TABLE I

EFFECT OF CHANGING FURNACE LENGTH

In all experiments, the end of the furnace was 0.5″ from the cold finger, the furnace temperature was 1000° and the flow rate was constant. In our experiments 10 cc. of gas measured at 30° and 760 mm. passed through the furnace per min.

Run no.	Furnace length[b]	Moles of product per mole of HN_3 consumed[a] N_2	H_2	NH_4N_3	NH_3	Color deposit	% decomp.
25	3	1.11	0.16	0.164	...	Deep blue	52.2
26	6	1.15	.16	.165	...	Deep blue	72.6
23	9	1.22	.15	.139	0.029	Very pale blue	86.5
11	12	1.26	.19	.087	0.099	White	91.3

[a] This is the amount of HN_3 entering the furnace minus the sum of the amounts of free and combined HN_3 frozen on the cold finger. [b] Length in inches.

TABLE II

EFFECT OF DISTANCE BETWEEN THE END OF FURNACE AND COLD FINGER

In all experiments, the furnace length was 3″ and the furnace temperature was 1000°. The flow rate was constant and the same as in Table I.

Run no.	Dist. from finger (inch)	Moles of product per mole of HN_3 consumed N_2	H_2	NH_4N_3	NH_3	Color deposit
37	0.5	1.20	0.14	0.148	..	Intense blue
38	3.5	1.10	.11	.182	..	Deep blue
41	6.5	1.07	.12	.183	..	Pale blue
42	9.5	1.09	.11	.183	..	White

TABLE III

EFFECT OF CHANGING FURNACE TEMPERATURE

In all experiments the furnace length was 12″ and the end of the furnace was 0.5″ from the cold finger. The flow rate was constant and the same as in Table I.

Run no.	Temp., °C.	Moles of product per mole of HN_3 consumed N_2	H_2	NH_4N_3	NH_3	Color deposit
4	850	1.05	0.10	0.188	....	Pale blue
5	850	1.03	.10	.191	....	Pale blue
6	900	1.09	.11	.190	....	Deep blue
7	900	1.09	.11	.198	....	Deep blue
8	900	1.11	.11	.194	....	Deep blue
10	900	1.09	.12	.192	....	Deep blue
15	950	1.23	.15	.128	0.0066	Very pale blue
16	950	1.22	.14	.114	.094	Very pale blue
11	1000	1.26	.19	.087	.099	White
12	1000	1.19	.19	.134	.028	White
14	1000	1.32	.18	.052	.156	White
21	1000	1.31	.18	.067	.127	White
19	1050	1.39	.21	...	.177	White

Discussion

It is very tempting to ascribe the following mechanism to the thermal decomposition of hydrazoic acid

$$HN_3 \longrightarrow NH + N_2$$

This represents the primary process. The imine radical is then carried to the cold finger where it condenses to form the blue solid. Since ammonium azide has the empirical formula $(NH)_4$, it would not be surprising to find ammonium azide as the product. It would be reasonable to expect that a large part of the NH would form ammonium azide on collision with the cold surface and only a small portion would form the blue substance which might be either the monomer or a polymer of NH.

Unfortunately, this simple picture is not in accord with our experimental results, particularly the formation of ammonia. We think now that the primary formation of NH is followed by reaction with HN_3 in steps leading finally to ammonia. The ammonium azide formed on the cold finger would then result from the combination of ammonia and undecomposed hydrazoic acid. We do not know the mechanism whereby NH became NH_3 although the experiments of Foner and Hudson[4k] indicate that di-imide is an intermediary; nor do we know the extent to which ammonium azide originates from the reaction either of ammonia with hydrazoic acid or of NH with itself.

As a second stage of our investigations we plan to repeat this work by decomposing hydrazoic acid electrically and also photochemically, in each case making complete mass balances.

[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT]

The Kinetics of the Homogeneous Gas Phase Thermal Decomposition of Ozone[1]

BY J. A. ZASLOWSKY, H. B. URBACH, F. LEIGHTON, R. J. WNUK AND J. A. WOJTOWICZ

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The homogeneous gas phase decomposition of concentrated ozone was studied manometrically over the pressure range 11.3 to 51.8 mm. at temperatures of 115, 120, 125 and 130°. The observed second order reaction rate constant is expressed as $k_{obsd.} = 1.6 \times 10^{13} (\exp - 24{,}300/RT)$ l./mole sec. Little variation in the reaction rate constant was noted over the initial 35 to 40% reaction. The results are consistent with previous[15,16] measurements in the temperature range of 70 to 110°.

