[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Kinetics of the Oxidation of Thiodiethanol by *t*-Butyl Hydroperoxide

JOHN O. EDWARDS AND DONALD H. FORTNUM

Received September 14, 1961

The rate of oxidation of thiodiethanol by *t*-butyl hydroperoxide in aqueous solution has been studied. The reaction is first order in each reactant and is catalyzed by hydrogen ion. Rate constants for the catalyzed and uncatalyzed reactions have been determined and activation quantities calculated. The reaction mechanism is discussed.

The oxidation of organic sulfides to sulfoxides has been carried out with various peroxide compounds. The kinetics of this reaction have been studied using hydrogen peroxide,[1,2] alkyl hydroperoxides,[3] and peroxybenzoic acid[4] as the oxidants. The reaction follows second order kinetics and acid catalysis is usually observed.

As part of a study of the reaction of nucleophiles with peroxides the oxidation in aqueous solution of 2,2′-thiodiethanol (hereafter sulfide) by *t*-butyl hydroperoxide (hereafter peroxide) has been investigated. This reaction is of interest because it involves neutral species and because comparative data with hydrogen peroxide as oxidant are available.[1] Specifically, we wished to find out (a) if this reaction followed the same kinetic pattern as the hydrogen peroxide oxidation, (b) the nature of the acid catalysis, and (c) the values of the activation thermodynamic quantities.

EXPERIMENTAL

Reagents. Reagent grade chemicals were used unless otherwise indicated. Three samples of peroxide were employed: two of these were commercial products and one was prepared in this laboratory; no difference in kinetics was observed due to the source of the peroxide. The sulfide was obtained from Eastman Kodak and redistilled under vacuum.

Procedure. Aqueous samples of the reactants were suspended in a constant temperature water bath maintained at 25.0 ± .1° or were packed in ice in a Dewar flask at 0.1 ± .1°. The reactants were mixed at constant temperature and 5-ml. aliquot samples were withdrawn at appropriate intervals of time and analyzed as indicated below. The *p*H of solutions having *p*H greater than 1.0 was measured with a Beckman Model G meter. The *p*H of more acid solutions was calculated from the concentrations and volumes of reagents in the reaction mixture. All *p*H measurements were made at room temperature.

Analytical. The aliquot sample to be analyzed for peroxide was added to about 50 ml. of glacial acetic acid in 250-ml. filter flask. The side arm of the flask was connected to a rubber tube, and the open end of the tube was submerged in a flask of water. The arrangement (after stoppering) permits the escape of gas, but prevents air from entering the flask containing the sample. Approximately 1.5 g. of sodium bicarbonate was added to the contents of the flask which was then tightly stoppered. When the evolution of carbon dioxide decreased (about 2 minutes), 2 ml. of a saturated solution of sodium iodide was added. The flask was then left in the dark for forty minutes. Then 100 ml. of water was added and the liberated iodine was titrated with standard sodium thiosulfate solution in the usual manner.

RESULTS

The rate of reaction was followed by measurement of peroxide concentration as a function of time. Conditions were generally chosen so that the sulfide was in excess and essentially constant throughout the course of the reaction. It was found that plots of the logarithm of the volume of standard thiosulfate required to titrate the iodine liberated by unreacted peroxide were linear. This indicates that the reaction is first order in peroxide concentration, and this was confirmed by the fact that the observed first order slopes were independent of peroxide concentration. The slopes were proportional to the concentration of sulfide. The rate law is, therefore

$$\frac{-d\,[\text{peroxide}]}{dt} = k\,[\text{peroxide}]\,[\text{sulfide}] \qquad (1)$$

The results of 25 kinetic experiments at 25.0° and 13 experiments at 0.1° are presented in Table I. Second order rate constants were obtained from the pseudo first order constants through division by the actual sulfide concentrations; in cases where the sulfide concentration was not in great excess, suitable correction was made.

The conditions for each kinetic run are also presented in Table I. During the course of this study, it was observed that the concentration of acetic acid affected the rate of reaction; therefore, this concentration is listed in column 2. Runs having appreciable amounts of acetic acid are listed at the end of the 25° runs in order of decreasing concentration. Column 3 lists the ionic strength. Columns 4 and 5 list the initial concentrations of reactants. Column 6 lists the measured or calculated *p*H of the reaction mixtures. The materials added to control *p*H and ionic strength are listed in column 7. The observed rate constants based on Equation 1 are given in column 8.

pH effect: It was observed that in the *p*H range from 3 to 6, the rate constant is constant, but in more acid solutions, *k* increases regularly and rapidly with an increase in hydrogen ion concen-

