presence of NO increases the basicity of the ion and increases the rate of loss of CN^-, but the uncharged intermediate has relatively high stability in both systems.[5]

Table IV
Positions (mμ) and Intensities of Absorption Bands of Cr–NO Species[a]

Species	λ	ε	λ	ε	λ	ε	λ	ε
$Cr(CN)_5NO^{3-}$	724	14.5	447	127	335	86		
$Cr(CN)_2(H_2O)_3NO$	630	23.6	453	103	358	293	285	247
$Cr(H_2O)_5NO^{2+}$	567	30.6	447	131	390	96	324	101
$Cr(NH_3)_5NO^{2+}$			457	101	348	69	302	157
$Cr(C_2H_5OH)_2NO^{2+}$	570	18	457	61	325	150		

[a] With the exception of $Cr(CN)_2(H_2O)_3NO$, these numbers are taken from ref 6.

Table IV[6] compares the spectrum of the product of the primary aquation, $Cr(CN)_2(H_2O)_3NO$, with ions containing the Cr–NO grouping. It is interesting that each of these species has a band near 450 mμ. The Cr–NO group dominates the MO splitting pattern for one of these species.[7] It seems reasonable to assign the band at 450 mμ to an internal ($d_{xz,yz} \rightarrow {}^*\pi$ NO) transition of the Cr–NO grouping.

Our present observation of the kinetic inertia of the Cr–NO grouping supplements the previous conclusion[8] that the Cr–NO grouping functions as an electrochemical unit.

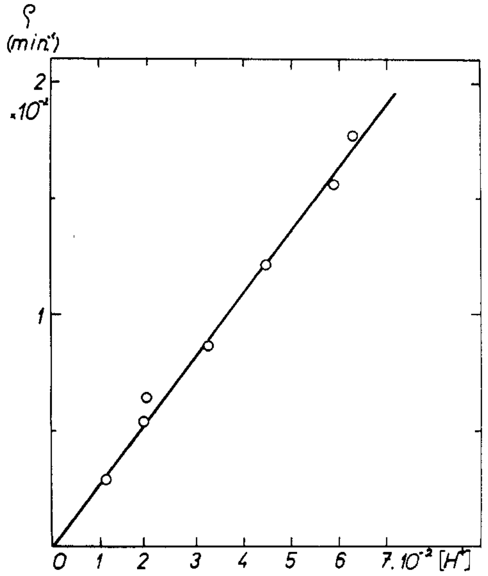

Figure 5.—Dependence of slope of the lines shown in Figure 4 on hydrogen ion concentration.

After this paper was submitted, an esr study of the aquation of $Cr(CN)_5NO^{3-}$ appeared.[9] The esr study gives more precise data on the subsequent aquation, but no kinetics on the primary aquation. Our data indicate that the solution resulting from adding an equivalent amount of acid to a solution of $Cr(CN)_5NO^{3-}$ should contain aquated species. This consideration may modify the discussion of some of the esr spectra.

Acknowledgment.—The portion of this work done at Georgetown University was supported by the Directorate of Chemical Sciences of the U. S. Air Force Office of Scientific Research under Grant AF-1225-67.

---

[5] W. B. Schaap and R. Krisnamurthy, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 36-O.

[6] W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).

[7] P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

[8] D. I. Bustin and A. A. Vlček, *Collection Czech. Chem. Commun.*, **32**, 1665 (1967) (paper II in this series).

[9] J. Burgess, B. A. Goodman, and J. B. Raynor, *J. Chem. Soc., A*, 501 (1968).

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Interaction of N,N-Bis(trifluoromethyl)hydroxylamine with Amines

By GERALD G. FLASKERUD and JEAN'NE M. SHREEVE

Received May 12, 1969

N,N-Bis(trifluoromethyl)hydroxylamine is a very weak acid with a dissociation constant of 1.5×10^{-9} in aqueous solution. It interacts with a variety of simple organic amines to form a series of weakly associated adducts which are liquids or low-melting, sublimable, crystalline solids at room temperature. These adducts are partially dissociated to the parent molecules in the gas phase. Proton nmr spectra, elemental analyses, and mole fraction plots indicate that 1:1 adducts are formed with ammonia, methylamine, dimethylamine, ethylamine, and triethylamine. Trimethylamine and diethylamine form adducts composed of 2 mol of $(CF_3)_2NOH$ per mole of amine.

