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The Rate of Oxidation of Thiodiglycol and Triethylamine by Hydrogen Peroxide

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Sulfides¹ and tertiary amines² are cleanly oxidized by aqueous hydrogen peroxide to give sulfoxides and amine oxides, respectively. Despite the formal simplicity of these reactions their mechanisms appear worth investigating because of the widespread occurrence of hydrogen peroxide as a product of natural oxidation-reduction processes. In order to study the effect of *pH* on these reactions measurements were made of the rate of oxidation of thiodiglycol by hydrogen peroxide in aqueous solution over the *pH* range 0.3–6, and of triethylamine by the same oxidizing agent in unbuffered water and at *pH* 1.

Experimental Results

The thiodiglycol was obtained from the Carbide and Carbon Chemicals Corporation. Only a constant boiling middle cut (b. p. 137° (5 mm.)) was used. The triethylamine was distilled several times and a middle cut boiling at 89.5–89.8° was used. All our kinetic measurements were made at 25 ± 0.05°. Initial time was taken as the time of addition of a solution of hydrogen peroxide, adjusted to 25.0° in the thermostat, to thiodiglycol or triethylamine in the appropriate aqueous solution at the same temperature. The aliquots, taken at appropriate time intervals, were analyzed directly for residual hydrogen peroxide by adding them to a solution containing 200 cc. of water, 20 cc. of 1:2 sulfuric acid and 2 g. of potassium iodide. Three drops of 3% ammonium molybdate were then added and, after standing for five minutes, the solution was titrated with standard sodium thiosulfate to a starch end-point.

The oxidation of thiodiglycol in water by hydrogen peroxide is bimolecular with a rate constant for the non-catalyzed reaction equal to 1.30 ± 0.07 × 10⁻¹ liters/mole-minute. As can be seen from Table I, the reaction shows acid catalysis at and below *pH* 1. This acceleration is not due simply to an increase in ionic strength at the lower *pH*'s, for to buffer at *pH* 4.7 the solution was made 0.5 *M* in both sodium acetate and acetic acid and, consequently, this solution is of higher ionic strength than the run at *pH* 1, where the solution was 0.1 *M* in hydrochloric acid.

The experimental data for a typical run at each *pH* are given in Tables II–VII. Here *a* and *b* refer to thiodiglycol and hydrogen peroxide, respectively. In all runs 5-cc. aliquots were taken. To indicate how closely the second order equation is followed throughout the course of a single run plots of log *Q* - *z*/*Q*(1 - *z*) vs. *t* for runs at three *pH*'s are presented in Fig. 1. Here *Q* = initial

TABLE I

Buffer	<i>pH</i>	<i>k</i> (bimolecular) liters/mole- minute
H ₂ O (not buffered)		0.123
Potassium acid phthalate-sodium potassium phthalate	6	.129
Sodium acetate-acetic acid	4.7	.137
Potassium acid phthalate-sodium potassium phthalate	4	.131
Hydrochloric acid	1	.273
Hydrochloric acid	0.3	.946

concentration of H₂O₂/initial concentration of thiodiglycol and *z* = fraction reacted.

TABLE II

a = 0.0500 *M*, not buffered;
b = 0.1406 *M*

Min.	0.0500 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
38	23.66	44.7
56	22.32	58.1
73	21.50	66.3
88	20.96	71.7
103	20.50	76.3

TABLE III

a = 0.1027 *M*, *b* = 0.1357
M, *pH* 6

Min.	0.0500 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
10.3	24.72	11.8
26.5	20.30	33.4
38.8	18.40	42.7
55.0	16.42	52.4
77.0	14.55	61.4
90.3	13.68	65.6
127	12.06	73.5

TABLE IV

a = 0.0822 *M*, *b* = 0.0873
M, *pH* 4.7

Min.	0.0999 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
10.6	7.70	12.6
35.3	6.24	30.4
52.7	5.60	38.2
83.3	4.68	49.4
112	3.90	58.8
150	3.34	65.6
201	2.85	71.6

TABLE V

a = 0.0907 *M*, *b* = 0.1338
M, *pH* 4

Min.	0.0500 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
7.00	24.66	11.7
16.4	22.60	23.0
25.3	21.00	31.8
35.4	19.42	40.5
44.0	18.32	46.6

TABLE VI

a = 0.0941 *M*, *b* = 0.1149
M, *pH* 1

Min.	0.0999 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
4.13	10.35	12.2
13.2	8.60	30.8
22.5	7.47	42.8
45.2	5.65	62.1
70.5	4.70	72.2
89.1	4.21	77.4

TABLE VII

a = 0.0956 *M*, *b* = 0.1179
M, *pH* 0.3

Min.	0.0999 <i>N</i> S ₂ O ₈ ²⁻ , cc.	% Reaction
4.80	8.22	37.5
13.2	5.70	63.8
23.6	4.68	74.4
25.6	4.18	79.6
32.0	3.80	83.6
42.4	3.30	88.8
56.5	2.99	92.1

The rate of oxidation of triethylamine by hydrogen peroxide in unbuffered aqueous solution is 2.0 × 10⁻² liters/mole-minute. At *pH* 1 no reaction had occurred after one hundred and

(1) Gazdar and Smiles, *J. Chem. Soc.*, **93**, 1833 (1908).