Introduction

A survey of the literature[2-21] indicates that considerable disagreement exists among various investigators concerning the thermal decomposition of ozone. Jahn[4] postulated the following

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(1) Work was performed under Air Force Contract AF-04(645)-72.

(2) Ozone Chemistry and Technology, Advances in Chemistry Series, No. 21, American Chemical Society, 1959, pp. 388–409.

(3) E. Warburg, *Ann. physik*, **9**, 1286 (1902).

(4) S. Jahn, *Z. anorg. Chem.*, **4B**, 260 (1906).

(5) O. R. Wulf and R. C. Tolman, THIS JOURNAL, **49**, 1183, 1202, 1650 (1927).

(6) H. E. Clarke and D. L. Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

(7) E. P. Perman and R. H. Greaves, *Proc. Roy Soc. (London)*, **80A**, 353 (1908).

(8) R. O. Griffith and A. McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

(9) D. L. Chapman and H. E. Jones, *ibid.*, **97**, 2463 (1910).

(10) K. J. Clement, *Ann. physik*, **14**, 341 (1904).

(11) J. W. Belton, R. O. Griffith and A. McKeown, *J. Chem. Soc.*, **129**, 3153 (1926).

(12) E. H. Riesenfeld and W. Bohnholtzer, *Z. physik. Chem.*, **130**, 241 (1927).

(13) E. H. Riesenfeld and H. J. Schumacher, *ibid.*, **138A**, 268 (1928).

mechanism to account for the second order kinetics which he observed in his study with dilute ozone at 127°

$$O_3 \xrightarrow{1} O + O_2 \qquad (1a)$$

$$\xleftarrow{2} \qquad (1b)$$

$$O + O_3 \xrightarrow{3} 2O_2 \qquad (2)$$

An equilibrium concentration of O atoms was postulated in steps 1a and 1b followed by the rate-determining step 3. The over-all rate equation therefore is

$$\frac{-d(O_3)}{dt} = \frac{2k_1k_3(O_3)^2}{k_2(O_2)} \qquad (I)$$

Jahn demonstrated an inverse relationship between the rate of ozone decomposition and the total pressure and presumed the inverse relationship of oxygen.

Other investigators[6–11] questioned these results and were unable to demonstrate a reasonable inverse relationship of rate with oxygen pressure. It was suspected that heterogeneous wall reactions were interfering with many of the kinetic studies. Inasmuch as the decomposition of ozone is known to be very susceptible to catalytic influences, the role of oxygen purity and materials of construction were investigated by Wulf and Tolman.[5] It was shown that the inverse relationship demanded by the Jahn mechanism was being masked by unknown catalysts in the oxygen. It was concluded that the Jahn hypothesis had merit and that much of the consistent work in the literature agreed fairly well with the above scheme. Ritchie,[19] however, found first order kinetics and suspected that the governing factor in the decomposition was the catalytic recombination of oxygen atoms on the walls of the container.

Riesenfeld and co-workers determined the rate of decomposition of concentrated ozone[12–14] and concluded that there were two simultaneous reactions proceeding. One was first, the other second order. Schumacher and Springer[20] maintained that the first-order decomposition observed by Riesenfeld was due to a heterogeneous reaction.

Glissman and Schumacher[15] determined the decomposition rate constants from 70 to 110° and found little or no heterogeneous reaction. Their calculated second order reaction rate constants increased as the reaction progressed. Energy chains were postulated for this increase in reaction rate. They also proposed a bimolecular ozone reaction leading to the simultaneous formation of three oxygen molecules.