N,N-Bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$,[1] is a useful reagent for introducing the N,N-bis(trifluoromethyl)nitroxide group into molecules which contain labile halogens. Also, $(CF_3)_2NOH$ has been found to form an adduct with cesium or potassium fluoride which has been used to prepare a large number of molecules containing the $(CF_3)_2NO$ moiety.[2-4] It also has been found to react with NaOH in tetrahydrofuran forming the sodium salt, $(CF_3)_2NONa$, which

---

[1] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).

[2] D. P. Babb and J. M. Shreeve, *Inorg. Chem.*, **6**, 351 (1967).

[3] L. L. Nash, J. J. Conville, D. P. Babb, and J. M. Shreeve, *J. Inorg. Nucl. Chem.*, **30**, 3373 (1968).

[4] J. A. Lott, D. P. Babb, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.* **7**, 2593 (1968).

reacts with CH_3I and $(CH_3)_3SiCl$ to form $(CF_3)_2NOCH_3$ and $(CF_3)_2NOSi(CF_3)_3$, respectively.[5] Thus, although considerable synthesis work has involved $(CF_3)_2NOH$, little has been reported concerning the acidity or reactivity of the hydroxyl proton.

N,N-Bis(trifluoromethyl)hydroxylamine is a very weak acid in aqueous solution ($K_a = 1.5 \times 10^{-9}$). It interacts with a variety of simple organic amines to form a series of weakly associated adducts. These adducts are not the high-melting solids typical of substituted ammonium salts, but are liquids or low-melting, sublimable crystalline solids which exhibit varying degrees of dissociation at room temperature. Mole fraction plots, proton nmr spectra, and elemental analyses indicate that either 1:1 or 2:1 (2 mol of $(CF_3)_2NOH$ per mole of amine) adducts are formed with ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, and triethylamine.

Experimental Section

Apparatus.—A standard Pyrex high-vacuum system was used for manipulation of volatile compounds. Glass stopcocks were lubricated with Kel-F No. 90 grease (3M Co.). Reactions were carried out in 20-ml tubes fitted with a Teflon stopcock (Fisher and Porter Co.).

Infrared spectra (Table I) were recorded for compounds in the gas and condensed (liquid or solid) phases with a Perkin-Elmer Model 137 Infracord and a Perkin-Elmer Model 621 spectrophotometer. The gaseous samples were contained in a Pyrex cell (5-cm path length) equipped with KBr windows. The liquid or solid was placed between two KBr windows for the condensed-phase spectra. High-resolution ^{19}F and ^1H nmr spectra (Table II) were obtained using a Varian Model HA-100 spectrometer operating at 94.1 Mc and a Varian Model A-60 spectrometer, respectively. Trichlorofluoromethane (Matheson Co.), which had been dried over P_4O_{10}, and tetramethylsilane were used as internal references. Mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-6E spectrometer at an ionization potential of 70 eV. Conductances were determined in dimethylformamide with a dipping-type conductivity cell (cell constant approximately 0.1 cm^{-1}). Melting points (Table III) were obtained by transferring the compound into a capillary tube in the vacuum system, sealing the tube, and determining the melting point with a standard melting point apparatus. The apparatus and techniques used in the mole fraction plots are essentially those described by Holmes.[6]

Reagents.—N,N-Bis(trifluoromethyl)hydroxylamine was prepared by the reaction of trifluoronitrosomethane with anhydrous ammonia.[7] CF_3NO was obtained from Peninsular Chem-Research, Inc., NH_3 was from Matheson Co., and all of the amines were from Eastman Organic Chemicals. All of the reagents were used without further purification.

