The Conductance of Nitronium Fluoroborate in Anhydrous Hydrogen Fluoride[1]

Mary L. Kilpatrick, Martin Kilpatrick, and John G. Jones[2]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. Received October 28, 1964

Nitronium fluoroborate, which in the solid state exists as nitronium ions and fluoroborate ions, NO_2^+ and BF_4^-, is in this paper shown to exhibit in solution in anhydrous hydrogen fluoride conductance almost identical with that of potassium fluoroborate, a strong electrolyte. Its molal conductance can be represented by the equation $\Lambda_m = 380 - 396\sqrt{m}$ up to molalities of ca. 0.2 at 20°, and the suggestion is made that the apparent conformity to the Onsager limiting law to such a high concentration may be due to ion pairing.

Introduction

For some years we have been interested in a nitrating system where nitronium ions could be, in effect, weighed out and dissolved in a solvent with which they did not react. We chose the stable nitronium fluoroborate as nitrating agent and hydrogen fluoride as the high-dielectric, ionizing solvent medium. The present paper contains evidence that NO_2BF_4 dissolves freely as a strong electrolyte in anhydrous hydrogen fluoride and is not decomposed by it. The use of the NO_2BF_4–HF nitrating system has been treated in a parallel paper in which kinetics and salt effect are discussed.[3]

The conductance method was used to study nitronium fluoroborate dissolved in hydrogen fluoride since conductance had already[4,5] proved a useful tool for examining the properties of substances dissolved in hydrogen fluoride. Due to its low viscosity (0.207 cp.[6] as against 1.002 for water, at 20°) electrolytes display high mobilities[7] in hydrogen fluoride, in accordance with Walden's rule.

Cook, Kuhn, and Olah,[8] and Evans, Rinn, Kuhn, and Olah[9] have shown that in the solid state nitronium fluoroborate exists as nitronium ions and fluoroborate ions. We carried out infrared absorption measurements on our samples of nitronium fluoroborate and obtained absorptions agreeing closely with those found by Cook, *et al.*, and by Evans, *et al.* All the absorptions could be ascribed to fluoroborate ion or nitronium ion.

Experimental

Hydrogen Fluoride. Hydrogen fluoride from the Harshaw Chemical Co. was purified in a metal and Kel-F vacuum line, the final distillation being through a Kel-F column packed with nickel helices, as described by Kilpatrick, Bett, and Kilpatrick.[10] This routinely produced hydrogen fluoride of specific conductance $(3 \pm 2) \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 20°. Such a specific conductance could be due to a 10^{-4} M concentration of uni-univalent salts, of which $H_3O^+HF_2^-$ is probably the chief constituent in view of the very basic nature of water in hydrogen fluoride.[11]

Potassium Fluoroborate. This was prepared from analytical grade reagents according to the instructions of van der Muellen and Van Mater,[12] but in polyethylene rather than platinum vessels. The product was was dried in a vacuum desiccator and kept in an airtight polyethylene bottle.

Nitronium Fluoroborate. This was made by Olah, Kuhn, and Mlinko's[13] adaptation of the method of Schmeisser and Elischer. Nitrogen pentoxide was prepared from dried N_2O_4 and ozonized oxygen by Gibson's[14] method and was stored at Dry Ice temperature. In a typical preparation of NO_2BF_4, 75 ml. of nitromethane, previously dried over $CaCl_2$ and then distilled, was used to dissolved 27 g. of solid N_2O_5. The solution was transferred to a Kel-F vessel containing 10 ml. of anhydrous HF and a Teflon-coated magnetic stirrer. The top of the vessel was fitted with two Kel-F valves, one leading to a Monel pressure-vacuum gauge and a cylinder of BF_3, the other leading to a vacuum pump *via* a Kel-F trap cooled in liquid nitrogen. The reactants were cooled in ice, and stirred, and on admission of BF_3 the pressure fell and crystals of NO_2BF_4 formed. When no more NO_2BF_4 was being produced, admission of BF_3 was discontinued, and the surplus HF was pumped off from the mush of NO_2BF_4 crystals. The reaction vessel was then transferred to the drybox and the NO_2BF_4 collected on a sintered glass filter. It was freed from $H_3O^+BF_4^-$ by washing with fresh nitromethane followed by Freon 113, a volatile liquid chlorofluorocarbon; after washing, it was transferred to a drying pistol and dried *in vacuo* over P_2O_5 at 140°. Finally the white, freely running crystals of NO_2BF_4 were transferred in the drybox from the pistol to glass ampoules with long necks which were subsequently sealed to protect the very deliquescent product from moisture.

