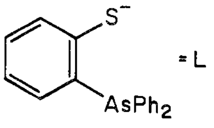
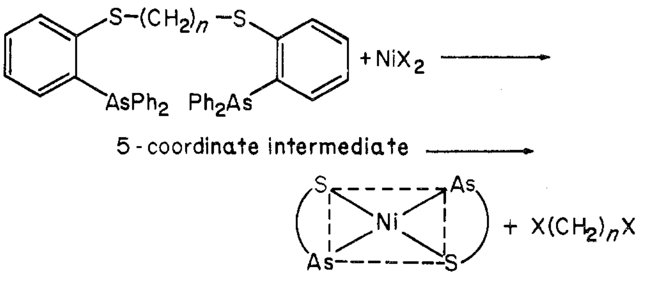
to a dinegative ligand (or ligands). The most obvious explanation was that the ligand had S-dealkylated and that two arsinosulfide ligands (L, I) were coordinated. This ex-



I

planation was confirmed by the analytical data, and further confirmation was obtained by the isolation of identical products from the reaction of *o*-mercaptophenyldiphenylarsine (LH) with the nickel(II) salts.

The $[NiL_2]$ complexes derived from either C_2, C_3, C_4, or LH all have identical infrared and electronic spectra, are nonelectrolytes in nitromethane, nitrobenzene, and dichloroethane, and are diamagnetic. It is known that arsinosulfide ligands form trans square-planar complexes,[6] and because the $[NiL_2]$ complexes prepared here from the quadridentate and bidentate ligands are alike in all respects, it is most likely that the $[NiL_2]$ complexes prepared from the C_2, C_3, and C_4 ligands are *trans*-$[NiL_2]$ species. The path of the reactions may be thus illustrated



Molecular models indicate that all the ligands fit more comfortably around a square-pyramidal structure than a planar structure, and the intense blue-purple color obtained upon initial reaction is reminiscent of the colors of low-spin pentacoordinate nickel(II) complexes with heavy donor atoms.

The visible spectra of reaction mixtures warmed to 30°, which had developed the blue-purple color, exhibit a broad band at *ca.* 19 kK, which is in the range accepted for low-spin square-pyramidal nickel(II) complexes.[7] Extreme difficulty was experienced in obtaining spectra of the blue-purple solutions; rapid precipitation of the green dealkylated complex continuously altered the intensity of absorption. Nevertheless, a laborious process of running small regions of the visible spectrum did build up a composite spectrum which indicated a band at *ca.* 19 kK. Dealkylation of the pentacoordinate intermediate followed by a slight rearrangement yields the complexes isolated. The visible spectra of the $[NiL_2]$ complexes are, as expected, identical and consist of a symmetrical absorption at 24,180 cm^{-1} (ϵ 680) and a band at 15,380 cm^{-1} (ϵ 290) accompanied by a shoulder at 14,300 cm^{-1}.

Evidence of the bis(dealkylation) has been obtained by glc identification of 1,2-dichloroethane and 1,3-dichloropropane in the solution obtained from the reaction of $NiCl_2$ with C_2 and C_3.[8] It is interesting to speculate on the fate of the $X(CH_2)_nX$ ($X = ClO_4$, NO_3) compounds formed during these reactions, but we have not followed this aspect of these reactions.

A number of attempts were made to isolate the blue-purple intermediates in the C_2, C_3, and C_4 ligand reactions. However, even careful control of the temperature of the reaction did not allow for any success. It is thus concluded that the initial reaction between NiX_2 and the quadridentate ligands is followed immediately by bis(dealkylation).

The S-dealkylation of a number of chelates containing thioether groups is known,[9-12] and these have usually employed heavy metal ions such as Au(III)[9] or Pd(II).[10] Two examples of S-dealkylation with nickel(II) halides are known,[11,12] but these, like the other examples,[9,10] have employed high-boiling solvents and long reflux times. Moreover, these are all examples of mono(S-dealkylation).

The present study has provided the first example of facile (30°) bis(S-dealkylation).

Registry No. Ni[o-$C_6H_4(AsPh_2)S]_2$, 41184-54-7; C_2, 16825-42-6; C_3, 41178-30-7; C_4, 41178-31-8; nickel, 7440-02-0; *o*-mercaptophenyldiphenylarsine, 16823-73-7.

