total of 42 for both 0.10 and 0.30 *F* $ZnCl_2$ is shown in Table IIb, c. These models have been selected so that the probability on the basis of an *F* test for the model with the highest variance should be higher than 5% as compared with the model with the lowest variance either for the 0.1 *F* $ZnCl_2$ or for the 0.3 *F* $ZnCl_2$ solutions. From this table it can be seen that on the basis of the *F* test it is not possible to distinguish between the best models even if the model involving $ZnCl_3^-$ is the only one with a reasonably high probability at both concentrations. However, if we include the stipulation that for a given model the p*K* values calculated for each concentration should agree, we find that only one model will fit these criteria, namely, the equilibrium $ZnCl_4^{2-} \rightleftarrows ZnCl_3^- + Cl^-$ with an average p*K* value of 2.15 ± 0.04. Furthermore the variance for this system is smaller than the variance found at high pCl^- for the KCl-$AlCl_3$ system but larger than the variance of 3×10^{-9} found at low pCl^- for the KCl-$AlCl_3$ system (last four measurements in Table Ia) where the reaction mechanism is unambiguous. This is a behavior which one would expect.

In view of the unexpected degree of success with which the polymers $Zn_3Cl_{10}^{4-}$ and $Zn_4Cl_{13}^{5-}$ represent the data, respectively, at 0.10 and 0.30 *F* $ZnCl_2$ it would have been interesting to include n_1 values higher than 6 in the above model fitting, but unfortunately this would have required excessive computer time. The ambiguity in choosing a preferred model on the basis of mathematical data fitting is obviously accentuated by the small variation in the degree of zinc coordination provided by the data, as illustrated in Figure 5. If the data had covered a wider range, the probability of the reaction $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$ would certainly have been vastly enhanced. However, as matters stand, we are left with trying to predict the total behavior of a function from an imperfect knowledge of only its first few derivatives. Physically there seems to be no way to get around this problem because of the low solubility of $ZnCl_2$ at high pCl^- values. However, the present measurements have not been performed all the way up to the saturation point of $ZnCl_2$.

It is noteworthy that the model equation

$$2ZnCl_4^{2-} \rightleftharpoons Zn_2Cl_7^{3-} + Cl^-$$

proved thoroughly inadequate as a representation of the data. This equation has been proposed[24,25] as the best representation of the structural situation in MCl-$ZnCl_2$ mixtures rich in MCl but it is a very poor representation of the buffering action of $ZnCl_2$ in KCl-$AlCl_3$ mixtures.

If we suppose that the structural reality behind the buffering action of $ZnCl_2$ is correctly represented by $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$, we can reconcile this behavior with that in MCl-$ZnCl_2$ through the additional supposition that $ZnCl_3^-$ is four-coordinate with the fourth chloride forming a bridge to aluminum so as to give an entity such as $Cl_3ZnClAlCl_3^{2-}$. Such an entity would, of course, be impossible in MCl-$ZnCl_2$ melts while perhaps being favored in the present case because of the high concentration of chloroaluminate species. The fact that this concentration is so high and, therefore, so slightly affected by solvation reactions obviously precludes the possibility of detecting solvation reactions by means of activity measurements.

Registry No. KCl, 7447-40-7; $AlCl_3$, 7446-70-0; $ZnCl_2$, 7646-85-7; $AlCl_4^-$, 17611-22-2; $ZnCl_4^{2-}$, 15201-05-5.

Acknowledgment. The authors wish to thank B. Lottrup-Knudsen for help with programming and F. W. Poulsen and G. P. Smith for valuable discussions. Further thanks are due to Statens tekniskvidenskabelige Fond for financial support for J. H. von Barner and to the Northern Europe University Computing Center (NEUCC) for computing time.