Infrared Absorption Measurements. Thin pastes of NO_2BF_4 were prepared with liquid paraffin (Nujol)

(1) Abstracted from the Ph.D. Thesis of J. G. Jones, Illinois Institute of Technology, June 1964.

(2) Department of Chemistry, The University, Sheffield 10, England.

(3) M. L. Kilpatrick, M. Kilpatrick, and J. G. Jones, to be published.

(4) K. Fredenhagen and G. Cadenbach, *Z. physik. Chem.*, **146**, 245 (1930).

(5) M. Kilpatrick and F. E. Luborsky, *J. Am. Chem. Soc.*, **76**, 5863, 5865 (1954).

(6) Extrapolation of the data of J. H. Simons and R. D. Dresdener, *ibid.*, **66**, 1070 (1944).

(7) M. Kilpatrick and T. J. Lewis, *ibid.*, **78**, 5186 (1956).

(8) D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, **33**, 1669 (1960).

(9) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).

(10) M. Kilpatrick, J. A. S. Bett, and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **85**, 1038 (1963).

(11) S. Kongpricha and A. F. Clifford, *J. Inorg. Nucl. Chem.*, **18**, 270 (1961).

(12) P. A. van der Muellen and H. L. Van Mater, *Inorg. Syn.*, **1**, 24 (1939).

(13) G. A. Olah, S. J. Kuhn, and A. Mlinko, *J. Chem. Soc.*, 4257 (1956).

(14) G. Gibson, C. D. Beintema, and J. J. Katz, *J. Inorg. Nucl. Chem.*, **15**, 110 (1960).

or fluorinated chlorocarbon oil (Fluorolube) and were mounted between plates of AgCl or NaCl. The best spectra resulted from very fine grinding of the NO_2BF_4 in a trough-like mortar and pestle of glass whose roughened grinding surfaces precisely fitted each other. Grinding and mounting operations were performed in the drybox.

The spectra were taken on a Perkin-Elmer 137 Infracord fitted with NaCl optics and covering the range 650–4000 cm.$^{-1}$, and on a similar machine fitted with KBr optics and covering the range 400–800 cm.$^{-1}$. Once found, the positions of the absorption maxima were determined more exactly with a Unicam SP 100. We are indebted to the University of Sheffield for the use of the two latter instruments.

Conductance Measurements. The conductance cell used was that employed by Kilpatrick, Bett, and Kilpatrick[10] and designated by them as cell II. It was made of Kel-F with a Kel-F valve at each end; it had bright platinum electrodes, and its cell constant, measured at 20°, was 1.83 ± 0.01 cm.$^{-1}$. With the bright electrodes, polarization affected the measured resistance to the extent of 2% for uni-univalent electrolytes in HF at a concentration of 0.15 m, and the effect fell rapidly as the concentration decreased.

The cell was immersed in an oil bath maintained at 20.00 ± 0.01°, temperature being read on a Beckmann thermometer which was calibrated against a standard platinum resistance thermometer. In all cases the conductance was recorded until it reached a value constant with time. Kel-F is a poor conductor of heat and in general 50 min. was required to establish equilibrium with the bath.

Resistance was measured at 1000 c.p.s. on a "Jones" bridge[15] from the Leeds and Northrup Co., using the oscillator, transformers, and amplifier supplied for that bridge. An oscilloscope was used to detect the null point in capacitance and impedance.

Preparation of Solutions. The conductance cell, thoroughly washed with HF and then evacuated, was weighed, and HF was condensed into it until it was nearly full, after which it was weighed again. Filled cell, a diamond-pointed glass cutter, a weighed ampoule of salt, and the special Kel-F needle valve and mixing chamber (Figure 1) were transferred to the drybox, where the ampoule was opened and an appropriate amount of salt was tipped into the mixing chamber. The needle valve was then screwed onto the mixing chamber and the assembly was screwed onto one of the valves of the conductance cell. Both valves between cell and mixing chamber were opened and HF was shaken back and forth between cell and mixing chamber until all salt had dissolved; NO_2BF_4 dissolved readily but KBF_4 took up to 20 min. to dissolve fully. The needle valve plus mixing chamber was unscrewed from the conductance cell, and after sealing the closed valve of the latter with a Kel-F cap, it was placed in the thermostat. The ampoule was resealed upon removal from the drybox and together with the cut-off neck was weighed to yield the mass of salt taken.

