The Addition Compounds of Some Sulfides with Boron Trifluoride and with Boron Trichloride

BY HARRIS L. MORRIS, NORMAN I. KULEVSKY, MILTON TAMRES, AND SCOTT SEARLES, JR.

A manometric method was used to investigate the addition compounds of dimethyl sulfide, diethyl sulfide, thiacyclopentane [$(CH_2)_4S$], and thiacyclohexane [$(CH_2)_5S$] with BF_3 and with BCl_3. Thiacyclobutane [$(CH_2)_3S$] polymerizes in the presence of these Lewis acids. The low stability of the BF_3 adducts and the low volatility of the BCl_3 adducts make these compounds difficult to study in the vapor phase. Physical characteristics and thermodynamic values for the dissociation of these adducts are presented. These data do not support a recent proposal of estimating relative donor strengths of the weak BF_3 adducts based on a principle involving "boiling points" and "Trouton constants" of the adducts.

Introduction

Electron donor properties of ethers, both acyclic and cyclic, have been studied extensively toward a large variety of acceptors. For example, hydrogen bonding[1,2] and iodine complexation[3,4] studies have established a ring size order of 4- > 5- > 6- > 3-membered ring, with diethyl ether falling between the 6- and 3-membered rings. Relative donor abilities of some open chain and the 5- and 6-membered ring ethers also have been established using stronger acids, *e.g.*, determining pK_a values[5] and forming adducts with BF_3.[6,7] The smaller ring ethers polymerize in the presence of these acids. Generally, good correlation of the donor ability order is found with all of these acceptors.

In a preliminary, condensed phase study on the interaction of cyclic sulfides with BF_3,[8] it was suggested that possibly the same basicity order held in this case as for the cyclic ethers. Later work showed that the donor ability of the cyclic sulfides toward iodine is in the order 5- > 6- > 4- > 3-membered ring,[9,10] with diethyl sulfide being almost as strong as thiacyclopentane [$(CH_2)_4S$], and dimethyl sulfide being somewhat weaker than thiacyclobutane [$(CH_2)_3S$].[11]

Few investigations of sulfide:BF_3 systems in the gas phase have been made, and it is reported that these adducts are highly dissociated.[12] Because of the difficulty in obtaining thermodynamic data, it was suggested[13] that use could be made of such properties as the "extrapolated boiling point" and "apparent Trouton constant" of the adduct to establish relative donor

ability. The order given for several sulfide:BF_3 adducts[13] is completely the reverse of that found toward iodine in solution.

It was thought desirable to study several sulfide:BF_3 adducts in the gas phase to establish at least the range of the thermodynamic properties, with the possibility of checking directly the thermodynamic results of the BF_3 adducts against those of the iodine complexes.

The study was extended to BCl_3 adducts also, since BCl_3 has been found to behave as a stronger Lewis acid than BF_3.[14]

Experimental Section

Apparatus and Procedure.—The vacuum line constant temperature manostat and the techniques employed to measure known quantities of reagents, to study the saturation pressures of the adducts, and to determine the melting points of the adducts have been described previously.[6,7,15]

The saturation pressure data measured in a small tensimeter are used to permit estimating the temperature at which a given quantity of adduct in the dissociation tensimeter would be completely in the vapor state. Such estimates, however, become less reliable for weak complexes[13] (see Discussion). Therefore, for the weak sulfide:BF_3 adducts, measured quantities of each component, usually close to 1:1 mole ratio, were condensed in the large tensimeter, and the dissociation measurements were begun at a temperature considered to be well into the vapor phase. The temperature was varied in random fashion to avoid the possibility of introducing systematic errors. The equilibrium pressure at each temperature was read several times, by varying the mercury levels in the manometer,[15] and the average value was used to calculate K. The time required to reach temperature equilibrium and determine K was of the order 20–30 min. A minimum of two runs was made on each adduct.

An older vacuum assembly, with a large tensimeter of approximately 400 cc. and a small tensimeter of 65 cc., and a Gaertner cathetometer were used to obtain the dissociation data for diethyl sulfide:BCl_3 and thiacyclopentane:BCl_3. A new line, with a large tensimeter of 358.5 cc. and a small tensimeter of variable volume of 46–47 cc., and a Wild cathetometer were used to study the dissociation of the other adducts. The new assembly was checked by measuring in the vapor phase the diethyl ether:BF_3 system, the thermodynamic properties of which are known: Found, $\Delta H° = 11.99 \pm 0.09$ kcal./mole, $\Delta S° = 30.6 \pm 0.3$ e.u., $\Delta G°_{100} = 580$ cal./mole; lit.,[6] $\Delta H° = 11.93 \pm 0.3$ kcal./mole, $\Delta S° = 30.2 \pm 0.8$ e.u., $\Delta G°_{100} = 665 \pm 30$ cal./mole.

Reagents.—Commercial boron trifluoride, obtained from the

(1) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

(2) S. Searles, M. Tamres, and E. R. Lippincott, *ibid.*, **75**, 2775 (1953).

(3) Sr. M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960).

(4) M. Tamres and Sr. M. Brandon, *ibid.*, **82**, 2134 (1960).

(5) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).

(6) D. E. McLaughlin and M. Tamres, *ibid.*, **82**, 5618 (1960).

(7) D. E. McLaughlin, M. Tamres, and S. Searles, *ibid.*, **82**, 5621 (1960).

