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Kinetics, Mechanism, and Activation Energy of the Cobaltous Ion Catalyzed Decomposition of Ozone[1]

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The rate of decomposition of ozone in an aqueous solution containing hydrogen peroxide and perchloric acid has been investigated by Taube and Bray.[2] The catalytic effect of cobaltous ion on the disappearance of ozone and hydrogen peroxide was noted and the rate constants determined. The purpose of the present investigation has been to study in detail the catalysis by cobaltous ion of the decomposition of ozone in the absence of hydrogen peroxide in order to determine the mechanism of the reaction.

The experimental evidence on the homogeneous catalysis by cobaltous ion is consistent with the mechanism

$$Co^{++} + O_3 + H_2O \longrightarrow CoOH^{++} + O_2 + HO \quad (1)$$

$$HO + O_3 \longrightarrow HO_2 + O_2 \quad (2)$$

$$HO_2 + CoOH^{++} \longrightarrow Co^{++} + H_2O + O_2 \quad (3)$$

Experimental

In each of the experiments, one liter of a solution containing cobaltous sulfate and perchloric acid at known concentrations was saturated with ozone at 0° by bubbling a stream of ozonized oxygen through the container. After a steady state had been achieved, samples of the solution were siphoned through a side arm of the container into calibrated 65 ml. reaction bottles and placed in a constant temperature bath. To each fourth sample was added immediately 3 ml. of a 0.2 *N* buffered potassium iodide solution and the iodide oxidized by the ozone titrated with standard 0.01 *N* thiosulfate.[3] The initial concentration of ozone was computed for each container from these data. The concentration of ozone remaining in the individual reaction vessels after different time intervals was determined using exactly the same procedure. In none of the ozone analyses did the concentration of cobalt ion exceed 1% of the total oxidizing agent present so no correction for oxidation of iodide by cobaltic ion was made.

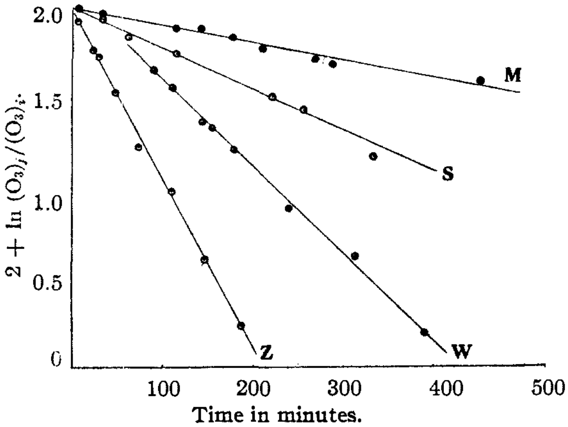

Fig. 1.—The decrease in concentration of ozone at different cobaltous sulfate concentrations: ○, S, $(Co^{++})_0 = 6 \times 10^{-5}$ *M*; ●, M, $(Co^{++})_0 = 12 \times 10^{-5}$ *M*; ◓, W, $(Co^{++})_0 = 18 \times 10^{-5}$ *M*; ◒, Z, $(Co^{++})_0 = 36 \times 10^{-5}$ *M*.

The concentration of cobaltous ion in the stock solution was determined by amperometric titration with α-nitroso-β-naphthol.[4] C. P. grades of perchloric, acetic and sulfuric acids and of cobaltous sulfate were used. Water, redistilled from Pyrex, was used in all experiments. The ozone was prepared by discharge of a 15,000-volt transformer across a battery of eight Berthelot tubes in series.[5]

Data and Discussion

The reaction was first order with respect to ozone as is shown in Fig. 1. The linear curves are plots of ln $(O_3)_f/(O_3)_i$ *vs.* time at different concentrations of cobaltous ion. The data for the upper curve on the graph include 8 additional co-linear points determined at longer times.

The reaction was proved homogeneous by experiments in which a 2.3-fold increase in surface area did not change the rate of the reaction appreciably. The reaction rate did not change with substitution of sulfuric acid for perchloric acid as the source of hydrogen ion.