Dilution of the solution of NO_2BF_4 or KBF_4 was carried out by allowing some of the solution to flow from the cell into a cooled trap when on the vacuum line, then taking the cell from the line and weighing it,

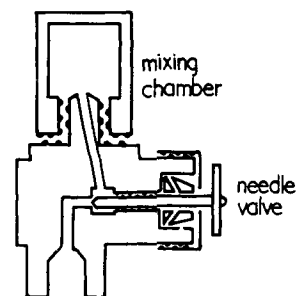(15) P. H. Dyke, *Rev. Sci. Instr.*, **2**, 379 (1931).

Figure 1. Special valve and mixing chamber of Kel-F.

filling it again by condensing HF from the fractionating column into it, and finally reweighing it. Solutions prepared by this technique exhibited conductances agreeing within the experimental error with those of similar concentration but prepared directly.

Results and Discussion

The results of the conductance measurements are given in Table I. To make a correction for conducting

Table I. Conductance Measurements in HF at 20°

Expt. no.	Concn., m	Λ_m	Λ_0'	Λ_m (calcd.)
		Molal conductance		
(a) Potassium Fluoroborate				
7	0.399	175	436	125
	0.206	218	400	196
	0.0951	248	369	253
	0.0523	274	364	285
	0.0249	302	363	313
	0.0121	320	363	332
	0.00327	355	388	352
11	0.0338	302	375	302
	0.0165	331	381	324
	0.00787	354	389	340
	0.00289	360	381	354
(b) Nitronium Fluoroborate				
6	0.114	250	384	246
	0.0744	275	381	262
	0.0435	294	376	297
	0.0197	319	375	324
	0.00943	324	363	342
5	0.200	229	409	203
	0.118	259	397	244
	0.0818	275	389	267
	0.361	305	380	305
	0.0234	323	384	319
	0.0124	336	380	336
	0.00486	332	388	352
	0.000867	367	379	362
1	0.211	228	414	198
2	1.075	120	609	−32
	0.593	151	497	71
	0.290	188	405	167
	0.134	222	366	235
3	0.169	241	407	217
4	0.300	207	431	173
	0.164	237	400	220
9	0.0724	264	374	262
	0.0399	303	382	301

species present in the solvent at the start or picked up during mixing or dilution, blank experiments were performed in which all operations were the same as in an actual run except that no solute was used. Ten "blanks" gave a solvent correction of $(1.05 \pm 0.18) \times$
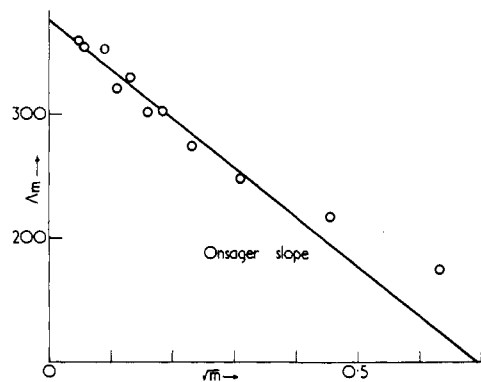
Figure 2. Molal conductance of KBF_4 dissolved in HF (20°).

Figure 3. Molal conductance of NO_2BF_4 dissolved in HF (20°).

10^{-4} ohm^{-1} cm.$^{-1}$. This figure was subtracted from the measured specific conductance to obtain the corrected specific conductance L, and the molal conductance listed in column 3 of Table I was calculated by the equation

$$\Lambda_m = 1000L/m \qquad (1)$$

where m is the molality of the NO_2BF_4 or KBF_4. It would have been preferable for theoretical reasons to have obtained the concentrations in moles per liter of solution rather than per 1000 g. of HF, but this would have added considerably to the experimental difficulty as HF boils at 19.5°, and was not done.

Table I shows that potassium and nitronium fluoroborates display high and similar molal conductances, from which it may be concluded that nitronium fluoroborate acts as a strong electrolyte when dissolved in HF.