Dissociation Constant of $(CF_3)_2NOH$.—Samples of $(CF_3)_2NOH$ in water were titrated with 0.1217 *N* NaOH. A Beckman expanded-scale pH meter, standardized against standard Beckman buffers, was used to determine the pH of the solution after addition of aliquots of NaOH. The K_a was determined either from the pH at the half-equivalence point as found from the titration curve or from the pH measured at the theoretical half-equivalence point. The dissociation constant is 1.5×10^{-9}.

TABLE I

INFRARED SPECTRAL DATA[a]

$(CF_3)_2NOH(g)$	3619 m, 1394 m, 1310 vs, 1270 vs, 1223 vs, 1046 s, 972 s, 710 s (PQR)
$NH_3 \cdot (CF_3)_2NOH(g)$	3619 m, 3317 w, 2750–3300 br, (2945 s, 3100, 3160, 3260 w), 1395 m, 1306 vs, 1272 vs, 1223 vs, 1065 s, 970 s, 650 s
$NH_3 \cdot (CF_3)_2NOH(l)$	3100–3450 m, br, 2400–2800 br, w, 1270 s, 1190 s, 1060 m, 965 s, 706 m
$CH_3NH_2 \cdot (CF_3)_2NOH(g)$	3619 w, 3173 w, br, 2400–3050 br, (2600 w, 2780 s, 2980 m), 1393 vw, 1300 vs, 1278 vs, 1220 vs, 1064 m, 972 s, 711 s
$CH_3NH_2 \cdot (CF_3)_2NOH(s)$	1270 s, 1180 m, 1055 w, 960 m, 702 w
$(CH_3)_2NH \cdot (CF_3)_2NOH(g)$	3619 m, 2400–3000 br, (2850, 2977 w), 1395 m, 1300 vs, 1272 vs, 1220 vs, 1049, 1060 m, 972 s, 710 m
$(CH_3)_2NH \cdot (CF_3)_2NOH(s)$	1270 vs, 1180 m, 1050 w, 960 w, 700 w
$(CH_3)_3N \cdot [(CF_3)_2NOH]_2(g)$	3619 w, 2350–3000 br (complex), 1393 w, 1292 vs, 1265 vs, 1210 vs, 1057 s, 963 s, 700 m
$(CH_3)_3N \cdot [(CF_3)_2NOH]_2(s)$	1270 m, 1180 w, 1050 vw, 963 vw, 700 vw
$C_2H_5NH_2 \cdot (CF_3)_2NOH(g)$	3619 vw, 3165 w, br, 2500–3000 br, (2600 w, 2770 m, 2980 m), 1395 w, 1300 vs, 1275 vs, 1220 vs, 1064 m, 973 s, 712 m
$C_2H_5NH_2 \cdot (CF_3)_2NOH(l)$	3305, 3370 w, 2977–2880 br, w, 1270 vs, br, 1185 s, br, 1057 m, 962 s, 704 m
$(C_2H_5)_2NH \cdot [(CF_3)_2NOH]_2(g)$	3619 w, 2400–3000 br, (2560 w, br, 2850, 2970 w), 1395 w, 1300 vs, 1270 vs, 1220 vs, 1048–1061 m, 970 s, 710 m
$(C_2H_5)_2NH \cdot [(CF_3)_2NOH]_2(s)$	1270 br, w, 1150 br, w
$(C_2H_5)_3N \cdot (CF_3)_2NOH(g)$	2750–3000 br, (2805 m, 2983 s), 1390 m, 1298 vs, 1275 vs, 1220 vs, 1068 m, 969 m, 708 w
$(C_2H_5)_3N \cdot (CF_3)_2NOH(l)$	3800–3020 br, (2850, 2880, 2940 w, 2980 m), 1270 br, s, 1190 br, s, 1057 m, 960 s, 702 m

[a] Taken from spectra obtained on the Perkin-Elmer Model 621 spectrometer.