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

Reactions of the Difluoramine-Potassium Fluoride Adduct, $HNF_2 \cdot KF$, with Sulfinyl and Perfluoroalkylsulfinyl Fluorides. Preparation of Perfluoroalkyl Perfluoroalkylthiosulfonates

RONALD A. De MARCO and JEAN'NE M. SHREEVE*[1]

Received January 22, 1973

The reaction of $HNF_2 \cdot KF$ with sulfinyl fluoride gave $FS(O)NF_2$ which was isolated and had sufficient stability to be characterized by spectroscopic methods. Attempts to prepare $CF_3S(O)NF_2$ and $C_2F_5S(O)NF_2$ resulted in the formation of N_2F_4 and the perfluoroalkyl perfluoroalkylthiosulfonate esters $CF_3SO_2SCF_3$ and $C_2F_5SO_2C_2F_5$. Efforts to synthesize additional thiosulfonate esters led to the characterization of $C_2F_5S(O)Cl$, ^{19}F nmr spectral identification of $C_2F_5SO_2SCF_3$ and $CF_3SO_2SC_2F_5$, and spectroscopic characterization of the previously reported $C_2F_5SO_2F$.

Introduction

In surveying the field of fluorinated sulfur-nitrogen compounds, the dearth of compounds which contain the difluoroamino moiety bound to sulfur became apparent. With the exception of CF_3SNF_2,[2] the known difluoroamino derivatives of this class of compounds are limited to cases in which sulfur is present in its maximum oxidation state.[3] Photolytic or thermal reactions of N_2F_4 for the preparation of sulfur(IV) difluoroamino compounds were not useful since oxidation of sulfur occurred with SF_4 derivatives or

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with SO_2,[3] while with sulfinyl halides,[4] no sulfur–nitrogen derivatives were isolated, *e.g.*

$R_fSF_3 + N_2F_4 \rightarrow R_fSF_4NF_2 \quad R_f = CF_3, F$

$SO_2 + N_2F_4 \rightarrow FSO_2NF_2$

$SOCl_2 + N_2F_4 \rightarrow NF_2Cl$

$SOBr_2 + N_2F_4 \rightarrow N_2F_2$

Generally the reactions of HNF_2 involved the use of strong acids or Lewis bases. For example, recently it was demonstrated that the NF_2 group can be readily introduced through the use of an $HNF_2 \cdot KF$ adduct. Thus, perfluoroamides or -amines were prepared in high yield with this adduct under mild reaction conditions[5,6]

$$R_fC(O)F + HNF_2 \cdot KF \xrightarrow{-23^\circ} R_fC(O)NF_2$$

$$CF_2(OF)_2 + HNF_2 \cdot KF \xrightarrow{-80^\circ} CF_2(OF)ONF_2 + CF_2(ONF_2)_2$$

The ease with which the $HNF_2 \cdot KF$ adduct reacted suggested its potential application in the preparation of sulfur(IV)–difluoroamino derivatives.

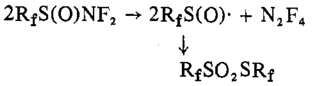
Results and Discussion

Difluoroaminosulfinyl fluoride, $F_2NS(O)F$, was obtained in low yield from the reaction of SOF_2 with the $HNF_2 \cdot KF$ adduct. The compound was unstable in the gas phase and in solution and, therefore, was usually isolated with varying amounts of sulfur dioxide as the major impurity. Although only minor amounts of $F_2NS(O)F$ were isolated, the reaction is believed to proceed in better than 75% yield based on the initial HNF_2 present. The major nitrogen-fluorine-containing compound isolated was N_2F_4 which almost certainly must arise from the decomposition of the sulfinamide and not from decomposition of HNF_2.