For strong uni-univalent electrolytes Onsager's limiting equation is

$$\Lambda = \Lambda_0 - (B_1\Lambda_0 + B_2)\sqrt{c} \qquad (2)$$

where c is the solute molarity and

$$B_1 = 8.204 \times 10^5/(\epsilon T)^{1/2}$$

$$B_2 = 82.5/\eta(\epsilon T)^{1/2}$$

ϵ being the dielectric constant of the solvent and η its viscosity. Re-extrapolation of the dielectric constant data of Fredenhagen and Dahmlos[16] and the viscosity data of Simons and Dresdener[17] gave for 20° $\epsilon = 67.5$, and $\eta = 0.207$ cp. Introducing these values eq. 2 becomes

$$\Lambda = \Lambda_0 - (0.295\Lambda_0 + 284)\sqrt{c} \qquad (3)$$

In Table I the molal concentration and molal conductance are listed rather than the molar properties used in the Onsager equation. Nevertheless, the density of liquid HF and its dilute solutions is close to 1 g./ml., and assuming that it is permissible to use the molal values in the present case, one has

$$\Lambda_m = \Lambda_0' - (0.295\Lambda_0' + 284)\sqrt{m} \qquad (4)$$

and on rearranging obtains

$$\Lambda_0' = (\Lambda_m + 284\sqrt{m})/(1 - 0.295\sqrt{m}) \qquad (5)$$

Values of Λ_0' calculated by (5) are given in the fourth column of Table I; it will be seen that they decrease with falling concentration until $m = 0.2$, approximately, after which they fluctuate randomly. If one averages the fluctuating values of Λ_0' found below 0.2 m for each salt and puts the average back into eq. 4, one obtains for KBF_4

$$\Lambda_m = (375 \pm 9) - (395 \pm 3)\sqrt{m} \qquad (6)$$

and for NO_2BF_4

$$\Lambda_m = (380 \pm 6) - (396 \pm 2)\sqrt{m} \qquad (7)$$

The values of λ_m calculated by eq. 6 and 7 are given in the last column of Table I as Λ_m (calcd.).

In Figures 2 and 3 the experimental values of Λ_m are shown plotted vs. $\sqrt{m}$, and the lines drawn represent eq. 6 and 7, respectively. It can be seen that there is very little difference between the two fluoroborates. It may well be that the slightly higher conductance of the nitronium salt is due to a higher mobility of the nitronium ion, a reflection of the slightly smaller size of that ion[18] as compared with the potassium ion (1.15 as against 1.33 Å.). But is would probably be more correct to say that the two salts are indistinguishable within the experimental error of our measurements.

Uni-univalent strong electrolytes dissolved in water tend to exhibit higher values of the equivalent conductance than predicted by the Onsager equation when the concentration exceeds ca. 0.001 M. However, if ion pairing occurs, this tendency is counteracted and the result may be empirical agreement with the Onsager equation to appreciably higher concentration, as in the case of silver nitrate.[19] It is suggested that the lower dielectric constant of hydrogen fluoride gives rise to ion pairing in our systems. Usuing Bjerrum's[20] or Fuoss's[21] method of calculating ion-pair association constants, values of K (association) of 1–1.5 can be obtained for our electrolytes in hydrogen fluoride at 20°, corresponding to a theoretical degree of ion-pair formation of ca. 5% at 0.1 m.

(16) K. Fredenhagen and J. Dahmlos, Z. anorg. allgem. Chem., 178, 272 (1928).
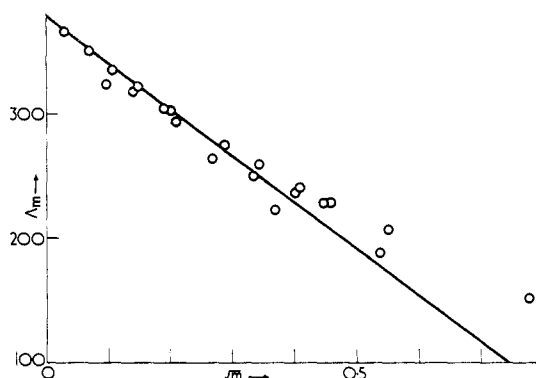(17) J. H. Simons and R. D. Dresdener, J. Am. Chem. Soc., 66, 1070 (1944).

(18) P. E. Grison, K. Ericks, and J. L. De Vries, Acta Cryst., 3, 290 (1950).
(19) T. Shedlovsky, J. Am. Chem. Soc., 54, 1411 (1932).
(20) N. Bjerrum, Kgl. Danske Videnskab. Selskab., 7, No. 9 (1926).
(21) R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958).

Kinetic Studies of Exchange between Metallic Mercury and Mercury Compounds in Solution. I

D. R. Pollard[1] and J. V. Westwood

Contribution from the Department of Chemistry, Sir John Cass College, London, England. Received December 12, 1964
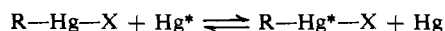
A kinetic study has been made of exchange between a stirred metallic mercury surface and diphenylmercury in solution. Results indicate that with careful selection of experimental conditions, diffusion control is avoided. Reaction has been shown to occur reproducibly, reversibly, and heterogeneously without complexity of products, and with a rate directly dependent on the mercury surface area. Anomalous mercury aryl concentration effects are explained in terms of inhibition by reaction product.

