject.

every case. The hypobromite was determined iodometrically by analyzing 10-cc. samples of the aqueous layer; the sulfate was determined gravimetrically as barium sulfate after separation of the carbon tetrachloride layer. Table I is a summary of seventeen experiments.

Examination of the ratio of moles of hypobromite ion used to moles of ethyl disulfide used, column 11, indicates that although the experimental error is larger than might be wished (approximately 2%), there is a variation in this ratio which is too great to be attributed entirely to this cause. From a comparison of the results of Expts. 1, 2, 3, 10, and 11, with those of Expt. 7, and of Expts. 4 and 6, with those of Expt. 9, it is apparent that this variation is independent of the disulfide concentration. In addition, the ratio seems to increase with increased hypobromite ion concentration and decrease with increasing hydroxide ion concentration, other factors remaining constant. These facts indicate that the value of the ratio depends in some manner upon the concentration of hypobromous acid present.

The initial hypobromous acid (Column 7) was obtained using Shilov's³ value of 2.06×10^{-9} for the dissociation constant of hypobromous acid. In calculating the final concentration of hypobromous acid, it was assumed that the reduction of two moles of hypobromite ion required one mole of hydroxide ion. That this assumed ratio of 2 to 1 is reasonable but possibly somewhat low will be shown by an examination of the equations for the oxidation of disulfide to sulfonic acid and to sulfates. An attempt to measure the ratio during the iodometric determination of the hypobromite ion was made by using a measured volume of standardized acid and back-titrating with standardized sodium hydroxide solution after the thio-sulfate titration. The results obtained for the ratio varied between 2 and 2.5, but the error involved in the method of determination is necessarily large. Fortunately, a value as high as 2.5 does not materially change the conclusion of the present work. The concentrations of hypobromous acid at the end of each experiment, calculated from the above assumption, are given in

(3) Shilov, *THIS JOURNAL*, **60**, 490 (1938).

TABLE I
 SUMMARY OF STOICHIOMETRY EXPERIMENTS

Expt.	G. R_2S_2	Initial R_2S_2	Initial OH^-	Initial BrO^-	Final OH^-	Final BrO^-	Initial $HOBBr \times 10^6$	Final $HOBBr \times 10^6$	Av. $HOBBr \times 10^6$	Moles BrO^- per mole R_2S_2	Moles SO_4^{2-} per mole R_2S_2	M
1	0.1122	0.0612	0.086	0.107	0.059	0.0522	6.21	4.42	5.32	6.03	0.271	12.6
2	.1139	.0620	.086	.103	.057	.0452	5.99	3.96	4.97	6.14	.267	13.5
3	.1296	.0707	.094	.10	.068	.0371	5.32	2.73	4.03	6.05	.230	14.1
4	.2721	.0445	.30	.205	.238	.0474	3.42	1.00	2.21	5.47	.212	9.5
5	.2720	.0445	.56	.23	.49	.0926	2.05	0.95	1.50	5.63		
6	.2275	.0414	.30	.18	.245	.0685	3.00	1.40	2.20	5.77	.257	11.0
7	.1147	.0313	.10	.097	.079	.0555	4.85	3.51	4.18	5.92	.323	10.7
8	.2272	.0620	.312	.100	.276	.0284	1.60	0.51	1.05	5.68		
9	1.3736	.113	.287	.214	.202	.0451	3.73	1.12	2.43	5.72		
10	0.6827	.0558	.10	.0982	.066	.0302	4.91	2.29	3.60	5.82	.262	11.2
11	.8094	.0662	.10	.1061	.057	.0198	5.31	1.73	3.52	5.95	.289	11.5
12	.7002	.0573	.10	.221	.0517	.124	11.0	12.0	11.5	6.76		
13	.7577	.0620	.10	.206	.0490	.104	10.3	13.3	11.8	6.58	.395	13.0
14	.7058	.0578	.10	.176	.0578	.0836	8.80	7.23	8.02	6.47	.371	12.9
15 ^a	1.3334	.109	.070	.238	.032	.162	17.0	25.3	21.1	1.82		
16 ^a	1.1045	.0903	.10	.222	.064	.150	11.0	11.7	11.4	3.04		
17 ^a	1.5203	.124	.10	.244	.031	.106	12.2	17.1	14.6	4.14		

^a Shaking stopped and solution analyzed before reaction was complete. Values of the ratio of moles of hypobromite used to moles sulfate ion produced are respectively 17.5, 17.0, 17.9.