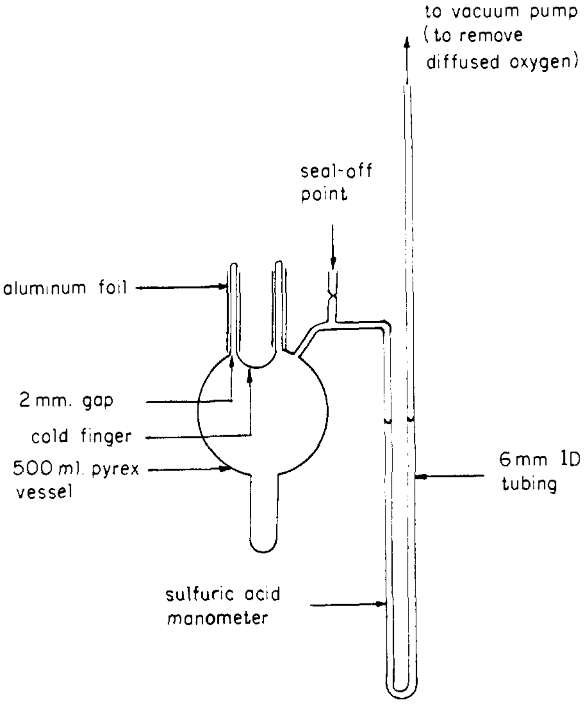

Fig. 1.—Apparatus for the manometric study of the decomposition of ozone formed *in situ*

Benson and Axworthy[16] accepted the Schumacher[22] and Garvin[21] modification of the Jahn mechanism by introducing an M body in the sequence of reactions

$$O_3 + M \xrightarrow{k_1} O + O_2 + M \qquad (3a)$$

$$\xleftarrow{k_2} \qquad (3b)$$

$$O + O_3 \xrightarrow{k_3} 2O_2 \qquad (4)$$

whence assuming a steady state oxygen atom concentration

$$\frac{-d(O_3)}{dt} = \frac{2k_1k_3(O_3)^2(M)}{k_2(O_2)(M) + k_3(O_3)} \qquad (II)$$

where $(M) = (O_3 + \alpha\, O_2)$ and α is the efficiency of oxygen relative to ozone as a third body. These investigators extracted the values of each of the k's and α's from the kinetics of the decomposition as determined by Glissman and Schumacher.[15] The value of k_3 was determined from k_1 and the thermodynamics of reaction 3. The equilibrium constant K_{eq} is given by the relationship

$$K_{eq} = \frac{k_1}{k_2} \qquad (III)$$

The value of α for oxygen was reported as 0.44.

Sutphen[18] recently has presented a mechanism which extends that of Benson and Axworthy by the additional bimolecular step proposed by Glissman and Schumacher[15]

$$O_3 + O_3 \xrightarrow{k_4} 3O_2 \qquad (5)$$

This leads to a term $k_4(O_3)^2$ which must be added to the rate expression (eq. II). The values obtained for the various reaction rate constants are not in good agreement with those of Benson and Axworthy.[16]

The results of an independent determination of the kinetics of the homogeneous gas phase thermal decomposition of concentrated ozone are reported in this paper. These results together with informa-

[14] E. H. Riesenfeld and E. Wassmuth, *ibid.*, **142A**, 397 (1929).

[15] A. Glissman and H. J. Schumacher, *ibid.*, **21B**, 323 (1933).

[16] S. W. Benson and A. E. Axworthy, *J. Chem. Phys.*, **26**, 1718 (1957).

[17] C. E. Thorp, "Bibliography of Ozone Technology," Vol. II, Armour Research Foundation, Chicago, Ill.

[18] W. T. Sutphen, Ph.D. Dissertation, Stanford University, 1955.

[19] M. Ritchie, *Proc. Roy. Soc.* (*London*), **146A**, 548 (1934).

[20] H. J. Schumacher and G. Springer, *Z. physik. Chem.*, **6B**, 446 (1930).

[21] D. Garvin, THIS JOURNAL, **76**, 1523 (1954).

[22] H. J. Schumacher, *ibid.*, **52**, 2377 (1930).

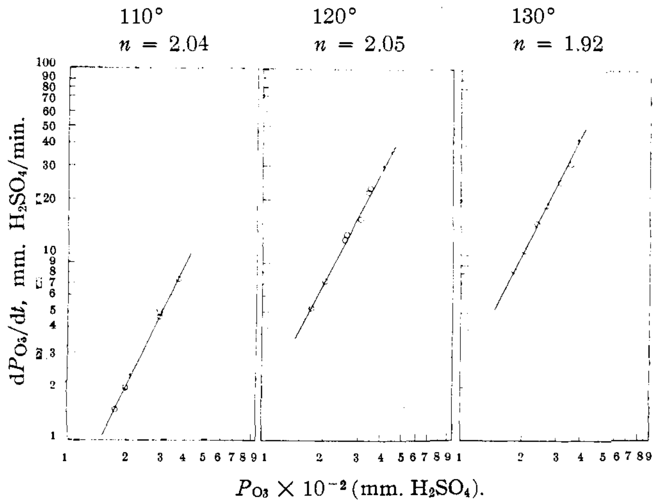

Fig. 2.—Determination of reaction order at 110, 120 and 130°.

tion to be presented in subsequent papers will, it is believed, establish the mechanism of ozone decomposition.