(8) M. Tamres, S. Searles, and R. F. Vance, Abstracts, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March 1953, p. 25M.

(9) J. D. McCullough and D. Mulvey, *J. Am. Chem. Soc.*, **81**, 1291 (1959).

(10) M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

(11) N. W. Tideswell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).

(12) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(13) T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 2989 (1959).

(14) H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).

(15) D. E. McLaughlin, Ph.D. Thesis, University of Michigan, 1959.

Matheson Co., Inc., was purified by a procedure described by Brown and Johannesen.[16] The vapor pressure of the BF_3 was 78.0 mm. at $-126.2°$ (lit.[17] 76.8 mm.), 157.0 mm. at $-119.1°$ (lit.[17] 157.0 mm.), and 302.0 mm. at $-111.8°$ (lit.[17] 301.4 mm.).

Boron trichloride, from the Matheson Co., Inc., was purified by the method of Brown and Holmes.[18] The vapor pressure of the BCl_3 was 170.5 mm. at $-22.9°$ (lit.[19] 170 mm.) and 476.0 mm. at $0°$ (lit.[19] 476 mm.).

Reagent grade CCl_4 from the Mallinckrodt Chemical Works was fractionated in the purification train of the vacuum line.

Research grade xenon from Air Products and Chemicals, Inc., was used directly. Its purity is reported to be 99.9914%.

Dimethyl sulfide and diethyl sulfide were obtained from the Eastman Kodak Co. They were distilled from sodium, with the middle fraction being used for the measurements. The syntheses of the cyclic sulfides have been given in a previous publication.[10] The refractive indices of the sulfides and their vapor pressures at several temperatures were in excellent agreement with literature values.[20] Also, analysis by vapor phase chromatography showed the absence of impurities, estimated to be less than 0.1%.

Results and Discussion

Physical Properties.—The sulfide:BF_3 adducts form white, slightly glassy solids which melt over a temperature range. The melting ranges are as follows: dimethyl sulfide:BF_3, -25 to $-23°$ (reported[12] to be a solid at $-78.5°$); diethyl sulfide:BF_3, -85 to $-80°$ (reported[13] to be a liquid at $-78°$); thiacyclopentane:BF_3, -30 to $-25°$ (reported[13] to be a solid at $-45°$ and a liquid at $-23°$); and thiacyclohexane:BF_3, -19 to $-15°$.

The white solids of the sulfide adducts with BCl_3 are higher melting and, in general, have sharper melting points than do the corresponding adducts with BF_3. The melting ranges are as follows: dimethyl sulfide:BCl_3, 85–90°; diethyl sulfide:BCl_3, 10–11°; thiacyclopentane:BCl_3, 43–44°; and thiacyclohexane:BCl_3, 65–69°.

Saturation Pressures.—Two methods are widely used to prepare the 1:1 adducts. In the first, equimolar amounts of the donor and acceptor species are measured out separately and are then transferred quantitatively to a smaller tensimeter where they are mixed (matched samples method). In the second, the individual species are measured out in approximate quantities with an excess of the more volatile species, usually the Lewis acid, e.g., BF_3, and the excess is pumped away at a temperature at which the adduct is a solid (pumping method).

The latter method is not satisfactory for preparing adducts that are weak. For these, the observed temperature dependence of the saturation pressure is not characteristic of the complex, but is dependent upon the ratio of sample size to volume of the tensimeter.[18] Therefore, a meaningful comparison can be made only if this ratio is maintained for the series being compared. That this could be so is not surprising since a

weak complex containing a highly volatile component, e.g., BF_3, can be considered as a system of a gas dissolved under pressure in a liquid. For a fixed quantity of complex, the gas pressure would be dependent on the free volume above the liquid. It is apparent for the sulfide:BF_3 adducts that most of the saturation pressure is due to BF_3 since the free sulfides, except $(CH_3)_2S$, have relatively low vapor pressures in the temperature range investigated. On cooling, the less volatile species may solidify rapidly, leaving an excess of the more volatile component which may not be able to diffuse sufficiently fast into the solid to maintain the 1:1 adduct. Pumping removes the volatile part, thereby changing the over-all ratio. It was found in the present study that when the pumping method was tried to prepare 1:1 adducts of sulfide:BF_3 the saturation pressure data were not reproducible. Other workers have observed that the donor/acceptor mole ratio is extremely critical in determining saturation pressures. According to the work of Palko and Drury[21] on the $(CH_3)_2S$:BF_3 adduct, even in cases where the sulfide/BF_3 mole ratio changed only from 0.99 to 0.96, the saturation pressures and the slope of the log P vs. $1/T$ plots changed markedly.

Consequently, only the matched samples method was employed to prepare sulfide:BF_3 adducts of fixed ratio of moles of adduct to volume of tensimeter. In the case of the adducts with BCl_3, which are more stable than those with BF_3, both the matching sample and the pumping techniques were used. The pertinent data on saturation pressures for the BF_3 and BCl_3 adducts are summarized in Table I,[22] the equations for the log P vs. $1/T$ plot being determined by the method of least squares. The temperature was varied in random fashion to avoid systematic error.

