mide. At 340° a reaction occurred, and 28 g. of yellow liquid was obtained over a period of seventy-two hours. The major part of this liquid distilled over the range of 148 to 208°. Trimethylgermanium bromide is the only methylgermanium bromide which has been described,[7] and its boiling point is 113.7°. The reaction product therefore appears to contain dimethylgermanium dibromide and methylgermanium tribromide, and isolation of these new compounds is planned.

From these four examples, it appears that the reaction of hydrocarbon halides with elementary germanium is a general one in which any such halide may react under specific conditions of temperature and catalysis to yield the corresponding organogermanium halides.

Summary

1. A general reaction of hydrocarbon halides with elementary germanium to produce the corresponding organogermanium halides is described.

2. The reaction of methyl chloride with germanium is described in detail to illustrate the effect of metallic copper as a catalyst.

3. The new compounds dimethylgermanium dichloride (b.p. 124°, m. p. −22°, d. 1.492 at 20° and 1.488 at 26°, n 1.4552 at 29°) and methylgermanium trichloride (b. p. 111°, d. 1.73 at 24.5°) are described as products of the above reaction.

SCHENECTADY, NEW YORK RECEIVED MARCH 24, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXVIII. Conductance of Some Salts in Nitrobenzene at 25°[1]

BY EDWARD G. TAYLOR[2] AND CHARLES A. KRAUS

I. Introduction

Conductance measurements in ethylene chloride have provided us with much information concerning the influence of specific constitutional factors upon the interactions of ions in a solvent medium of relatively low dielectric constant. Nitrobenzene is a solvent of moderately high dielectric constant, the molecules of which, like those of ethylene chloride, contain no active hydrogen atoms and lack basic properties. Nitrobenzene has a low vapor pressure and is easily obtained in a high state of purity. It is thus suitable for accurate conductance measurements. On account of its relatively high dielectric constant, it has been possible to obtain accurate values for the limiting conductance and dissociation constant of salts which are too weak to permit of accurate evaluation in ethylene chloride. Moreover, a number of salts of inorganic cations are sufficiently soluble to permit of measurement. The dissociation constants of the strongest salts cannot be accurately evaluated because of their almost complete dissociation.

The influence of cationic size on the characteristic constants of electrolytes has been investigated by measurements with a series of homologous tetra-alkylammonium picrates. In order to ascertain the effect of substituting ethyl, hydrogen, hydroxyl, methoxy and phenyl, respectively, for one of the methyl groups in the tetramethylammonium ion, the picrates of ethyltrimethylammonium, trimethylammonium, trimethylhydroxyammonium, trimethylmethoxyammonium and phenyltrimethylammonium have been studied.

Choline picrate and bromomethyltrimethylammonium picrate have been employed to study the effect of replacing an alkyl hydrogen atom by hydroxyl and bromine, respectively. Methoxymethyltrimethylammonium picrate, an isomer of choline picrate, phenyldimethylhydroxyammonium picrate and phenyldimethylammonium picrate have also been investigated.

For the purpose of determining ion conductances, measurements were subsequently carried out by Mr. M. B. Reynolds, of This Laboratory, with tetrabutylammonium triphenylborofluoride. The results of these measurements are included in this paper.

II. Experimental

Apparatus.—Details of the measuring apparatus have been fully described in earlier papers of this series. The conductance cells were of the type described by Cox, Kraus and Fuoss.[3] They were provided with bright platinum electrodes.

Materials.—Nitrobenzene[3a] was fractionally frozen three times, about one-third of the total being poured off as a liquid each time. It was then washed successively with sulfuric acid (1:1), water and sodium hydroxide. The treatment with caustic was continued until the washings were no longer colored. After thoroughly washing with water, the nitrobenzene was dried over calcium chloride. The filtered liquid was fractionated twice under low pressure (<2 mm.). The pale yellow fraction was allowed to stand over powdered barium oxide, filtered and again fractionated (under reduced pressure), this time from activated aluminum oxide. Following the above procedure, solvent having a specific conductance of 2-4 $\times 10^{-10}$ was readily obtained.

The following tetraalkylammonium picrates were prepared and purified by the usual methods: tetramethylammonium picrate, m. p. 318–319°; ethyltrimethylammonium picrate, m. p. 307–308° (dec.); tetraethylam-

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(1) This paper comprises part of the subject matter of a thesis submitted by Edward G. Taylor in partial fulfillment of the requirements for the Degree of Master of Science in the Graduate School of Brown University, May, 1938.