Although it was reported that HNF_2 was converted to N_2F_4 in high yield by such catalysts as stainless steel, copper, urea, and LiH after a contact time of more than 68 hr at temperatures greater than 0°,[7a] a subsequent paper showed that HNF_2 in contact with KF at 25° decomposed to N_2F_2 exclusively.[7b] When HNF_2 was allowed to contact urea at −80°, the pressure decreased but on warming to 25° all the HNF_2 was recovered. In our previous work with $HNF_2 \cdot KF$-perfluoroacyl fluoride reactions at −23° and below, no trace of N_2F_4 was observed.[5] Since in our present study, reactions were carried out in glass vessels at −78° with reaction times of 6-12 hr, there is no reason to expect the HNF_2 to behave in a different manner. Although it is not possible to exclude the possibility completely that the sulfur compounds could act as decomposition catalysts, the N_2F_4 is a likely product in the decomposition of $F_2NS(O)F$ because of the weak sulfur-nitrogen bond. The fate of the $FS(O)\cdot$ radical, which would be expected to form, is not clear. The decomposition of this radical is much more complex as is suggested by the formation of solids ranging from yellow to violet and red during the reaction and nmr spectral runs. A sample of $F_2NS(O)F$ which was allowed to decompose in an infrared cell resulted in the formation of SO_2 and SOF_2. Both of these compounds would be expected in $FS(O)\cdot$ decomposition and disproportionation. The N-F stretching region in the infrared spectrum was too complex to readily assign N_2F_4 as a product but ^{19}F nmr spectral studies do confirm the formation of SOF_2 and N_2F_4 as the decomposition products in addition to some N_2F_2 which can also arise from NF_2 radicals. The stability of $F_2NS(O)F$ varies with its physical state. Essentially complete decomposition in the gas phase occurred in about 8 hr, while complete decomposition in an SO_2F_2 solution occurred within 1 hr.

The very low recovery and poor reproducibility of this reaction prevented complete characterization of $F_2NS(O)F$, but the spectral properties readily confirmed the assigned structure. The infrared spectrum consists of bands at 1305 (s, d), 925 (sh, br), 905 (s), 885 (sh, br), 860 (s), and 765 (m) cm^{-1}. The complex region between 925 and 860 cm^{-1} can be assigned to the asymmetric and symmetric NF_2 stretching frequencies. The doublet at 1305 cm^{-1} corresponds to the S=O stretch and the band at 765 cm^{-1} to the S–F stretch. In comparison the S=O stretching frequencies for SOF_2 and SOFCl are doublets centered at 1330 and 1290 cm^{-1}, respectively. The S–F stretch in SOFCl is at 750 cm^{-1}. The ^{19}F nmr spectrum of $F_2NS(O)F$ consists of a triplet at ϕ −19.6 (J_{NF_2-SF} = 9.5 Hz) and a typically broadened NF_2 resonance at ϕ −29.8 with the area ratio 1:1.9.

The reactions of perfluoroalkylsulfinyl fluorides with $HNF_2 \cdot KF$ were carried out in an attempt to prepare stable *N*-fluorosulfinamide derivatives. The reactions are comparable to the sulfinyl fluoride reaction in that N_2F_4 was the major product isolated but no corresponding sulfinamide was found. The only sulfur-containing compound isolated from both $CF_3S(O)F$ and $C_2F_5S(O)F$ was the symmetrical perfluoroalkyl perfluoroalkylthiosulfonate, $R_fSO_2SR_f$. These esters could arise from the interaction of the corresponding $R_fS(O)\cdot$ radicals



$$\begin{array}{l} 2R_fS(O)NF_2 \rightarrow 2R_fS(O)\cdot + N_2F_4 \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad R_fSO_2SR_f \end{array}$$

Isolation of these esters as very stable compounds suggests that the difference in products observed for the decomposition of $NF_2S(O)F$ and the hypothetical $R_fS(O)NF_2$ is due to the greater stability of the $R_fS(O)\cdot$ radical compared to that of $FS(O)\cdot$ which permits dimerization and rearrangement to occur.

The unfluorinated sulfinamides ($RS(O)NR_2$) and trifluoromethyl sulfinamides ($CF_3S(O)NR_2$) are stable to 100°, but with the introduction of the electron-withdrawing NF_2 group, in addition to the perfluoroalkyl group or fluorine, the net effect is to weaken the sulfur–nitrogen bond. For $NF_2S(O)F$, the yield of N_2F_4 accounted for about 80% of the HNF_2 initially consumed in the reaction. The yields of the thiosulfonate esters were more variant and although the trifluoromethyl derivative accounted for 80% of the N_2F_4, the pentafluoroethyl compound gave only 30% of the ester based on N_2F_4.