General Procedure.—Nearly the same method of preparation was used for all of the adducts. In all cases adduct formation was essentially quantitative and only a single product was formed. In a typical reaction, 4.25 mmol of dimethylamine was condensed onto 3.84 mmol of $(CF_3)_2NOH$. The reaction mixture was allowed to warm to room temperature, and the resulting solution was agitated thoroughly. The mixture was refrozen and, while warming slowly, was caused to pass through a trap-to-trap distillation apparatus. After purification, the yield, based on the amount of $(CF_3)_2NOH$ consumed, was 95% (3.65 mmol). An excess of the amine was used in all reactions. When an excess of the hydroxylamine was used, it was found that its solubility in and affinity for the adduct was such that the excess was removed from the adduct only with great difficulty. The quantities of reactants, trap temperatures, adduct formed, and yields are listed in Table III. Elemental analyses (Table IV) were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Results and Discussion

The adducts are either clear, colorless liquids or colorless, low-melting, sublimable, crystalline solids. The physical state of the adducts and the melting points

---

(5) R. E. Banks, R. N. Haszeldine, and D. L. Hyde, *Chem. Commun.*, 413 (1967).

(6) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960).

(7) S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, *Dokl. Akad. Nauk SSSR*, **160**, 1319 (1965).

TABLE II

NMR SPECTRA

Compound	^{19}F ϕ^*	^1H δ			^1H δ	
	CF_3	CH_3	CH_2	$J_{CH_3-CH_2}$, cps	NH_x	Rel area (protons)
$NH_3\cdot(CF_3)_2NOH$	69.67	...	...	...	4.15, s	...
$CH_3NH_2\cdot(CF_3)_2NOH$	69.41	2.45, s	...	...	5.37, s	1.0:1.0
$(CH_3)_2NH\cdot(CF_3)_2NOH$	69.62	2.43, s	...	...	7.56, s	6.0:2.1
$(CH_3)_3N\cdot((CF_3)_2NOH)_2$	69.60	2.37, s	...	...	12.78, s	9.0:1.9
$C_2H_5NH_2\cdot(CF_3)_2NOH$	69.48	1.13, tr	2.76, q	7.0	5.13, s	3.1:2.0:2.9
$(C_2H_5)_2NH\cdot((CF_3)_2NOH)_2$	69.51	1.22, tr	2.80, q	7.0	9.27, s	6.2:4.0:3.1
$(C_2H_5)_3N\cdot(CF_3)_2NOH$	69.89	1.03, tr	2.57, q	7.0	11.7, s	8.9:6.0:0.9
$(CF_3)_2NOH$	70.02	5.9, OH	...	...	...	...

TABLE III

PREPARATION AND PROPERTIES OF HYDROXYLAMINE–AMINE ADDUCTS

Amt of reactants, mmol			Bath temp, °C				Physical		
	$(CF_3)_2NOH$	Amine	Trap 1	Trap 2	Trap 3	Adduct formed	state	Mp, °C	Yield, %
NH_3	3.52	4.00	−30	−80	−183	$NH_3\cdot(CF_3)_2NOH$	Liquid	...	94
CH_3NH_2	3.84	4.25	−15	−30	−183	$CH_3NH_2\cdot(CF_3)_2NOH$	Solid	28.0–28.5	~99
$(CH_3)_2NH$	3.99	4.31	−7	−30	−183	$(CH_3)_2NH\cdot(CF_3)_2NOH$	Solid	35.0	~98
$(CH_3)_3N$	3.16	3.95	−10	−80	−183	$(CH_3)_3N\cdot((CF_3)_2NOH)_2$	Solid	28.0–28.5	98
$C_2H_5NH_2$	2.59	3.09	−15	−30	−183	$C_2H_5NH_2\cdot(CF_3)_2NOH$	Liquid	...	>99
$(C_2H_5)_2NH$	3.94	4.71	−7	−30	−183	$(C_2H_5)_2NH\cdot((CF_3)_2NOH)_2$	Solid	41.5–42.5	~98
$(C_2H_5)_3N$	3.04	4.15	−30	−80	−183	$(C_2H_5)_3N\cdot(CF_3)_2NOH$	Liquid	...	~93