(2) Commonwealth Fellow at Brown University, 1936–1937, 1937–1938. Present address: Williams College, Williamstown, Mass.

(3) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(3a) Oil of Mirbane, kindly donated by the Calco Chemical Company, of Bound Brook, New Jersey.

monium picrate, m. p. 255.5°; tetra-*n*-propylammonium picrate, m. p. 115–116.5°; tetra-*n*-butylammonium picrate, m. p. 89.5°; and tetra-*n*-amylammonium picrate, m. p. 74.0–74.5°.

Trimethylhydroxyammonium picrate was prepared by neutralization of a solution of the hydroxide with picric acid. Trimethylhydroxyammonium hydroxide is readily obtained by the action of hydrogen peroxide on trimethylamine in aqueous solution at room temperature. The picrate was recrystallized from alcohol–water mixtures, m. p. 207–208°.

Trimethylmethoxyammonium iodide was prepared by the interaction of methyl iodide with a solid hydrate of trimethylhydroxyammonium hydroxide in methyl alcohol solution. The hydroxide was prepared by evaporation of its aqueous solution *in vacuo* over calcium chloride and phosphorus pentoxide, m. p. 60–70°. The methoxytrimethylammonium iodide was metathesized with silver picrate in aqueous solution. The picrate was recrystallized from aqueous alcohol and also from alcohol, m. p. 219°.

Phenyldimethylhydroxyammonium picrate was obtained by the interaction of picric acid with dimethylaniline oxide. The latter was prepared by the oxidation of dimethylaniline with hydrogen peroxide.[4] The picrate was recrystallized from alcohol, m. p. 139° (dec.).

Phenyldimethylammonium picrate was recrystallized from alcohol–water mixtures and also from acetone, m. p. 160°. Trimethylammonium picrate was recrystallized from alcohol, m. p. 223°.

Phenyltrimethylammonium picrate was prepared from the corresponding bromide. It was recrystallized from alcohol, m. p. 122.5–123°.

Bromomethyltrimethylammonium picrate, m. p. 236°; choline picrate, m. p. 247–247.5°; and methoxymethyltrimethylammonium picrate, m. p. 200°, were products of this Laboratory. The bromo compound was further purified by recrystallization from water while the other two salts were recrystallized from alcohol.

Tetra-*n*-butylammonium triphenylborofluoride was prepared by Mr. G. L. Brown by the method of Fowler.[5] It was dissolved in sufficient hot alcohol to put it into solution; crystals were obtained upon cooling, m. p. 165–166°.

All salts were dried by long standing *in vacuo* over phosphorus pentoxide at room temperatures.

TABLE I

CONDUCTANCE OF SOME SUBSTITUTED AMMONIUM SALTS IN NITROBENZENE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Tetramethylammonium picrate		Tetraethylammonium picrate	
50.80	26.85	39.47	27.81
18.83	29.38	14.00	29.60
7.846	30.87	5.901	30.60
3.498	31.75	2.431	31.27
1.475	32.36	1.034	31.68
0.5152	32.80	0.3937	31.98
.1555	33.11	.1164	32.21
Tetra-*n*-propylammonium picrate		Tetra-*n*-butylammonium picrate	
35.74	25.28	28.69	24.25
14.38	26.77	11.89	25.49
5.916	27.74	5.187	26.29
2.535	28.36	2.323	26.81
1.062	28.75	1.069	27.15
0.4418	29.02	0.4589	27.41
.1936	29.21	.1972	27.58
Tetra-*n*-amylammonium picrate		Tetra-*n*-butylammonium triphenylborofluoride	
23.98	23.49	25.31	20.37
10.77	24.54	9.553	21.55
5.371	25.19	3.209	22.33
2.660	25.66	1.752	22.63
1.293	26.00	0.7569	22.90
0.5982	26.24		
.2714	26.43		
Phenyltrimethylammonium picrate		Ethyltrimethylammonium picrate	
39.07	26.08	39.77	27.77
15.96	28.13	17.26	29.66
6.854	29.42	7.425	30.98
2.678	30.32	3.231	31.82
0.8550	30.95	1.438	32.35
.2195	31.32	0.6214	32.71
		.2280	33.00
Hydroxyethyltrimethylammonium picrate		Bromomethyltrimethylammonium picrate	
37.33	22.31	35.95	24.49
15.80	25.87	14.27	27.53
7.053	28.36	5.635	29.55
3.089	30.02	2.157	30.78
1.387	30.99	0.7123	31.52
0.5580	31.63	.2343	31.92
.2026	32.03		
Methoxymethyltrimethylammonium picrate		Trimethylmethoxyammonium picrate	
43.53	26.62	35.33	27.69
15.89	29.28	15.63	29.80
5.348	31.07	7.501	31.12
1.770	32.07	3.740	31.99
0.5237	32.68	1.854	32.58
.1303	32.95	0.9591	32.97
		.4301	33.30
Trimethylhydroxyammonium picrate		Phenyldimethylhydroxyammonium picrate	
43.29	2.177	33.13	2.381
17.50	3.292	14.48	3.389
8.016	4.688	6.883	4.646
3.760	6.554	3.025	6.538
1.802	8.960	1.230	9.345
0.7591	12.64	0.4850	13.13
.3178	17.19	.1828	17.86
Trimethylammonium picrate		Phenyldimethylammonium picrate	
44.35	6.086	36.35	2.893
18.47	8.849	13.73	4.141
8.974	11.844	5.288	5.536
4.186	15.70	2.089	6.830
1.762	20.67	0.7605	7.932
0.6802	26.05	.2659	8.827
.2364	30.65		