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TABLE I

SUMMARY OF RATE DATA

Run	[HAC][a]	u[b]	[peroxide][a]	[sulfide][a]	pH	Other	$k \times 10^{4d}$
				Part I; 25°			
1	0	0.35	0.112	0.72	0.46	$HClO_4$	6.85
2	0	0.21	0.030	0.69	0.68	$HClO_4$	4.69
3	0	0.13	0.085	0.53	0.90	$HClO_4$	3.30
4	0	0.12	0.101	0.52	0.91	$HClO_4$	3.10
5	0	0.07	0.037	0.45	1.14	HNO_3	2.43
6	0	0.07	0.084	0.57	1.18	$HClO_4$	2.30
7	0	0.03	0.060	0.44	1.58	$HClO_4$	1.80
8	0	0.01	0.111	0.80	2.03	$HClO_4$	1.54
8a	0	0.01	0.114	0.80	2.03	$HClO_4$ and t-C_4H_9OH	1.0
10	0	0.001	0.114	0.80	3.00	$HClO_4$	1.40
11	0.05	0.05	0.116	0.24	4.55	NaAc	1.42
12	0.05	0.40	0.125	0.97	4.58	NaAc and $NaClO_4$	1.37
13	0.05	0.05	0.057	0.48	4.66	NaAc	1.41
14	0.05	0.05	0.113	0.48	4.70	NaAc	1.26
15	0.05	0.05	0.067	0.48	4.70	NaAc	1.41
16	0	0	0.104	0.52	5.7–5.2		1.38
17	11.7	0.69	0.112	0.67	2.68	NaAc	7.43
18	7.1	1.67	0.138	0.81	4.04	NaAc	2.70
19	3.5	2.5	0.138	0.81	4.82	NaAc	1.68
20	2.9	0.01	0.099	0.67	1.98	NaAc	2.11
21	2.7	0.01	0.104	0.62	1.95		2.02
22	1.7	0.01	0.074	0.48	2.10		1.78
23	0.85	0.004	0.075	0.48	2.31		1.49
24	0.59	0.60	0.176	0.57	4.68	NaAc	1.33
25	0.58	0.06	0.088	0.55	3.62	NaAc	1.53
				PART II; 0.1°			
							$k \times 10^{5d}$
1	0	0.43	0.174	2.33	0.37	$HClO_4$	13.36
2	0	0.28	0.145	2.53	0.56	$HClO_4$	5.77
3	0	0.13	0.170	2.15	0.89	$HClO_4$	4.60
4	0	0.07	0.176	2.28	1.17	$HClO_4$	2.94
5	0	0.04	0.189	2.33	1.38	$HClO_4$	2.60
6	0	0.01	0.193	2.39	1.84	$HClO_4$	1.97
7	0	0.01	0.194	2.39	1.84	$HClO_4$	1.83
7a	0	0	0.088	1.08	2.41	$HClO_4$	1.62
8	0	0	0.038	0.45	3.27	$HClO_4$	1.60
9	0	0	0.087	1.31	*ca.* 5[e]		1.48
10	0	0	0.088	1.10	*ca.* 5[e]		1.52
11	0	0	0.186	2.42	*ca.* 5[e]		1.47
12	0.025	0.03	0.101	2.66	*ca.* 4.5	NaAc	1.41
13	0	0	0.117	4.84	*ca.* 5[e]		1.35

[a] Initial molar concentration. HAc is acetic acid. [b] Ionic strength. [c] Other materials present in the reaction mixture to control pH or ionic strength. NaAc is sodium acetate. [d] Observed second order rate constant in units of l. mole^{-1} sec.$^{-1}$. [e] Solution was not buffered. pH at room temperature varied from 5.5 to 4.5 during the course of reaction.

tration. A graph of log k *vs.* pH is shown in Fig. 1. This behavior may be explained by assuming the rate law where the second term represents catalysis

$$\text{rate} = k_2\,[\text{peroxide}]\,[\text{sulfide}] + k_3\,[\text{H}^+]\,[\text{peroxide}]\,[\text{sulfide}] \qquad (2)$$

by hydrogen ion. For each experimental run, the observed rate constant is given by

$$k = k_2 + k_3[\text{H}^+] \qquad (3)$$

The lines in Figure 1 represent the variation of rate constant with pH calculated with equation 3 using the values of k_2 and k_3 given in Table II. The dots in the figure represent values of k determined experimentally. The agreement between experimental points and the calculated curves supports the above explanation of the behavior of the second order rate constant as a function of pH.

Medium effects. The reacting species are nonionic, and no salt effect was expected. No large effect was observed, although some of the runs with considerable electrolyte present seem to have slightly lower rate constants (compare numbers 11 and 12, and also 24 and 25).