TABLE I

SATURATION PRESSURE EQUATIONS FOR LIQUID ADDUCTS OF SULFIDES WITH BF_3 AND BCl_3

Adduct	Ratio[a] $\left(\dfrac{\text{cc. of adduct}}{\text{cc. of tensimeter}}\right)$	log $P = -A/T + B$ A	B
Dimethyl sulfide:BF_3	0.308[b]	2168	9.602
Diethyl sulfide:BF_3	0.308[b]	1743	7.918
Thiacyclopentane:BF_3	0.308[b]	1598	7.316
	0.308[b]	1590	7.287
Thiacyclohexane:BF_3	0.308[b]	1584	7.424
	0.308[b]	1579	7.406
Dimethyl sulfide:BCl_3	Pumping method	3294	10.119
Diethyl sulfide:BCl_3	0.216[c]	3356	10.286
	Pumping method	3371	10.315
Thiacyclopentane:BCl_3	0.214[c]	3369	9.856
	Pumping method	3430	9.954
Thiacyclohexane:BCl_3	0.238[c]	3246	9.482
	Pumping method	3735	10.648

[a] Ratios are given for the matched samples method. The quantity of adduct is expressed as cc. of gas at S.T.P. [b] Tensimeter volume range of 46–47 cc. [c] Tensimeter volume of 65 cc.

(16) H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **72**, 2934 (1950).

(17) R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," Elsevier Publishing Co., 1954, p. 203.

(18) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

(19) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(20) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Research Institute, Project 44, Vol. VII.

(21) A. A. Palko and J. S. Drury, *J. Chem. Phys.*, **33**, 779 (1960).

(22) The original data have been deposited as Document No. 8579 with the A.D.I. Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

The saturation pressure data for dimethyl sulfide: BF_3 are in excellent agreement with the results of Graham and Stone,[12] but are slightly lower than the values reported by Palko and Drury.[21] For both diethyl sulfide: BF_3 and thiacyclopentane: BF_3, the saturation pressures obtained in this study are slightly lower than those found by Coyle, Kaesz, and Stone.[13]

Dissociation Data.—The weakness of the interaction of BF_3 with sulfides results in the formation of very small concentrations of adduct in the vapor phase, thereby making quantitative study very difficult. In most cases, as much of each component was taken ($\sim$30 mm. at 0°) as could conveniently be studied in the tensimeter in order to favor the formation of adduct. Even so, as may be seen in Table II, the concentration of adduct formed is quite small. These results are in accord with those of Graham and Stone[12] and also of Coyle, Kaesz, and Stone,[13] who reported that, for their pressures of sulfide and BF_3, the adducts were very extensively dissociated at room temperature (above 95% in the case of dimethyl sulfide and 98% in the case of diethyl sulfide and of thiacyclopentane).

Nevertheless, the presence of adduct in the vapor phase seems real. The maximum standard deviation of an individual pressure measurement was of the order of 0.01 to 0.02 mm. The measured pressure of adduct lies outside the realm of the cumulative errors. Of course, there is the possibility that the differences from additivity may be due to nonideal gas behavior or to nonquantitative transfer of a component. To test these possibilities, the same experimental techniques were tried on the thiacyclopentane–CCl_4 and on the xenon–BCl_3 systems. In the former case, some deviation from ideal gas behavior was noted just above the temperature at which the system entered the vapor phase. This lasted only for a few degrees, and then the dissociation pressure leveled off to a constant value within several hundredths of a millimeter of the initial total pressure (which may have been due in part to cumulative errors or to a slight transfer loss).[23] For the xenon–BCl_3 system, there is no interaction under the conditions of measurement, the observed total pressure being exactly equal to the sum of the component pressures.

The sulfide adducts with BCl_3 are much less volatile than are those with BF_3, making it necessary to study the dissociation at elevated temperatures. For some of the adducts, smaller pressures of components were measured out in order to stay within a temperature range for convenient operation of the constant temperature manostat. The conditions of small sample and high temperature are unfavorable for adduct formation and, indeed, in these cases the concentration of adduct in the gas phase is quite small. Thus, the comments made on the BF_3 adducts apply equally well here.

(23) Actually, the carbon tetrahalides may act as electron acceptors toward the sulfides. Unpublished work in this laboratory shows that diethyl sulfide–CBr_4 forms a charge-transfer complex in *n*-heptane. The equilibrium constant is so small, however, that if the same constant applied in the gas phase as in solution, the pressure of adduct formed under the conditions of the manometric study would be $\sim$0.01 mm.

TABLE II

EXPERIMENTAL CONDITIONS FOR THE ADDUCTS OF SULFIDES WITH BF_3 AND WITH BCl_3

Run	Temp range, °C.	Sum of component press., mm. at 0°	Range[b] in adduct press., mm. at 0°
Dimethyl Sulfide: BF_3			
1	44.7–85.9	61.34	0.33–0.22
2	36.5–85.5	60.71	0.33–0.19
3	47.2–85.5	59.55	0.26–0.14
Diethyl Sulfide: BF_3			
1	30.0–55.6	61.07	1.03–0.79
2[a]	32.3–58.1	32.39	0.38–0.30
3[a]	37.3–56.5	31.59	0.32–0.19
Thiacyclopentane: BF_3			
1	44.5–65.3	61.91	0.57–0.38
2	45.6–64.6	60.33	0.50–0.35
3	46.8–63.7	62.03	0.47–0.31
Thiacyclohexane: BF_3			
1	57.6–85.3	59.77	0.72–0.63
2[a]	46.3–66.1	28.67	0.17–0.13
3[a]	45.8–64.4	29.22	0.19–0.16
Dimethyl Sulfide: BCl_3			
1	134.5–165.7	60.58	2.31–0.90
2	135.7–165.5	52.83	1.99–0.88
Diethyl Sulfide: BCl_3			
1[a]	118.0–140.9	29.47	0.79–0.36
2[a]	116.1–125.4	23.62	0.57–0.39
Thiacyclopentane: BCl_3			
1[a]	134.5–149.8	22.08	0.37–0.17
2[a]	134.2–149.2	21.72	0.46–0.21
Thiacyclohexane: BCl_3			
1	141.1–168.3	28.12	0.44–0.16
2	140.6–169.6	26.56	0.34–0.13
Thiacyclopentane–CCl_4			
	54.0–93.9	60.86	0.09–0.03
Xenon–BCl_3			
	33.2–58.1	80.60	0.01–0.00