Procedure.—The dilution method as described in earlier papers was adopted. Corrections for solvent in the vapor phase were negligible and vacuum corrections were unnecessary. All measurements were made in an oil thermostat maintained at 25 ± 0.01°.

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[4] Bamberger and Tschierner, *Ber.*, **32**, 346 (1899).

[5] Fowler and Kraus, THIS JOURNAL, **62**, 1143 (1940).

In no instance was there any appreciable change of resistance with time. The salts were recrystallized until concordant results (0.1%) were obtained with samples from two consecutive recrystallizations.

III. Results

Values of the equivalent conductance, Λ, and the concentration, C, in gram equivalents per liter of solvent, are given in Table I. The densities of the solutions have been taken to be the same as that of the pure solvent, 1.1986.[6] Although two independent series of measurements were made with each salt, the results of only one series are recorded here.

IV. Discussion

Electrolytes having very large ions conform closely to the Debye–Hückel–Onsager equation[7] in nitrobenzene. Assuming 0.01811 for the viscosity[6] and 34.5 for the dielectric constant[8] at 25°, the Onsager equation becomes

$$\Lambda = \Lambda_0 - (0.784\Lambda_0 + 44.6)\sqrt{C}$$

The limiting conductance of the electrolyte may be evaluated by extrapolating the linear plot to the Λ-axis. Plots for a number of salts are shown in Fig. 1.

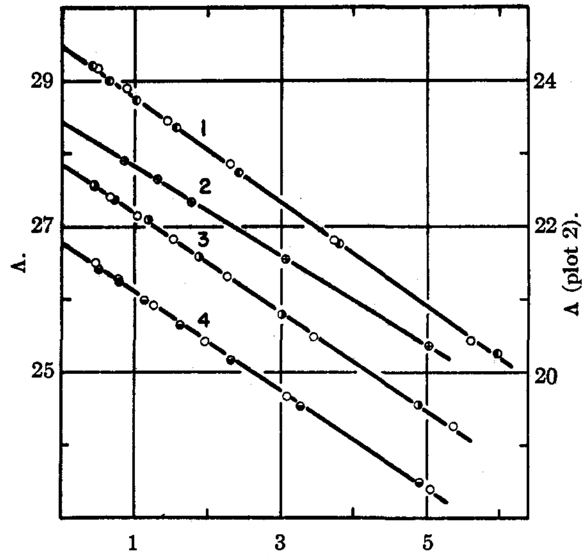

Fig. 1.—Square root plots for strong salts: 1, (n-$C_3H_7)_4$NPi; 2, (n-$C_4H_9)_4$NFB$(C_6H_5)_3$; (right-hand scale); 3, (n-$C_4H_9)_4$NPi; and 4, (n-$C_5H_{11})_4$NPi.

Salts having small ions, although they usually yield a linear plot of Λ against $\sqrt{C}$ in the accessible concentration range, deviate widely from the theoretical slope due to short-range interactions between the ions and the formations of ion-pairs. The results with such salts are best treated by the method of Fuoss.[9] From the intercept of the plot on the F/Λ-axis, the value of Λ_0 is obtained and from the slope of the plot, the value of the dissociation constant, K, may be evaluated. A number of typical plots are shown in Fig. 2; the steeper the plot, the lower is the value of K.

