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

The Kinetics and Mechanism of Hydroxide Ion Catalyzed Ozone Decomposition in Aqueous Solution[1]

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Introduction

Although the kinetics of the decomposition of gaseous ozone have been found to be represented best by a bimolecular reaction with possible first and second order characteristics[3-8] dependent upon surface and pressure effects, investigators of the decomposition in aqueous media have interpreted their data to represent $^1/_2$,[9] $^3/_2$,[9] first[10] and second[11,12] order dependence on ozone concentration.

The observed reaction rates have been interpreted to involve direct and inverse integral dependencies upon the hydroxyl ion concentration. A fractional dependence of the rate constant upon the hydroxyl ion concentration has also been reported.[9]

These contradictory results were sufficient to initiate an investigation of the kinetics of ozone decomposition in aqueous solutions over a specific *p*H range.

Experimental Procedure

For a given solution, the kinetic data were obtained by two methods: (1) a spectrophotometric measurement of the ozone concentration and (2) an iodometric determination of the total concentration of reducible constituents in the solution. Both sets of concentration data were obtained as functions of time.

One-tenth and 0.2 *N* solutions of perchloric acid were prepared by diluting reagent grade perchloric acid with conductivity water. The solutions were saturated with a 20 mole % mixture of ozone and oxygen for two hours. A variation of saturation time from one and one-half to seven hours produced no appreciable change in the ozone concentration of the saturated solutions. Solutions were saturated and analyzed at constant temperature.

The spectrophotometric method was based on the experimental fact (Fig. 1) that ozone molecules dissolved in aqueous solutions retain essentially the same absorption maximum as that found in the gas phase. The maximum is seen to be independent of ozone concentration and occures at 260 mμ. This value is in good agreement with the gas phase absorption maximum of 255 mμ.[9,13,14] An oxygen saturated 0.1 *N* acid solution served as a blank and gave no absorption in the range 240–300 mμ.

Percentage transmission measurements as a function of *t* were made by using silica absorption cells in a Beckmann Model DU spectrophotometer equipped with a constant temperature unit. Solutions employed were prepared by neutralizing the ozone saturated acid solution to the desired calculated *p*H value with reagent grade sodium hydroxide. To check for specific effects due to the sodium hydroxide a few measurements were made using acid diluted to the same calculated *p*H as that obtained by neutralization. Figure 2 shows the agreement of the results obtained.

Transmission measurements were made immediately following neutralization of the ozone saturated acid solution to the desired *p*H. Corresponding values of the ozone concentration were obtained from an experimentally determined % transmission *versus* ozone concentration curve.

The iodometric method was employed to determine the total concentration of reducible constituents in a given solution. Titers obtained represented the ozone concentration plus the corresponding concentration of reducible intermediates. Solutions of the same *p*H value but saturated with oxygen only served as the blank runs. The ozone saturated solutions were sampled into calibrated vessels and stored until analysis[15] at constant temperature. The reaction was stopped by the addition of an excess potassium iodide to reduce the ozone present. Reagent grade chemicals and conductivity water were used for all solutions employed. Analyses were made at 0° and 27°.

Results

Figure 3 is a plot of the logarithm of the fraction of the original ozone present at time *t* as a function of *t*. The rate data therefore represent a first order dependence on ozone concentration or

$$\mathrm{d}[\mathrm{O}_3]/\mathrm{d}t = -k_0[\mathrm{O}_3]; \quad \ln\,([\mathrm{O}_3]/[\mathrm{O}_3]_0) = -k_0t$$

where k_0 is the observed rate constant and $[\mathrm{O}_3]_0$ is the ozone concentration at $t = 0$. The first order dependence is found to persist over the *p*H range investigated. Figure 4 shows the same first order dependence derived from earlier data taken in water[11,12] and carbon tetrachloride[16] media.

Kinetic data obtained iodometrically (Fig. 3) indicate first order dependence of the rate constant on the total oxidizing capacity of the solutions. This can be expressed as

$$\mathrm{d}([\mathrm{O}_3] + C)/\mathrm{d}t = -k_0'([\mathrm{O}_3] + C)$$
$$\ln\,([\mathrm{O}_3] + C)/([\mathrm{O}_3]_0 + C) = -k_0't$$

where k_0' is the observed rate constant and C is essentially a constant representing the steady state concentration of reducible intermediates

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[2] Taken in part from a thesis to be submitted to the Graduate School of the University of Utah by Marilyn Grace Alder in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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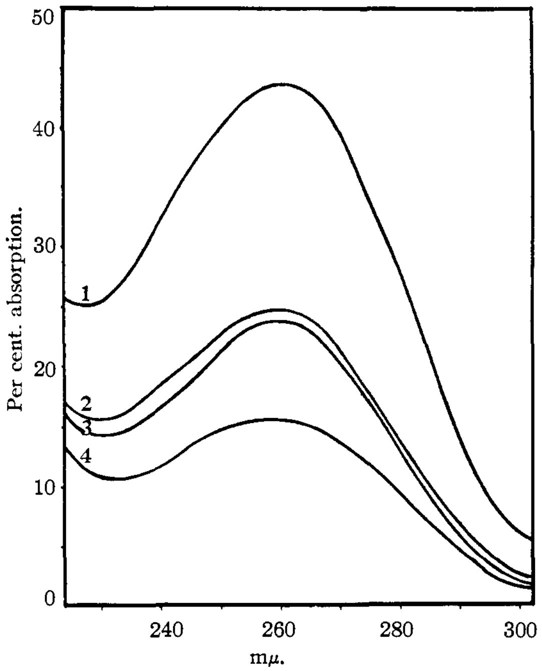