Column 8. In Column 9 are the average concentrations of the acid.

An examination of the plot of average hypobromous acid concentration against the values of moles hypobromite ion used per mole of disulfide oxidized (Fig. 1) shows that within the limits of experimental error the relationship is a linear one.

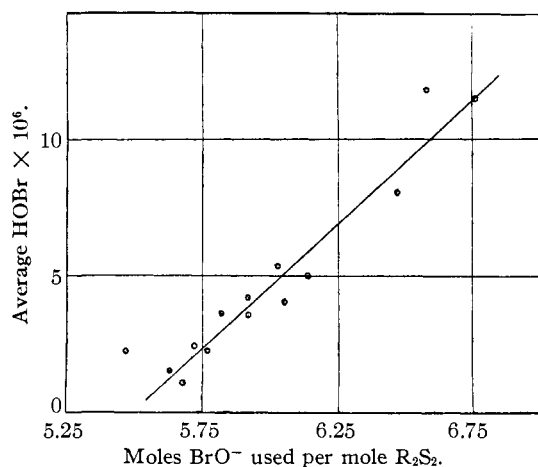


Fig. 1.—Dependence of hypobromite ion requirement upon concentration of HOBr.

In column 12 are given the values of moles of sulfate ion produced per mole of disulfide oxidized, and it is seen that they increase as the hypobromite-disulfide ratios increase. The plot of the values of the sulfate-disulfide ratio against average hypobromous acid concentration is shown in

Fig. 2, and again the relationship appears to be a linear one.

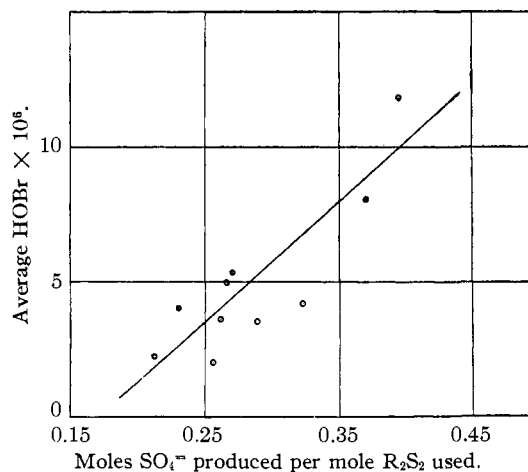


Fig. 2.—Dependence of sulfate production on concentration of HOBr.

The fact that values of the ratio of moles of hypobromite ion used to moles of disulfide used did not increase over those tabulated, even though some of the experiments were allowed to shake for many hours, is evidence that the sulfate ion production is an independent rather than a follow reaction to the production of sulfonate. This conclusion is strengthened by the results of Expts. 15, 16, and 17, in which the reaction was stopped when the values of moles of hypobromite used per mole of disulfide were approximately 2, 3, and 4,

respectively. The resulting values of moles hypobromite used per mole of sulfate ion produced were constant within the limits of error, being 17.5, 17.0, and 17.9, respectively.

The Rate of the Reaction

Experimental.—The rate of disappearance of hypobromite ion during the early stages of the reaction was measured by the following experiments. Freshly prepared hypobromite solutions were pipetted into the reaction vessel, consisting of an indented 500-cc. round-bottomed Pyrex flask, fitted with a mercury-sealed glass stirrer and a side neck of small diameter for withdrawing samples. Freshly prepared solutions of ethyl disulfide, made by dissolving weighed amounts of disulfide in a known volume of carbon tetrachloride, were added by means of a pipet, and the electric stirrer started. The stirring was at constant speed and sufficiently fast to emulsify the two layers. At various times the stirrer was stopped, the carbon tetrachloride layer allowed to settle out, a 10-cc. sample of the water layer removed by means of a pipet, and the hypobromite determined iodimetrically. This procedure of sampling seemed justified, since experiments indicated that there was no decrease in the hypobromite ion concentration when there was no stirring.

The temperature at which the rate experiments were carried out was $25.0 \pm 0.1^\circ$, maintained by a water thermostat. All reagents were brought to reaction temperature before each experiment by immersion in the thermostat.