TABLE IV

ELEMENTAL ANALYSES

Compound	% C		% H		% N		% F	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$NH_3\cdot(CF_3)_2NOH$	12.91	13.05	2.17	2.19	15.06	14.92	61.27	61.0
$CH_3NH_2\cdot(CF_3)_2NOH$	18.01	18.38	3.02	2.98	14.00	13.37	56.97	57.3
$(CH_3)_2NH\cdot(CF_3)_2NOH$	22.44	22.48	3.77	3.86	13.08	12.95	53.24	53.5
$(CH_3)_3N\cdot((CF_3)_2NOH)_2$	21.17	21.51	2.79	2.90	10.58	10.75	57.40	57.5
$C_2H_5NH_2\cdot(CF_3)_2NOH$	22.44	22.59	3.77	3.80	13.08	13.45	53.24	52.3
$(C_2H_5)_2NH\cdot((CF_3)_2NOH)_2$	23.37	23.85	3.19	3.10	10.22	9.31	55.44	55.1
$(C_2H_5)N\cdot(CF_3)_2NOH$	35.56	35.54	5.97	5.90	10.37	10.22	42.18	42.1

of the solids are given in Table III. The compounds are, except for the triethylamine adduct, reasonably stable at room temperature, but with the exception of the ammonia adduct, they decompose at about 50°. The triethylamine adduct decomposes in light at room temperature, depositing a nonvolatile yellow-brown oil typical of amine decompositions caused by light. The ammonia adduct does not decompose at elevated temperatures and undergoes a reversible dissociation over a long temperature range. For all of the adducts, if some decomposition has occurred, pure adduct can be recovered by a trap-to-trap distillation of the remaining compound. Trace impurities of amines hasten their decomposition.

The compounds are not particularly moisture sensitive, and, initially, the solids appear to repel water. This phenomenon is due to the CF_3 groups of the $(CF_3)_2NOH$ portion of the molecule. However, after a few hours $(CF_3)_2NOH$ and the free amine are formed. The compounds are all dissociated in the vapor phase at 25° although to varying degrees as indicated by infrared analysis at room temperature. The adduct formed with ammonia shows the greatest dissociation (approximately 50%), while the dimethylamine adduct is only about 5% dissociated under the same conditions. All appear to be completely associated in the condensed phase.

The band at 3619 cm^{-1} in the infrared spectrum (Table I) is assigned to the OH stretching frequency of $(CF_3)_2NOH$. This band can be used to obtain a semiquantitative measure of the extent of adduct dissociation, since it should arise from free, unassociated hydroxylamine only. Any associated hydroxylamine present, assuming association occurs through the hydroxyl proton, should show a shift in the OH frequency from 3619 cm^{-1} to a lower frequency. The weak absorbances in the gas- and liquid-phase spectra of $NH_3\cdot(CF_3)_2NOH$ at 3317 and 3400 cm^{-1} and in the liquid-phase spectrum of $C_2H_5NH_2\cdot(CF_3)_2NOH$ at 3370 and 3305 cm^{-1} are probably due to the OH stretching frequency of $(CF_3)_2NOH$ in the adducts, shifted from 3619 cm^{-1} in the gas phase, but the band is absent or at least not discernible in the condensed phase.

