Interactions of Nitrosonium Salts with Crown Ethers

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Interactions of nitrosonium tetrafluoroborate and hexafluorophosphate with 18-crown-6, 15-crown-5, and 12-crown-4 in dichloromethane, acetonitrile, and nitromethane have been probed by a combination of proton magnetic resonance spectroscopy, infrared spectroscopy, and conductance measurements. The stoichiometries of the crown ether-nitrosonium salt complexes were one mole of 18-crown-6 per mole of nitrosonium salt and two moles of 12-crown-4 per mole of nitrosonium salt in all solvents. For 15-crown-5, the one-to-one stoichiometry observed in acetonitrile and nitromethane changed to two moles of crown ether per mole of nitrosonium salt in dichloromethane. The nature of these complexes is discussed. Treatment of a solution of equimolar nitrosonium hexafluorophosphate and 18-crown-6 in dichloromethane with water produced hydronium hexafluorophosphate·18-crown-6 complex.

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Since Pederson's pioneering reports (1,2) of viable synthetic routes to macrocyclic polyethers (crown ethers), the complexation of numerous cationic species by these multidentate ligands has been studied (3,4). The list of complexed cations includes: alkali and alkaline earth cations, as well as other metal ions (3,4); ammonium and substituted ammonium ions (4); aryldiazonium ions (5); quanidinium ions (6); and even hydronium ions (7). The recent use of crown ether-complexed nitronium ions in aromatic nitrations (8) prompts us to report our studies of the interactions of nitrosonium cations with crown ethers (9).

Results.

Interactions of nitrosonium tetrafluoroborate and hexafluorophosphate with 18-crown-6, 15-crown-5, and 12-crown-4 in dichloromethane, acetonitrile, and nitromethane have been probed by a combination of proton magnetic resonance (^{1}H nmr) spectroscopy, infrared (ir) spectroscopy, and conductance measurements.

The ^{1}H nmr absorptions for the protons of 18-crown-6, 15-crown-5, and 12-crown-4 were found to shift downfield in the presence of nitrosonium tetrafluoroborate and hexafluorophosphate. Observation of only a single, sharp absorption for the crown ether protons reveals that exchange between free crown ether molecules and those complexed by nitrosonium salt is rapid on the nuclear magnetic resonance time scale.

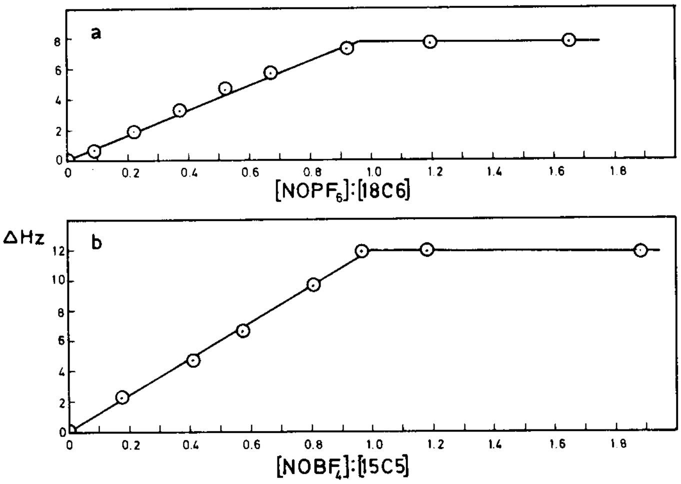

Figure 1. Chemical shift change of crown ether protons *vs.* [nitrosonium salt]:[crown ether] for (a) nitrosonium hexafluorophosphate and 18-crown-6 in dichloromethane, (b) nitrosonium tetrafluoroborate and 15-crown-5 in nitromethane.