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A New Synthesis of NF_4^+ Salts and Its Mechanistic Interpretation Involving a New and Exceptionally Powerful Oxidizing Species

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Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[1] for BrF_3.

$$BrF_3 + SbF_5 \rightarrow BrF_2^+SbF_6^- \tag{1}$$

In the case of NF_4^+ salts, this approach was impossible since the parent molecule NF_5 is unknown and unlikely to exist owing to the validity of the octet rule for first row elements such as nitrogen and fluorine. The synthesis of NF_4^+ from NF_3 and F^+ is preempted by the fact that fluorine is the most electronegative element and, hence, F^+ should be extremely difficult, if not impossible, to prepare by chemical means. In 1965, Christe and coworkers experimentally confirmed that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of an activation energy source.[2] Presently, three methods are known which are capable of producing NF_4^+ salts. These are (1) glow discharge at low temperature,[3,4] (2) heating under high pressure,[5,6]

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and (3) bremstrahlung at −196°.[7] In this note, we describe a fourth method, *i.e.*, uv photolysis, which is capable of producing NF_4^+ salts.

In addition to the great challenge which the preparation of NF_4^+ salts presented to the synthetic chemist, the NF_4^+ formation is of unusual interest from a mechanistic point of view. In view of the second and fourth methods of formation (see above), the originally suggested[3] mechanism cannot be considered satisfactory and a more plausible mechanism is offered. Based on the revised mechanism, we postulate a new intermediate of unusual oxidizing power comparable to that[8] of PtF_6.

Experimental Section

Materials and Apparatus. The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrogen trifluoride (Air Products), BF_3 (Matheson Co.), and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation. Antimony pentafluoride (Ozark Mahoning Co.) was purified by distillation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl windows in the form of pressed disks. The pressing operation was carried out using a Wilks mini pellet press. Raman spectra were recorded on a Cary Model 83 double monochromator using the 4880-Å exciting line and Kel-F capillaries as sample containers. Reactions were carried out either in a sapphire reaction tube brazed to a 304 stainless steel tube (Varian, Model CS-4250-3) having a volume of 23 ml or in a flamed out 1-l. quartz bulb. For the photolyses, unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury vapor arc was used.

Reactions in Quartz. Preparation of $NF_4^+SbF_6^- \cdot xSbF_5$. Antimony pentafluoride (26.43 mmol) was loaded into the flamed out and passivated (with ClF_3) quartz bulb in the glove box. Nitrogen trifluoride (30.6 mmol) and F_2 (30.6 mmol) were added at −196°. The mixture was allowed to warm to 25°. When exposed to uv irradiation, clouds of suspended solid appeared within seconds inside the bulb. Within 1 hr layers of a white solid formed. Irradiation of the contents was continued for 3 days until the last droplets of liquid (SbF_5) had disappeared and no signs of cloudiness in the gas phase could be detected. The contents of the bulb were cooled to −196° and O_2 and unreacted F_2 (3.1 mmol total) and unreacted NF_3 (25.2 mmol) were removed and separated by fractional condensation. The absence of unreacted SbF_5 was established by pumping for 2 hr at 25° on the solid, resulting in no detectable weight change. Compared to the bulb with SbF_5 only, the bulb containing the solid product had gained 403 mg in weight. The solid was removed from the walls of the reactor by immersion of the bulb into an ultrasonic cleaning bath and removed from the bulb in the glove box. The resulting white powder (~6.1 g) was shown by vibrational spectroscopy to be an approximately equimolar mixture of $SbF_6^- \cdot xSbF_5$ salts of NF_4^+ [9,10] and O_2^+.[11]

The NF_3-F_2-AsF_5 System. An equimolar mixture of NF_3, F_2, and AsF_5, when exposed in a quartz bulb to uv irradiation, produced a white solid product. It was identified by vibrational spectroscopy[11] and its X-ray diffraction powder pattern[12] as $O_2^+AsF_6^-$. No NF_4^+ salt could be detected by these methods.

Reactions in Sapphire. Preparation of $NF_4^+AsF_6^-$. An equimolar mixture of NF_3, F_2, and AsF_5, when kept for 3 days at 25° in a sapphire reactor in the dark, at an autogenous pressure of 6.5 atm, showed no detectable trace of solid formation. Upon exposing the sapphire section of the reactor to unfiltered uv radiation, clouds of suspended solid appeared within seconds inside the reactor resulting in an instant coating on the reactor walls. Continued exposure (for several days) of the reactor to uv radiation did not significantly increase the solid formation. After removal of the volatile reaction products, the weight gain of the reactor varied from 2 to 8 mg in several experiments. The solid residue was identified by vibrational spectroscopy[9,10] as $NF_4^+AsF_6^-$ and in all cases did not show any detectable impurities.

