was added a solution of 5.0 g. (0.0227 mole) of [α-carboranyl]benzene in 100 ml. of methylene chloride. Stirring was continued for 18 hr. Vapor phase chromatography of the methylene chloride phase on a Carbowax column at 215° with a flow rate of 40 ml./min. of argon showed that the final reaction mixture contained 4% *o*-, 26% *m*- and 70% *p*-[α-carboranyl]-nitrobenzene. No dinitration products were detected. After separation of the methylene chloride phase from the concentrated acids phase, it was washed twice with water and dried over anhydrous sodium sulfate; the solvent was removed at reduced pressure. Two recrystallizations from carbon tetrachloride afforded 3.1 g. (50.2% of theory) of a white solid (m.p. 167–168°). The proton n.m.r. spectra of this compound showed an A_2B_2 pattern in the aromatic region confirming that it was *p*-[α-carboranyl]nitrobenzene.

Anal. Calcd. for $B_{10}C_8H_{15}NO_2$: B, 40.75; C, 36.22; H, 5.66; N, 5.28. Found: B, 40.84; C, 36.16; H, 5.89; N, 5.30.

After removal of the solvent from the first carbon tetrachloride supernatant from above, the residue was crystallized twice from glacial acetic acid to afford 0.30 g. (5.0% of theory) of a yellow-white product (m.p. 140–141°). The aromatic portion of the proton n.m.r. spectrum was very similar to that observed for the known *meta*-substituted carboranylbenzenes reported above.

Anal. Calcd. for $B_{10}C_8H_{15}NO_2$: B, 40.75; C, 36.22; H, 5.66; N, 5.28. Found: B, 40.72; C, 36.43; H, 5.86; N, 5.03.

The small peak (4%) observed to come first off the v.p.c. column was never isolated and was tentatively identified as *o*-[α-carboranyl]nitrobenzene.

p-[α-Carboranyl]aniline. One gram of *p*-[α-carboranyl]nitrobenzene was reduced to *p*-[α-carboranyl]-aniline over a platinum chloride–sodium borohydride catalyst as reported by Brown and Brown[14] to afford 0.80 g. (90.2% of theory) of a white solid (m.p. 104–105°).

Anal. Calcd. for $B_{10}C_8H_{17}N$: B, 46.00; C, 40.81; H, 7.24; N, 5.95. Found: B, 45.84; C, 40.88; H, 7.42; N, 6.22.

m-[α-Carboranyl]aniline. One gram of *m*-[α-carboranyl]nitrobenzene was converted to *m*-[α-carboranyl]aniline by the same procedure as described above for its *para* isomer to afford 0.81 g. (91.4% of theory) of a white solid (m.p. 81–82°).

Anal. Calcd. for $B_{10}C_8H_{17}N$: B, 46.00; C, 40.81; H, 7.24; N, 5.95. Found: B, 45.74; C, 41.02; H, 7.22; N, 5.81.

Ionization Constants of Benzoic Acids. Apparent ionization constants of the substituted benzoic acids were obtained at 25.0° in 25% water–75% ethyl alcohol (by volume) as described by Roberts and co-workers[16] using a Leeds and Northrop pH meter. The data are presented in Table I.

Ionization Constants of Anilinium Ions. Ionization constants (pK_a) of substituted anilinium ions were measured at room temperature in 40% methyl alcohol–60% water sulfuric acid solutions by the procedure of Hammett, as modified by Roberts and co-workers.[15] A Cary Model 14 recording spectrophotometer was used to measure the spectra. The standard employed was *m*-chloroaniline. The data are given in Table I.

Determination of ^{19}F Chemical Shifts of Fluorobenzenes. The ^{19}F chemical shifts relative to fluorobenzene were obtained in cyclohexane solution at room temperature at concentrations of 0.15, 0.10, and 0.05 mole % using fluorobenzene as an internal standard. A Varian HR-60 n.m.r. spectrophotometer was employed in these measurements. The normal side-band technique was employed to determine the chemical shifts in c.p.s. No concentration dependence was observed. The internal standard employed for *p*-[β-carboranyl]-fluorobenzene was *m*-[α-carboranyl]fluorobenzene.

Acknowledgment. This investigation was supported in part by Public Health Service Predoctoral Fellowship 1-Fl-GM-23,433-01 from the National Institute of General Medical Sciences to T. E. B. and by the Army Research Office (Durham).