[a] Older apparatus used; all other runs made with newer apparatus. [b] With the newer apparatus the extremes in adduct pressures generally corresponded with the extremes in temperature. With the older apparatus, where there was greater scatter in the data, this often was not the case.

It was noted for the thiacyclopentane: BF_3 adduct that reproducible data for the log K *vs.* $1/T$ plot were obtained so long as the adduct was taken quickly into and maintained in the vapor phase. The adduct was colorless initially, but gave a yellow color when it was cooled to a liquid after the vapor phase measurements had been taken. The yellow color darkened to an orange-yellow on standing. Upon re-entering the vapor state, the dissociation constants were lower. Repetition of the condensation and vaporization processes continually diminished the dissociation constants. These data are shown in Figure 1 (corresponding to run 1 in Tables II and III). Similar observations were made for the thiacyclohexane: BF_3 adduct, but no such difficulty was encountered with dimethyl sulfide or with diethyl sulfide and BF_3. The data for the adducts are presented in Figure 2.

TABLE III

THERMODYNAMIC DATA FOR THE DISSOCIATION OF
SULFIDE ADDUCTS WITH BF$_3$ AND WITH BCl$_3$

Run[a]	ΔH°,[b] kcal./mole	ΔG°_{60}, kcal./mole	ΔS°,[b] e.u.
	Dimethyl Sulfide:BF$_3$		
1	2.8 ± 0.3	-1.07	11.6 ± 0.8
2	3.3 ± 0.1	-1.16	13.4 ± 0.4
3	4.4 ± 0.2	-1.27	16.9 ± 0.7
Av.	3.5 ± 0.5	-1.17 ± 0.06	14.0 ± 1.6
	Diethyl Sulfide:BF$_3$		
1[c]	2.9 ± 0.1	-0.42	9.9 ± 0.4
2[d]	$(2.2 \pm 1.1)^e$	-0.21	$(7.1 \pm 3.3)^e$
3[d]	$(3.7 \pm 1.4)^e$	-0.45	$(12.4 \pm 4.3)^e$
	Thiacyclopentane:BF$_3$		
1	4.6 ± 0.3	-0.86	16.4 ± 0.9
2	5.3 ± 0.3	-0.89	18.5 ± 1.0
3	5.8 ± 0.2	-0.98	20.5 ± 0.6
Av.	5.2 ± 0.4	-0.91 ± 0.04	18.5 ± 1.3
	Thiacyclohexane:BF$_3$		
1[c]	1.5 ± 0.1	-0.44	5.9 ± 0.3
2[d]	$(1.3 \pm 0.9)^e$	-0.51	$(5.4 \pm 2.8)^e$
3[d]	$(0.5 \pm 0.7)^e$	-0.42	$(2.6 \pm 2.1)^e$
		ΔG°_{150}, kcal./mole	
	Dimethyl Sulfide:BCl$_3$		
1	12.3 ± 0.7	-0.14	29.4 ± 1.6
2	11.9 ± 0.5	0.00	28.0 ± 1.1
Av.	12.1 ± 0.5	-0.07 ± 0.07	28.7 ± 1.2
	Diethyl Sulfide:BCl$_3$		
1[d]	12.6 ± 0.7	-0.39	30.8 ± 1.7
2[d]	13.6 ± 1.4	-0.45	33.3 ± 3.5
Av.	13.1 ± 0.9	-0.42 ± 0.03	32.1 ± 2.3
	Thiacyclopentane:BCl$_3$		
1[d]	19.7 ± 0.7	-0.29	47.1 ± 1.7
2[d]	18.6 ± 1.7	-0.06	44.2 ± 4.0
Av.	19.2 ± 1.1	-0.18 ± 0.12	45.7 ± 2.6
	Thiacyclohexane:BCl$_3$		
1	13.5 ± 1.4	-0.20	32.5 ± 3.3
2	13.4 ± 0.8	-0.25	32.2 ± 2.0
Av.	13.5 ± 0.8	-0.23 ± 0.03	32.4 ± 1.9

^{a} The number of the run corresponds to that in Table II. ^{b} Given with standard error. ^{c} Considered to be the best run; error limits similar to those of dimethyl sulfide:BF$_3$. ^{d} Older apparatus used; all other runs made with newer apparatus. ^{e} In using the older apparatus, the combination of smaller sample and greater scatter of data makes these results less reliable. This is particularly so in the case of thiacyclohexane:BF$_3$ where the measured change in adduct pressure over the temperature range was only 0.04 to 0.03 mm. (Table II), which lies within the range of cumulative experimental error. Nevertheless, the data are useful in establishing a check on ΔG°_{60}.