The rate of reaction is independent of hydrogen ion for solutions more acid than *p*H 1.6. From *p*H 1.6 to 3.5 the rate of reaction increases; at the higher value a sol, believed to be $Co(OH)_3$, forms and a heterogeneous reaction no longer first order with respect to ozone ensues. The increased rate with decreasing hydrogen ion can be explained by assuming that the species $CoOH^+$, produced by hydrolysis of Co^{++} in solutions of low acidity, has a higher specific rate of reaction with ozone than does the unhydrolyzed ion.

The rate expression for the disappearance of ozone in acid solution is obtained from equations (1) through (3) as follows

$$-\,d(O_3)/dt = k_1(O_3)(Co^{++}) + k_2(O_3)(HO)$$

At the steady state

$$\frac{d(C_0{}^{++})}{dt} = \frac{d(HO)}{dt} \approx O$$

Therefore

$$k_1(O)_3(Co^{++}) = k_2(O_3)(HO) = k_3(CoOH^{++})(HO_2)$$

Since $(Co^{++})_0$, (total cobalt ion) $= (Co^{++}) + (CoOH^{++})$

$$(Co^{++}) = (Co^{++})_0/1 + \frac{k_1(O_3)}{k_3(HO_2)}$$

and

$$\frac{-\,d(O_3)}{dt} = \frac{2k_1(O_3)(Co^{++})_0}{1 + \frac{k_1(O_3)}{k_3(HO_2)}} = \frac{2k_1(O_3)(Co^{++})_0}{1 + \frac{(CoOH^{++})}{(Co^{++})}}$$

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[1] Presented before the Pacific Division of the American Chemical Society meeting in conjunction with the American Association for the Advancement of Science at San Diego, California, June 16–22, 1947.

[2] Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

[3] Treadwell and Hall, "Analytical Chemistry, Volume II, Quantitative Analysis," 8th ed., John Wiley and Sons, Inc., New York, N. Y., 1935, p. 620.

[4] Kolthoff and Langer, THIS JOURNAL, **62**, 3172 (1940).

[5] L. E. Smith, *ibid.*, **47**, 1844 (1925).

This expression will give first order dependence on initial cobaltous ion concentration and on ozone concentration if the second term in the denominator does not change appreciably during a given experiment. The value of $2k_1/1 + [(\mathrm{CoOH}^{++})/(\mathrm{Co}^{++})]$ at 0° as determined from a plot of rate *vs.* cobalt ion concentration is 28 mole^{-1} min.$^{-1}$. Spectrophotometric rate measurements leading to the explicit evaluation of k_1 are now being undertaken.

Determination of Activation Energy.—In order to evaluate the heat, entropy, and free energy of activation for the reaction, additional experiments were undertaken at 17.4°, 24.1° and 30.6°. It was found that the spontaneous decomposition of ozone was important at these temperatures and the rate of that reaction determined. The uncatalyzed reaction was found to be of the same order with respect to ozone as the catalyzed reaction.[6] In Table I are given the values for total rate of ozone decomposition, the rate of the uncatalyzed reaction, and the rate of and rate constant for the catalyzed reaction. From a plot of the rate constants (divided by the frequency factor kT/h) *vs.* reciprocal temperature, the following data were obtained: $\Delta H^\ddagger = 9{,}000$ cal., $\Delta S^\ddagger = -19$ E. U., $\Delta F^\ddagger_{298.1} = 14{,}700$ cal. The constants in terms of the Arrhenius equation are: $E_{\mathrm{exp}} = 9{,}600$ cal. and $A = 2 \times 10^8$.

