[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Kinetics of the Oxidation of Cobaltous Ion by Ozone[1]

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The cobaltous ion catalyzed decomposition of ozone in perchloric and acetic acids is satisfactorily explained by the mechanism[2]

$$Co^{++} + O_3 + H_2O \xrightarrow{k_1} CoOH^{++} + O_2 + HO \quad (1)$$

$$CoOH^{++} + HAc \overset{K}{\rightleftarrows} CoAc^{++} + H_2O \quad (2)$$

$$HO + O_3 \xrightarrow{k_2} HO_2 + O_2 \quad (3)$$

$$HO_2 + CoAc^{++} \xrightarrow{k_3} Co^{++} + O_2 + HAc \quad (4)$$

The decomposition in the absence of acetic acid differs only in the reaction regenerating Co^{++}.

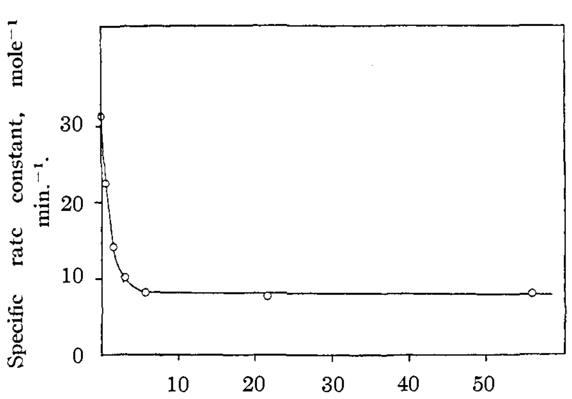

Fig. 1.—Variation in rate constant with acetic acid concentration: $(Co^{++})_0 = 1.4 \times 10^{-4}$ *M*; $(H^+) = 0.2$ *M*; $T = 0°C$.

Figure 1 illustrates the effect of very small concentrations of acetic acid on the specific rate constant upon which the equilibrium (2) and chain terminating step (4) are based. The steady state solution of decomposition equations (1) through (4) is

$$\frac{-d(O_2)}{dt} = \frac{2k_1(O_3)(Co^{++})_0}{1 + \frac{k_1(O_3)}{k_3(HO_2)}\left[1 + \frac{1}{K(HAc)}\right]} = \frac{2k_1(O_3)(Co^{++})_0}{1 + \frac{(CoAc^{++})}{(Co^{++})}\left[1 + \frac{1}{K(HAc)}\right]} \quad (5)$$

The data upon which the mechanism is based were obtained by determining the rate of disappearance of ozone from solutions containing steady-state concentrations of all intermediates. The rate constants so determined[2] are not simple, but are combinations of two specific rate constants. To evaluate k_1 explicitly, and to give an independent check on the mechanism, spectrophotometric measurements of the rate of formation of $CoAc^{++}$ have been made.

Absorption curves for aqueous solutions of ozone in 0.2 *M* perchloric acid, of Co^{++} and of electrolytically prepared $CoOH^{++}$[3] in 0.2 *M* perchloric acid and of $CoAc^{++}$ in perchloric acid plus acetic acid were determined with a Beckman Model DU spectrophotometer at several concentrations of each of the colored constituents. Pertinent curves are given in Fig. 2. The absorption spectrum of cobalti-acetate complex ion (curve S, Fig. 2) possesses a maximum at 330 mμ at which wave length ozone is colorless, and cobaltous ion is virtually so. The color due to $CoOH^{++}$ in these solutions would be negligible in comparison to that of the acetate complex ion. This wave length was selected for the rate measurements and an absorption–concentration curve for cobalti-acetate complex ion was prepared.

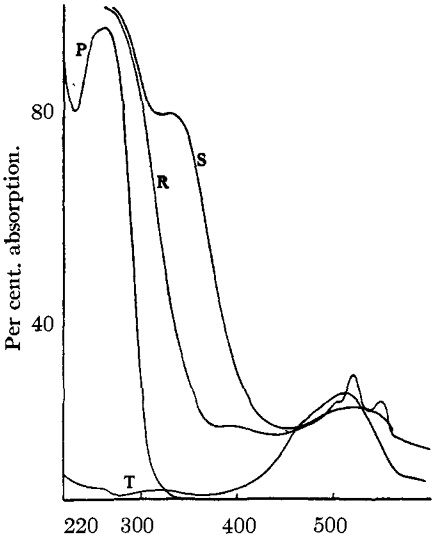

Fig. 2.—Absorption spectra: P, ozone in perchloric acid; R, $CoOH^{++}$; S, $CoAc^{++}$; T, Co^{++}.

Rate measurements for evaluating k_1 were made by adding a solution containing Co^{++}, $HClO_4$ and HAc at known concentrations from a calibrated pipet to a known volume of solution of ozone in perchloric acid and acetic acid in a 3.7-ml. silica cuvette in the spectrophotometer. Time of mixing was taken as t_0 and readings of the transmission were taken at 30-second intervals. The temperature for all experiments was 0–2°.