Preparation of $NF_4^+BF_4^-$. The NF_3-F_2-BF_3 reaction was carried out in the same way as described for NF_3-F_2-AsF_5. The reactants behaved similarly and the reaction rate decreased sharply with increasing solid deposition on the inside walls of the reactor. The yield of $NF_4^+BF_4^-$ was between 1 and 2 mg. The infrared spectrum of the solid was in excellent agreement with that previously reported[7] for $NF_4^+BF_4^-$.

Results and Discussion

When gaseous mixtures of NF_3, F_2, and the strong Lewis acids SbF_5, AsF_5, or BF_3 are exposed to unfiltered uv irradiation, the corresponding NF_4^+ salts are formed rapidly and reproducibly. Using AsF_5 or BF_3 and sapphire reactors, the following reactions occurred.

$$NF_3 + F_2 + AsF_5 \rightarrow NF_4^+AsF_6^- \qquad (2)$$

$$NF_3 + F_2 + BF_3 \rightarrow NF_4^+BF_4^- \qquad (3)$$

However, the yield of the NF_4^+ salt was less than 1%. This low yield appears not to be caused so much by a low reaction rate but by deposition of the solid product on the reactor walls, thus preventing further irradiation of the reactants. In the case of SbF_5 and a quartz reactor, all of the SbF_5 starting material was consumed in less than 3 days. In addition to NF_4^+ formation, the following side reaction occurred.

$$\begin{array}{l} 4F_2 + 2SiO_2 \rightarrow 2SiF_4 + 2O_2 \\ 2O_2 + F_2 + 4SbF_5 \rightarrow 2O_2^+Sb_2F_{11}^- \\ \hline 5F_2 + 2SiO_2 + 4SbF_5 \rightarrow 2SiF_4 + 2O_2^+Sb_2F_{11}^- \end{array}$$

Based on the observed material balance and its vibrational spectrum, the product contained approximately equimolar amounts of NF_4^+ and O_2^+ salts.[9–11] As generally the case with SbF_5, polymeric anions,[13] such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$, were formed. Attempts to use the quartz reactor for the synthesis of $NF_4^+AsF_6^-$ were unsuccessful. The attack of the quartz reactor occurred at a rate much faster than that of the NF_4^+ formation, thus resulting in $O_2^+AsF_6^-$ as the principal product.

The relatively low intensity of the uv lamp used in our experiments and the high yield of $NF_4^+SbF_6^- \cdot xSbF_5$ suggest a quantum yield larger than one, *i.e.*, a chain reaction. Taking all the presently available experimental data on the synthesis of NF_4^+ compounds into consideration, additional conclusions concerning a plausible reaction mechanism can be reached. Based on the glow-discharge synthesis, we had originally invoked the intermediate formation of a F^+ or NF_3^+ cation.[3] Whereas these cations might indeed be produced under glow-discharge conditions, the high ionization potentials of NF_3 (13.00 eV),[14] F_2 (15.69 eV),[15] or $F\cdot$ (17.44 eV)[16] preclude their formation in the uv photolysis, since the maximum energy available from the uv source does not exceed 7 eV.

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Even stronger evidence for an alternate mechanism stems from the thermal synthesis (method 2). Heating to about 120° cannot provide the activation energies required for the formation of NF_3^+, F_2^+, or F^+. However, it has been found for the Cl_2-F_2 dark reaction[17,18] that a temperature of about 120° is sufficient to dissociate some of the F_2 into $F\cdot$ radicals [$D°(F_2)$ is only 37.5 kcal mol^{-1} = 1.62 eV].[19] In spite of the very low $F\cdot$ atom concentrations expected at 120°, a chain reaction may result in relatively fast reaction rates. Based on these considerations and the observed fast reaction rate in the NF_3-F_2-SbF_5 photolysis, it seems safe to postulate F_2 dissociation as the first reaction step in the NF_4^+ salt syntheses.