The chemical shift changes for the crown ether protons were used to determine the stoichiometry of crown ether-nitrosonium salt complexes. In plots of the chemical shift change (ΔHz) relative to that for the crown ether itself *vs.* the [nitrosonium salt]:[crown ether] ratio, two types of behavior were observed for 18-crown-6 and 15-crown-5. Type 1: The additions of nitrosonium salt produced regular chemical shift changes for the crown ether protons until a ratio of 0.95 ± 0.05 was reached (Figure 1). After that point further additions of nitrosonium salt produced inhomogeneity and no change in the chemical shift of the crown ether protons. Type 2: The added nitrosonium salt dissolved readily in the crown ether solution and the chemical shift of the crown ether protons changed regularly until [nitrosonium salt]:[crown ether] = 0.45 ± 0.05 (Figure 2). With further additions of nitrosonium salt, a

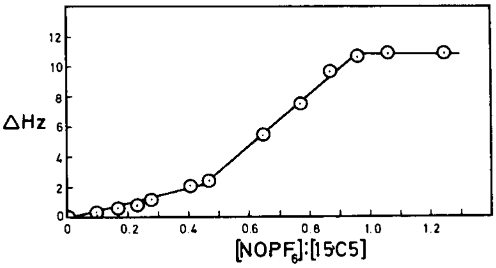

Figure 2. Chemical shift change of crown ether protons *vs.* [nitrosonium hexafluorophosphate]:[15-crown-5] in dichloromethane.

line of increased slope was defined until [nitrosonium salt]:[crown ether] = 0.95 ± 0.05, after which additional nitrosonium salt produced inhomogeneity and no further changes in chemical shift.

For a variation of the nitrosonium salt anion from hexafluorophosphate to tetrafluoroborate, there was no noticeable effect upon the magnitude of the chemical shift changes produced by adding the nitrosonium salt to dichloromethane solutions of 18-crown-6 or 15-crown-5.

For additions of nitrosonium salt to solutions of 12-crown-4 in dichloromethane (Figure 3) and acetonitrile, Type 2 behavior was observed with the modification that inhomogeneity and gas evolution were noted after [nitrosonium salt]:[crown ether] = 0.45 ± 0.05. The behavior in nitromethane (Figure 4) was unique in that additional nitrosonium salt produced chemical shift changes even after [nitrosonium salt]:[crown ether] = 0.95 ± 0.05 was surpassed.

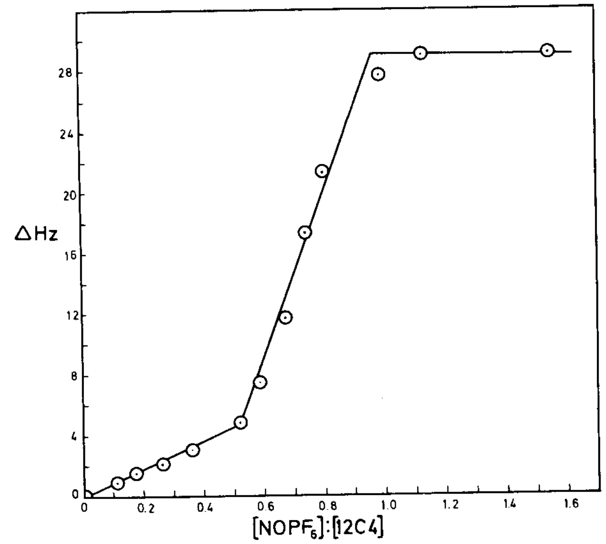

Figure 3. Chemical shift change of crown ether protons *vs.* [nitrosonium hexafluorophosphate]:[12-crown-4] in dichloromethane.