Experimental

Apparatus.—The apparatus used to study the kinetics of ozone decomposition is illustrated in Fig. 1.

Materials.—High purity oxygen (containing less than 20 p.p.m. water and less than 1 p.p.m. hydrocarbon, nitrogen and hydrogen) produced by the electrolysis of 15% aqueous sodium hydroxide was employed in all the decomposition studies. The method of analysis for impurities in the oxygen is a modification of that described by Shepherd[23] and will be reported in a subsequent publication.

Sulfuric acid, which was used as the manometric fluid, was thoroughly deaerated before use.

Procedure.—The apparatus was washed with distilled water and dried. The manometer was filled with sulfuric acid after which the entire apparatus was evacuated to approximately 5×10^{-3} mm. The system was alternately filled with oxygen and evacuated several times to insure a quality of oxygen comparable to the source. After charging the bulb with oxygen, the system was closed at the seal-off point. The upper cold finger was filled with liquid nitrogen. A Tesla coil was attached to the outer aluminum foil while the inner foil was grounded. When the Tesla coil was actuated ozone was produced and condensed on the inner walls of the cold finger. When practically 100% conversion of oxygen to ozone was achieved, as noted by the pressure, the ozone was vaporized and the pressure at room temperature measured. The reaction vessel was immersed in a thermostated ethylene glycol bath heated by two 500-watt heating elements. The temperature was controlled to within 0.1° by means of a Thermocap relay. Zero time was selected when the gas pressure reached the calculated pressure at the bath temperature. Since it was established that thermal equilibration was attained in less than 30 sec. after insertion of the bulb into the heating bath, the error due to decomposition was negligible.[24] Several different reaction vessels were used to study the decomposition rates. Inasmuch as no differences were noted, it was presumed that heterogeneous catalysis was effectively eliminated. The data obtained at various initial ozone pressures and temperatures are summarized in Table II.

Calculations.—To ascertain the order of reaction, the logarithm of the observed rate, $-d(O_3)/dt$, was plotted against the logarithm of the ozone concentration.

The resulting lines, whose slopes give the reaction order, are plotted for 110, 120 and 130° in Fig. 2.

The second order specific reaction rate constant in l. mole^{-1} sec.$^{-1}$ was calculated in the conventional manner by plotting the reciprocal of the ozone pressure against time, obtaining the slope and converting to appropriate units by assuming that ozone behaves as an ideal gas at the pressures studied.

Data for two typical experiments at different initial pressures in two reactors are illustrated in Fig. 3.

A plot of log $k_{obsd.}$ against $1/T$ is illustrated in Fig. 4. From the slope and intercept of the line the equation for $k_{obsd.}$ was obtained in terms of the pre-exponential and the activation energy values.

When systems containing stopcocks (lubricated with fluorocarbon grease) were employed, non-reproducible and markedly increased rates of decomposition were noted. Similarly, experiments in contact with mercury manometers (even when protected with sulfuric acid) gave high and non-reproducible rates of decomposition. When commercial oxygen was used instead of the high purity product, the data were erratic. This could be due to the formation of nitrogen oxides by the discharge technique employed. Surprisingly, water (5 mole %) had no detectible effect on the decomposition kinetics.

The technique described in this paper insures that the ozone concentration at any time is known directly from the pressure reading. There is no chance for inadvertent contamination of the system and the same oxygen could be used repetitively.

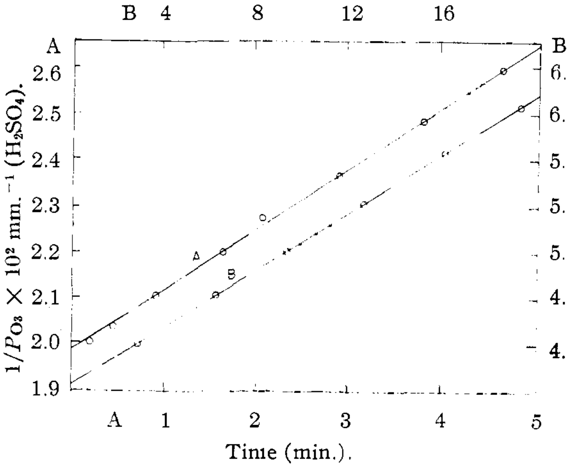

Fig. 3.—Determination of $k_{obsd.}$ at two different initial ozone pressures at 120°.