Dimethylselenium Dihalides and Their Adducts with Boron Trihalides

Kenneth J. Wynne and John W. George

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts. *Received May 17, 1965*

To test the possible coordinate bond-forming ability of the unshared electron pair associated with the central atom of a trigonal bipyramidal molecule, 1:1 adducts of dimethylselenium dihalides and boron trihalides have been prepared and the infrared spectra of these adducts examined. These data indicate that the electron pair is not involved in a classical Lewis acid–base sense, but that halide transfer occurs leading to monohalogenodimethylselenium(IV) tetrahaloborate ionic substances.

Introduction

Structural investigation of those chalcogen tetrahalides, and alkyl and aryl derivatives of these tetrahalides, existing in molecular form has revealed in each case a trigonal bipyramidal structure having an unshared electron pair in the trigonal plane.[1] As with

---

(1) A few references to typical molecules in this category are: (a) $TeCl_4$(g), D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, 62, 1267 (1940); (b) SeF_4(l), J. A. Rolfe, L. A. Woodward, and D. A. Long,

other molecules having at least one unshared electron pair associated with a central atom it might be expected that this electron pair could form a coordinate bond with appropriate Lewis acids. However, for the various adducts of group VIb tetrahalides which have been examined, ionic formulations resulting from halide ion transfer are found exclusively.[2]

Only very limited information is available regarding the complexing behavior of organo-substituted selenium tetrahalides. Thus, dimethylselenium dibromide has been reported[3] to react with platinum(IV) bromide to form $[SeBr(CH_3)_2]^+{}_2PtBr_6{}^{-2}$, or $[(CH_3)_2Se]_2PtBr_4$ plus Br_2, depending upon reaction conditions.

The general question regarding the possible Lewis base behavior of trigonal bipyramidal species having an unshared pair suggested the examination of the behavior of $(CH_3)_nSeX_{4-n}$ (X = Cl, Br; n = 0–3) molecules with the strong Lewis acids boron trichloride and boron tribromide. In this paper evidence is presented which suggests the configuration of dimethylselenium dihalide, $(CH_3)_2SeX_2$, and which establishes the structural formulation of adducts of these selenium compounds with the aforementioned Lewis acids.

Experimental Section

Materials. The atmospheric moisture sensitivity of materials used in this study required that handling be carried out *in vacuo* and/or in a dry atmosphere.

1. *Adducts of Dimethylselenium Dihalides.* The BCl_3 adduct of $(CH_3)_2SeCl_2$[4] was prepared by mixing CH_2Cl_2 solutions of the reactants at room temperature and cooling to −25°. Colorless, needle-shaped crystals, which begin to decompose at 58°, were obtained. *Anal.* Calcd. for $(CH_3)_2SeCl_2 \cdot BCl_3$: Se, 26.6; Cl, 59.7. Found: Se, 26.7; Cl, 58.8. The BBr_3 adduct of $(CH_3)_2SeBr_2$, pale lemon needles, was prepared similarly and decomposed at 66°. *Anal.* Calcd. for $(CH_3)_2SeBr_2 \cdot BBr_3$: Se, 15.2. Found: Se, 15.2.

An attempt to prepare the chloride adduct by direct reaction, with stirring, of liquid BCl_3 and solid $(CH_3)_2SeCl_2$ at temperatures up to 12° in the vacuum line gave evidence of only a limited reaction at the surface of the selenium compound.

2. *Adducts of Dimethyl Selenide.* The adducts of $(CH_3)_2Se$ with BCl_3 and BBr_3 were prepared without using a solvent by direct reaction in the vacuum line. Measurements of relative amounts of reactants used indicated 1:1 adducts, $(CH_3)_2Se \cdot BCl_3$ and $(CH_3)_2Se \cdot BBr_3$, to have formed in each case. These adducts, previously unreported, are white solids having a vapor pressure below 1 mm. at 20° and melting at 101–102 and 119–120° for chloride and bromide, respectively. Slow decomposition and hydrolysis on exposure of these substances to the atmosphere was evidenced by the odor of volatile selenium-containing compound(s) and by the appearance of a B–O stretching frequency in the infrared spectra of the samples.