$$\mathrm{F_2 \rightarrow 2F\cdot} \tag{4}$$

The next step could involve the reaction of $F\cdot$ with either NF_3 or a Lewis acid such as AsF_5. Since the hypothetical $NF_4\cdot$ containing only first row elements would violate the octet rule, its formation is very unlikely. Therefore, the second step should be

$$\mathrm{F\cdot + AsF_5 \rightarrow AsF_6\cdot} \tag{5}$$

This step appears plausible since AsF_5 generally acts as an excellent acceptor molecule and changes from a trigonal-bipyramidal to an energetically more favorable octahedral AsF_6 configuration. The $AsF_6\cdot$ radical is pseudo-isoelectronic with SF_6^+ and, hence, a rough estimate for the exothermicity of the reaction

$$\mathrm{AsF_6\cdot + e \rightarrow AsF_6^-}$$

can be obtained from the known[20] photoionization threshold of SF_6 (15.29 eV). This high value strongly suggests that the $AsF_6\cdot$ radical is the only likely intermediate capable of oxidizing NF_3, which has a first ionization potential of 13.00 eV.[14] Consequently, the third reaction step in the $NF_4^+AsF_6^-$ formation should be

$$\mathrm{AsF_6\cdot + NF_3 \rightarrow NF_3^+AsF_6^-} \tag{6}$$

In order to maintain a chain reaction, the $NF_3^+AsF_6^-$ could react with F_2 according to

$$\mathrm{NF_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F\cdot} \tag{7}$$

A crude estimate of the bond energy changes involved in this step can again be obtained by comparison between the isoelectronic species

$$\mathrm{NF_3^+ + F\cdot \rightarrow NF_4^+} \tag{8}$$

and

$$\mathrm{CF_3\cdot + F\cdot \rightarrow CF_4} \tag{9}$$

Since the CF_3-F bond energy (139.4 kcal mol^{-1})[21] is considerably higher than that of the F-F bond (37.5 kcal mol^{-1}),[19] reaction 7 should also be exothermic. Chain termination steps could occur by combination of any two of the radicals involved in this mechanism. The overall sequence, eq 4-7, appears to be a very plausible mechanism requiring only a low activation energy for (4), in excellent agreement with the experimental observations.

Solomon and coworkers have studied[22] the kinetics of the thermal decomposition of $NF_4^+AsF_6^-$ to NF_3, F_2, and AsF_5 in the temperature range 175-222° at low pressure. Since Tolberg, *et al.*, have shown[5] that $NF_4^+AsF_6^-$ can be formed in this temperature range from NF_3, F_2, and AsF_5 under high pressure, reversibility of these reactions is indicated. Consequently, the $NF_4^+AsF_6^-$ formation mechanism should allow us also to better understand the thermal decomposition. Solomon, *et al.*, observed[22] that both NF_3 and AsF_5 inhibit the decomposition reaction and suggest that the decomposition mechanism involves the reversible dissociation of the solid to NF_5 and AsF_5, followed by the irreversible decomposition of NF_5 as the rate-determining step. However, the observed fractional-order kinetics could not be explained by an elementary reaction mechanism. The mechanism, suggested[22] by Solomon and coworkers, has several shortcomings. In our opinion, the most serious ones are (1) NF_5 violates the octet rule which is strictly valid for first row elements—promotion of nitrogen electrons to the 3s level would result in a prohibitively large activation energy for the NF_5 formation, (2) the $NF_4^+AsF_6^-$ formation, and (3) the inhibition of the $NF_4^+AsF_6^-$ decomposition by NF_3 addition suggests that the steps involving NF_3 cannot be irreversible. For these reasons and by analogy with the mechanism discussed above for the $NF_4^+AsF_6^-$ formation, a more plausible decomposition mechanism would be

$$\mathrm{NF_4^+AsF_6^- \rightleftarrows NF_3^+AsF_6^- + F\cdot} \tag{10}$$

$$\mathrm{NF_3^+AsF_6^- \rightleftarrows NF_3 + AsF_6\cdot} \tag{11}$$

$$\mathrm{AsF_6\cdot \rightleftarrows F\cdot + AsF_5} \tag{12}$$

$$\mathrm{2F\cdot \rightarrow F_2} \tag{13}$$

Because the steady-state F atom concentration would be determined by a number of reactions, including the reverse of reaction 7, a very complex rate expression might be expected. The recombination of F atoms could occur either homogeneously *via* a three-body collision or heterogeneously. The inhibiting effects of NF_3 and AsF_5 could result from the reduction of the steady-state F atom concentration caused by the shifting of the equilibria 10-12 to the left.