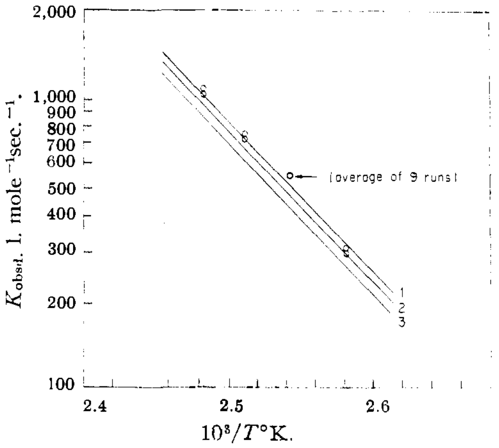

Fig. 4.—Activation energy for $k_{obsd.}$: 1, this research; 2, Glissman and Schumacher; 3, Benson and Axworthy.

Discussion and Results

The plot of the reciprocal of the ozone pressure *versus* time was essentially linear up to 35% reaction.

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[23] M. Shepherd, *Natl. Bur. Standards* (*U. S.*), *J. Research*, **12**, 185 (1934).

[24] This was established with an oxygen blank by determining the time required to give the equilibrium pressure at the pressures employed.

This proves that at the experimental conditions employed equilibrium does not exist among ozone, oxygen and oxygen atoms as suggested by the original Jahn mechanism. If such an equilibrium existed the formation of oxygen would immediately retard the rate of decomposition as

$$\frac{-\,d(O_3)}{dt} = \frac{k_{\text{obsd.}}\,(O_3)^2}{(O_2)} \qquad \text{(IV)}$$

$$\left(\text{Eq. IV is the same as eq. I, } k_{\text{obsd.}} = \frac{2k_1k_3}{k_2}\right)$$

Assuming Benson's mechanism, (3) and (4) and eq. II, we now are in a position to determine the relative magnitudes of $k_2(O_2)(M)$ and $k_3(O_3)$. In order to obtain second order kinetics $k_3(O_3)$ must be considerably larger than $k_2(O_2)(M)$. Benson's data support this conclusion in the concentration range under discussion. In concentrated ozone (M) is the ozone concentration. It can be concluded that under these experimental conditions a steady state concentration of oxygen atoms is obtained rather than an equilibrium concentration as demanded by the Jahn mechanism.

Equation II therefore simplifies to eq. V which defines k_{obsd}.

$$\frac{-\,d(O_3)}{dt} = 2k_1(O_3)\,(M) = 2k_1(O_3)^2 = k_{\text{obsd.}}\,(O_3)^2 \qquad \text{(V)}$$

The experimental activation energy, 24.3 kcal., is similar to the endothermic heat of reaction at constant volume, 24.6 kcal., for the reaction

$$O_3 \xrightarrow{k_1} O + O_2 \qquad \text{(1a)}$$

There is some uncertainty in the value of the above heat of reaction. It appears that the best value according to the literature[25–27] is about 25.4–RT kcal. in the temperature range studied. The value obtained by Glissman and Schumacher[28] for the initial second order reaction rate constant,

$$k_{\text{obsd.}} = 1.7 \times 10^{13} e^{-24{,}400/RT} \text{ l./mole sec.} \qquad \text{(VI)}$$

is (over the temperature range 70–110°) in agreement (see Fig. 4) with the value reported in this research over the range 115 to 130°

$$k_{\text{obsd.}} = 1.6 \times 10^{13}\, e^{-24{,}300/RT} \text{ l./mole sec.} \qquad \text{(VII)}$$

It is therefore probable that the same mechanism is controlling over the temperature range 70 to 130°.