Fig. 1.—Absorption spectrum maximum of ozone in water: $(O_3) \times 10^4$ m./l. for 1, 2.58; 2, 1.29; 3, 1.20; 4, 0.775.

excluding oxygen. Titers obtained were corrected for the slow reaction of iodide ion with molecular oxygen. Absolute values of $[O_2]$ and $[O_3]$ were not determined.

The *p*H dependence of the rate constants for ozone disappearance at 0° as shown in Fig. 2 is best represented by a one-half order dependence on hydroxyl ion concentration. The empirical equation is

$$-\ln([O_3]/[O_3]_0)/t = k'[OH^-]^{1/2} = k_0$$

where k' is the rate constant for the ozone disappearance.

As seen in Fig. 2, the rate constants representing the change of total oxidizing capacity of the solutions are essentially independent of *p*H.

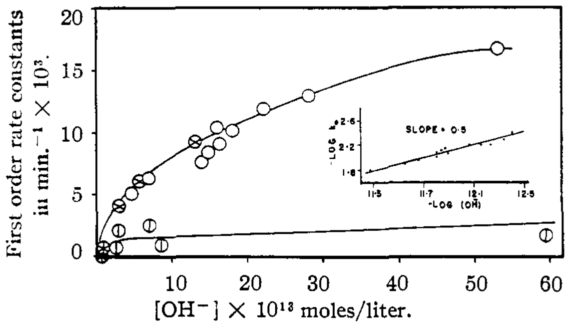

Fig. 2.—Dependence of first order rate constants on hydroxyl ion: O, spectrophotometric determination of k_0 at 0°; Ⓘ, iodometric determination of k_0' at 0°; crosses indicate $[OH^-]$ fixed by dilution. Inset shows logarithmic plot of $k_0 = [OH^-]^a$ with slope $= a = 0.5$.

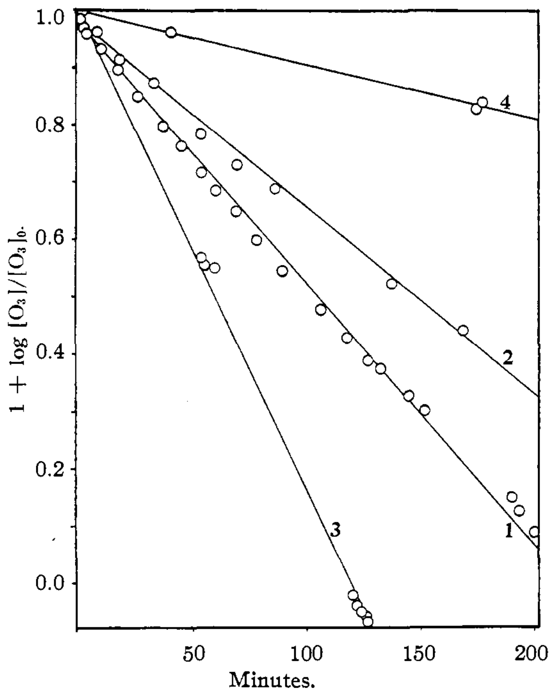

Fig. 3.—First order rate constants: 1, spectrophotometric run at 0° and $(OH^-) = 16 \times 10^{-13}$ mole/liter; 2, spectrophotometric run at 0° and $(OH^-) = 13.9 \times 10^{-13}$ mole/liter; 3, spectrophotometric run at 27° and $(OH^-) = 0.513 \times 10^{-13}$ mole/liter; 4, iodometric run at 27.5° and $(OH^-) = 1.00 \times 10^{-13}$ mole/liter.

Discussion

Results pointing to a chain type mechanism are (1) the rate of ozone disappearance is of first

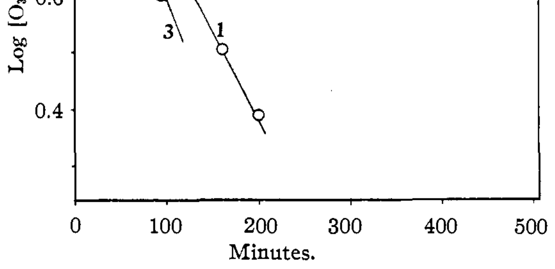

Fig. 4.—Decomposition of ozone showing first order dependence over variation of media, *p*H and temperature: 1, ozone in carbon tetrachloride at 71°, ref. 16; 2, same at 54.7°, ref. 16; 3, ozone in water at 0° and *p*H 5.29, ref. 11; 4, same at 0° and *p*H 4, ref. 12.

order with respect to ozone in both water and carbon tetrachloride media, (2) the rates of decomposition are different in the two media and much faster than that found in the gas phase, (3) an essentially constant concentration of reducible intermediates is found to exist in the water solutions investigated.