In the case of thiacyclobutane and BF$_3$, an irreversible decomposition occurred immediately on warming the mixture to room temperature. A nonvolatile clear liquid was produced which could not be removed from the vacuum line by pumping.

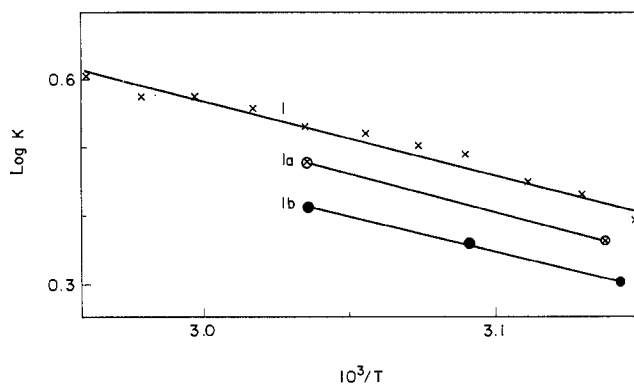A similar reaction was obtained with thiacyclobutane

Figure 1.—Effect of condensation on the dissociation measurements of thiacyclopentane:BF$_3$: (1) adduct brought quickly into vapor phase and all points taken in this phase, (1a) data taken after adduct had been cooled to room temperature, (1b) data taken after adduct was kept at room temperature for 1 day.
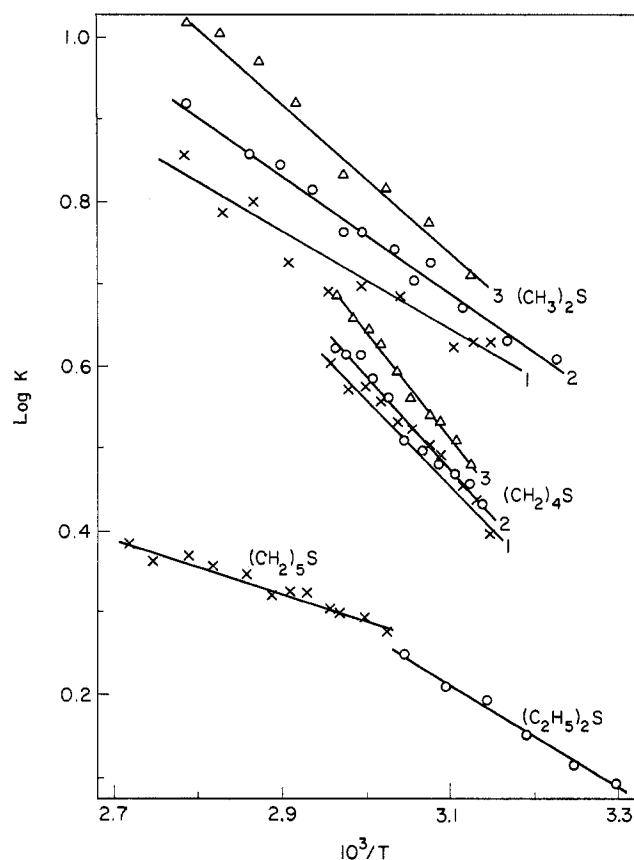

Figure 2.—Log K vs. $1/T$ for BF$_3$ adducts with dimethyl sulfide, diethyl sulfide, thiacyclopentane, and thiacyclohexane.

and BCl$_3$. For the other BCl$_3$ adducts, no secondary reactions were observed; the dissociation data were reproducible after the adduct was condensed and revaporized. These data are shown in Figures 3 and 4.

Thermodynamic Results.—It should be pointed out that because of the low concentration of adduct in the vapor phase, small experimental errors such as those cited could have a large effect on the dissociation constant and, hence, on ΔG°. Further, the change in concentration of adduct over the temperature range investigated was quite small, particularly for the adducts with BF$_3$ where the over-all change in some cases was
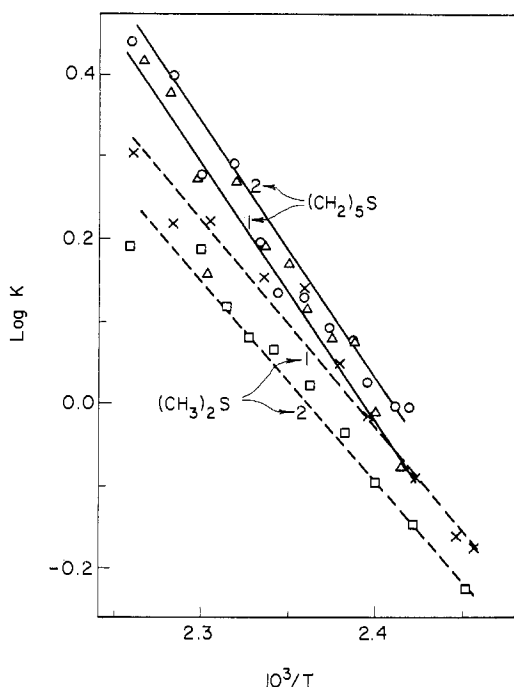
Figure 3.—Log K vs. $1/T$ for BCl_3 adducts with dimethyl sulfide and thiacyclohexane.
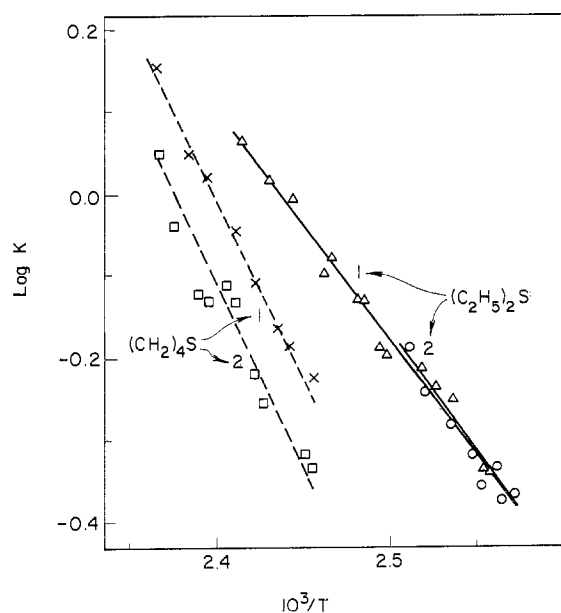