The following is a comparison of rate constants obtained by different investigators as functions of temperature:

$$k_1 \text{ (ref. 16)} = 4.61 \times 10^{12}\, e^{-24{,}000/RT} \text{ l./mole sec.} \qquad \text{(VIII)}$$

$$k_1 \text{ (this research)} = 8 \times 10^{12}\, e^{-24{,}300/RT} \text{ l./mole sec.} \qquad \text{(IX)}$$

$$k_1 \text{ (ref. 28)} = 8.5 \times 10^{12}\, e^{-24{,}400/RT} \text{ l./mole sec.} \qquad \text{(X)}$$

The second order reaction rate constants in l./mole sec. calculated from the above equations at 110, 120 and 130° are:

Temp., °C.	This research	Ref. 16	Ref. 28,15
110	1.07×10^{-1}	0.93×10^{-1}	1.02×10^{-1}
120	2.41×10^{-1}	2.08×10^{-1}	2.38×10^{-1}
130	5.23×10^{-1}	4.46×10^{-1}	5.00×10^{-1}

The agreement with the original data of Glissman and Schumacher[15] is excellent, while the correlation with the interpretation of the same data by Benson and Axworthy[16] is satisfactory.

A value of α can be ascertained from the extensive data of Glissman and Schumacher[15] in the latter part of the reaction when marked increases in reaction rate occur because of the effect of oxygen as an M body.

If (M) is given by (O_3) plus α (O_2) then from (V)

$$\frac{-\,d(O)_3}{dt} = 2k_1(O_3)^2 + 2k_1\alpha(O_2)(O_3) \qquad \text{(XI)}$$

providing that the concentration of ozone is sufficiently high so that $k_3(O_3) >> k_2(O_2)M$.

From thirty experiments of Glissman and Schumacher[15] a value of 0.3 ± 0.05 was obtained for α.

We may calculate the equilibrium constant for the reversible reaction 3 by extrapolation of the data contained in ref. 25, 26 and 29.

Table I summarizes the thermodynamic data for the reaction.

TABLE I[a]

Temp., °C.	ΔF (kcal./mole)	Keq. (mole/liter)	ΔH (kcal./mole)
115	13.33	9.75×10^{-10}	25.41
120	13.18	14.54×10^{-10}	25.42
125	13.01	21.79×10^{-10}	25.43
130	12.85	31.7×10^{-10}	25.44

[a] $\Delta H_0{}^0 = 23.95$, $\Delta H^\circ{}_{25} = 25.16$ kcal./mole.

The values of k_2 shown in Table II were obtained from the above values of Keq. and the values of k_1 obtained in this study.

TABLE II

THE RATE CONSTANTS k_1 AND k_2 FOR THE DECOMPOSITION OF CONCENTRATED OZONE AT VARIOUS TEMPERATURES

Temp., °C.	Init. O_3 press., mm. H_2SO_4	$k_{\text{obsd.}} \times 10^3$ l./mole sec.	k_1 ($^1/_2 k_{\text{obsd.}} \times 10^3$) l./mole sec.	$k_2 \times 10^{-8}$ l.^{2} mole^{-2} sec.
115	256	318	159	1.63
115	264	300	159	1.54
120	376	532	266	1.83
120	376	512	256	1.76
120	84	553	277	1.90
120	84	507	254	1.75
120	256	547	274	1.88
120	190	520	260	1.79
120	195	544	272	1.86
120	249	513	262	1.80
120	263	538	269	1.86
125	266	720	360	1.65
125	250	780	380	1.74
130	386	1068	534	1.68
130	386	1089	545	1.72
130	252	1058	529	1.67

The data for k_2 (by least square treatment of the grouped values) satisfies the equation

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(25) Selected Values of Chemical Thermodynamics Data, National Bureau of Standards, Circular 500, 1952.

(26) Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Research Institute, Project 44, 1953.

(27) G. A. Cook, E. Spedinger, A. D. Kiffer and V. Klumpp, *Ind. Eng. Chem.*, **48**, 736 (1956).

(28) Tables of Chemical Kinetics, Homogeneous Reactions, National Bureau of Standards, Circular 510, 1951, p. 463.

(29) Linde Air Products, Research on the Properties of Ozone, U. S. Navy Contract No. NO(a)S 10945, May 1, 1955.

$$k_2 = 2.57 \times 10^8 e^{-320/RT} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$$

The result is in reasonably good agreement with the value obtained by Benson and Axworthy[16]

$$k_2 = 6.00 \times 10^7 e^{+600/RT} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$$

The ΔE of reaction 3a is 25.4 $-$ RT or 24.6 kcal. The activation energy for reaction 3a is 24.3 kcal. Therefore the conclusion is warranted that the reaction proceeds, as expected for atomic reactions of this type, with little or no positive energy of activation. It is in fact possible[16] that a small negative activation energy is actually involved in this energy transfer reaction.

