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better vibrational and rotational constants will evolve; further studies of this molecule are in progress.

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Separation of Boron Isotopes.* VIII. BF_3 Addition Compounds of Dimethyl Ether, Dimethyl Sulfide, Dimethyl Selenide, Dimethyl Telluride, Dibutyl Ether, and Ethyl Formate

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Studies were made of the physical and chemical properties of molecular addition compounds formed by BF_3 and Group VIb donors. The dimethyl telluride complex was too unstable to exist at temperatures above −30°C. The freezing point of the 1:1 dimethyl selenide·BF_3 compound was −43°C. From room temperature to its freezing point, the saturation pressure of the 1:1 dimethyl selenide complex was given by $\log_{10} P=9.945-(1824/T)$. The 1:1 butyl ether and ethyl formate complexes formed at 25°C but deteriorated slowly with the formation of noncondensible gases. The freezing points of these complexes were −30° and −8°C, respectively. Between room temperature and their freezing point, the saturation pressures of freshly prepared $Bu_2O\cdot BF_3$ and $HCOOEt\cdot BF_3$ were given by $\log P=5.65-(1010/T)$ and $\log P=5.70-(1330/T)$, respectively. For the same temperature range, the equilibrium constant for the isotopic exchange reaction

$$^{10}BF_3(g)+A\cdot{}^{11}BF_3(l)={}^{11}BF_3(g)+A\cdot{}^{10}BF_3(l)$$

was given by $\log K_{eq}=(8.13/T)-0.0131$, when A was dimethyl selenide and $\log K_{eq}=(1.6/T)+0.0059$, when A was dibutyl ether. Previously reported equilibrium constants for the Me_2O and Me_2S exchange reactions were redetermined: for Me_2O, $\log K_{eq}=(8.76/T)-0.0179$, and for Me_2S, $\log K_{eq}=(10.7/T)-0.0200$. Related thermodynamic data were also computed.

INTRODUCTION

A SYSTEMATIC study has been undertaken of the exchange of boron isotopes between BF_3 gas and a molecular addition compound, $A\cdot BF_3$, where A is one of a variety of Lewis bases. In previous studies a search was made for donors whose use resulted in the largest isotopic equilibrium constants for the exchange reaction. In the present study, we sought to gain additional insight into the factors influencing isotopic fractionation by comparing the behavior of similarly substituted chalcogen donors. To provide a common basis of comparison, previously reported factors for the Me_2O system were recomputed, and additional experimental determinations were made of the isotopic fractionation occurring in the Me_2S system.

EXPERIMENTAL

Methods and Materials

The Analytical Chemistry Division of Oak Ridge National Laboratory supplied both the dimethyl selenide and the dimethyl telluride used in these experiments. The method of Bird and Challenger[1] was utilized to prepare the selenide: sodium selenide was first formed by treating metallic selenium with sodium formaldehyde sulfoxylate in aqueous solution. Methyl iodide was then added to this product to form methyl selenide by metathesis. The crude dimethyl selenide was removed by distillation. After purification, the dimethyl selenide boiled at 58°C (760 torr) and had the following composition:

Element	% Found	% Theoret.
C	21.9	22.0
H	5.5	5.55
Se	72.6	72.4 .

The dimethyl telluride was prepared from metallic tellurium and methyl iodide as directed by Vernon.[2] The resulting dimethyl telluronium di-iodide was then treated with hydrated sodium sulfite and sodium car-

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[1] M. L. Bird and F. Challenger, J. Chem. Soc. **1942,** 570.
[2] R. H. Vernon, J. Chem. Soc. **117,** 86 (1920).

bonate to produce $(CH_3)_2Te$. The composition of the telluride thus prepared was:

Element	% Found	% Theoret.
C	15.5	15.2
H	3.8	3.8
Te	76.7	80.9 .

The boiling point of the product was 92°–93°C (760 torr).

Boron trifluoride for these experiments came from the same batch as that for earlier determinations; it was treated as previously described.[3]

The dimethyl sulfide was furnished by Crown Zellerbach Corporation, Camas, Washington. It was purified as in earlier experiments.[4]

The dibutyl ether and ethyl formate were white label Eastman Kodak Company products. Both were dried by azeotropic distillation and fractionally distilled before use.