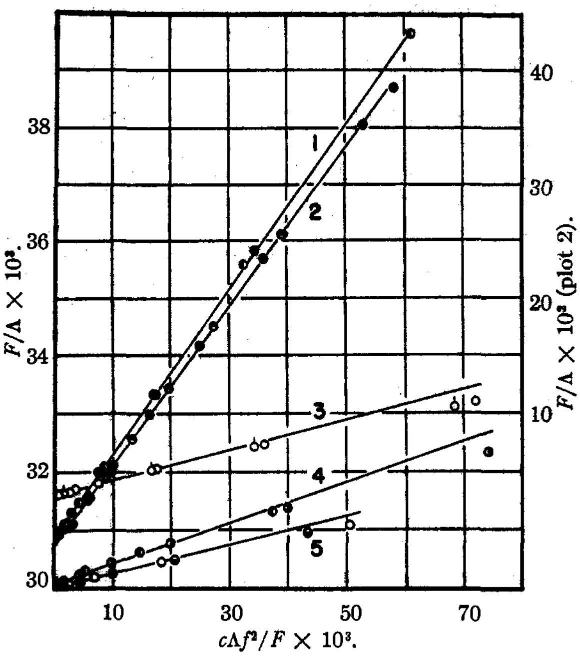

Fig. 2.—Fuoss plot for weaker salts: 1, (HOC_2H_4)-$(CH_3)_3$NPi; 2, $(C_6H_5)(CH_3)_2(HO)$NPi; (right hand scale); 3, $(C_6H_5)(CH_3)_3$NPi; 4, $(CH_3OCH_2)(CH_3)_3$NPi; and 5; $(CH_3)_4$NPi.

Values of Λ_0 for salts of large ions, as determined by means of Onsager plots, are given in Table II. For salts having small ions, values of both Λ_0 and K, as determined by means of Fuoss plots, are given in the same table.

TABLE II

CONDUCTANCE OF SOME ELECTROLYTES IN NITROBENZENE AT 25°

Salt	Λ_0	Λ_0^+	Δ%	$K \times 10^4$
(n-$C_4H_9)_4N(C_6H_5)_3$BF	23.4	(11.7)	−4	..
(n-$C_5H_{11})_4$NPi	26.8	10.6	+3	..
(n-$C_4H_9)_4$NPi	27.9	(11.7)	5	..
(n-$C_3H_7)_4$NPi	29.5	13.3	6	..
$(C_2H_5)_4$NPi	32.4	16.2	10	1400
$(CH_3)_4$NPi	33.3	17.1	31	400
$(C_6H_5)(CH_3)_3$NPi	33.3	17.1	25	440
$(C_6H_5)(CH_3)_3$NPi	31.6	15.4	25	410
$(CH_3O)(CH_3)_3$NPi	33.7	17.5	..	250
$(CH_3OCH_2)(CH_3)_3$NPi	33.2	17.0	..	240
$(BrCH_2)(CH_3)_3$NPi	32.3	16.1	..	120
$(HOC_2H_4)(CH_3)_3$NPi	33.4	17.2	..	70
$(CH_3)_3$NHPi	34.8	18.6	..	1.5
$(C_6H_5)(HO)(CH_3)_2$NPi	27.3	11.1	..	0.19
$(CH_3)_3$(HO)NPi	33.1	16.9	..	.17

The dissociation of the first four salts of Table II was so nearly complete that they could not be treated by the Fuoss method. The following four

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(6) Walden and Birr, *Z. physik. Chem.*, **163A**, 281 (1932).

(7) Onsager, *Physik. Z.*, **28**, 296 (1927).

(8) Lattey and Gattey, *Phil. Mag.*, **7**, 985 (1929).

(9) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

salts were treated by both methods but the Λ_0 values given are due to the Fuoss method, since the Onsager plot, for these salts, yields Λ_0 values that are somewhat too high. It may be noted that the value of K for tetraethylammonium (0.14) is of necessity a rough approximation; the value is considered to be a lower limit. Constants below 0.05 may be evaluated within reasonable limits.

When short-range interaction occurs between the ions, the experimental $\Lambda-\sqrt{C}$ plots are steeper than the theoretical. In column 4 is given the percentage deviation from the theoretical slope for each of a number of salts. The picrates of tetra-amylammonium and tetrabutylammonium ions deviate but little from the theoretical, being only 3 and 5%, respectively. As the ions become smaller, the deviations become greater, reaching a value of 31% for tetramethylammonium picrate.

For tetrabutylammonium triphenylborofluoride, the slope is less than the theoretical by 4%. This negative deviation, if not real, can only be due to residual impurities in the salt.