In order to obtain sufficient amounts of $C_2F_5SO_2SC_2F_5$ for complete characterization, other less hazardous methods were attempted. The most direct method to prepare compounds of the $R_fSO_2SR_f$ type is by the reaction of the corresponding sulfinyl chloride with mercury.[8] Although this reaction gave good yields for $CF_3SO_2SCF_3$, it is not very effective for the formation of $C_2F_5SO_2SC_2F_5$. The two main products were $C_2F_5SO_2Cl$ and $(C_2F_5S)_2$. The pentafluoroethyl pentafluoroethylthiosulfonate was isolated

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in quantities to enable spectroscopic identification only. The infrared spectrum consisted of bands at 1425 (ms), 1330 (sh, m), 1320 (ms), 1242 (s), 1140 (ms), 1128 (sh, m), 977 (sh, m), 952 (ms), 756 (m), 535 (ms), 545 (w), and 524 (w) cm^{-1}. The ^{19}F nmr spectrum contained four resonances which are listed in Table I.

The trifluoromethyl[9] and pentafluoroethyl thiosulfonate esters are the only reported perfluoro examples of this class of compounds which contain sulfur in different oxidation states. Since each contains only one kind of perfluoroalkyl group, it was of interest to attempt the preparation of unsymmetrical analogs for spectroscopic comparison. Unfortunately, neither the reaction of a mixture of $CF_3S(O)Cl$ and $C_2F_5S(O)Cl$ with mercury nor the reaction of $(CF_3S(O)O)_2Zn$ with C_2F_5SCl was consistent or occurred in sufficiently high yield to allow such a comparison. The reaction of equimolar amounts of the sulfinyl chlorides with mercury did result in the formation of a mixture of two compounds which, after purification *via* gas chromatography, were studied with ^{19}F nmr. Based on nmr spectral shifts and coupling constants compared with the symmetrical $CF_3SO_2SCF_3$ and $C_2F_5SO_2SC_2F_5$ and other CF_3 and C_2F_5 sulfonyl and sulfenyl derivatives, the mixture was shown to contain $CF_3SO_2SC_2F_5$ and $C_2F_5SO_2SCF_3$ (Table I). As can be seen these values are in good agreement with reported values.

The ^{19}F nmr spectra of sulfinyl derivatives which contain the $-CF_2S(O)-$ group have been interpreted as having nonequivalent methylene fluorines due to the asymmetric center at the sulfur atom.[10-12] Although the methylene fluorines in both $CF_3CF_2S(O)F$ and $CF_3CF_2S(O)Cl$ exhibit this nonequivalence, the effect is more pronounced in the latter case. Since the presence of an asymmetric center should not account for this difference, it is possible that a rotational factor also contributes.

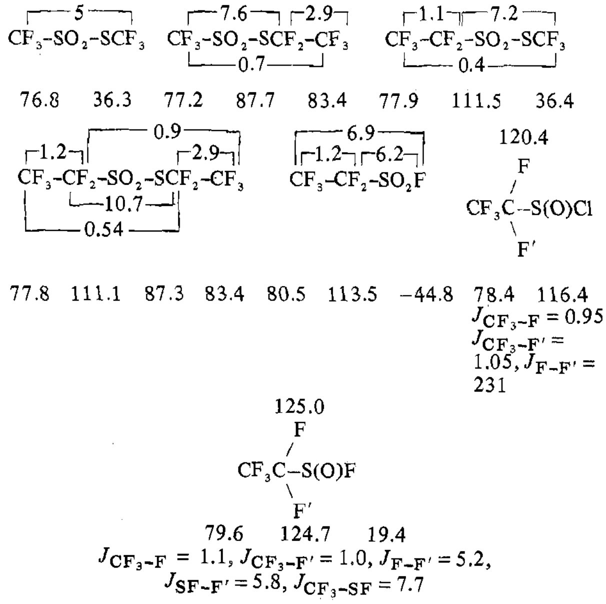
Experimental Section

Apparatus. Volatile liquids and gaseous materials were handled in a standard Pyrex vacuum line equipped with a Heise Bourdon tube gauge. The reactions were carried out in 25-ml Pyrex flasks equipped with Fischer-Porter stopcocks. The products were purified by fractional condensation or gas chromatography with 0.25-in. copper columns packed with FS-1265 or Kel-F No. 3 oil on Chromosorb P.