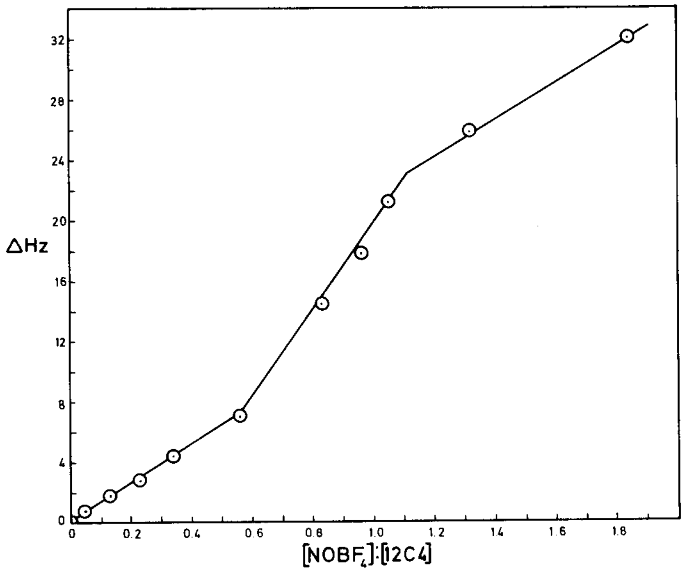

Figure 4. Chemical shift change of crown ether protons *vs.* [nitrosonium tetrafluoroborate]:[12-crown-4] in nitromethane.

Based upon the ^{1}H nmr studies, the preferred stoichiometries of the nitrosonium salt-crown ether complexes as a function of the crown ether, solvent, and anion are summarized in Table I.

Table I

Preferred Stoichiometries of Nitrosonium Salt-Crown Ether Complexes in Solution

Crown Ether	Solvent	X^- of NO^+X^-	Stoichiometry (a)	Method
18-crown-6	CH_2Cl_2	PF_6^-	1:1	^{1}H NMR
18-crown-6	CH_2Cl_2	BF_4^-	1:1	^{1}H NMR
18-crown-6	MeCN	BF_4^-	1:1	^{1}H NMR
15-crown-5	CH_2Cl_2	PF_6^-	2:1	^{1}H NMR
15-crown-5	CH_2Cl_2	BF_4^-	2:1	^{1}H NMR
15-crown-5	MeCN	BF_4^-	1:1	^{1}H NMR
15-crown-5	$MeNO_2$	BF_4^-	1:1	^{1}H NMR, conductance
12-crown-4	CH_2Cl_2	PF_6^-	2:1	^{1}H NMR
12-crown-4	MeCN	BF_4^-	2:1	^{1}H NMR
12-crown-4	$MeNO_2$	BF_4^-	2:1	^{1}H NMR, conductance

(a) Moles of crown ether:moles of nitrosonium salt.

To verify the conclusions reached in the ^{1}H nmr experiments, the changes in conductivity caused by adding nitrosonium tetrafluoroborate to solutions of 15-crown-5 and 12-crown-4 in nitromethane were determined (10). Results are depicted as plots of specific conductance *vs.* [nitrosonium salt]:[crown ether] in Figures 5 and 6. For 15-crown-5 (Figure 5) the addition of $NOBF_4$ produced

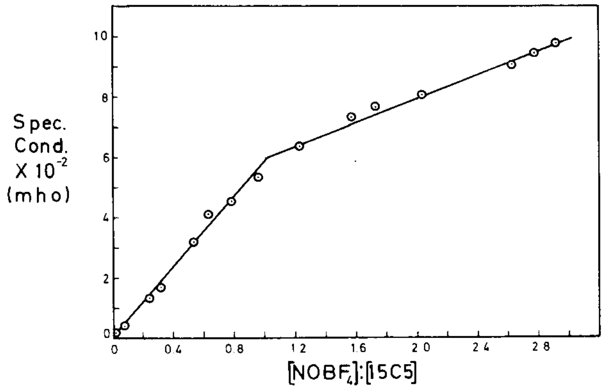

Figure 5. Specific conductance *vs.* [nitrosonium tetrafluoroborate]:[15-crown-5] in nitromethane.