To intercompare conductance values, it is necessary to evaluate the conductance of the individual ions. Since reliable transference measurements in non-aqueous solvents are extremely difficult, if not impossible, it is necessary to resort to the method of Fowler.[10] This method consists in measuring the conductance of an electrolyte having, as far as possible, two large ions of high symmetry, of equal size and similar constitution. A close approximation to the conductances of the two ions is then obtained by simply halving the conductance of the electrolyte. We have employed tetrabutylammonium triphenylborofluoride, a salt which Fowler employed earlier in ethylene chloride. This salt was prepared by Mr. G. L. Brown and the measurements were carried out by Mr. M. B. Reynolds. The salt was of high purity and several independent preparations yielded results that were in good agreement.

The conductance of tetrabutylammonium triphenylborofluoride was found to be 23.40. This yields a value of 11.7 for the conductance of the tetrabutylammonium ion. Using this value as a basis, and the conductance of tetrabutylammonium picrate (27.9), we obtain 16.2 as the conductance of the picrate ion. Employing this value for the conductance of the picrate ion, the conductance values of the different cations, as they appear in column 4 of Table II, were computed.[11]

For the homologous series of quaternary ammonium ions, from methyl to *n*-amyl, inclusive, the conductance change on adding a CH_2 group to each of the substituent alkyl groups is, respectively, 0.9, 2.9, 1.6 and 1.1. The conductance change in going from the tetramethyl- to the tetraethylammonium ion is only 0.9 unit, while the change in going from the ethyl to the propyl derivative is 2.9. With increasing number of carbon atoms in the substituent groups, the effect, beyond the propyl derivative, decreases regularly. The tetramethylammonium ion evidently experiences retardation to its motion in much greater degree in proportion to its size than do larger ions. Doubtless, this is, in the main, due to interaction between the charge on the small tetramethylammonium ion and the dipoles of the solvent molecules. With larger ions, this effect disappears. It is of interest to note that the conductance of the trimethylammonium ion is 1.5 units greater than that of the tetramethylammonium ion.

Considering other cations, they have much the same conductance if they contain the same number of atoms other than hydrogen, although the effect of constitutional factors is apparent. It is somewhat surprising to find the conductance of the methoxytrimethylammonium ion slightly higher than that of the tetramethylammonium ion. The conductance of the hydroxyethyltrimethylammonium ion (17.2) is slightly higher than that of its isomer methoxymethyltrimethylammonium (17.0). The conductance of the trimethylhydroxyammonium ion is nearly the same as that of the tetramethylammonium ion. The conductance of the bromomethyltrimethylammonium ion is markedly lower than that of the comparable ethyltrimethylammonium ion; in fact, it is the same as that of the tetraethylammonium ion.

The dissociation constant of the normal quaternary ammonium picrates decreases with decreasing ionic dimensions. For picrates of ions larger than the tetraethylammonium ion, the constant cannot be evaluated and, indeed, for the largest ions, the constant ceases to have a physical meaning. The constant for tetramethylammonium picrate is about one-fourth that of tetraethylammonium picrate. It is surprising that the constant for phenyltrimethylammonium picrate should be practically the same as that of tetramethylammonium picrate.

The introduction of polar groups into the quaternary ammonium ion leads to lower dissociation constants. The constant for methoxytrimethylammonium picrate is smaller than that of tetramethylammonium picrate. More striking is the fact that the constant for hydroxyethyltrimethylammonium picrate is only about one-fourth that of its isomer, methoxymethyltrimethylammonium picrate. This lowering of the constant must be due to interaction of the hydroxy group with the picrate ion. In similar fashion, the constant of bromomethyltrimethylammonium picrate is less than half that of the corresponding tetramethylammonium salt.

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[10] Fowler and Kraus, THIS JOURNAL, 62, 2237 (1940).

[11] *Added in Proof.*—A redetermination of the conductance of tetrabutylammonium triphenylborofluoride yields a Λ_0 value of 23.78 for the salt and 11.9 for the tetrabutylammonium ion. Ion conductances in Table II need to be increased to 0.2 unit for positive ions and decreased by the same amount for negative ions. The slope of the $\Lambda-\sqrt{C}$ plot is 0.6% greater than the theoretical.