Analysis. Infrared spectra were taken with a Perkin-Elmer Model 457 infrared spectrometer using a 10-cm Pyrex glass cell equipped with KBr windows or a 10-cm stainless steel cell equipped with AgCl windows. High-resolution ^{19}F nmr spectra were obtained with a Varian Model HA-100 spectrometer operating at 94.1 MHz. Fluoride analyses were done by sodium fusion and the fluoride ion determined by the use of an Orion specific ion electrode Model 94-09A or by Beller Mikroanalytisches Laboratorium, Gottingen, Germany.

Starting Materials. Difluoramine was prepared from trityldifluoramine[13] (PCR, Inc.) and was complexed as previously described.[5] Sulfinyl fluoride was prepared by exposing SF_4 (K & K Laboratories) to moist air in a Pyrex vessel and then isolated by fractional condensation. Sulfuryl fluoride was prepared by the reaction of SO_2 and fluorine. Trifluoromethyl- and pentafluoroethylsulfinyl fluorides,[14] trifluoromethylsulfuryl chloride, and zinc trifluoromethylsulfonate[9] were prepared by the literature methods. Diglyme was purchased from Aldrich Chemical Co. and stored over molecular sieves. Potassium fluoride (J. T. Baker) was dried at 350° and CsF (American Potash and Chemical Corp.) was dried *in vacuo* at 150°. Tetrafluoroethylene and pentafluoroethyl iodide (Hynes Chemical Co.) were used as received and the bis(pentafluoroethyl) disulfide was prepared *via* the published method.[15] *Warning*! Care should be exercised in handling HNF_2 since it is known to exhibit explosive properties especially when condensed at −183 or −196°. Liquid HNF_2 is more shock sensitive than nitroglycerine and should be handled in small quantities. Adequate shielding should be used at all times including the cleaning of reaction vessels since in one case the exposure of the solid residue to air resulted in a violent explosion.

Table I. ^{19}F Nmr Spectra[a]



[a] Chemical shifts in ϕ (internal CCl_3F reference); J values in hertz.

Reaction of SOF_2. Approximately 18 mmol of SOF_2 was condensed at −138° onto 4.0 mmol of $HNF_2 \cdot KF$ and then warmed to −78° for 6-12 hr. The volatile products were removed at −78°, then at −23°, and finally at 25°. The difluoroaminosulfinyl fluoride was isolated usually by fractional condensation in a trap cooled to −108° and was invariably contaminated with SO_2 and occasionally with some HNF_2 (0.1-0.2 mmol). All attempts to purify the sample further by physical or chemical methods resulted in further decomposition. Also isolated from the reaction mixture were unreacted SOF_2 and HNF_2 which were then recylced. It was impossible to determine the amounts of the two compounds since they were both trapped at −128° but HNF_2 was present in less than 1-mmol amounts. Approximately 1.6 mmol of N_2F_4 was also found.

Reaction of $CF_3S(O)F$. This reaction was carried out under essentially the same conditions as with SOF_2 (18 mmol of $CF_3S(O)F$–4 mmol of $HNF_2 \cdot KF$). Fractional condensation with traps at −91, −138, and −196° resulted in the isolation of 1.4 mmol of $CF_3SO_2SCF_3$ (identified by the reported infrared[9] and ^{19}F nmr spectra), unreacted starting materials and 1.8 mmol of N_2F_4.

