The Rates of Oxidation of Ethyl Disulfide and Ethyl Mercaptan by Bromine
Effect of Hydrogen Ion

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

In recent papers[1] the oxidation of a carbon tetrachloride solution of ethyl disulfide by bromine in the presence of a water layer has been discussed. In that discussion it was pointed out that the initial rate of disappearance of bromine might be represented by the expression $-dBr_2/dt = k[R_2S_2 \cdot (Br_2)_2]$ in the absence of hydrogen ion, but that in the presence of hydrogen ion an increase in the rate of the reaction was apparent. Further measurements on the effect of hydrogen ion upon this initial rate have been obtained and are now presented, together with the results of some experiments on the rate of oxidation of ethyl mercaptan by bromine. The effect of varying the volume of the carbon tetrachloride layer also has been determined.
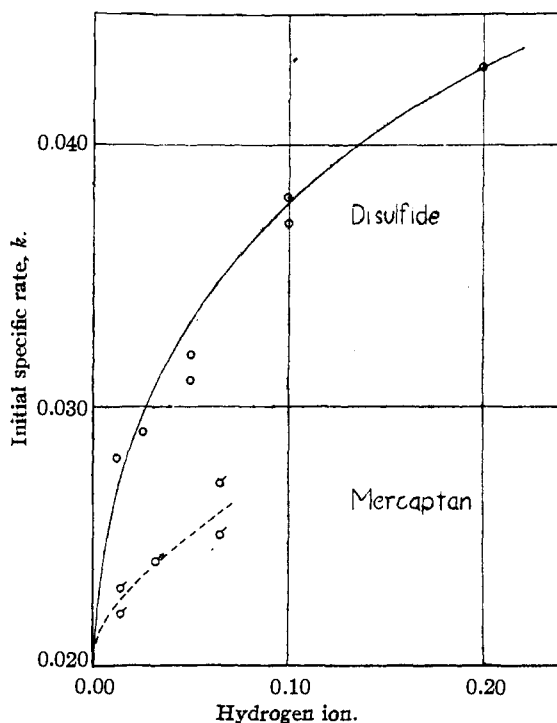

Fig. 1.—Initial specific rate plotted against initial hydrogen ion concentration.

The experimental results which were obtained by the method previously described[1b] are summarized in Table I.

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

TABLE I

SUMMARY OF RESULTS

DISULFIDE EXPERIMENTS

In Expts. 1 to 7 the volume of the carbon tetrachloride layer was 67.7 cc.; in Expt. 8 it was 35.0 cc. All concentrations in moles per liter.

Expt.	Br_2 initial	R_2S_2 initial	H^+ initial	k, exptl	k, calcd.
1	0.0368	0.00988	0.20	0.043	0.044
2	.0501	.00964	.10	.038	.038
3	.0366	.00985	.05	.032	.034
4	.0314	.00875	.025	.029	.031
5	.0331	.00729	.012	.028	.028
6	.0132	.0519	.05	.032	.034
7	.0130	.0501	.10	.037	.038
8	.0309	.00679	.0	.035	

MERCAPTAN EXPTS.

In Expts. M-1 to M-7 the volume of the carbon tetrachloride layer was 67.7 cc.; in Expts. M-8 and M-9 it was 42.0 cc. In Expt. M-7 initial H^+ was 0.05 M.

| Expt.	Initial Br_2 Calcd.	Initial R_2S_2 Calcd.	H^+ from RSH	k, exptl.
M-1	0.0230	0.01085	0.0140	0.022
M-2	.0554	.01085	.0140	.023
M-3	.0531	.0246	.0318	.024
M-4	.0153	.0246	.0318	.024
M-5	.00765	.0492	.0646	.027
M-6	.0148	.0492	.0646	.025
M-7	.0106	.0525	.01175	.035
M-8	.0595	.00691	.00585	.034
M-9	.0295	.00690	.00581	.036

Effect of Hydrogen Ion on Rate of the Ethyl Disulfide–Bromine Reaction.—The results of the seven experiments in which the original concentration of hydrogen ion in the water layer varied from 0.012 to 0.20 M are shown graphically in the upper curve of Fig. 1. The initial rates may be represented fairly well by the expression

$$-dBr_2/dt = [R_2S_2(Br_2)_2][0.020 + 0.043(H^+)^{1/2.68}]$$

as may be seen by comparing the experimentally determined values of $-(dBr_2/dt)/R_2S_2(Br_2)_2$ (column 5, Table I) with the values of k calculated from $k = 0.020 + 0.043 (H^+)^{1/2.68}$ (column 6, Table I). The value of 0.038 for k when hydrogen ion is 0.1 M is somewhat lower than the single value of $k = 0.051$ given for this concentration in a previous paper, but in all other respects the present experiments behaved in a manner exactly similar to those previously described.