Figure 4.—Log K vs. $1/T$ for BCl_3 adducts with diethyl sulfide and thiacyclopentane.

of the order of 0.1 mm. Here, quite small changes in K could affect appreciably the least-squares calculation of $\Delta H°$ from the log K vs. $1/T$ plot. Consequently, many determinations of K were made over the temperature range to get a better statistical evaluation of $\Delta H°$. Even so, omission of one or two points, which still fell within the experimental limits, could alter the $\Delta H°$ by as much as 1 kcal./mole. In spite of these limitations, the data obtained[22] permit a reasonable estimate of the thermodynamic properties of the adducts. These are given in Table III.

Even allowing for the fact that the high degree of dissociation of adducts makes difficult a precise deter-

mination of $\Delta H°$, it seems reasonable to estimate from the data that the enthalpy of reaction of the sulfides with BF_3 has a maximum value of approximately 5 kcal./mole. Clearly, $\Delta H°$ is smaller for the BF_3 than the BCl_3 adducts and confirms that BCl_3 is a stronger Lewis acid toward sulfides than BF_3.

The increase in entropy on adduct dissociation is due to the change of three vibrational degrees of freedom into translational. For stable adducts, the vibrational frequencies are too high to contribute appreciably to the over-all entropy. This is the case for the sulfide:BCl_3 adducts, the entropy changes being in the range expected. For the BF_3 adducts, the enthalpy and entropy changes are much smaller, being of the order of magnitude observed for ether–iodine complex formation in solution.[3,4] The small entropy change on dissociation requires that the adduct possess some rather low frequencies corresponding in magnitude to those found in pure rotation. No direct evidence for this has been reported as yet in the literature. There has appeared[24] one result for thiacyclopentane:BF_3 which suggests that the enthalpy and entropy values may be larger than those found in the present study, namely, $\Delta H° = 9.6$ kcal./mole, $\Delta G°_{50} = -1.35$ kcal./mole, and $\Delta S° = 29.4$ e.u. The high value calculated for $\Delta S°$ is due predominantly to the experimental result for $\Delta H°$. The latter seems unusually high, considering the great instability of this adduct as found in the present study and by others.[13]

Donor Ability.—The sequence of donor ability of a series of electron donors is dependent on the choice of reference acid and the conditions of measurement. When these are varied, it is not uncommon to find reversals in the sequence of donor strength, being due mainly to such factors as steric and solvation effects.

In studies on the interaction of tetrahydrofuran, tetrahydropyran, and diethyl ether with iodine in n-heptane solution[3] and with BF_3 in the vapor phase,[6,7] the same sequence of donor ability is observed. In fact, a linear correlation exists between the enthalpies of reaction for the two sets of data.[7] It would seem somewhat unexpected if a marked reversal for these same two acids were to be found for the corresponding sulfide system.

The fact that variation in $\Delta H°$ of somewhat more than 1 kcal./mole between different runs on the same sulfide:BF_3 adduct is observed makes it difficult to assign a unique sequence of donor strengths which could be compared with the corresponding data for the iodine complexes. For the latter, a sequence of thiacyclopentane $>$ diethyl sulfide $>$ thiacyclohexane has been reported,[9,10] with dimethyl sulfide probably being still weaker.[11] In many interactions, particularly in the absence of steric factors, it has been noted that any two of the thermodynamic functions $\Delta H°$, $\Delta S°$, and $\Delta G°$ show a linear correlation for a series of related compounds.[25] Unfortunately, such a correlation was not obtained in the present study (Table III).

(24) J. F. Carpenter, Ph.D. Thesis, St. Louis University, 1960.
(25) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

Nevertheless, the data permit making a few comparisons, even if the entire sequence of strengths is not established. A sequence based on the dissociation constant can be changed depending upon the temperature chosen for the comparison. For the BF_3 adducts, that formed with dimethyl sulfide was the most highly dissociated over the entire temperature range. Its $\Delta H°$ appears somewhat smaller than that for the thiacyclopentane adduct. These data would indicate that dimethyl sulfide probably is a weaker donor than thiacyclopentane toward BF_3.

The stronger BCl_3 adducts do not show quite the same trends in $\Delta H°$ and $\Delta G°$ as do the BF_3 adducts. Here, both sets of thermodynamic functions support the conclusion that, toward BCl_3, thiacyclopentane is a better donor than diethyl sulfide.