(2) Dunstan and Goulding, *ibid.*, **75**, 1004 (1899).

twenty hours. The data for a typical run are given in Table VIII.

TABLE VIII

0.08399 *M* hydrogen peroxide, not buffered; 0.06643 *M* triethylamine.

Min.	0.0971 <i>N</i> S ₂ O ₈ ²⁻ cc.	% Reaction
52.7	7.85	11.7
105.1	7.40	18.3
185.7	6.88	26.0
324.1	6.00	38.7
385.4	5.85	40.9
600	5.05	52.6
724	4.70	57.7
1348	3.43	76.3

Discussion

In the oxidation of a tertiary amine by hydrogen peroxide, which is quite analogous to the formation of sulfoxides, the direct product is a base of the type (R₃NOH)⁺OH⁻, from which an amine oxide may be produced by dehydration.³ The action of hydrogen peroxide is, therefore, analogous to that of a methylating agent in the formation of quaternary ammonium (or tertiary sulfonium) salts, and its effectiveness is dependent upon the ease with which it can donate the group (OH)⁺ to the basic nitrogen or sulfur atom.

In the oxidation of thiodiglycol the rate was faster at and below *pH* 1. The effect of acid on the rate of oxidation is explained by supposing that the neutral molecule HOOH, which must produce a hydroxyl ion in the oxidation can accomplish this oxidation at a constant rate which is less than the rate at which its conjugate acid, HOOH₂⁺, can do it. Only in strongly acid solution is there enough of this species present to make a difference in rate. It is faster because the other product of its oxidation is not the OH⁻ ion, involving a separation of charge in the critical step of the reaction, but a neutral water molecule.

In the oxidation of triethylamine an additional factor becomes important. With thiodiglycol the shift in favor of HOOH₂⁺ is not counteracted by a shift in favor of (HOCH₂CH₂)₂SH⁺. With triethylamine which has a *K_B* of 4.35 × 10⁻⁴ at 25°,⁴ the ratio R₃NH⁺/R₃N is equal to 4.35 ×

(3) Meisenheimer, *Ann.*, **397**, 273 (1913).

(4) Moore, *J. Chem. Soc.*, **91**, 1383 (1907).

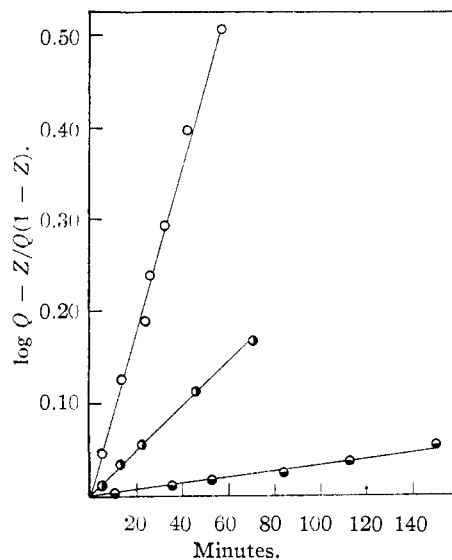


Fig. 1.—Second order plots of runs at three *pH*'s: 0.1179 *M* H₂O₂ and 0.0956 *M* thiodiglycol at *pH* 0.30; 0.1149 *M* H₂O₂ and 0.0941 *M* thiodiglycol at *pH* 1.0; 0.0873 *M* H₂O₂ and 0.0822 *M* thiodiglycol at *pH* 4.7.

10⁹ at *pH* 1. The conjugate acid of triethylamine, R₃NH⁺, is much less susceptible to oxidation than triethylamine itself and as a result no reaction occurs at *pH* 1.

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Summary

The oxidation of thiodiglycol in water is bimolecular and shows acid catalysis at and below *pH* 1. The rate constant for the non-catalyzed reaction is 1.30 ± 0.07 × 10⁻¹ liters/mole-minute at 25.0°.

The rate constant for the oxidation of triethylamine by hydrogen peroxide in water is 2.0 × 10⁻² liters/mole minute at 25°. At *pH* 1 the oxidation is too slow for convenient measurement.

The mechanism of these reactions is briefly discussed.

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