Results.—Preliminary experiments showed that the decomposition of hypobromite ion to bromate ion could be neglected if the concentration of hydroxide ion was kept reasonably high. Experiments in which the hydroxide ion concentration at any time became appreciably lower than 0.03 *N* gave low results for both stoichiometric and rate measurements. Consequently, in the later experiments it seemed advisable to adopt the concentration of 0.03 *N* as the lower limit for hydroxide ion. That the rate of decomposition of hypobromite ion to bromate ion increases sharply with decreasing hydroxide ion has been shown by Liebhafsky and Makower⁴ and more recently by Skrabal and Skrabal.⁵

The experiments indicated that the rate of disappearance of hypobromite ion was proportional to the concentrations of disulfide and hypobromite

ion and inversely proportional to the hydroxide ion concentration.

If the stoichiometric relationship may be represented by the equation $L \text{ BrO}^- + L/2\text{OH}^- + \text{R}_2\text{S}_2 \longrightarrow$, where *L* is a function of the hypobromous acid concentration and is known from the stoichiometry experiments, the following formulation may be made for any one time interval. Let the initial concentrations of hypobromite, disulfide, and hydroxide be *a*, *b*, and *c*, respectively. Then if the volumes of the aqueous layer and of the carbon tetrachloride layer are *V* and *V*₁, respectively, and *x* is the concentration of hypobromite ion at time *t*, the concentration of disulfide at time *t* will be $b - \frac{(a-x)}{L} \left(\frac{V}{V_1}\right)$ and that of hydroxide ion will be $c - (a-x)/2$.

The rate law may then be expressed as

$$-\frac{dx}{dt} = \frac{k[x] \left[b - \frac{a-x}{L} \left(\frac{V}{V_1}\right) \right]}{\left[c - \frac{a-x}{2} \right]}$$

or more simply

$$-\frac{dx}{dt} = \frac{k(x)(D + Ex)}{F + Gx}$$

where

$$\begin{aligned} D &= b - \frac{a}{L} \frac{V}{V_1} & E &= \frac{1}{L} \frac{V}{V_1} \\ F &= c - \frac{a}{2} & G &= \frac{1}{2} \end{aligned}$$

Integration of *dx* between the limits *a* and *x*, and of *dt* between 0 and *t* leads to the expression

$$kt = \frac{F}{D} \ln \left(\frac{D + Ex}{x} \right) - \frac{G}{E} \ln (D + Ex) - \frac{F}{D} \ln \left(\frac{D + Ea}{a} \right) + \frac{G}{E} \ln (D + Ea)$$

A plot of

$$\left[2.303 \frac{F}{D} \log \frac{D + Ex}{x} - 2.303 \frac{G}{E} \log (D + Ex) \right]$$

(denoted *H*) as ordinate against time as abscissa should then be a straight line for each time interval. Because of the variation in *V*, the results of a single experiment would result in a series of line segments with the initial abscissa of each differing from the final abscissa of the preceding one. If the rate law is correct, translation of each line segment by an amount equal to the summation of the preceding differences should result in a single straight line. That such is the case is shown in Fig. 3, where are plotted the results of two typical experiments. The details of calculation are in Table II.

(4) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1044 (1933).

(5) Skrabal and Skrabal, *Monatsh.*, **71**, 251 (1938).