Table II

Infrared Absorptions of Crown Ethers, Nitrosonium Salts, and Crown Ether-Solubilized Nitrosonium Salts (a) in Solution

Entry	Solvent	Crown Ether	X^- of NO^+X^-	ν NO (cm^{-1}) (b)	ν CO (cm^{-1}) (b)	ν X^- (cm^{-1}) (b)
1	CH_2Cl_2	18-crown-6	—	—	1117	—
2	CH_2Cl_2	18-crown-6	PF_6^-	1850	1100	840
3	CH_2Cl_2	18-crown-6	BF_4^-	1852	1105	(c)
4	CH_2Cl_2	15-crown-5	—	—	1130	—
5	CH_2Cl_2	15-crown-5	PF_6^-	1851	1105	843
6	CH_2Cl_2	12-crown-4	—	—	1133, 1103, 1076	—
7	CH_2Cl_2	12-crown-4	PF_6^-	1850	1139, 1101	842
8	MeCN	—	PF_6^-	1879	—	845
9	MeCN	—	BF_4^-	1877	—	(d)
10	MeCN	18-crown-6	—	—	1120	—
11	MeCN	18-crown-6	PF_6^-	1876	1103	840
12	MeCN	18-crown-6	BF_4^-	1876	1096	(c)
13	MeCN	15-crown-5	—	—	1123	—
14	MeCN	15-crown-5	BF_4^-	1876	1096	(c)
15	MeCN	12-crown-4	—	—	1136, 1103	—
16	MeCN	12-crown-4	BF_4^-	1876	1142, 1099	(c)

(a) [Nitrosonium salt]:[crown ether] $\geq$ 1.0. (b) Uncertainty = ± 3 cm^{-1}. (c) ν BF_4^- overlaps with ν CO. (d) Not measured.

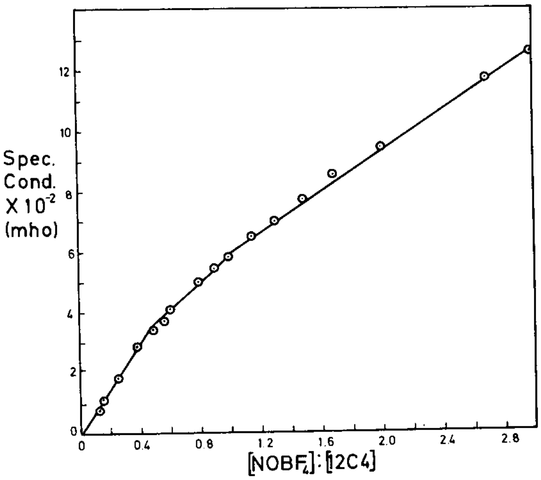

Figure 6. Specific conductance *vs.* [nitrosonium tetrafluoroborate]:[12-crown-4] in nitromethane.

regular changes in the specific conductance until [nitrosonium salt]:[crown ether] = 1.0. At this point, a pronounced inflection was evident. On the other hand, a similar plot for 12-crown-4 (Figure 6) exhibited inflections at ratio values of 0.5 and 1.0. These results are in complete agreement with those obtained in the ^{1}H nmr studies (Table I).

Infrared spectra were measured for crown ether-solubilized nitrosonium tetrafluoroborate and hexafluorophosphate in dichloromethane and acetonitrile. In addition, ir spectra of the three crown ethers in both solvents and of the uncomplexed nitrosonium salts in acetonitrile were obtained. Results are recorded in Table II. Although the solutions of nitrosonium salts solubilized by 18-crown-6 and 15-crown-5 showed no changes in ir spectra over a period of several hours, additional peaks became evident in the ir spectra for the 12-crown-4-solubilized nitrosonium salts after 30 minutes.