For those cases where thermodynamic data are unavailable, comparison of stabilities of addition compounds has been made by using the rule[26] that for adducts of similar structure and molecular weight the weaker adduct will be more volatile. This criterion, if applied to the BF_3 adducts of thiacyclopentane, diethyl sulfide, and even thiacyclohexane, again leads to the conclusion that thiacyclopentane forms the strongest adduct.

In the case of *weak* complexes, still other criteria have been proposed to compare stabilities.[13] The first is based on the difference in the boiling points of the complex and the free ligand, namely, for two bases B and B′ adding to the same reference Lewis acid A, the base strength of B is greater than that of B′ if

$$(\text{"b.p."}_{B:A} - \text{b.p.}_B) > (\text{"b.p."}_{B':A} - \text{b.p.}_{B'}) \quad (1)$$

or

$$[\Delta_{(b.p.)} > \Delta'_{(b.p.)}]$$

The second criterion is based on[27]

$$\text{Trouton constant}_{B:A} > \text{Trouton constant}_{B':A}$$

It is the use of these criteria which led to a proposed stability sequence of $(CH_3)_2S > (C_2H_5)_2S > (CH_2)_4S$ toward BF_3 in the gas phase, which is not in accord with the thermodynamic data of the present study and is the reverse of the sequence toward I_2 in solution.[9-11]

The pertinent boiling point and Trouton constant data are given in Table IV. It is difficult to attach physical significance to either of these quantities for the adducts because, although the sulfide and BF_3 are measured out in a 1:1 mole ratio for the saturation pressure measurements, neither the vapor nor the liquid phase has this ratio. The combination of high volatility of BF_3 and low volatility of sulfide can give an "extrapolated boiling point" of the adduct which is lower than that of the free ligand. When the sulfide is very volatile, as dimethyl sulfide, the high "apparent Trouton constant" could result from the relatively low "extrapolated boiling point."

The criterion of eq. 1 depends upon two differences: (a) the difference in the "extrapolated boiling points"

(26) H. C. Brown and H. Pearsall, *J. Am. Chem. Soc.*, **67**, 1765 (1945).
(27) A more complete discussion of the Trouton constant criterion is given by H. D. Kaesz, Ph.D. Thesis, Harvard University, 1958.

TABLE IV
BOILING POINT AND TROUTON CONSTANT DATA FOR ADDUCTS OF SULFIDES WITH BF_3 AND WITH BCl_3

Adduct	Work[a]	B.p. of adduct,[b] °C.	B.p. of ligand, °C.	$\Delta_{b.p.}$, °C.	Trouton constant,[b] e.u.
Dimethyl sulfide:BF_3	A	49.4 ± 2.0	37.3	+12.1	30.8 ± 0.2
	C	48.4		+11.1	31.6
	D	30.2[c]		− 7.1	33.2[c]
Diethyl sulfide:BF_3	A	73.0 ± 4.7	92.1	−19.1	23.1 ± 0.4
	E	61.6		−30.5	25.9
Thiacyclo-pentane:BF_3	A	87.1 ± 1.2	121.2	−34.1	20.3 ± 0.1
	A	87.8 ± 3.9		−33.4	20.2 ± 0.3
	E	73.0		−48.2	23.6
Thiacyclo-hexane:BF_3	A	75.4 ± 2.5	141.7	−66.3	20.8 ± 0.2
	A	75.9 ± 2.5		−65.8	20.7 ± 0.2
Dimethyl sulfide:BCl_3	B	181.9 ± 3.1			33.1 ± 0.3
Diethyl sulfide:BCl_3	A	180 ± 11			33.9 ± 1.0
	B	180 ± 22			34.0 ± 1.9
Thiacyclo-pentane:BCl_3	A	210 ± 30			31.9 ± 2.3
	B	212 ± 23			32.4 ± 1.8
Thiacyclo-hexane:BCl_3	A	219 ± 9			30.2 ± 0.7
	B	208 ± 14			35.5 ± 1.2

[a] A, this research, matched samples method; B, this research, pumping method; C, Graham and Stone, ref. 12; D, Palko and Drury, ref. 21; E, Coyle, Kaesz, and Stone, ref. 13. [b] Given with standard error. [c] Calculated from the data for the 0.99 ratio of BF_3 to $(CH_3)_2S$, ref. 21.

of the adducts and (b) the difference in boiling points of the free ligands. The first of these is relatively small due predominantly to the ready volatility of the BF_3 and covers a range of less than 40° for the extreme case of the BF_3 adducts with dimethyl sulfide and thiacyclopentane. The second, on the other hand, is quite large, the difference in the boiling points of dimethyl sulfide and thiacyclohexane being more than 100°. Thus, in this study, the latter seems to dominate and leads to eq. 1 giving an apparent stability order which parallels the boiling points of the free base.

Equation 1 does give a stability order for the 5- and 6-membered ring adduct with BF_3 in accord with some of the thermodynamic results. But, as pointed out, so does the criterion[26] of comparing volatilities of complexes of similar structure and molecular weight. It would seem preferable to retain this criterion, or rephrasing it in a fashion particularly applicable to weak complexes, to compare the vapor pressures of complexes whose free ligands are of comparable volatility.

It may be concluded from the composite data, *e.g.*, enthalpy values and volatility considerations, that thiacyclopentane probably forms the strongest adduct with BF_3. The enthalpy values for the BCl_3 adducts suggest a sequence which is closely in line with that found for iodine complexation. Furthermore, the observation that thiacyclobutane polymerizes in the presence of BF_3 (and also BCl_3), thereby giving a lower than usual pressure for the system, could account for the early observation[8] that the 4-membered ring thioether formed a more stable BF_3 adduct than did the 5- or the 6-membered ring. Consequently, this discrepancy can be considered to be removed.