TABLE II
TYPICAL EXPERIMENTS
-2.303G/E 2.303F/D

<i>t</i>	<i>V</i> , cc.	<i>x</i>	<i>D</i> + <i>E_x</i>	$\frac{\log D + E_x}{D + E_x}$	$\frac{-D + E_x}{x}$	$\frac{\log D + E_x}{D + E_x}$	<i>H</i>	ΔH	Corrn. factor	<i>H</i> , corr.
Expt. 1										
Av. HOBr = 2.32×10^{-6} , <i>L</i> = 5.8, <i>V</i> ₁ = 49.75, <i>F</i> = 0.1468										
0	190.0	0.0983	0.0359	2.257	0.3653	5.13	7.657			7.657
4	190.0	.0965	.0347	2.553	.360	5.22	7.773			7.773
4	180.0	.0965	.0347	2.696	.360	5.89	8.586	0.813	0.813	
12	180.0	.0934	.0328	2.740	.351	6.10	8.840			8.027
12	170.0	.0934	.0328	2.854	.351	6.92	9.774	0.934	1.747	
24	170.0	.0893	.0304	2.921	.341	7.13	10.051			8.304
24	160.0	.0893	.0304	3.151	.341	8.29	11.441	1.390	3.137	
39	160.0	.0840	.0275	3.264	.328	8.59	11.854			8.717
39	150.0	.0840	.0275	3.482	.328	10.14	13.622	1.768	4.905	
54	150.0	.0798	.0253	3.540	.317	10.43	13.970			9.065
Expt. 7										
HOBr = 2.45×10^{-6} , <i>L</i> = 5.8, <i>V</i> ₁ = 49.75, <i>F</i> = 0.213										
0	190.0	0.1500	0.0421	2.408	0.2807	4.789	7.197			7.197
6	190.0	.1458	.0393	2.459	.268	4.960	7.419			7.419
6	180.0	.1458	.0393	2.598	.268	5.43	8.028	0.609	0.609	
14	180.0	.1414	.0366	2.657	.259	5.57	8.227			7.518
14	170.0	.1414	.0366	2.765	.259	6.18	8.945	0.718	1.327	
24	170.0	.1369	.0339	2.830	.248	6.39	9.220			7.893
24	160.0	.1369	.0339	3.050	.248	7.10	10.150	0.930	2.257	
36	160.0	.1320	.0312	3.127	.237	7.34	10.467			8.210
36	150.0	.1320	.0312	3.335	.237	8.22	11.555	1.088	3.345	
48	150.0	.1275	.0289	3.409	.227	8.47	11.879			8.534

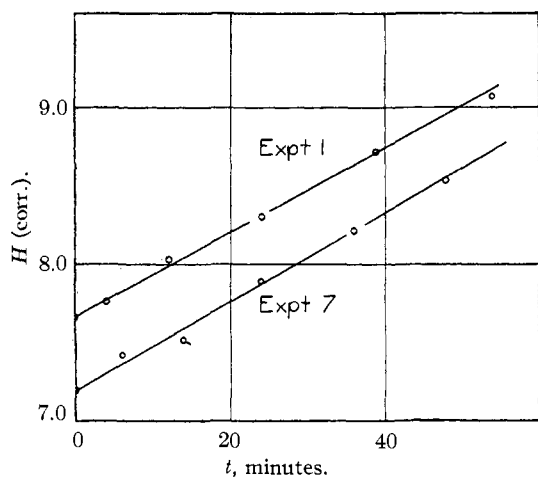


Fig. 3.—Typical rate results. Corrected value of *H* plotted against time in minutes.

Discussion of Results

An explanation for the above stoichiometric and rate results would be a reaction system which has, as a single rate-determining step, a reaction between disulfide and hypobromous acid. This rate-determining step is probably followed by several rapid reactions, among which must be two competing ones of comparable rates, the first in-

volving hypobromous acid and eventually leading to sulfate ion, the second involving water and leading to sulfonate ion.

Although the authors realize the need for caution in interpreting the results obtained in such a complicated reaction system, it is felt that these experiments seem to prove that the principal rate determining step is not the hydrolysis of the disulfide. The possibility of the establishment of a rapid equilibrium involving water and disulfide as a precursor to further oxidation also seems to be remote, since not only is the solubility of ethyl disulfide in water not materially affected by hydroxide ion, but experiments in which carbon tetrachloride solutions of disulfide were stirred with water for several minutes resulted in water layers which did not reduce hypobromite ion. Any sulfenic acid formed in the latter experiments might reasonably be expected to be in the water layer, and, because of solubility relations, in appreciable quantities.

The conclusion that sulfenic acid formation is not involved in the primary oxidation is in accord with the results of Shinohara and Kilpatrick,⁶ who have shown that the rate determining step in oxi-

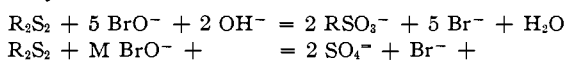
(6) Shinohara and Kilpatrick, *THIS JOURNAL*, **56**, 1466 (1934).

dation of cystine by iodine is a simple second order reaction between cystine and iodine (or triiodide ion). Since Shinohara and Kilpatrick worked entirely in acid solution, however, their results do not preclude the possibility of the establishment of a rapid equilibrium involving cystine and water and the formation of a sulfenic acid. But also, the above conclusion is not contradictory to the work of Schöberl and his colleagues. They have shown that symmetrical disulfides which contain a carboxyl group and the sulfur atom attached to the same carbon atom decompose to yield the corresponding sulfhydryl compound, a keto acid, and hydrogen sulfide when heated in alkaline or, in some cases, neutral, solutions.