The rate is influenced by the amount of acetic acid present in the reaction mixture. Runs 17 through 25 at 25° had concentrations of acetic acid greater than 0.1M. The rate increases with an increase in the concentration of acetic acid, however this increase is not in direct proportion to the concentration of acetic acid. The nature of this effect will be discussed below.

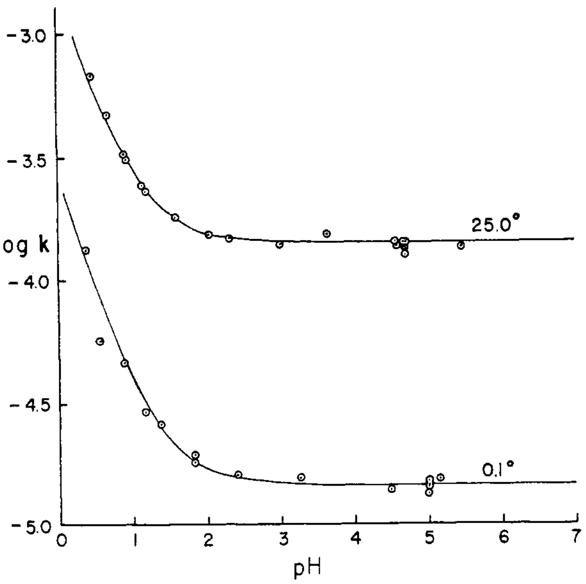

Fig. 1. Values of observed second order rate constant as a function of *p*H for two temperatures

One run, 8a, was made in a solution containing 21% (by volume) *t*-butyl alcohol. The observed rate constant was lowered by about 35% from an otherwise identical run (8) made without the alcohol.

Temperature effects. Using the rate constants at 25° and 0°, activation thermodynamic quantities were calculated.[5] These values are tabulated in Table II, and are consistent with expectation in that the catalyzed reaction has a lower activation energy than the uncatalyzed reaction.

TABLE II

Data for the Catalyzed and Uncatalyzed Processes[a]

	Uncatalyzed Reaction	Acid-Catalyzed Reaction
Rate constant (0°)	1.45×10^{-5}	2.6×10^{-4}
Rate constant (25°)	1.40×10^{-4}	1.5×10^{-3}
Ea	14.8	11.4
ΔH^*	14.2	10.8
ΔS^*	−29	−35

[a] Rate constants for the uncatalyzed reactions are in l. mole^{-1} sec.$^{-1}$; rate constants for the catalyzed reaction are in l.^{2} mole^{-2} sec.$^{-1}$; units of Ea and ΔH^* are in kcal. mole^{-1}; units of ΔS^* are in cal. mole^{-1} deg.$^{-1}$

DISCUSSION

There does not appear to be any evidence for a different mechanism on changing oxidant from hydrogen peroxide[1] to *t*-butyl hydroperoxide. The rate laws for sulfide oxidation are the same in the two cases and the entropies of activation obtained here are in the same range as those observed previously.[2,3] We conclude therefore that the mechanism here is the nucleophilic attack by sulfur on the oxygen bonded to hydrogen of the peroxide as this mechanism seems favored by previous workers.

The difference in rate constants for the two peroxides seems to be a result of the difference of the basicity of the leaving anion. Because of its greater basicity, *t*-butoxide ion would be expected to be a poorer leaving group than hydroxide ion; as expected, *t*-butyl hydroperoxide reacts more slowly than hydrogen peroxide.

In view of the fact that general acid catalysis was found in the oxidation of sulfite ion by hydrogen peroxide[6] but not found in the oxidation of thiocyanate ion by hydrogen peroxide,[7] it is of interest to look at the present rate data for those runs containing acetic acid. Using the Brønsted equation and the data for k_2 and k_3, it is possible to estimate the rate change due to addition of acetic acid to the reaction mixture if general acid catalysis were operative. The calculated result is that the rate should double on going from zero to one molar acetic acid. This is not the case for the change in rate with one molar acid is negligible (see run number 23). The behavior of acetic acid in our solutions seems therefore to be more like a solvent effect, for there is a sharp change in rate when the amount of acetic acid becomes quite large.

Rate laws of the type of Equation 2 are quite common for reactions which appear to be nucleophilic displacements on peroxide oxygen. Other reducing agents which show such behavior are thiocyanate ion,[7] iodide ion,[8] bromide ion,[8] chloride ion[8] and thiosulfate ion.[9] As general acid catalysis does not prevail either here or in the thiocyanate ion case and that the ratio of k_3 to k_2 is fairly constant for·all of these cases, we conclude that specific acid catalysis is operative in these cases involving six nucleophiles and two peroxides.

Acknowledgment. We wish to thank the U. S. Atomic Energy Commission for financial support.

Providence 12, R. I.

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