3. *Diphenyl Selenide and Diphenylselenium Dihalides.* $(C_6H_5)_2SeCl_2$ and $(C_6H_5)_2SeBr_2$ were prepared from $(C_6H_5)_2Se$, Eastman White Label, according to standard procedures.[5] The chloride melted at 187° (sealed tube), lit. m.p. 187–188°, and the bromide at 144–147° (sealed tube), lit. m.p. 148°.[6]

Physical Measurements and Decomposition Behavior. Infrared data on the solid materials were obtained using mineral oil mulls between KBr plates or Marlex 50 polyethylene disks. Solution and pure liquid spectra were secured using cells equipped with KBr windows or polyethylene cells (Barnes Instrument Co.). Spectra were recorded using Perkin-Elmer Model 21, Model 237B, and Infracord spectrometers.

The molecular weights of $(CH_3)_2SeCl_2$ and $(CH_3)_2SeBr_2$ were determined using standard vapor pressure depression and cryoscopic techniques.

Decomposition behavior of the adducts was observed by warming the adducts *in vacuo* and identifying the volatile and nonvolatile products by their spectroscopic characteristics and general physical properties.

Results

General Properties. The existence of $(CH_3)_2SeCl_2$ and $(CH_3)_2SeBr_2$ as monomeric, molecular species in the solvents of low dielectric strength employed in this work is supported by the experimental molecular weights of 185 and 260, respectively, of these substances. All of the adducts described in this paper undergo hydrolysis when exposed to atmospheric moisture but possess moderate thermal stability. The boron trihalide adducts of dimethylselenium dihalides decompose thermally beginning at 58 and 66° for the chloride and bromide adducts, respectively, giving elementary selenium, methyl halide, and boron trihalide in each case. In addition, a very small amount of a yellow oil of low volatility and odor characteristic of dimethyl diselenide was formed in the decomposition of each adduct. No yellow oil is formed when the dimethylselenium dihalides decompose; elementary Se and methyl halides are the only products when the dichloride and dibromide are heated above their melting points of 61 and 86°, respectively.

Attempts to measure molecular weights of the dimethylselenium dihalide adducts in methylene chloride were unsuccessful owing to extensive dissociation of the adducts in solution. Spectroscopic examination of bromide adduct solutions indicated that at least 85% of the BBr_3 originally present in the adduct was free in the solution. Similarly, vapor pressure increases for chloride adduct solutions as compared to pure solvent indicated substantial dissociation to dimethylselenium dichloride and boron trichloride.

Infrared Spectra. The frequencies and estimated intensities of infrared absorptions of $(CH_3)_2SeCl_2$, $(CH_3)_2SeBr_2$, and their adducts are summarized in Table I. For purpose of comparison these data for $(CH_3)_2Se$, and its adducts with BCl_3 and BBr_3, are also given. Owing to the coincidence of a strong Nujol band the observation of C–H stretching frequencies was prevented in mull samples. Table II gives observed frequencies for diphenyl selenide and diphenyl-

---

Trans. Faraday Soc., **49**, 1388 (1955); (c) $(C_6H_5)_2TeBr_2(s)$, G. D. Christofferson and J. D. McCullough, *Acta Cryst.*, **11**, 249 (1958).

(2) The following are examples of well-characterized substances: (a) $SF_3{}^+BF_4{}^-$ [L. D. Calvert and J. R. Morton, *Acta Cryst.*, **17**, 613 (1964)] and (b) $TeCl_3{}^+AlCl_4{}^-$ [H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **73**, 737 (1954)].

(3) P. Spinoglio and M. DeGasperi, *Gazz. chim. ital.*, **67**, 318 (1937).

(4) K. J. Wynne and J. W. George, *Inorg. Chem.*, **4**, 256 (1965).

(5) H. M. Leicester, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 290.

(6) F. Krafft and R. E. Lyons, *Chem. Ber.*, **27**, 1765 (1894).

Table I. Infrared Absorption Frequencies (cm.$^{-1}$) for Dimethyl Selenide, Dimethylselenium Dichloride, Dimethylselenium Dibromide, and Boron Trihalide Adducts of These Compounds