When a hydrogen atom or a hydroxyl group is joined directly to the central nitrogen atom of the ammonium ion, the constant reaches very low values. This may be ascribed to hydrogen bonding with the negative ion. Thus, the dissociation constant of trimethylammonium picrate is only 1.5×10^{-4}. In the case of ions having an —OH group directly attached to the nitrogen atom, the bonding effect is even greater, the dissociation constants for trimethylhydroxyammonium picrate and phenyldimethylhydroxyammonium picrate being 1.7×10^{-5} and 1.9×10^{-5}, respectively. Clearly, here we have energy effects of considerable magnitude appearing as a result of other than coulombic interaction.

Some preliminary measurements were carried out with phenyldimethylammonium picrate. On extrapolation of the Fuoss plot, which was found to be linear, a Λ_0 value of 9.54 was obtained. It seems evident that this salt dissociates into free acid and base in nitrobenzene solution. The conductance of solutions of this salt was greatly increased by adding either picric acid or dimethylaniline. The same salt undergoes acid–base dissociation in tricresyl phosphate as Elliott and Fuoss[12] have shown. The results of a detailed study of systems of this kind will be presented in another paper of this series.

V. Summary

1. A method is described for the preparation of nitrobenzene having a specific conductance of $2–4 \times 10^{-10}$.

2. The results of conductance measurements at concentrations below $2 \times 10^{-3}N$ are given for the following salts: the picrates of tetramethylammonium, tetraethylammonium, tetra-*n*-propylammonium, tetra-*n*-butylammonium, tetra-*n*-amylammonium, trimethylammonium, trimethylhydroxyammonium, methoxytrimethylammonium, ethyltrimethylammonium, bromomethyltrimethylammonium, hydroxyethyltrimethylammonium, methoxymethyltrimethylammonium, phenyltrimethylammonium, phenyldimethylhydroxyammonium and phenyltrimethylammonium picrate and for tetra-*n*-butylammonium triphenylborofluoride.

3. The higher members of the homologous series of tetraalkylammonium picrates give results which closely approximate the Debye–Hückel–Onsager equation. For these salts, values of Λ_0 have been obtained by extrapolation of the Λ_0–$\sqrt{C}$ plots to the Λ-axis.

4. The results for other picrates, which show ion-pair association, have been treated by the method of Fuoss to obtain values of Λ_0 and K.

5. The conductance of various ions in nitrobenzene has been approximated by the method of Fowler and Kraus.

6. The influence of various constitutional factors on ion conductance and on dissociation constants is discussed.

7. It has been shown that phenyldimethylammonium picrate dissociates into free acid and base, which dissociation is repressed by addition of these constituents.

PROVIDENCE, R. I. RECEIVED APRIL 5, 1947

[12] Elliott and Fuoss, THIS JOURNAL, **61**, 294 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Study of the Kinetics of the Reaction between Nitrogen Pentoxide and Nitric Oxide[1,2]

BY J. HAROLD SMITH[3] AND FARRINGTON DANIELS

The reaction between nitrogen pentoxide and nitric oxide has been observed previously only in a qualitative manner,[4,5] and it has been described as an extremely rapid, perhaps instantaneous, gas phase reaction. Busse and Daniels[4] in 1927 observed that "nitric oxide reacts immediately with nitrogen pentoxide" to produce brown nitrogen dioxide. Sprenger[5] refers to the reaction as being "immeasurably rapid." No attempt to follow the rate of this very rapid reaction in a quantitative manner has heretofore been reported.

The nitrogen pentoxide–nitric oxide reaction is of interest as a gas-phase reaction which takes place at a rapid rate even at room temperature. Furthermore, this reaction is of special interest in connection with the thermal decomposition of nitrogen pentoxide. The nitrogen pentoxide–nitric oxide reaction is assumed to be a rapid secondary step in a mechanism proposed to account for the first order nature of the nitrogen pentoxide decomposition,[4,6] but a question has been raised[7] regarding the possibility that this reaction may be slow enough at very low pressures to limit the rate of the nitrogen pentoxide decomposition.

This paper describes a method and apparatus devised for the measurement of the rate of the

[1] From a dissertation submitted by J. Harold Smith to the Graduate School faculty of the University of Wisconsin in June, 1941, in partial fulfillment of the requirements for the Ph.D. degree.

[2] Presented to the Div. of Phys. and Inorg. Chem. at the St. Louis, Mo., meeting of the A.C.S., April, 1941.

[3] Present address: University of Massachusetts, Amherst, Mass.

[4] Busse and Daniels, THIS JOURNAL, **49**, 1257 (1927).

[5] Sprenger, *Z. physik. Chem.*, **49**, 136 (1928).

[6] Bodenstein, *ibid.*, **105**, 51 (1923).

[7] Daniels "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, p. 71.