Addition of the nitrosonium salts to solutions of 18-crown-6, 15-crown-5, and 12-crown-4 in dichloromethane and acetonitrile produced new absorptions at 1850-1852 cm^{-1} in the former and at 1876 cm^{-1} in the latter solvent. The positions of these absorptions did not change with variation of the anion (compare entries 2 and 3 or 11 and 12) or when the [nitrosonium salt]:[crown ether] ratio was varied from a ratio of 1.0 to 0.5 or less. The ir absorption frequency of the hexafluorophosphate anion was the same, within experimental uncertainty, for nitrosonium hexafluorophosphate in the absence and presence of crown ether (compare entry 8 with entries 2, 5, 7, and 11).

Addition of nitrosonium tetrafluoroborate and hexafluorophosphate to solutions of 18-crown-6 and 15-crown-5 in dichloromethane and in acetonitrile produced shifts of 12-27 cm^{-1} to lower frequency in the C-O stretching absorptions for the crown ethers. The more complex C-O stretching absorption pattern for 12-crown-4 was also influenced by the presence of nitrosonium salt. These changes are listed in Table II and are depicted in Figures 7 and 8 for nitrosonium hexafluorophosphate in dichloromethane and acetonitrile, respectively.

After a solution of nitrosonium hexafluorophosphate which had been solubilized by equimolar 18-crown-6 in dichloromethane was allowed to stand in contact with room air for several hours, the ir absorption at 1850 cm^{-1} disappeared even though the C-O stretching absorptions (1143

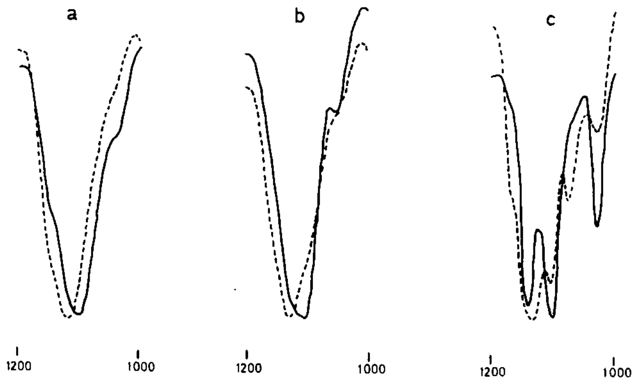

Figure 7. Infrared spectra of crown ethers in dichloromethane in the absence (dashed lines) and presence (solid lines) of equimolar nitrosonium hexafluorophosphate for (a) 18-crown-6, (b) 15-crown-5, and (c) 12-crown-4.

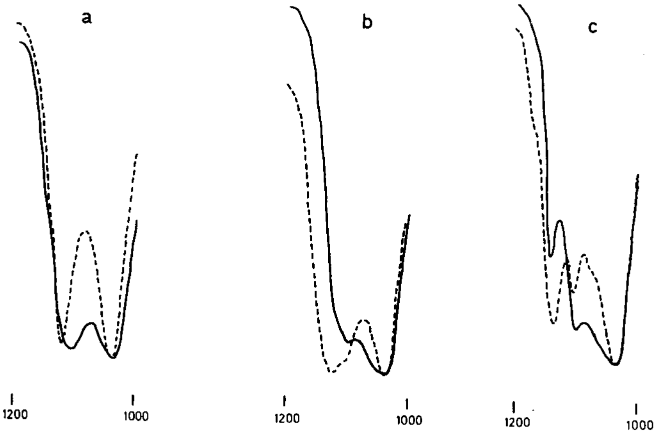

Figure 8. Infrared spectra of crown ethers in acetonitrile in the absence (dashed lines) and presence (solid lines) of equimolar nitrosonium hexafluorophosphate for (a) 18-crown-6, (b) 15-crown-5, (c) 12-crown-4. The solvent absorbs at 1030 cm^{-1}.

and 1093 cm^{-1}) showed evidence of continued crown ether complexation as did the presence of the absorption for the hexafluorophosphate anion (839 cm^{-1}). The ^{1}H nmr spectrum of the solution consisted of singlets at δ 3.64 and 10.84 with relative areas of 8:1. Upon addition of deuterium oxide, the low field ^{1}H nmr absorption disappeared. The observed ir and ^{1}H nmr spectral properties were identical with those of a hydronium hexafluorophosphate·18-crown-6 complex prepared by an independent route (11). Also, addition of diethyl ether gave a white solid which had the same melting point as the known 1:1 complex of hydronium hexafluorophosphate with 18-crown-6 (11).