$(CH_3)_2Se^a$	$(CH_3)_2Se \cdot BCl_3{}^b$	$(CH_3)_2Se \cdot BCl_3{}^c$	$(CH_3)_2SeCl_2{}^b$	$(CH_3)_2SeCl_2 \cdot BCl_3{}^b$	$(CH_3)_2Se \cdot BBr_3{}^{b,d}$	$(CH_3)_2SeBr_2{}^b$	$(CH_3)_2SeBr_2 \cdot BBr_3{}^b$
			270 s	280 w		~265 s?	286 s
			293 s	311 s			
	370 w	371 m		378 w–m		338 w	
				403 s			408 vw
526 w							
585 w	589	573 sh	573 w	572 w–m		568 w	571 s
601 vw	612 s, broad	595 s broad	589 w	589 w–m		585 w	604 s
673 w	640	614 sh		644 vs, broad	642 vs		638 w
				692	674 s		
	731 s, broad	789 s, sh on solvent band					
	766						
	884 w			893 w	885 w	910 vw	829 w
908 m	936 m	939 m	925 m	927 m–s	937 m–s	931 w	923 m–s
954 m	979 m	982 m	978 m	988 m–s	979 m–s	980 m	984 m–s
1261 s	1271 w		1260 w	1264 m	1273 w	1256 w	1265 m
1360 w	1295 m	1302 sh on solvent band	1283 w	1283 w	1295 m	1278 w	1285 m
1418 vs	1414 m		1403 s	1400 vs	1414 m	1399 w	1399 m

[a] Data from ref. 17. [b] Nujol mull. [c] CH_2Cl_2 solution. [d] 265–600-cm.$^{-1}$ region not examined.

selenium dichloride and dibromide in the 265–625-cm.$^{-1}$ region. With regard to the intensity estimates given in Tables I and II it should be noted that care was taken to prepare mulls in such a way that the concentration of an adduct mull was much less than that of a mull of the appropriate selenium-containing compound alone and, while sample thickness cannot be accurately controlled, it is believed that the reported intensity estimates may be assigned limited reliability with respect to comparative use between compounds. Intensity estimates given for the spectra of those substances run as liquids or in solution are, of course, not comparable with those of the mulls.

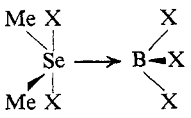
Table II. Infrared Absorption Frequencies (cm.$^{-1}$) for Diphenyl Selenide, Diphenyl Selenium Dichloride, and Diphenylselenium Dibromide

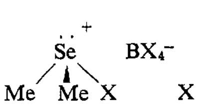
$(C_6H_5)_2Se^a$	$(C_6H_5)_2SeCl_2{}^b$	$(C_6H_5)_2SeBr_2{}^b$
317 s	277 s	<265 vs
400 m	310 vs	307 s
454 vs	331 s	323 s
477 vs	466 s	464 s
544 vw	478 s	471 s
564 w	609 vw	610 vw
615 w		

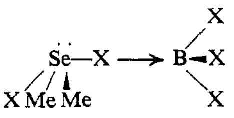
[a] Liquid sample. [b] Nujol mull.

Discussion

Of possible structural formulations for the adducts of dimethylselenium dihalides and boron trihalides, there are three models of particular interest. These, shown below, are a coordinate bond arrangement utilizing selenium's unshared electron pair (I), an ionic formulation (II), and a halogen-bridged structure (III).


I


II


III

Boron–Halogen Stretching Frequencies. Several observations concerning the infrared spectra are pertinent to a choice of formulation. First, the position and shape of the broad absorption envelope in the 630–750-cm.$^{-1}$ regions with peaks at 644 and 692 cm.$^{-1}$ for the $(CH_3)_2SeCl_2 \cdot BCl_3$ adduct correspond well with those reported for typical tetrachloroborates, $KBCl_4$, $CH_3NH_3BCl_4$, $C_5H_5NHBCl_4$, etc.[7] In contrast, for those compounds in which the boron atom of BCl_3 is bonded directly to a central atom of a Lewis base molecule such as trimethylamine,[7] pyridine,[7] amides,[8] and nitriles,[9] the broad absorption characteristic of the BCl_3 portion of the adduct is found in the 700–800-cm.$^{-1}$ region. This broad absorption envelope, whether due to $-BCl_3$ or BCl_4^-, is composed of the antisymmetric boron–chlorine stretching frequency, ν_3, and of an infrared-allowed combination band of the symmetric boron–chlorine stretching frequency, ν_1, and a deformation frequency, ν_4.[10] Accordingly, the absorptions at 730 and 765 cm.$^{-1}$ noted in Table I for a Nujol mull sample of $(CH_3)_2Se \cdot BCl_3$ may be assigned to "BCl_3" modes. Although strong solvent absorptions made impossible the observation of the complete spectrum of $(CH_3)_2Se \cdot BCl_3$ in methylene chloride solution, the close correspondence of the spectra of mull and solution samples suggests the existence of this adduct in largely undissociated form in solution. This is in sharp contrast to the previously mentioned behavior of $(CH_3)_2SeCl_2 \cdot BCl_3$ and $(CH_3)_2SeBr_2 \cdot BBr_3$ adducts in CH_2Cl_2 solution.