Preparation of $C_2F_5S(O)Cl$. A mixture of 13.8 mmol of $C_2F_5S(O)F$ and 16.0 mmol of HCl was warmed slowly to 25° in a 1-l. Pyrex vessel and allowed to remain at this temperature for 45 min. After fractional condensation at −78°, the sample was purified by gas chromatography using a 17-ft column packed with 20% FS-1265 on Chromosorb P. The infrared spectrum consists of bands at 1340 (m), 1250 (s), 1228 (s), 1140 (m), 943 (m), 753 (mw), 505 (mw), and 478 (m) cm^{-1}. A molecular weight of 203.7 (202.6) was found and the fluoride analysis yielded 45.7% (46.1% required). From vapor pressure data represented by the equation $\log P_{\mathrm{Torr}} = 7.974 - 1707.4/T$°K (valid in the range 0-65°), a boiling point of 62.2° was obtained. The heat of vaporization was calculated to be 7.8 kcal/mol and the Trouton constant is 23.3 eu. ^{19}F nmr data for both $C_2F_5S(O)F$ and $C_2F_5S(O)Cl$ are listed in Table I.

Preparation of $C_2F_5SO_2F$. A mixture of 20 mmol of C_2F_4 and 46 mmol of SO_2F_2 was condensed into a 30-ml Hoke bomb which

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contained dried CsF and about 7 ml of diglyme. After heating the bomb at 80° for 4 days, the volatile portion was fractionated (−98°) and then further purified by gas chromatography by using an 8-ft column packed with 20% Kel-F oil on Chromosorb P. The pentafluoroethylsulfuryl fluoride[16] (30%) was further characterized by ^{19}F nmr spectra (Table I) and by its infrared spectrum which has bands at 1476 (vs), 1336 (m), 1255 (vs), 1240 (sh, vs), 1208 (m), 1152 (s), 999 (m), 817 (s), 754 (w), 644 (sh, w), and 610 (sh, w) cm^{-1}. Its experimental molecular weight was 203 (202).

Preparation of C_2F_5SCl. A mixture of $(C_2F_5S)_2$ (4.75 mmol) and Cl_2 (6.0 mmol) was heated at 90-100° for 6 hr in a Pyrex vessel. Separation of the mixture by fractional condensation gave unreacted disulfide (−78°), C_2F_5SCl (−108°), and a mixture of Cl_2 and C_2F_5SCl at −196°. The infrared spectrum consists of bands at 1330 (m), 1230 (vs), 1168 (m), 1122 (s), 980 (s), 965 (sh), 753 (m), and 550 (w) cm^{-1}.

Reaction of C_2F_5SCl and $(CF_3S(O)O)_2Zn$. Approximately 1 mmol of C_2F_5SCl was condensed onto $(CF_3S(O)O)_2Zn$ in a Pyrex vessel and the volatile products were monitored every 6 hr over a 36-hr period. The major products identified were CF_3Cl, $(C_2F_5S)_2$, $C_2F_5SCF_3$,[10] and some unreacted C_2F_5SCl. No $CF_3SO_2SC_2F_5$ was detected during this period.

Preparation of $CF_3SO_2SC_2F_5$ and $C_2F_5SO_2SCF_3$. A mixture of 5 mmol each of $CF_3S(O)Cl$ and $C_2F_5S(O)Cl$ was condensed at −183° into a 500-ml Pyrex flask equipped with a Teflon stopcock and then warmed to 25°. Over a period of 1.5 hr approximately 3.5 ml of mercury was added with shaking. The mixture was fractionated through traps cooled to −63, −78, and −196°. Further purification of the materials retained in the traps at −63 and −78° was accomplished with gas chromatography using an 8-ft column packed with Kel-F No. 3 oil on Chromosorb P. This resulted in the isolation of 0.4 mmol of a mixture of the thiosulfonates. Additional attempts to separate the mixture by gas chromatography were unsuccessful and attempts to reproduce or alter this reaction resulted in no isolation of the two products.