Small deviations (on the high side) of the experimental rate obtained by Glissman and Schumacher[15] have been attributed by Benson and Axworthy[16] to the presence of thermal gradients in the reactor. No evidence for this hypothesis exists in the pressure range of the present ozone systems operating between 115 to 130°.

Conclusions

The thermal decomposition of concentrated ozone follows second order kinetics over the temperature range 70 to 130°. There is little deviation in the observed rate constant over the first 35% decomposition.

The data obtained in this research are in excellent agreement with the data previously reported by Glissman and Schumacher[15] and Benson and Axworthy.[16] When concentrated ozone decomposes, a steady state concentration of oxygen atoms rather than an equilibrium concentration is present.

Support is given for a modified Jahn mechanism of ozone decomposition suggested by Benson and Axworthy,[16] Schumacher[22] and Garvin.[21]

From the best available thermodynamic data values for k_2 have been calculated.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Nuclear Magnetic Resonance Line Shifts of Fluorine in AgF and Ag$_2$F[1,2]

BY Q. WON CHOI[3]

RECEIVED NOVEMBER 12, 1959

A new method of preparing silver fluoride solution without any contamination is described and a procedure for preparing very finely divided silver subfluoride is given. Nuclear magnetic resonance absorption lines are shifted by +0.014% and $-$0.009% for AgF and Ag$_2$F, respectively, with respect to the fluorine resonance line in KF aqueous solution. The positive shift corresponds to the higher magnetic resonant field at constant frequency. Possible interpretations for these data are provided.

Introduction

The magnetic resonance frequency of a given nucleus varies with its electronic environment. This arises because, as an external magnetic field H_0 is applied to an atom or molecule, its electrons acquire an induced diamagnetic circulation which produces a magnetic field $-\sigma H_0$ at the position of nucleus, partly cancelling the applied field. As pointed out by Ramsey,[4] the second-order paramagnetism partly cancels the diamagnetic shielding effect. Saika and Slichter[5] and Yosida and Moriya[6] correlated the contribution of the second order paramagnetism in an ionic compound with its degree of covalency of the binding. Gutowsky and McGarvey[7] have studied the resonance absorption spectra of Rb^{187} and Cs^{133} nuclei in various halides and have confirmed the parallel relation between the values of the relative line shift and the electronegativity differences of the metal and halogen involved. Yosida and Moriya[6] have found good agreement between their calculated values of shifts for halogen nuclei in alkali halides and the experimental results of Kanda.[8] In metallic conductors, however, there is another type of paramagnetic effect caused by the contact interaction of the conduction electron and the magnetic nuclei, known as the Knight shift.[9]

The F^{19} resonance shifts reported here appear to be the first provided for AgF and Ag$_2$F crystals. The n.m.r. study of the F^{19} nucleus in Ag$_2$F crystals is of particular interest since the compound is quite metallic in character, judging from measurements of the electrical resistivity[10] and of magnetic susceptibility.[11]

Experimental

Preparation of Pure AgF Solution.—The procedure adopted here is a modification of the one developed by Tapilov and Abdulaev[12] which consists of dissolving silver oxide, obtained by the oxidation of metallic silver with hydrogen peroxide, in hydrofluoric acid. Since hydrogen peroxide decomposes very readily in the presence of silver oxide, it is difficult to adjust the conditions so as to assure complete oxidation. In order to avoid such a difficulty, the silver

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[2] This work was supported by a grant from the Research Corporation.

[3] Department of Chemistry, Cornell University, Ithaca, N. Y.

[4] N. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

[5] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

[6] Kei Yosida and Toru Moriya, *J. Phys. Soc. Japan*, **11**, 33 (1956).

[7] H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.*, **21**, 1423 (1953).

[8] Teinosuke Kanda, *J. Phys. Soc. Japan*, **10**, 85 (1955).

[9] W. D. Knight, *Phys. Rev.*, **76**, 1259 (1949).

[10] R. Hilsch, G. v. Minnegerode and H. v. Wartenberg, *Naturwissenschaften*, **44**, 463 (1957).

[11] S. Freed, N. Sugarman and R. P. Metcalf, *J. Chem. Phys.*, **8**, 225 (1940).

[12] Sh. T. Tapilov and D. A. Abdulaev, *Chem. Abstr.*, **49**, 6757 (1955).