Reports of infrared spectra of compounds containing BBr_3 and BBr_4^- groups assist also in the discussion of the $(CH_3)_2SeBr_2 \cdot BBr_3$ adduct. The BBr_4^- ion in NH_4BBr_4 has been assigned frequencies appearing in the strong, broad absorption envelope in the 580–610-cm.$^{-1}$ region,[7] while absorptions centered at 683, 674, and 677 cm. for the acetamide,[8] N-methylacet-

---

[7] W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1772 (1960).

[8] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *ibid.*, 2144 (1960).

[9] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *ibid.*, 2182 (1960).

[10] T. C. Waddington and F. Klanberg, *ibid.*, 2339 (1960).

amide,[8] and trimethylamine[11] adducts of BBr_3, respectively, are associated with the antisymmetric B–Br stretching frequency. As reported in Table I the $(CH_3)_2Se\cdot BBr_3$ adduct absorbs strongly from 640 to 700 cm.$^{-1}$. The peak at 642 cm.$^{-1}$, like that at 640 cm.$^{-1}$ for the $(CH_3)_2Se\cdot BCl_3$ adduct, may be due in part to the selenium–boron stretching frequency. Calculation using Gordy's rule[12] suggests that a Se–B vibration should have a frequency of about 630 cm.$^{-1}$. The absorption at 697 cm.$^{-1}$ is then associated with the antisymmetric B–Br stretching frequency of the BBr_3 group in $(CH_3)_2Se\cdot BBr_3$. For the $(CH_3)_2SeBr_2\cdot BBr_3$ adduct, however, the strong absorption envelope with maxima at 571 and 604 cm.$^{-1}$ is in the expected region for the BBr_4^- ion. The selenium–carbon stretching frequencies, discussed below, of $(CH_3)_2SeBr_2$ are very similar in value to the BBr_4^- frequencies, but are much weaker in intensity and hence not considered a serious complication in the interpretation of the spectrum of the $(CH_3)_2SeBr_2\cdot BBr_3$ adduct. For this adduct, then, as for the corresponding chloride substance, the presence of BX_4^- ion is strongly indicated.

Selenium–Halogen and Selenium–Carbon Stretching Frequencies. The literature provides a few selenium–chlorine stretching frequency assignments. For $SeCl_4$,[2b] the $AlCl_3$ adduct[13] of $SeCl_4$, and the SO_2Cl_2 adduct[14] of $SeCl_4$, all of which are reported to contain the $SeCl_3^+$ ion having C_{3v} symmetry, the symmetric and antisymmetric Se–Cl stretching frequencies have been assigned as 388 and 346 cm.$^{-1}$, 416 and 398 cm.$^{-1}$, and 417 and 398 cm.$^{-1}$, respectively. These relatively large frequency differences for $SeCl_3^+$-containing compounds may have their source in limited association effects, which might be expected for the substance containing a small chloride ion as compared to the larger $AlCl_4^-$ and SO_3Cl^- ions, and/or in the crystal packing requirements of the solids.

With respect to the selenium–carbon stretching frequency, Raman[15,16] and infrared[17] data on dimethyl selenide lead to the association of the 601 and 585 cm.$^{-1}$ absorptions with the symmetric and antisymmetric Se–C stretching modes. These modes are readily identified in $(CH_3)_2SeCl_2$, $(CH_3)_2SeBr_2$, and in the $(CH_3)_2SeCl_2\cdot BCl_3$ adduct, but are obscured by B–X frequencies in the other adducts listed in Table I.

Because the structures of diphenylselenium dichloride[18] and dibromide[19] have been determined by X-ray examination, infrared data for diphenyl selenide, $(C_6H_5)_2SeCl_2$, and $(C_6H_5)_2SeBr_2$ are of assistance, both in identifying the selenium–halogen stretching frequencies and in suggesting the configuration of the corresponding dimethyl compounds. The appearance of a sharp doublet in the 455–475-cm.$^{-1}$ region of the spectrum of each of these three compounds, and the absorption at 317 cm.$^{-1}$ (shoulder at 312 cm.$^{-1}$) for $(C_6H_5)_2Se$, are clearly associated with vibrations of the selenium–carbon skeletons of the molecules.[20] It is tentatively suggested that the 317-cm.$^{-1}$ band in $(C_6H_5)_2Se$ appears as a well-resolved doublet in $(C_6H_5)_2SeCl_2$ and $(C_6H_5)_2SeBr_2$ with peaks at 310 and 331 cm.$^{-1}$ for the former, and 307 and 323 cm.$^{-1}$ for the dibromide. It is interesting that the 585-cm.$^{-1}$ (shoulder at 601 cm.$^{-1}$) band of $(CH_3)_2Se$ shows a similar resolution into a doublet when additional bonds are formed by the selenium atom.