Registry No. $HNF_2 \cdot KF$, 13841-05-9; SOF_2, 7783-42-8; $FS(O)NF_2$, 39937-04-7; $CF_3S(O)F$, 812-12-4; $CF_3SO_2SCF_3$, 358-15-6; $C_2F_5S(O)F$, 20621-31-2; HCl, 7647-01-0; $C_2F_5S(O)Cl$, 39937-08-1; C_2F_4, 116-14-3; SO_2F_2, 2699-79-8; $C_2F_5SO_2F$, 354-87-0; $(C_2F_5S)_2$, 679-77-6; Cl_2, 7782-50-5; C_2F_5SCl, 39937-11-6; $[CF_3S(O)O]_2Zn$, 39971-65-8; $CF_3S(O)Cl$, 20621-29-8; $CF_3SO_2SC_2F_5$, 39937-13-8; $C_2F_5SO_2SCF_3$, 39937-14-9; Hg, 7439-97-6; $C_2F_5SO_2SC_2F_5$, 39937-15-0.

Acknowledgment. Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research.

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Contribution from Ames Laboratory—USAEC and the Department of Chemistry,
Iowa State University, Ames, Iowa 50010

Spectrophotometric Study of the Platinum(II) Chloride-Aluminum Chloride Vapor Complex

G. N. PAPATHEODOROU[1]

Received February 1, 1973

The reaction of solid *cluster* platinum(II) chloride (Pt_6Cl_{12}) with gaseous aluminum chloride to form a purple gaseous complex has been studied spectrophotometrically. Thermodynamic considerations suggest the stoichiometry for the reaction: $^1/_6Pt_6Cl_{12}(s) + Al_2Cl_6(g) \rightarrow PtAl_2Cl_8(g)$ ($\Delta H^R = 7.8$ kcal/mol, $\Delta S^R = 6.4$ eu). The visible electronic absorption spectrum of the gaseous complex was compared with the spectrum of Pt(II) centers in liquid LiCl and interpreted in terms of a square-planar $PtCl_4$ group sharing edges with two tetrachloroaluminates.

Introduction

It has been shown[2-6] that gaseous aluminum chloride reacts with many MCl_k metal chlorides to form gaseous complexes with the general formula $(MCl_k)_m(Al_2Cl_6)_n$. In most cases studied $m = 1$ while the value of n varies between $^1/_2$ and 2.

Among the different metal chlorides investigated by vapor pressure equilibrium measurements were some alkali and alkaline earth chlorides (M = Na, K, Mg, Ca)[2,3] and some chlorides of 3d metal cations (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)).[3] The chlorides of Nd(III),[4a] U(III), U(V),[4b] and Pd(II)[5] have been studied spectrophotometrically.

In the present report the existence of a purple vapor complex of platinum chloride with aluminum chloride has been established. Furthermore, the equilibrium

$$(m/6)Pt_6Cl_{12}(s) + nAl_2Cl_6(g) \rightarrow (PtCl_2)_m(Al_2Cl_6)_n(g) \tag{1}$$

has been studied by measuring spectrophotometrically the partial pressures of the gaseous complex(es) over the "cluster" platinum chloride (Pt_6Cl_{12}). The thermodynamic quantities of the above equilibrium and the electronic absorption spectrum of the gaseous complex are discussed in terms of the stoichiometry and possible structure of the gaseous molecule.

Experimental Section

Chemicals and Equipment. High-purity anhydrous aluminum chloride was prepared from Baker Analytical reagent $AlCl_3$ by slow sublimation in silica tubes under vacuum. The sublimation was repeated six times.

The platinum(II) chloride was prepared as previously described.[7a] Large quantities of the cluster platinum chloride Pt_6Cl_{12} were prepared by recrystallization of $PtCl_2$ from its dilute solutions in liquid Al_2Cl_6.[7b] The spectrophotometric measurements were performed on a Cary Model 14 spectrophotometer equipped with a high-temperature cell compartment[8] (15-cm maximum path length). The quartz cells were the uv-type cylindrical cells, purchased from Pyrocell. The

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