Stirring an equimolar solution of 18-crown-6 and nitrosonium hexafluorophosphate in dichloromethane with an excess of water for five minutes, followed by separation, drying, and addition of diethyl ether to the dichloromethane layer gave a white precipitate. Washing this precipitate with diethyl ether and drying gave a nearly quantitative yield of the hydronium hexafluorophosphate·18-crown-6 complex.

Discussion.

The ^{1}H nmr and conductance measurements clearly establish that the preferred stoichiometry of nitrosonium salt-crown ether complexes in solution is controlled by the identity of the crown ether and the solvent polarity (Table I). With 18-crown-6, nitrosonium tetrafluoroborate and hexafluorophosphate form 1:1 complexes in dichloromethane and acetonitrile. For 12-crown-4 in dichloromethane, acetonitrile, and nitromethane, there is preferential formation of 2:1 complexes which contain two molecules of crown ether per one nitrosonium salt species. However, the situation for 15-crown-5 is intermediate with 1:1 complexes being formed in acetonitrile and nitromethane, but a 2:1 complex being preferred in the less polar solvent dichloromethane.

The pronounced effect of crown ether ring size upon the stoichiometry is consistent with the recent report by Elsenbaumer and Wasserman (8) concerning the stoichiometries of crown ether complexes of nitrosonium tetrafluoroborate in dichloromethane. These authors detected a 1:1 complex with 18-crown-6 and a 3:1 complex with 12-crown-4, but no well-defined complex with 15-crown-5.

In the ir spectra of nitrosonium tetrafluoroborate and hexafluorophosphate measured by Sharp and Thorley (12) as mulls in Fluorolube grease, nitrosonium ion absorptions at 2387 and 2378 cm^{-1}, respectively, were observed. In contrast, the new absorptions which arise when these nitrosonium salts are added to dichloromethane and acetonitrile solutions of the crown ethers (Table II) are in the region of 1850-1880 cm^{-1}. The magnitude of this change is much larger than would be anticipated for a simple complexation of a nitrosonium cation by a crown ether (13).

The NO stretching absorptions of covalent nitrosyl chloride and fluoride (14) are at 1799 and 1844 cm^{-1}, respectively. Therefore, the positions of the nitrosyl stretching absorptions for the crown ether-solubilized nitrosonium salts (Table II) and for nitrosonium tetrafluoroborate and hexafluorophosphate dissolved in acetonitrile (entries 8 and 9, Table II) indicate that the nitrosyl groups are covalently linked to strongly electron-withdrawing atoms. We suggest that these species are $R_2{}^+O\text{-}NO$ and $CH_3\text{-}C{\equiv}N^+\text{-}NO$, respectively.

Since the ^{1}H nmr experiments reveal an equivalency of all oxygens of a complexed crown ether, the covalently-bound nitrosyl group must exhibit fluxional behavior. For crown ethers with larger cavity sizes, such as 18-crown-6, the fluxional behavior of the nitrosyl groups involves the oxygen atoms of a single crown ether molecule. However, for the small polyether cavity of 12-crown-4, the fluxional interactions of the nitrosyl group encompass the oxygen atoms of two crown ether molecules, presumably in a sandwich type (15) of complex.

Evaporation of the solvent from equimolar solutions of 18-crown-6 and nitrosonium tetrafluoroborate or hexafluorophosphate in dichloromethane produced solids which melted with decomposition. Due to the extreme moisture sensitivity of these solids it was not possible to obtain elemental analyses.