Comparing the $(C_6H_5)_2SeBr_2$ spectrum to that of $(C_6H_5)_2Se$, the beginning of a moderately intense absorption is noted at the lower frequency limit of our instrumentation, about 265 cm.$^{-1}$. Taking this as one of the Se–Br stretching frequencies, the other must then appear at a lower frequency. For $(C_6H_5)_2SeCl_2$ the Se–Cl stretching frequency, corresponding to the 265-cm.$^{-1}$ band for Se–Br, must lie at a higher frequency. Inspection of the spectrum for $(C_6H_5)_2SeCl_2$ showed a broad absorption at 277 cm.$^{-1}$, but also the doublet with peaks at 310 and 331 cm.$^{-1}$ is seen to have a greater intensity in the lower frequency branch. For $(C_6H_5)_2SeBr_2$ the peaks of the doublet are of comparable intensity. It is possible, then, that the Se–Cl stretching frequencies are at approximately 310 and 277 cm.$^{-1}$, and the Se–Br absorptions appear at ~265 cm.$^{-1}$ and lower. A report of the Raman examination of Se_2Br_2[21] gives 292 and 204 cm.$^{-1}$ for the antisymmetric and symmetric Se–Br frequencies, respectively. While limited in scope, the infrared data are thus compatible with the C_{2v} model proposed from X-ray examination of these diphenylselenium dihalides.

For the dimethylselenium dihalides the frequencies at 293 and 270 cm.$^{-1}$ in the spectrum of $(CH_3)_2SeCl_2$, and the beginning of a band at ~265 cm.$^{-1}$ for $(CH_3)_2SeBr_2$, may be associated with Se–X stretching frequencies. Considered together with the Se–C absorption frequencies previously noted for these substances, these data point to a C_{2v} symmetry for the dimethylselenium dihalides also.

Turning to the boron trihalide adducts of $(CH_3)_2SeCl_2$ and $(CH_3)_2SeBr_2$, the cationic species accompanying the BX_4^- ion is initially assumed to be $[SeX(CH_3)_2]^+$ previously depicted in structural model II. These cations would be expected to have a pyramidal configuration and display C_s symmetry. Accordingly, two Se–C frequencies are active in the infrared, and these are readily associated with the 589- and 572-cm.$^{-1}$ absorptions in the spectrum of the dichloride adduct. The intense absorption of the BBr_4^- envelope precludes observation of the Se–C absorption frequencies in the bromide adduct. The single Se–X fundamental of these cations appears at 403 cm.$^{-1}$ in the dichloride adduct and at 286 cm.$^{-1}$ for that of the dibromide. The increase in both Se–Cl and Se–Br frequencies with adduct formation may be correlated with the increased s character of the selenium orbital participating in the Se–X bond when the halogen atom shifts from an apical position in a trigonal bipyramidal molecule to a pyramidal position in the cationic species.

Two other absorptions in the dichloride adduct spectrum should be noted. The strong band at 311 cm.$^{-1}$ is assigned to the deformation mode, ν_4, of

---

(11) R. C. Taylor, "Boron-Nitrogen Chemistry," American Chemical Society, Washington, D. C., 1964, p. 64.

(12) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(13) H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **73**, 759 (1954).

(14) H. Gerding and H. Houtgraaf, *ibid.*, **75**, 589 (1956).

(15) P. Donzelot, *Compt. rend.*, **203**, 1069 (1936).

(16) H. Siebert, *Z. anorg. Chem.*, **271**, 65 (1952).

(17) H. P. Fritz and H. Keller, *Chem. Ber.*, **94**, 1524 (1961).

(18) J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **64**, 508 (1942).

(19) J. D. McCullough and G. Hamburger, *ibid.*, **63**, 803 (1941).