TABLE I

RATE CONSTANT DATA FOR OZONE SOLUTIONS CONTAINING 0.0 AND 1.4 × 10^{-4} *M* $\mathrm{CoSO_4}$

Temp., °C.	Total rate of decomposition (ln $(\mathrm{O_3})$/time)	Rate of uncatalyzed decomposition	$k'(\mathrm{Co}^{++})_0$, rate of catalyzed decomposition	k'
0	3.3×10^{-3}	0	3.3×10^{-3}	28
17.4	9.7×10^{-3}	0.02×10^{-3}	9.68×10^{-3}	69
24.1	17.5×10^{-3}	1.0×10^{-3}	16.5×10^{-3}	118
30.6	28.7×10^{-3}	4.1×10^{-3}	24.6×10^{-3}	176

Reaction in the Presence of an Inhibitor, Acetic Acid.—The reaction remains very nearly first order with respect to ozone—in a particular run the rate increases slightly as the ozone concentration becomes low. The data in Fig. 2 show that the rate of decomposition of ozone decreases with increasing acetic acid concentration to a limiting value of 8 mole^{-1} min.$^{-1}$ at 0°. The concentration of perchloric acid and of cobalt sulfate were the same as in the uninhibited reactions. A ratio of acetic acid to cobaltous ion of 2:1 effects a decrease in the rate to 10 mole^{-1} min.$^{-1}$. These data suggest that in the equilibrium $\mathrm{CoOH^{++} + HAc \rightleftarrows CoAc^{++}\ H_2O}$, whose constant is very large, the cobalti–hydroxide complex is converted to cobalti–acetate complex and that the latter is reduced more slowly by $\mathrm{HO_2}$ than is the hydroxide complex. The rate expression for decomposition of ozone in the solution containing acetic acid is

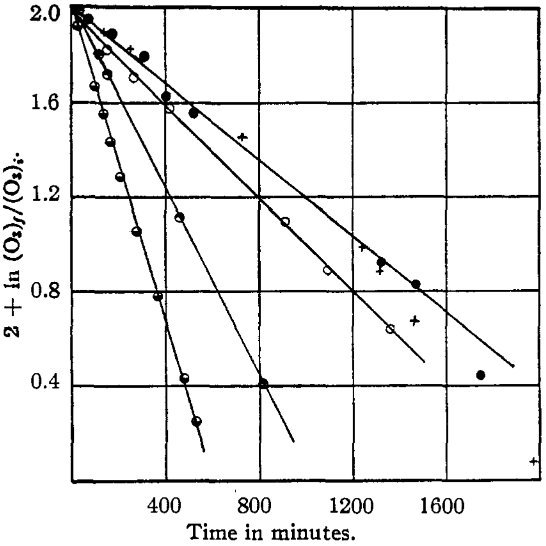

Fig. 2.—Decrease in concentration of ozone at different concentrations of acetic acid: ●, (HAc) = 56 × 10^{-4} *M*; +, (HAc) = 5.6 × 10^{-4} *M*; ○, (HAc) = 2.8 × 10^{-4} *M*; ◓, (HAc) = 0.28 × 10^{-4} *M*; ⊖, (HAc) = 0.0 *M*. $(\mathrm{Co}^{++})_0$ = 1.4 × 10^{-4} *M* and (H^+) = 0.2 *M* in each run.

$$-\frac{d(\mathrm{O_3})}{dt} = \frac{2k_1(\mathrm{O_3})(\mathrm{Co}^{++})_0}{1 + \frac{(\mathrm{CoAc}^{++})}{(\mathrm{Co}^{++})}\,[1 + 1/K(\mathrm{HAc})]}$$

A decrease in the ratio $(\mathrm{CoAc}^{++})/(\mathrm{Co}^{++})$ during the run would account for the observed increase in rate at low ozone concentrations.

Summary

1. The heat, entropy, and free energy of activation have been determined for the cobaltous ion catalyzed decomposition of ozone in acid solution.

2. A mechanism involving HO and $\mathrm{HO_2}$ radicals and cobaltous and cobaltic ions is proposed to account for the observed rate dependence of the homogeneous catalyzed reaction on the concentrations of ozone, cobaltous ion and hydrogen ion.

3. The effect of acetic acid in inhibiting the cobaltous ion catalyzed reaction is explained and the rate of the reaction determined at 0°.

4. Differential equations have been obtained which represent the rates of the reactions in the presence and in the absence of acetic acid.

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[6] Sennewald, *Z. physik. Chem.*, **A164**, 305–317 (1933).