The gaseous spectra of the primary amine adducts $CH_3NH_2\cdot(CF_3)_2NOH$ and $C_2H_5NH_2\cdot(CF_3)_2NOH$ exhibit a weak, broad absorption at 3173–3165 cm^{-1}, probably due to a C–H vibration. They also have a medium, broad absorption in the N–H and C–H region, with similar fine structure. The absorption covers the ranges 2400–3050 and 2550–3000 cm^{-1}, respectively. In this region both compounds have a weak peak at 2600 cm^{-1} and a medium peak at 2980 cm^{-1}. The methylamine adduct has an additional strong band at 2780 cm^{-1}, while the ethylamine adduct has a medium band at 2770 cm^{-1}. Definite assignments of these bands cannot be made, but, because of the similarity of the fine structure, the bands are probably due to N–H rather than C–H vibrations. The secondary amine adducts $(CH_3)_2NH \cdot (CF_3)_2NOH$ and $(C_2H_5)_2NH \cdot ((CF_3)_2NOH)_2$ exhibit no well-defined peaks in the N–H and C–H regions. They do have broad, weak bands covering the region 2400–3000 cm^{-1}, probably due to N–H vibrations. The tertiary amine adduct $(CH_3)_3N \cdot ((CF_3)_2NOH)_2$ has a broad, rather complex absorption band in the N–H region 2350–3000 cm^{-1}. In the case of $(C_2H_5)_3N \cdot (CF_3)_2NOH$, there is a broad peak covering the region 2750–3000 cm^{-1} and containing a strong peak at 2983 cm^{-1} and a medium peak at 2805 cm^{-1}, which are assigned to N–H vibrations.

The additional major peaks in both the gas- and condensed-phase spectra are due to vibrations in the $(CF_3)_2NO$ portion of the adducts. The three very strong absorptions in the range 1200–1350 cm^{-1} in the gas-phase spectra and the two strong, broad absorptions at approximately 1180 and 1265 cm^{-1} in the condensed-phase spectra occur in all seven adducts and are due to the C–F stretching modes.[2,8] Comparison with spectra of similar compounds containing the $(CF_3)_2NO$ moiety, reported by other workers,[2,9–11] allows bands at 1061 cm^{-1} in the gas phase and 1051 cm^{-1} in the condensed phase to be assigned to the N–O stretching vibration. The strong absorption at approximately 970 cm^{-1} in the gas phase and 960 cm^{-1} in the condensed phase is characteristic of compounds containing the $(CF_3)_2N$ group[2,12] and is assigned to the C–N stretching vibration. The moderate band at approximately 707 cm^{-1} in the gas phase and the weak peak at approximately 703 cm^{-1} in the condensed phase are characteristic of CF_3 deformation.

The gaseous infrared spectra of the adducts contain bands which can be attributed to all of the possible components, *i.e.*, the amine, the hydroxylamine, and the adduct. That the adduct is in equilibrium with its components is shown most effectively by the spectrum of $NH_3 \cdot (CF_3)_2NOH$. Peaks due to NH_3, $(CF_3)_2NOH$, and $NH_3 \cdot (CF_3)_2NOH$ exist in approximately equal proportions and indicate that the adduct is about 50% dissociated in the gas phase at room temperature. The other adducts exhibit only weak bands which may be attributed to the reactants and are thus dissociated to a smaller extent.

The fluorine nmr spectrum of each of the adducts consists of a singlet due to the $(CF_3)_2NO$ group at a reasonably nonvariant value of ϕ^* 69.9–70.0. This value is consistent with the shifts reported for other molecules containing the $(CF_3)_2N$[13] or $(CF_3)_2NO$[2] groups, where the resonances fall in a range ϕ^* 66–74. No spin–spin coupling between the CF_3 fluorines and the protons of the amine portion of the adduct is observed.

The proton nmr spectra are entirely consistent with the proposed adducts. All of the adducts exhibit a reasonably sharp single resonance at widely variant positions (δ 5.13–12.68), which can be assigned to the proton or protons on the nitrogen atom. The sharpness of the peak is due to rapid exchange of the N–H protons. Although the peaks due to the N–H protons do not exhibit any nitrogen–proton coupling, the relative areas of the peaks are in agreement with the proposed formulas. The relative areas of the peaks of the 1:1 adducts correspond to an addition of one proton to the amine, and the 1:2 adducts have relative areas corresponding to the addition of two protons to the amine. The methylamine adducts exhibit a singlet at $\delta \simeq 2.4$ ppm which is typical of amines which contain a methyl group. The ethylamine adducts possess a triplet due to CH_3–CH_2 coupling centered at $\delta \simeq 1.0$–1.2 ppm and a quartet due to the CH_2 coupled with CH_3 at $\delta \simeq 2.6$–2.8 ppm, with a coupling constant of 7.0 cps, all of which are consistent with typical ethyl amines. Gradual cooling of the nmr samples used for ^1H spectra does not change the appearance of the resonance peaks significantly. Even at the freezing point, little broadening and no splitting occur.