(20) D. H. Brown, A. Mohammed, and D. Sharp, *Spectrochim. Acta*, **21**, 659 (1965).

(21) H. Stammreich and R. Forneris, *ibid.*, **8**, 46 (1956).

BCl_4^-. Instrumental characteristics make difficult the assessment of the intensity of the absorption at 377 cm.$^{-1}$ but, if it is weak as has been assumed, it could be the symmetric B–Cl stretching frequency, ν_1, of BCl_4^-. This is an infrared-forbidden band in the isolated species of T_d symmetry but may become weakly allowed owing to crystal perturbations. This effect has been proposed in the interpretation of the infrared spectrum of potassium tetrafluoroborate.[22]

The increases in Se–X absorption frequencies attending adduct formation would not be expected if the adducts were represented by structural formulation III. For a halogen-bridged structure little change in the disposition of groups about the selenium atom would be required, and fundamental frequency shifts would be unexpected, except possibly for the Se–X bridging bond. Viewing this bridging as the coupling of two oscillators for which the force constant k_{Se-X} is less than k_{B-X}, a decrease in the value of k_{Se-X} would be expected when the coupling occurs. This should result in a decrease in the absorption frequency of the bridging Se–X group.

A final point of interest in the infrared data presented in Table I is the apparently enhanced intensities of Se–C stretching frequencies of the dimethylselenium dihalide adducts as compared to the dimethylselenium dihalides themselves. Since band intensity depends upon the change in electric dipole moment with stretching motion along the bond axis, an intensity increase is in accord with the formation of a charged species, the $[SeX(CH_3)_2]^+$ cation.

The infrared evidence provided here is thus best interpreted in favor of the ionic formulations II for these adducts.

Conclusions

While it might be argued that the presence of two electron-releasing groups, *e.g.*, methyls, in a four-coordinated molecule having selenium (or sulfur or tellurium) as the central atom should result in the enhancement of the bond-forming capacity of the unshared electron pair, it develops in the present case that the rupture of an Se–X bond and transfer of a halide ion is the preferred reaction route, as it is with the tetrahalide molecules. That classical Lewis basicity for those molecules in which the central atom possesses five electron pairs, one of which is stereochemically active but not involved in bond formation, has not yet been reported is perhaps not surprising, since the attachment of two chlorine atoms to the selenium atom in the $(CH_3)_2Se \cdot BCl_3$ adduct would work against the formation and maintenance of a stable Se–B bond through both the steric and electron-withdrawing effects of the added atoms. Other related systems are under investigation and will be reported upon in due course.

Acknowledgment. The authors wish to thank the Selenium–Tellurium Development Association, Inc., and the National Science Foundation for financial support.

---

[22] N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

Mass Spectrometric Studies at High Temperatures. VIII. The Sublimation Pressure of Iron(II) Fluoride

Richard A. Kent and John L. Margrave

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received May 26, 1965*

Mass spectrometric studies of FeF_2 sublimation from a Knudsen cell have established $FeF_2(g)$ as the vapor species and ΔH°_{298} (sublimation) = 75.6 ± 1.0 kcal. mole^{-1}.

I. Introduction

It has been pointed out in previous papers in this series[1,2] that, in general, reliable Knudsen or Langmuir vaporization or sublimation rates for the transition metal fluorides have not been available. Because of this, the review of Brewer, Somayajulu, and Brackett[3] on the thermodynamic properties of the gaseous metal dihalides includes many estimated heats of sublimation. In this work, the sublimation rate of FeF_2 has been measured and the vapor species identified by the Knudsen technique employing a mass spectrometer.

II. Experimental Section

The mass spectrometer employed in this work has been described previously.[4] Temperatures below 800° were measured with a Ray-Tek R-7S infrared pyrometer equipped with a lead sulfide detector and an achromatic lens. This instrument operates in the spectral region from 1.8 to 2.5 μ and can be focused on a 1-mm. black body hole from a distance of 15 in. Both the infrared and optical pyrometers were used to measure temperatures in the range 800 to 900°, and for all temperatures the measurements differed by no more than ±3°.

The FeF_2 powder was obtained from the Ozark-Mahoning Co. of Tulsa, Okla., and the only impurity

---

[1] R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **86**, 5090 (1964).

[2] T. C. Ehlert, R. A. Kent, and J. L. Margrave, *ibid.*, **86**, 5093 (1964).

[3] L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).

[4] G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, *J. Phys. Chem.*, **67**, 877 (1963).