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[1] Presented in part before the American Chemical Society Division of Physical and Inorganic Chemistry at Portland, Oregon, September 15, 1948.

[2] Hill, THIS JOURNAL, **70**, 1306 (1948).

[3] Swann and Xanthakos, *ibid.*, **53**, 400 (1931).

Data and Discussion

According to the reaction mechanism, plots of log $(Co^{++})/(Co^{++})_0$ *vs.* time should give an initial portion which is almost linear as $CoAc^{++}$ is formed. As the concentration of this ion becomes appreciable, reaction (4) becomes important and the concentration of the $CoAc^{++}$ approaches a steady state. This would be indicated on the experimental curves by a decrease in the slope to zero. The initial slope should be dependent upon ozone concentration and independent of concentrations of acetic acid and cobaltous ion. Figure 3 gives three of the experimental curves for different acetic acid and ozone concentrations. The curves have the properties predicted by the mechanism.

In Table I are given the concentrations of cobaltous ion and acetic acid for which k_1 was evaluated. Columns 3 and 4, not used in the calculation of k_1, list the steady state concentrations of Co^{++} and $CoAc^{++}$ for each run. It is to be noted that although the relative steady state concentrations of $CoAc^{++}$ depend upon the acetic acid concentrations, the rates of formation of $CoAc^{++}$ (see Fig. 3) do not. k_1 was evaluated as $\frac{2.3}{(O_3)}\left[\frac{\log (Co^{++})/(Co^{++})_0}{\text{time}}\right]$, the term in brackets being the slope of the linear portion of the experimental curve. The concentration of ozone was large compared to $(CoAc^{++})$, being 1×10^{-3} molar in each run.

TABLE I

SPECTROPHOTOMETRIC DETERMINATION OF SPECIFIC RATE CONSTANT

$(Co^{++})_0 \times 10^4$	$(HAc) \times 10^3$	$(CoAc^{++}) \times 10^5$ at steady state	$(Co^{++}) \times 10^5$ at steady state	k_1
1.05	40	6	4.5	23
2.60	30	15	11	34
5.10	20	27	24	48
5.84	1	3.5	55.4	32
5.84	1	9.2	49.2	39
5.80	1.97	21	37	37
11.3	1	21	92	37
11.3	1.95	42	71	42
			Average	37

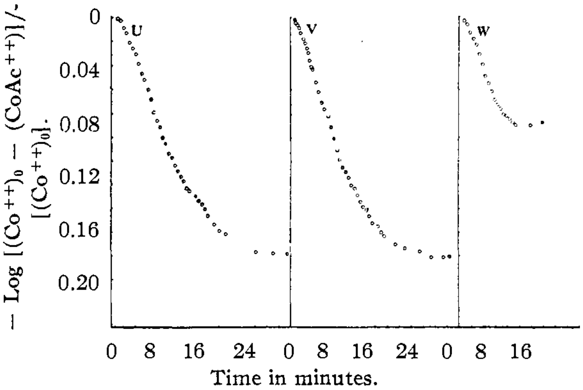

Fig. 3.—Rate of formation of $CoAc^{++}$: U, $[Co^{++}]_0 = 5.84 \times 10^{-4}$; $[O_3] = 0.97 \times 10^{-3}$; $[HAc] = 1.97 \times 10^{-3}$; V, $[Co^{++}]_0 = 1.13 \times 10^{-3}$; $[O_3] = 0.95 \times 10^{-3}$; $[HAc] = 1.95 \times 10^{-3}$; W, $[Co^{++}]_0 = 1.13 \times 10^{-3}$; $[O_3] = 1.0 \times 10^{-3}$; $[HAc] = 1.0 \times 10^{-3}$.

The concentration ratio $CoAc^{++}/Co^{++}$ was measured in a solution through which ozone was passed until steady state conditions were achieved. The ratio observed was 7.0. Using this value and the values for $k_1 = 37$ mole^{-1} min.$^{-1}$ and $k' = 28$ mole^{-1} min.$^{-1}$ [2] in the integrated solution of equation (5), a value of 4×10^3 is obtained for the equilibrium constant in equation (2).

The measured ratio for $CoOH^{++}/Co^{++}$ in a solution without acetic acid was 0.8. The insensitivity in the determination of the concentration of $CoOH^{++}$ spectrophotometrically renders this value very approximate. Nevertheless the value for k_1 calculated from this ratio and k', is 25 mole^{-1} min.$^{-1}$ which compares favorably with the better value 37 mole^{-1} min.$^{-1}$ obtained directly from the initial rate measurements.

Summary

1. Absorption spectra for solutions of ozone, Co^{++}, $CoOH^{++}$ and $CoAc^{++}$ in 0.2 *M* perchloric acid are given.

2. The specific rate constant for the oxidation of cobaltous ion by ozone has been measured.

3. The hydrolysis constant reciprocal for the cobalti-acetate complex ion has been determined.

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