Although the mass spectra of the adducts do not contain peaks attributable to fragments of the adducts, they do contain peaks due to the components of the adducts. The major peak in the spectra, the CF_3^+ peak, is also the major peak in the spectrum of $(CF_3)_2NOH$.

The equivalent conductance of a 0.005 *M* solution of $(CH_3)_3NH \cdot (CF_3)_2NOH$ was 1.9 ohm^{-1} cm^2, that of a 0.003 *M* solution of $(CH_3)_3N \cdot ((CF_3)_2NOH)_2$ was 0.4 ohm^{-1} cm^2, and that of a 0.002 *M* solution of $NH_3 \cdot (CF_3)_2NOH$ was 1.6 ohm^{-1} cm^2. The equivalent conductance of a 0.002 *M* solution of triphenylchlorogermane, a nonelectrolyte in dimethylformamide, is 1.6 ohm^{-1} cm^2.[14] This indicated that the adducts are not ionized in dimethylformamide.

The mole fraction plots of the adducts formed between ammonia, methylamine, dimethylamine, and ethylamine with $(CF_3)_2NOH$ exhibit a marked rise in the pressure just after the $X = 0.5$ point is reached (X = mole fraction of amine). A rapid rise in the pressure which is observed just after the concentrations of amine and hydroxylamine are equal indicated that these amines form 1:1 adducts with $(CF_3)_2NOH$. A plot of the other 1:1 adduct, $(C_2H_5)_3N \cdot (CF_3)_2NOH$, exhibits a moderate rise in the observed pressure at $X = 0.5$ because $(C_2H_5)_3N$ is soluble in $(C_2H_5)_3N \cdot (CF_3)_2NOH$, and $(C_2H_5)_3N$ has approximately a 20-Torr vapor pressure at 0°.

The two 2:1 adducts, $(CH_3)_3N \cdot ((CF_3)_2NOH)_2$ and $(C_2H_5)_2NH \cdot ((CF_3)_2NOH)_2$, show increases in pressure

---

(8) J. Mason, *J. Chem. Soc.*, 4531 (1963).

(9) J. Jander and R. N. Haszeldine, *ibid.*, 696 (1954).

(10) R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *ibid.*, 901 (1966).

(11) H. A. Dinwoodie and R. N. Haszeldine, *ibid.*, 1681 (1965).

(12) J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 396 (1960).

(13) W. D. Blackley and R. R. Rheinhard, *ibid.*, **87**, 802 (1965).

(14) C. L. Frye, R. M. Salinger, and T. J. Patin, *ibid.*, **88**, 2343 (1966).

beginning at $X = 0.45$. The rate of rise is less pronounced for the diethylamine adduct, but this is to be expected, since the equilibrium vapor pressures of the two amines at 0° are quite different (700 Torr for trimethylamine *vs.* 90 Torr for diethylamine). The plots also show pressure decreases from $X = 0$ to a low at $X = 0.33$. Thus, there is a minimum in the equilibrium pressure extending from $X = 0.33$ to $X = 0.45$. The existence of the pressure minimum and the fact that the equilibrium pressure begins to rise before the $X = 0.5$ point are significant when one considers the method used to prepare the adducts (trap-to-trap distillation). Because substances volatile at the chosen trap temperature are removed during the distillation, the product obtained with this technique would be the least volatile one. Since an excess of amine was used in every case and more and more amine is removed as the distillation progresses, the concentration of amine in the trap decreases. One can visualize the system as moving toward greater concentrations of hydroxylamine, approaching the least volatile composition as amine is removed. The formation of the 1:1 adduct is precluded since the pressure minimum lies at $X < 0.5$, and, therefore, amine will continue to be removed when the $X = 0.5$ point is reached. The system would follow the mole fraction plot along the pressure minimum from $X = 0.45$ to $X = 0.33$.