The postulate of an $AsF_6\cdot$ radical intermediate which can act as a powerful oxidizer could also explain the following two previously reported[23-25] and highly unusual reactions

$$\mathrm{2O_2 + F_2 + 2AsF_5 \xrightarrow[\text{or uv}]{130°} 2O_2^+AsF_6^-} \tag{14}$$

and

$$\mathrm{Xe + F_2 + AsF_5 \xrightarrow{uv} XeF^+AsF_6^-} \tag{15}$$

Both reactions proceed again under very mild conditions, resulting in the oxidation of two species, O_2 and Xe, with very high first ionization potentials of 12.06 and 12.13 eV, respectively. Reactions 14 and 15 are directly comparable to the following known[8,26,27] PtF_6 reactions

$$\mathrm{O_2 + PtF_6 \rightarrow O_2^+PtF_6^-} \tag{16}$$

and

$$\mathrm{Xe + 2PtF_6 \rightarrow XeF^+Pt_2F_{11}^-} \tag{17}$$

This analogy suggests that the oxidizing power of a Lewis acid-F· radical, such as $AsF_6\cdot$, is comparable to that of PtF_6,

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which is one of the strongest oxidizing fluorinators[8] known. The applicability of the Lewis acid-activated F_2 system, however, seems to be limited to starting materials which themselves do not form stable adducts with the Lewis acid. The given examples demonstrate that the oxidizing power of fluorine can be promoted significantly by the simultaneous use of a strong Lewis acid and an energy source promoting dissociation of F_2 into $F\cdot$ atoms. Consequently, many reactions previously requiring the use of the prohibitively expensive PtF_6 may now be carried out at a reasonable expense by the use of Lewis acid promoted activated fluorine.

Acknowledgment. We wish to express our gratitude to Drs. D. Pilipovich and C. J. Schack for stimulating discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. F_2, 7782-41-4; NF_3, 7783-54-2; SbF_5, 7783-70-2; AsF_5, 7784-36-3; BF_3, 7637-07-2; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4.

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Bis(fluorosulfato)bromates(I) of Lithium and Sodium

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Chung and Cady[1] have shown that the solid compound, cesium bis(fluorosulfato)bromate(I) [$CsBr(SO_3F)_2$] is produced when $BrSO_3F$ combines with $CsSO_3F$ and have found qualitative evidence that a single fluorosulfate ion, when introduced into liquid bromine(I) fluorosulfate, probably becomes associated with more than one molecule of $BrSO_3F$. Quereshi and Aubke[2] have confirmed the existence of $CsBr(SO_3F)_2$ and have reported its Raman spectrum.

In the present study solutions of the fluorosulfates of Li, Na, K, Rb, or Cs in excess bromine(I) fluorosulfate were subjected to dynamic vacuum at room temperature. In each case the removal of $BrSO_3F$ left behind a liquid more viscous but less highly colored than pure liquid bromine(I) fluorosulfate. As evaporation occurred a solid phase appeared. For the systems involving potassium or rubidium, the solid which formed was KSO_3F or $RbSO_3F$, respectively. For systems involving lithium or sodium, the solids which first formed were $LiBr(SO_3F)_2$ or $NaBr(SO_3F)_2$.

Experimental Section

System $NaSO_3F$-$BrSO_3F$. A mixture of $NaSO_3F$ (2.233 mmol) and $BrSO_3F$ (30.06 mmol) was held in a glass vessel at 90° for 1.5 hr and was later subjected to dynamic vacuum at about 23° to remove $BrSO_3F$. At first the vessel lost weight rapidly, but the rate of loss decreased greatly after the ratio of $BrSO_3F$ to $NaSO_3F$ fell below 2:1. Much solid was then present, but the material obviously was partially liquid down to a ratio of 1.4. Possibly liquid was present down to a ratio of about 1.0. Pumping was continued until the weight of the residue fell to 0.6870 g, corresponding to a molar ratio of $BrSO_3F$ to $NaSO_3F$ of 1.04. During the last part of the pumping operation, the solid was not homogeneous in color. Some parts were much darker than others. The Raman spectrum of one nearly white region contained lines characteristic of $NaSO_3F$. When the flask was then held at 65° for 18 hr, but with no pumping, the solid became homogeneous and was pale yellow. The Raman spectrum of $NaSO_3F$ was no longer found and the spectrum was much like that for $CsSO_3F\cdot BrSO_3F$. Raman spectra taken with the laser beam directed at several random locations in the homogeneous 1:1 solid were identical.