When exposed to atmospheric moisture for several hours, an equimolar solution of 18-crown-6 and nitrosonium hexafluorophosphate in dichloromethane was converted into a solution of the hydronium hexafluorophosphate complex of 18-crown-6. Formation of this complex was inferred from the ^{1}H nmr and ir spectra of the solution and demonstrated by precipitation of the known 1:1 complex of hydronium hexafluorophosphate with 18-crown-6 (11) when diethyl ether was added.

In a deliberate synthesis, an equimolar solution of nitrosonium hexafluorophosphate and 18-crown-6 dissolved in dichloromethane was stirred with an excess of water. Workup provided an essentially quantitative yield of the hydronium hexafluorophosphate·18-crown-6 complex. Thus the hydrolysis (16) of crown ether-solubilized nitrosonium salts is a new method for the synthesis of hydronium salt-crown ether complexes.

EXPERIMENTAL

Materials.

The 12-crown-4, 15-crown-5, and 18-crown-6 were obtained from Aldrich Chemical Company and were used without further purification. Nitrosonium tetrafluoroborate and hexafluorophosphate from Aldrich Chemical Company or Columbia Organic Chemical Company were dried under vacuum over phosphorus pentoxide for several hours before use. Reagent grade dichloromethane (MC&B, Omnisolve) was purified by simple distillation, refluxing over lithium aluminum hydride, and distillation through a long fractionation column. Acetonitrile (MC&B, Omnisolve) was subjected to simple distillation, stirring overnight with calcium hydride, and distillation twice from phosphorus pentoxide. Nitromethane (Aldrich, Gold Label) was purified by simple distillation followed by two distillations from phosphorus pentoxide under reduced pressure. Anhydrous diethyl ether (MC&B) was used as received.

^{1}H NMR Measurements.

In a nitrogen-flushed dry bag, incremental amounts of the nitrosonium salt were added to a 0.2-0.8 *M* solution of the crown ether in a ^{1}H nmr tube. To eliminate weighing errors attributable to the loss of solvent by evaporation, the contents of the tube were frozen using liquid nitrogen before the tube was opened. After adding the portion of nitrosonium salt, the tube was capped and again weighed once the contents had thawed. The chemical shift of the crown ether protons relative to that for the protons of the solvent was then measured with either a Varian EM-300 or XL-100 nuclear magnetic resonance spectrometer.

Conductance Measurements.

Using an Industrial Instruments Inc. conductivity bridge (Model RC16B2) and a platinum conductivity cell with a cell constant of 0.10, the changes in specific conductance caused by the addition of nitrosonium tetrafluoroborate to a stirred solution of 15-crown-5 (5.4 mM) or 12-crown-4 (7.3 mM) in nitromethane were measured.

IR Measurements.

In a nitrogen-flushed dry bag, solutions of the nitrosonium salt and crown ether in the desired solvent were prepared and transferred to a liquid infrared cell (0.10 mm pathlength) with sodium chloride windows. Infrared spectra were recorded with a Perkin-Elmer model 457 infrared spectrophotometer.

Preparation of Hydronium Hexafluorophosphate·18-Crown-6 Complex.

Into a polyethylene test tube were weighed 0.20 g (0.76 mmole) of 18-crown-6 and 0.13 g (0.76 mmole) of nitrosonium hexafluorophosphate and 4 ml of dry methylene chloride were added. Vigorous agitation with a vortex mixer for 5 minutes produced a yellow solution to which 0.5 ml of water was added producing a green color and a vigorous evolution of brown gas. After approximately 5 minutes the two phase solution became colorless. The methylene chloride layer was separated and dried with magnesium sulfate. Addition of anhydrous diethyl ether precipitated a white solid which was filtered, washed with anhydrous diethyl ether, and dried under vacuum. The resultant white solid (0.31 g, 95% yield) had mp = 130-131°, reported (11) 131-132°.

Acknowledgements.

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