No chemical evidence can be cited to explain the formation of the 2:1 adducts. Formation of the 2:1 adducts cannot be correlated with the structure of the amine with the least crowded electron pair on the nitrogen showing the greatest tendency to form a 2:1 adduct. Since both $(CH_3)_3N$ and $(C_2H_5)_2NH$ possess an electron pair on the nitrogen surrounded by bulky groups, they should show less tendency to form a 2:1 adduct than CH_3NH_2, $(CH_3)_2NH$, or $C_2H_5NH_2$. Thus, if the availability of the electron pair was the determining factor, there would be a larger number of 2:1 adducts.

Acknowledgments.—This work was supported in part through a contract with the Office of Naval Research. We are indebted to the National Science and the Max C. Fleischmann Foundations for grants to purchase the HA-100 nmr spectrometer. The authors wish to thank Mr. L. M. Zaborowski for the ^{19}F nmr spectra and Mr. R. L. Boyd for the mass spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH 84601

High-Pressure Th_3P_4-Type Polymorphs of Rare Earth Sesquichalcogenides[1]

BY NORMAN L. EATOUGH,[2] ALAN W. WEBB, AND H. TRACY HALL

Recieved December 4, 1968

Th_3P_4-type polymorphs of the sesquisulfides of holmium, erbium, thulium, ytterbium, lutetium, and yttrium were made from the normal forms at 77 kbars and 2000°. Holmium and erbium sesquiselenides of the Th_3P_4 type were formed from the elements at 68 kbars and 1800°.

Introduction

The crystal structures of rare earth sesquisulfides, sesquiselenides, and sesquitellurides prepared near atmospheric pressure have been systematically investigated by Flahaut and coworkers.[3–5] A summary of the polymorphic forms of the sesquichalcogenides is given in Table I. This table is similar to one given by Flahaut but has been expanded and updated.

There is a large density difference between the crystal form of the light rare earth sesquichalcogenides and the modification found in the heavy rare earth compounds. This difference is quite evident when the theoretical densities are plotted against ionic radius of the rare earth elements[6] as in Figure 1. Extrapolation of the densities of the light rare earth compounds suggests that the heavy rare earth chalcogenides might be converted to the crystal form of the lighter compounds by high pressure. This has been found to be true for the sesquioxides by Hoekstra[7] and Sawyer, Hyde, and Eyring[8] and has been accomplished in this work for six sesquisulfides and two sesquiselenides.

Theoretical densities of the sesquiselenides and sesquitellurides are shown in Figure 2. They indicate that a transformation from the Sc_2S_3 type to either the Th_3P_4 type or the U_2S_3 type might also be made for the heavy rare earth sesquiselenides and sesquitellurides.

Experimental Section

The studies on the rare earth sesquisulfides were carried out in a tie-bar type of cubic anvil press equipped with an anvil guide for synchronizing anvil motion.[9] The square faces of the tungsten carbide anvils were 9.9 mm on each edge. Cubes made of pyrophyllite were used to hold the sample and form the compressible gasket. The cubes had 12.0-mm edges and a 4.0-mm sample hole.

---

[1] This research was supported by the National Science Foundation and the Army Research Office, Durham, N. C.

[2] NSF traineeship recipient.

[3] M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **2**, 221 (1960).

[4] J. Flahaut, P. Laruelle, M. P. Pardo, and M. Guittard, *ibid.*, 1399 (1965).

[5] G. Collin and J. Loriers, *Compt. Rend.*, **260**, 5043 (1965).

[6] D. H. Templeton and C. H. Dauben. *J. Am. Chem. Soc.*, **76**, 5237 (1954).

[7] H. R. Hoekstra, *Inorg. Chem.*, **5**, 754 (1966).

[8] J. O. Sawyer, B. G. Hyde, and L. Eyring, *ibid.*, **4**, 426 (1965).

[9] H. T. Hall, *Rev. Sci. Instr.*, **33**, 1278 (1962).