Table I. Raman Spectra for $MBr(SO_3F)_2$ Salts

$LiBr(SO_3F)_2$		$NaBr(SO_3F)_2$		$CsBr(SO_3F)_2$	
ν, cm^{-1}	Intens[a]	ν, cm^{-1}	Intens[a]	ν, cm^{-1}	Intens[a]
				40	6.2
				69	24.2
96	16.2				
124	8.2	108	13.8	109	12.8
		(174)	6.9	(182)	1.2
246	100	263	51.4	262	100
412	3.1	398	3.5	399	1.2
446	55.8	443	44.1	437	42.8
557	7.5	554	5.9	557	3.1
583	6.2	578	11.0	573	3.1
626	48.7	624	100	617	79.4
803	12.2	827	14.8	778	2.5
1062	6.9	1023	0.9	1018	1.9
1280	8.5	1238	22.3	1220	13.2
1339	5.5	1379	7.3	1373	7.2
		1395	10.8		

[a] Uncorrected Raman intensities; ( ) probably an impurity.

Analysis. The salt was allowed to react with aqueous sodium hydroxide solution. Sulfur was then determined gravimetrically as $BaSO_4$ and bromine as AgBr. Fluorine was determined by titrating with thorium nitrate solution and the end point was observed with the help of an Orion fluoride-ion-selective electrode. *Anal.* Calcd for $NaSO_3F\cdot BrSO_3F$: S, 21.3; Br, 26.5; F, 12.6. Found: S, 22.6; Br, 25.7; F, 12.7.

System $LiSO_3F$-$BrSO_3F$. Bromine(I) fluorosulfate (25.5 mmol) was mixed with dry lithium fluorosulfate (4.543 mmol) in a glass vessel. While this 5.61 to 1 mixture was held at 65° for 1.5 hr, it was completely liquid. As it cooled to room temperature, part of the material crystallized. The system was then subjected to dynamic vacuum at about 23° with $BrSO_3F$ distilling away. Although the rate of removal of $BrSO_3F$ decreased somewhat when the ratio of $BrSO_3F$ to $LiSO_3F$ fell below about 3 to 1, the rate remained higher than for the systems involving $NaSO_3F$ and $CsSO_3F$. As $BrSO_3F$ was removed, one could easily see a liquid phase down to a molar ratio of about 1.9, and the solid continued to look wet down to a ratio of about 1.3. After the molar ratio of $BrSO_3F$ to $LiSO_3F$ had fallen to 1.02, pumping was stopped and the mixture was allowed to stand for 5 days. The resulting solid was a homogeneous pale yellow, dry, flaky material which had a Raman spectrum resembling those of $CsSO_3F\cdot BrSO_3F$ and $NaSO_3F\cdot BrSO_3F$. No bands attributable to $LiSO_3F$ were observed. *Anal.* Calcd for $LiSO_3F\cdot BrSO_3F$: S, 22.5; Br, 28.0; F, 13.3. Found: S, 23.4; Br, 27.6; F, 13.0.

Spectra. Raman spectra were recorded using the 5145-Å exciting line of a Coherent Model 52 Ar-Kr ion laser in conjunction with a Spex 1401 double monochromator and a thermoelectrically cooled F.E.-130 phototube. The observed spectra are reported in Table I.

^{19}F nmr spectra of solutions of alkali metal fluorosulfates in $BrOSO_2F$ were obtained using a Varian Associates Model V-4311 nmr spectrometer at 56.4 MHz. The samples were sealed in 5-mm Pyrex glass tubes, and trichlorofluoromethane was used as an external standard. All of the samples gave only a single "line" spectrum. The chemical shift was somewhat dependent upon concentration and decreased as the ratio $BrSO_3F$:MSO_3F became smaller. The chemical shift observed for pure bromine(I) fluorosulfate was −34.9 ppm. For the solutions the values ranged down to −37.9 ppm. Apparently exchange occured so rapidly that only one line was obtained for each solution. As the temperature was lowered, the line became so broad below about −45° that the "peak" disappeared.[3]

Discussion

The above experiments clearly indicate the existence of the new solid compounds $LiBr(SO_3F)_2$ and $NaBr(SO_3F)_2$. The materials appear to be homogeneous and have characteristic Raman spectra similar to that of $CsBr(SO_3F)_2$. Since lines for MSO_3F are lacking and since the ratio of $BrSO_3F$ to

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