The observed data are consistent with the mechanism

$$O_3 + H_2O \xrightarrow{k_1} HO_3^+ + OH^- \qquad (1)$$

$$HO_3{}^+ + OH^- \underset{k_2'}{\overset{k_2}{\rightleftarrows}} 2HO_2 \qquad (2)$$

$$O_3 + HO_2 \xrightarrow{k_3} HO + 2O_2 \qquad (3)$$

$$HO + HO_2 \xrightarrow{k_4} H_2O + O_2 \qquad (4)$$

The assumptions made in solving for the rate of disappearance of the ozone are (1) that reactions 1 and 3 are responsible for the ozone disappearance and are presumably relatively slow and rate determining, (2) that reaction 2 represents an equilibrium which is maintained as long as there is any ozone in the system, and (3) that reaction 4 is the chain breaking step.

The rate of ozone disappearance is given by

$$d[O_3]/dt = -k_1[O_3][H_2O] - k_3[O_3][HO_2] \qquad (5)$$

and the steady state condition can be described by

$$d[HO]/dt = 0 \quad d[HO_2]/dt = 0 \quad d[HO_3{}^+]/dt = 0 \quad (6)$$

Application of equations 6 to 1–2–3–4 results in the expression for the ozone disappearance

$$d[O_3]/dt = -3k_3[HO_2][O_3] \qquad (7)$$

From the equilibrium assumption of 2 where K is the equilibrium constant, equation 7 becomes

$$d[O_3]/dt = -3k_3K^{1/2}[HO_3{}^+]^{1/2}[OH^-]^{1/2}[O_3] \quad (8)$$

and integration gives

$$-\ln([O_3]/[O_3]_0) = 3k_3K^{1/2}[HO_3{}^+]^{1/2}[OH^-]^{1/2}t$$

Therefore a plot of $\ln([O_3]/[O_3]_0)$ *versus* t should be a straight line of slope $= -3k_3K^{1/2}[HO_3{}^+]^{1/2}[OH^-]^{1/2} = k_0$. Since $K^{1/2}$ and $[HO_3{}^+]^{1/2}$ are indeterminate, the rate determining step is reported as

$$k' = k_0/[OH^-]^{1/2} = 3k_3K^{1/2}[HO_3{}^+]^{1/2}$$

The heat of activation, $\Delta H^{\ddagger}$, can be obtained by plotting $\ln k'h/kT$ *versus* $1/T$ and determining the slope of the line. For $k' = 5.17 \times 10^{14}$ min.$^{-1}$ mole$^{-1/2}$ at 300° A. and $k' = 0.905 \times 10^{14}$ min.$^{-1}$ mole$^{-1/2}$ at 273° A., $\Delta H^{\ddagger}$ is found to be 9,900 cal./mole. The indeterminancy of values for $K^{1/2}$ and $[HO_3{}^+]^{1/2}$ precludes the possibility of deriving values for $\Delta S^{\ddagger}$ and $\Delta F^{\ddagger}$.

The difference in the magnitudes of the specific rate constants as measured iodometrically and spectrophotometrically gives a good indication as to the validity of the postulated chain reaction mechanism. From Fig. 2 it is apparent that an increase of hydroxyl ion increases the rate of ozone disappearance but has little effect on the rate of change of the total oxidizing capacity of the solution. This can be interpreted as implying the existence of a relatively small ozone concentration as compared with the ($[O_3] + [HO] + [HO_2] + [HO_3{}^+]$) steady state concentration where ($[HO] + [HO_2] + [HO_3{}^+]$) is assumed to remain constant until near the end of each run.

Summary

Over a sixty-fold variation of hydroxyl ion concentration the rate constant for the decomposition of ozone in aqueous solutions has been shown to be of first order with respect to ozone concentration. The first order dependence occurs at 0° and 27°.

The observed reaction rates are shown to be dependent upon the one-half power of the hydroxyl ion concentration. A chain type mechanism is proposed and is shown to predict the observed dependencies upon ozone and hydroxyl ion concentrations.

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The Effect of Fluorine Substitution on Medicinal Agents. II.[1] Synthesis of Some Fluorine-Containing α- and α,γ-Substituted Glycerol Ethers

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Because of the increasing interest in the behavior of fluorine-containing medicinals and in compounds possessing central depressant action, we have undertaken the preparation and a study of the pharmacological properties of various fluorine-containing α- and α,γ-substituted glycerol ethers. The present work deals with a study of compounds in which the *meta* directing trifluoromethyl group and the *ortho-para* directing fluorine atom, substituted at the various positions in the phenyl group, replace the methyl group in the central depressant 3-(2-methylphenoxy)-propan-1,2-diol (Myanesin).[3,4,5,6] The following compounds were prepared and tested for central depressant activity: 3-(2-fluorophenoxy)-propan-

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[1] For the first paper in this series, see Bradlow and VanderWerf, THIS JOURNAL, **70**, 654 (1948). The authors are indebted to the Office of Naval Research for a grant which made this and continuing investigations possible.

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