For this result, the assumption of an alkaline cleavage of the original disulfide leads to a satisfactory and reasonable mechanism, as they have pointed out. However, the authors feel that there is at present a regrettable tendency in the chemical literature to assume that all disulfides undergo cleavage in alkali. Aside from the evidence of the present paper that such a cleavage is not of importance in the oxidation of ethyl disulfide, Schöberl has pointed out two other disulfides, both of which contain carboxyl groups but only one of which is in the proper position, which do not show any tendency to decompose upon heating with alkali² (p. 1187).

If the two over-all reactions for the oxidation of ethyl disulfide are written



values of M may be determined from the stoichiometry measurements of Table I, since it may be readily shown that

$$M = \frac{\left(\frac{\text{BrO}^-}{\text{R}_2\text{S}_2}\right) - 5 + \frac{5}{2} \left(\frac{\text{SO}_4^{2-}}{\text{R}_2\text{S}_2}\right)}{\frac{1}{2} \left(\frac{\text{SO}_4^{2-}}{\text{R}_2\text{S}_2}\right)}$$

where $\text{BrO}^-/\text{R}_2\text{S}_2 =$ moles hypobromite used per

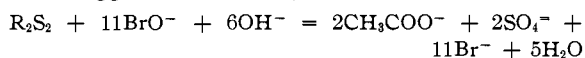
TABLE III
SUMMARY OF RATE EXPERIMENTS

Expt.	Initial			HBrO		L	k	
	BrO ⁻	OH ⁻	R ₂ S ₂	× 10 ⁶ Final	× 10 ⁶ Av.			
1	0.0983	0.196	0.0359	2.51	2.14	2.32	5.8	0.027
2	.0994	.098	.0321	5.07	4.69	4.88	6.1	.027
3 ^a	.0493	.098	.0321	2.51	1.75	2.13	5.8	.030
4 ^a	.0915	.100	.0454	4.57	3.79	4.18	6.0	.029
5 ^a	.0912	.100	.0454	0.46	3.84	4.20	6.0	.027
6	.152	.191	.0454	3.98	3.49	3.73	5.9	.026
7	.150	.288	.0421	2.60	2.30	2.45	5.8	.028
8	.0992	.288	.0421	1.72	1.43	1.58	5.7	.029
9 ^a	.0730	.288	.0421	1.27	0.97	1.12	5.6	.030
10 ^a	.0989	.292	.0650	1.69	1.28	1.49	5.7	.030
11	.0388	.292	.0365	1.69	1.35	1.52	5.7	.031
12	.0977	.392	.0365	1.25	1.04	1.15	5.6	.029

^a These experiments unfortunately embraced concentration ranges in which D became zero, resulting in a singularity in the integrated expression. However, in the neighborhood of the singularity, the rate constants could be determined by using the simplified rate law— $dx/dt = k(x)(Ex)/(F + Gx)$. Such calculations were made and the rate constants so determined did not differ appreciably from those determined in the usual manner.

mole R_2S_2 used, and $\text{SO}_4^{2-}/\text{R}_2\text{S}_2 =$ moles sulfate ion produced per mole R_2S_2 used.

Although the values of M (column 14, Table I) vary quite widely, it is observed that, except for Expts. 4 and 5, the values lie between 10.70 and 13.50. The average value of M , 12.1, is at least suggestive of the equation



Conclusion

1. The oxidation of ethyl disulfide by hypobromous acid involves at least two independent reactions, one of which produces ethyl sulfonate ion and the other sulfate ion.

2. The rate of oxidation has been studied at 25° and the following rate law obtained

$$-\frac{d \text{BrO}^-}{dt} = \frac{k(\text{R}_2\text{S}_2)(\text{BrO}^-)}{(\text{OH}^-)}$$

where k has the value of $0.028 \approx 0.002$.

3. These experiments give no evidence for the formation of a sulfenic acid by the hydrolysis of the disulfide.

DAVIS, CALIF.

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