The techniques and equipment used in the present study were similar to those described previously.[3,4]

RESULTS AND DISCUSSION

Saturation-Pressure Measurements

Over the temperature range, +25° to −30°C, only trace quantities of BF_3 were absorbed by dimethyl telluride. If the molecular addition compound formed at all, it was highly dissociated at these temperatures. Two indications of irreversible decomposition were noted: (1) immediately upon the addition of BF_3, the solution assumed a brilliant red hue, and (2) a volatile orange-colored sublimate quickly formed on the wall of the reaction vessel above the liquid phase.

The addition of BF_3 to dimethyl selenide was more successful. Solutions were formed containing 1 mole of BF_3 per mole of donor. There was no visible evidence of irreversible decomposition. Saturation pressures of several mixtures of BF_3 and dimethyl selenide were measured over the temperature range +30° to −35°C. Variables, a and b, of the equation $\log P = a - (b/T)$ were fitted to the data by the method of least squares. Results of these calculations are tabulated in Table I along with results previously obtained for the $Me_2O \cdot BF_3$ and the $Me_2S \cdot BF_3$ complexes.[5,6]

Both Bu_2O and HCOOEt added BF_3 readily and with little visible change other than a slight discoloration. However, the measured saturation pressures of these compounds were not reproducible, and it was soon evident that a slow, irreversible decomposition was occurring, even near the freezing points of the complexes. The saturation pressures of freshly prepared solutions of these complexes are given in Table I.

From the temperature dependence of the vapor pressures of pure Me_2Se and Me_2S, estimates of −7.5 and −7.1 kcal $mole^{-1}$ were obtained for the heat of vaporization of these solvents.

Similarly, the changes of enthalpy for the exothermic reactions,

$$BF_3(g) + \text{donor}\ (l) = \text{donor} \cdot BF_3(l), \qquad (1)$$

were estimated: Me_2O, −12.7; Me_2S, −10.2; Me_2Se, −8.3; HCOOEt, −6; and Bu_2O, −5 kcal $mole^{-1}$. Since all of these complexes except $Me_2O \cdot BF_3$ are completely dissociated in the vapor phase, the principal contribution to the ΔH term should be due to the formation of the coordinate bond in the complex. Accordingly, we took the ΔH estimate as a first approximation of the strength of this bond in the various complexes. On this basis it may be seen from the above data that the boron–ligand bond strength decreases in the order $Me_2O > Me_2S > Me_2Se > HCOOEt \geq Bu_2O$. The order of the dimethyl-substituted donors is as expected from a consideration of donor radii and is in agreement with quantitative determinations obtained through the use of other techniques.[5] The position of Bu_2O with respect

TABLE I. Saturation pressures of the $Me_2Se \cdot BF_3$, $Me_2S \cdot BF_3$, $Me_2O \cdot BF_3$, $Bu_2O \cdot BF_3$, and $HCOOEt \cdot BF_3$ complexes from the freezing point to room temperature, $\log P = a - (b/T)$.

Donor	Solution composition (moles BF_3/mole donor)	a	b	Reference
Me_2Se	0	7.861 ±0.008	1643 ±36	
	0	7.747	1610	5
	0.09	9.552 ±0.004	2013 ±16	
	0.36	10.376 ±0.005	2146 ±23	
	0.42	10.215 ±0.004	2084 ±9	
	0.93	10.444 ±0.004	1991 ±21	
	1.00	9.945 ±0.005	1824 ±20	
Me_2O	1.00	9.806	2775	6
Me_2S	0	7.878 ±0.009	1546 ±5	
	0.99	10.164 ±0.001	2209 ±70	
	1.00	9.806	2227	5
Bu_2O	1.0	5.65	1010	
HCOOEt	1.0	5.70	1330	

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[3] A. A. Palko, J. Chem. Phys. **30**, 1187 (1959).

[4] A. A. Palko and J. S. Drury, J. Chem. Phys. **33**, 779–781 (1960).

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

[6] D. E. McLaughlin and M. Tamres, J. Am. Chem. Soc. **82**, 5618 (1960).

TABLE II. Isotopic equilibrium constants and related thermodynamic data for the reaction $^{10}BF_3(g)+A\cdot{}^{11}BF_3(l)={}^{11}BF_3(g)+A\cdot{}^{10}BF_3(l)$, $\log K_{eq}=(b/T)-a$.