Rate of Oxidation of Ethyl Mercaptan by Bromine.—As previously shown[1a] bromine in-

stantaneously and completely oxidizes ethyl mercaptan to ethyl disulfide according to the equation

$$2RSH + Br_2 = R_2S_2 + 2HBr$$
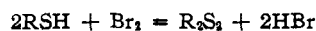
The initial rate of disappearance of bromine as it reacts with ethyl mercaptan should then be interpreted readily in terms of the known rates of oxidation of ethyl disulfide in the presence of hydrogen ion. The results of experiments M-1 to M-6 shown by the lower curve in Fig. 1 indicate that the rate law $-dBr_2/dt = k[R_2S_2 \cdot (Br_2)_2]$ is being followed fairly well, but that the initial specific rate does not increase with the liberated hydrogen ion as rapidly as might be expected. Apparently the hydrogen ions which are liberated throughout the carbon tetrachloride layer as hydrobromic acid are not as effective in increasing the initial reaction rate as are those originally introduced into the water layer.

Change in Rate with Surface of Carbon Tetrachloride Layer.—Since the carbon tetrachloride remained a contiguous layer throughout the experiments, the amount of surface per mole of intermediate was conveniently increased by decreasing the volume of the carbon tetrachloride. As the conical flasks used throughout the experiments were constructed so that they were nearly cylindrical in their lower parts, decreasing the volume of the carbon tetrachloride layer should result in an almost proportionate increase in contact area per mole. As indicated by the result of Expt. 8, decreasing the volume of the carbon tet-

rachloride from 67.7 to 35.0 cc. increased the experimental value of k from 0.020 (as previously determined) to 0.035. The two mercaptan experiments M-8 and M-9, when corrected for effect of hydrogen ion, also show an approximately proportionate increase in the value of k with a decrease in the total volume of the carbon tetrachloride. These results support the assumption that the rate determining reaction is one occurring at the boundary of the water and carbon tetrachloride layers.

Conclusion

The previous suggestion that the rate determining step in the oxidation of ethyl disulfide by bromine in this two phase system is initially the hydrolysis of an intermediate product at the surface of the carbon tetrachloride layer, and is finally the rate of diffusion of the intermediate from the carbon tetrachloride, is strengthened by the following observations:

1. The relationship between the initial specific rate and the initial hydrogen ion concentration.

2. The fact that initial rate of oxidation of ethyl mercaptan follows the same law as does that of the disulfide, except that the hydrogen ions liberated throughout the carbon tetrachloride layer are not completely available for accelerating the initial rate.

3. Increasing the amount of surface per mole of intermediate increases the initial rate of the reaction.
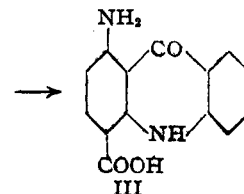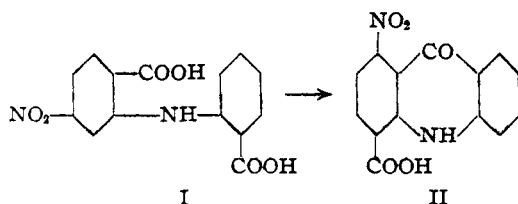
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1-Aminoacridine-4-carboxylic Acid[1]

BY KONOMU MATSUMURA

In pursuance of a pharmacological investigation of amino-acridine carboxylic acids, 1-nitroacridone-4-carboxylic acid was synthesized according to the following scheme

In conformity with the expected behavior of a product of type II, the intermediary product in dilute alcoholic potassium hydroxide develops a deep orange yellow color. On reduction with stannous chloride, followed with decarboxylation, II yields an aminoacridone (m. p. 289–290°).