Complex Compounds of Uranium Hexafluoride with Sodium Fluoride and Potassium Fluoride[1,2]

BY JOHN G. MALM, HENRY SELIG, AND STANLEY SIEGEL

The reaction of UF_6 with NaF goes to completion rapidly if the NaF is suspended in an inert solvent, C_7F_{16}. Two compounds are formed, $NaUF_7$ and Na_2UF_8. Single crystals of Na_2UF_8 have been obtained. The Na_2UF_8 phase is body-centered tetragonal with $a = 5.27$ Å. and $c = 11.20$ Å. A model based on this symmetry and cell size leads to an eightfold coordination of fluorine atoms around each uranium atom, with all U–F distances equivalent. The preparation of the analogous compounds KUF_7 and K_2UF_8 is also described.

Introduction

In 1946 Martin and Albers[3] reported the formation of stable complexes between uranium hexafluoride and a number of inorganic fluorides. Further work,[4–7] primarily with the sodium fluoride complex, indicated its composition to be Na_3UF_9. Exchange studies using F^{18}, however, pointed to the formula Na_2UF_8.[8] Recently, Katz has prepared pure Na_2UF_8 by means of a gas–solid reaction.[9] Exchange studies with several other fluorides including KF gave no evidence for complex formation. Nikolaev and Sukhoverkhov[10] reported the preparation of complexes of the type M-UF_7 (M = Cs, NH_4) by combining the reactants dissolved in chlorine trifluoride. They proposed a tentative scheme whereby ClF_3 acted as an ionizing solvent in which intermediate species of the type $(ClF_2)_n$-UF_{6+n} were formed which combined with the simple fluorides to form the isolated complexes. Volavsek,[11] however, also prepared NH_4UF_7 by treating UF_6 with a suspension of NH_4F in tetrachloroethane. In this case, an ionic reaction mechanism appears unlikely.

We report here studies which confirm the formula obtained by F^{18} exchange work, Na_2UF_8. In addition, we have prepared the new compound $NaUF_7$, as well as the analogous complexes K_2UF_8 and KUF_7.

Experimental Section

Materials.—Reagent grade sodium fluoride powder (J. T. Baker Co.) of greater than 99% purity was used. Potassium fluoride was obtained by decomposing reagent grade potassium bifluoride (J. T. Baker Co.) at 500°. The powders had a particle size range of 3–15 μ. The materials were loaded into the reactor (the KF in a drybox) and outgassed at 350° under vacuum. A tank of pure UF_6 was obtained from Oak Ridge. It was additionally purified by repeated sublimations under reduced pressure as described previously.[12] The inert solvent, n-perfluoroheptane, C_7F_{16}, was obtained from Carbide and Carbon Chemicals Co. This was dried over P_2O_5 for 24 hr. with intermittent heating to 100°. The C_7F_{16} was pretreated with UF_6. The mixture was then contacted with NaF to remove the UF_6, and after several distillations the C_7F_{16} was transferred to a thoroughly outgassed glass storage vessel.

Procedure.—Reactions were carried out in 10-ml. glass erlenmayer flasks connected *via* housekeeper seals to brass Hoke valves. The glass reactors contained glass enclosed magnetic stirring bars. Reaction flasks and storage containers were attached to a metal manifold described elsewhere.[12] The weighed glass reactor was loaded with about 0.20 g. of NaF or KF and heated at 350° overnight under high vacuum and weighed. About 5 ml. of C_7F_{16} was distilled onto the NaF or KF. With an ice bath surrounding the reactor, the suspension was magnetically stirred, and about 2.5 g. of UF_6 was distilled into the reaction vessel. The valve was closed, and the reaction was allowed to proceed under various conditions. The unreacted UF_6 and the C_7F_{16} were then distilled off under reduced pressure until constant weight was obtained. The extent of conversion of the alkali fluoride to UF_6 complex was determined from the increase in weight of the starting materials. Occasionally the reactor was opened in a drybox, and a small amount of the

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

(3) H. Martin and A. Albers, *Naturwissenschaften*, **33**, 370 (1946).

(4) H. Martin, A. Albers, and H. P. Dust, *Z. anorg. allgem. Chem.*, **265**, 128 (1951).

(5) R. E. Worthington, United Kingdom Atomic Energy Authority, IGR-R/CA 200, 1957.

(6) G. I. Cathers, M. R. Bennett, and R. L. Jolley, *Ind. Eng. Chem.*, **50**, 1709 (1958).

(7) F. Massoth and W. E. Hensel, Jr., *J. Phys. Chem.*, **62**, 479 (1958).

(8) I. Sheft, H. H. Hyman, R. M. Adams, and J. J. Katz, *J. Am. Chem. Soc.*, **83**, 291 (1961).

(9) S. Katz, *Inorg. Chem.*, **3**, 1598 (1964).

(10) N. S. Nikolaev and V. F. Sukhoverkhov, *Dokl. Akad. Nauk SSSR*, **136**, 621 (1961).

(11) B. Volavsek, *Croat. Chem. Acta*, **33**, 181 (1961).

(12) B. Weinstock and J. G. Malm, *J. Inorg. Nucl. Chem.*, **2**, 380 (1956).