Donor (A)	a	b	$-\Delta H$ (cal mole^{-1})	$-\Delta F_{30}$ (cal mole^{-1})	$-\Delta S$ (eu)	K_{eq}		mp of 1:1 compound (°C)
						30°C	0°C	
Me_2O	0.018±0.005	8.8±1.5	40	15	0.08	1.026	1.033	−12
Bu_2O	(−0.0059)	(1.6)	(7)					−30
Me_2S	0.020±0.004	10.7±1.1	49	22	0.09	1.037	1.046	−20
Me_2Se	0.013±0.001	8.1±0.36	37	19	0.06	1.033	1.040	−43

to HCOOEt as well as the position of both with respect to the dimethyl-substituted donors may be explained by steric considerations. In the HCOOEt complex, boron trifluoride is probably coordinated to the ether-linked oxygen.[7] In such a model, weakening of the donor–boron bond would be expected because of the substantial degree of interference which occurs with the terminal carbon of the ethyl group. In the Bu_2O complex, the presence of two bulky butyl groups—each having an interfering β-carbon atom—appears to weaken the donor–ligand bond in the $Bu_2O\cdot BF_3$ complex to an even greater extent. It should be noted that the steric influence in $Bu_2O\cdot BF_3$ is opposed by the inductive effect which, in the absence of the former, would tend to make the coordinate bond in the $Bu_2O\cdot BF_3$ complex stronger than that in $Me_2O\cdot BF_3$. Thus, in the $Bu_2S\cdot BF_3$ complex, where the larger size of the S atom affords a greater degree of freedom from steric interference, the inductive effect is dominant and the coordinate bond in the $Bu_2S\cdot BF_3$ complex is slightly stronger than that in $Me_2O\cdot BF_3$ (12.8 vs 12.7 kcal/mole).[3,7]

Freezing-Point Measurements

The dimethyl selenide addition compound was a pale, straw-colored liquid which froze to a clear crystalline solid at −43°C. This value was obtained from cooling curves of the 1:1 complex as well as from direct observations.

The butyl ether and ethyl formate complexes were colorless, viscous liquids which froze to clear crystalline solids at −30° and −8°C, respectively. Upon standing, the ether complex soon developed a yellow color characteristic of irreversible decomposition. The ester complex did not exhibit this behavior. The liquid ether complex dissolved a considerable amount of BF_3 in excess of that required for the 1:1 compound. The freezing points of the dimethyl-substituted ether, sulfide, and selenide complexes were linearly related to their molecular weight. From an extrapolation of this curve, it may be seen that the freezing point of the hypothetical dimethyl telluride molecular addition compound should be near −65°C.

Isotopic-Equilibrium-Constant Measurements

Measurements were made of the equilibrium constants for the isotopic exchange reactions

$$^{10}BF_3(g)+A\cdot{}^{11}BF_3(l)={}^{11}BF_3(g)+A\cdot{}^{10}BF_3(l) \quad (2)$$

where A was dimethyl selenide, dimethyl sulfide, or dibutyl ether. In each case the light isotope of boron concentrated in the liquid phase. Results of these measurements, as well as revised values for dimethyl ether–BF_3 system, are given in Table II, along with values for related thermodynamic functions.

The variables a and b in Table II represent the least-squares fit of straight lines to the experimental data between the freezing points of the molecular addition compounds and 35°C. The maximum error for all complexes except $Bu_2O\cdot BF_3$ was estimated to be ±0.003 or less. The data for the $Bu_2O\cdot BF_3$ reaction were quite scattered, presumably because of irreversible decomposition, and should be considered qualitative in nature. Nevertheless, it seems safe to conclude that the equilibrium constant for the $Bu_2O\cdot BF_3$ exchange reaction is equal to, or slightly smaller than, that for the $Me_2O\cdot BF_3$ complex at the same temperature. (Thus, at 20°C our estimate of the equilibrium constant for the $Bu_2O\cdot BF_3$ reaction is 1.025. Ribnikar[8] reports 1.029.) Further, it seems reasonably well established that the equilibrium constants for reactions with different donors vary in the following manner: $Me_2S>Me_2Se>Me_2O>Bu_2O$. This sequence differs from that expected on the basis of stabilities deduced from observed saturation pressures, and our rule[9] that equilibrium constants for Reaction (2) vary inversely with the strength of the boron–donor bond. From these considerations, the expected order would be $Me_2Se>Me_2S>Me_2O\geq Bu_2O$.

From the standpoint of our rule, the position of the Me_2Se complex is surprising and requires explanation.