Introduction

In recent years mercury organic compounds have been of interest owing to their application to the study of electrophilic substitution. In particular, Nesmeyanov and Reutov[2] and Ingold[3] have made detailed investigations of homogeneous mercury aryl exchange reactions and proposed mechanisms for electrophilic substitution analogous to the well-characterized nucleophilic types.

Few workers have considered heterogeneous exchange reactions quantitatively, mainly owing to experimental difficulties in dealing with large uniform surface areas under controlled conditions. Haissinsky[4] first used a tagged metallic mercury layer to investigate exchange with inorganic mercury compounds in aqueous solution. He concluded diffusion control but did not attempt a rigorous kinetic investigation.

We noted that reactions involving the homogeneous decomposition of mercury aryl compounds in solution proceeded faster following the appearance of metallic mercury droplets. A similar effect was reported by Reutov.[5] Reutov and Ostapchuk[6] and Reutov and Yan-tsei[7] have reported the exchange of mercury organic compounds with a stirred metallic mercury layer.

$$R—Hg—X + Hg^* \rightleftharpoons R—Hg^*—X + Hg$$

and

$$R_2Hg + Hg^* \rightleftharpoons R_2Hg^* + Hg$$

They produced evidence to show that free radicals were not involved but omitted the rigorous kinetic data needed for quantitative analysis of the reaction mechanism.

To account for the observed dipole moment, Hampson[8] suggested that mercury organic compounds were not strictly linear "sp" hybrids in solution. Dessy and Kim[9] have invoked nonlinearity to account for reactions with HCl. More direct evidence has been given by Schneider and Buckingham,[10] who showed large chemical shifts (82 p.p.m.) by n.m.r. studies when $Hg(CH_3)_2$ was diluted with pyridine and attributed this to changes of hybridization by solvent coordination. Similar effects in mercury aryl molecules require investigation. It was hoped that heterogeneous exchange reactions might provide further evidence, as molecular orientation effects may be involved in any adsorption process.

This paper is mainly concerned with the establishment of experimental techniques and factors affecting the exchange
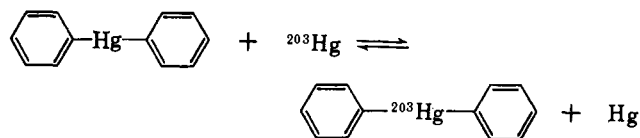
prior to a systematic kinetic investigation of possible mechanisms of exchange for diphenylmercury and its symmetrically monosubstituted derivatives.

Experimental

1. Materials. Diphenylmercury was prepared from bromobenzene in xylene solution by the sodium amalgam method,[11] with ethyl acetate as catalyst, and purified by double recrystallization from benzene (m.p. 123–124°; lit. m.p. 122°,[12] 125–126°[13]). Di-*o*-tolylmercury was prepared by converting *o*-bromobenzene to the Grignard reagent and treating it with mercuric chloride in ether–benzene solution. Purification was effected

(1) Part of this material was taken from a thesis of D. R. Pollard, submitted in fulfillment of the degree of Ph.D.. University of London at Sir John Cass College.

(2) O. A. Reutov and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 655 (1953).

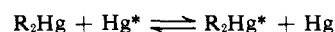(3) C. K. Ingold, *J. Chem. Soc.*, 2523 (1959).

(4) M. Haissinsky and M. Cottin, *J. chim. phys.*, **45**, 224 (1948); **46**, 476 (1949).

(5) O. A. Reutov, *Tr. Inst. Fiz. Khim. Akad. Nauk SSSR* **22**, 3315 (1951).

(6) O. A. Reutov and G. M. Ostapchuk, *Dokl. Akad. Nauk SSSR*, **117**, 826 (1957).

(7) O. A. Reutov and U. Yan-tsei, *ibid.*, **117**, 1003 (1957).

(8) G. C. Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

(9) R. E. Dessy and J. Y. Kim, *J. Am. Chem. Soc.*, **82**, 686 (1960).

(10) W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, **34**, 147 (1962).

(11) E. Dreher and R. Otto, *Ber.*, **2**, 542 (1869).

(12) E. Dreher and R. Otto, *Chem. Zentr.*, **2**, 822 (1912).

(13) M. O. Forster, *J. Chem. Soc.*, **73**, 783 (1898).