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[7] H. C. Brown, H. I. Schlesinger, and A. B. Burg, J. Am. Chem. Soc. **61**, 673 (1939).

[8] S. V. Ribnikar, Proc. Intern. Symp. Isotope Separation, Amsterdam 1957, 206 (1958).

[9] A. A. Palko and J. S. Drury, J. Chem. Phys. **40**, 278 (1964).

Thus, for a simplified two-atom model,[10] the donor–boron force constant should decrease and the equilibrium constant for Reaction (2) should increase as the size of the donor atom increases. A quantitative assessment of the failure of the selenide molecule to respond in the expected manner requires spectroscopic data not yet obtained. However, we believe the anomaly may be understood qualitatively in terms of two opposing effects whose contributions to the isotopic equilibrium constants for Reaction (2) vary with increasing size of the donor atom. These effects are: (1) the electron-pair donating powers of the donor atoms which decrease with increasing radii, and (2) the polarizabilities of the donor atoms which increase with increasing radii. For oxygen, the first effect is quite strong,[11] and the second is quite weak.[12] A strong boron–donor bond is thus formed and the resulting isotopic equilibrium constant is relatively small. For sulfur, the electron-pair donating power is sharply reduced and the polarizability is increased. The net effects are a boron–donor bond weaker than that with oxygen and an increase in the value of the isotope equilibrium constant for Reaction (2). For selenium, the electron-pair donating power is somewhat smaller than for sulfur, but the large increase in polarizability of this atom permits sufficient incremental overlap of the orbitals along the coordinate bond axis that a bond results which is slightly stronger than with sulfur. This stronger bond results in an isotopic equilibrium constant slightly smaller than that for the sulfur complex, but larger than that for the oxygen complex.

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[10] The two-atom model is convenient for discussion and leads to conclusions which are qualitatively valid. Valid quantitative conclusions require complete spectroscopic analysis of the participating molecules, as it is well known that the asymmetric B–F stretches, rather than the symmetric boron–donor stretch, make the major contributions to the pertinent vibrational partition functions.

[11] H. P. Fritz and H. Keller, Chem. Ber. **94**, 1524 (1961).

[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 951ff.

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Forbidden Transitions in Molecular Crystals: The Cameron System of Solid α-CO

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A crystal splitting has been observed in the (0, 0) band of the Cameron system ($a\,^3\Pi \leftarrow X\,^1\Sigma^+$) of solid α-CO at 20°K, using a well-annealed sample. We believe that this is the first reported example of a triplet exciton splitting in a nonaromatic, the only previously reported examples having been in naphthalene and *p*-di-iodobenzene. A spin–orbit calculation has been carried out which demonstrates that the spectroscopic activity of this transition is primarily due to spin–orbit mixing of the $^3\Pi_1$ and $^1\Pi_1$ levels of the $a\,^3\Pi$ and $A\,^1\Pi$ states, respectively. The same calculation shows that the mixing of the ground and first triplet states can give intensity to this transition, but such intensity will be many times less than that induced via the first mechanism.

The electric-dipole character gained by the transition is insufficient to account for the observed splitting, i.e., as a Davydov splitting. Instead, it is concluded that molecules undergoing this transition are coupled via an intermolecular-exchange interaction. An estimate of the magnitudes of the exchange integrals in solid CO, relative to those in aromatic crystals, results in a prediction of a triplet exciton splitting for CO which is of the order of magnitude of the observed splitting. A vibronic interaction mechanism within the CO crystal may also account for the splitting. Experiments are discussed which can distinguish between the two coupling mechanisms and which can confirm one or the other as that responsible for the observed splitting.

INTRODUCTION

THE utility of absorption spectroscopy in condensed states has been well established, its principal advantage being, of course, the absence of molecular rotation and its concomitant complicating spectral features. Rotational fine structure in gas-phase spectra (when resolved) is, of course, of great benefit to the spectroscopist. It may be used to determine whether the observed transition is electronically allowed or vibronically induced. In favorable cases, the polarization of the transition may be identified, and thus the assignment (specification of the combining terms) may be completed. In the best of circumstances, parameters of molecular geometry may be evaluated. Except when very high-resolution instrumentation is available, such determinations are frequently subject to considerable error, both experimental and interpretive.

Condensation usually results in more bothersome spectral effects than the simple quenching of rotation. In the gas phase the only routes available to the molecule for relaxation are emission, internal conversion, and inelastic collision. In the solid state there will be, in principle, a whole new set of internal states available