values of Dq and B' is observed. These results, in addition to those reported by Cotton, *et al.*,[5] and by Madan, *et al.*,[25,26] for sulfur donors, illustrate that this concept is valid for a large number of pseudo-tetrahedral cobalt(II) complexes.[27-29] This agreement is indeed surprising because low-temperature mull spectra exhibit splitting of the near-infrared band greater than can be expected from spin–orbit coupling suggesting a low-symmetry component. The high-energy band has at least six components.

Solid-State Behavior of the Complexes.—While the solid-state and solution electronic spectral data for $Co(TMNO)_4^{2+}$ are essentially identical, there are differences in the same sets of data for the $Co(TMNO)_2X_2$ complexes (Table II). While the moments are in the range expected for tetrahedral cobalt(II) (Table VI), with the exception of the thiocyonate complex, values calculated for λ' (after correcting for TIP[5]) are higher than those normally calculated for tetrahedral cobalt(II) complexes,[5] being even higher than the gas-phase value. This indicates inappropriate use of the model for T_d complexes on these lower symmetry complexes and renders the interpretations of λ' values for other than T_d complexes questionable. Even then, accurate magnetic moments are needed. The λ' value for the $Co(TMNO)_4^{2+}$ species (-158 cm^{-1}) is in the normal range[5] of 130–170 cm^{-1} usually encountered.

In other pseudo-tetrahedral cobalt(II) complexes of the type CoL_2X_2 (L = pyridine, HMPA, triphenylphosphine) it was found that the positions of maximum absorbance did not change upon change of state. The spectral data are not indicative of halide bridging, as is the case with $Co(py)_2Cl_2$ (py = pyridine),[13] but evidently lattice effects are causing changes in the ligand fields around the cobalt(II) ion.

Acknowledgment.—The authors gratefully acknowledge the generous support of this research by the Atomic Energy Commission through Contract No. AT(11-1)-758.

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[25] S. K. Madan and M. Sulich, *Inorg. Chem.*, **5**, 1662 (1966), and the references therein.

[26] S. K. Madan and D. Mueller, *J. Inorg. Nucl. Chem.*, **28**, 177 (1966).

[27] It is interesting to note that a study of $Co(DMA)_2X_2$ (DMA = N,N-dimethylacetamide, X^- = halide) complexes[28] yields Dq values for DMA which are much smaller than those observed in $Co(DMA)_4^{2+}$. Spectral and magnetic evidence have been presented for the four-coordinated complex[29] to indicate possible distortion from a tetrahedral configuration. This discrepancy in average-field Dq values is consistent with such findings.

[28] S. K. Madan and A. M. Donohue, *J. Inorg. Nucl. Chem.*, **28**, 1617 (1966).

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Gas-Phase Enthalpies of Adduct Formation: Dimethylamine–Chloroform and Ethyl Acetate–Boron Trifluoride

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The gas-phase thermodynamic data for formation of the adduct of ethyl acetate with boron trifluoride and for the hydrogen-bonding interaction of chloroform with dimethylamine are reported. For the chloroform–dimethylamine adduct an enthalpy of dissociation, $\Delta H_D = 5.8 \pm 1.1$ kcal/mol, and an entropy of dissociation, $\Delta S_D = 22.5$ eu, were obtained. Values of $\Delta H_D = 12.8 \pm 0.7$ kcal/mol and $\Delta S_D = 37$ eu were obtained for the ethyl acetate–boron trifluoride adduct. Toward chloroform, dimethylamine is a stronger donor than triethylamine. Previously,[4] we have been able to assign two parameters to an acid, E_A and C_A, and two to a base, E_B and C_B, which when substituted into the following equation reproduce the enthalpy of adduct formation: $-\Delta H = E_AE_B + C_AC_B$. The systems reported here have been incorporated into this correlation and some interesting insight into the existence of steric effects in the donor–acceptor interactions is provided.

Introduction

In contrast to the many studies on donor–acceptor interactions in solution, relatively little work has been reported on such systems in the gas phase. Limitations on volatility of reactants and adducts, difficulties in purchasing or constructing the requisite high-vacuum equipment, and operational problems all mitigate against gas-phase measurements when other methods are available. Yet gas-phase thermodynamic data are singularly important, particularly for testing the common assumption that solvation effects can be neglected (here, specifically, for donor–acceptor interactions) if a nonpolar solvent is employed. These studies were initiated, in part, to provide a test for this assumption. At that time we knew of no studies providing reliable thermodynamic data for adduct formation both in the gas phase and in solution. Subsequent to the completion of this work, reports appeared[2,3] indicating that similar enthalpies are obtained in the gas phase and in carbon tetrachloride or hexane solution. This evidence supported the use of data obtained in these nonpolar solvents along with gas-phase data for correla-

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[1] Abstracted in part from the Ph.D. theses of L. J. Sacks and D. P. Eyman, University of Illinois, Urbana, Ill., 1964.

[2] J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

[3] F. T. Lang and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965).

tion of enthalpies of interaction.[4] Empirical constants C_A, C_B, E_A, and E_B were determined to predict enthalpies of reaction (within 0.2 kcal/mol) according to the equation

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

where A and B refer to acceptor and donor, respectively. In the formalism employed, it was tentatively proposed that C represents the covalent and E the electrostatic parts of the interaction.[4] The E and C parameters are quite complex and include reorganization and electron–electron repulsion energies.

Chloroform was chosen as the reference acid for the study of hydrogen bonding in the gas phase for several reasons: (1) it was reported[5] and is confirmed by our isochores to be essentially unassociated in the gas phase under conditions of our experiment; (2) it offers but a single hydrogen-bonding site; (3) reported[6–11] enthalpies of its hydrogen bonding ability are available from a variety of methods and we felt some of these results were questionable;[7,8] (4) reported heats for such reactions (*ca.* 5 kcal/mol for strong donors) suggested that these interactions would be quite weak and thus would provide a rigorous test for any use to which our apparatus might be put; (5) the equilibrium constant for chloroform adducts is generally small and such large excesses of base are needed in the solution studies that one can question whether the excess base or "inert" solvent is the solvent. Consequently, in order to incorporate $CHCl_3$ into the E and C correlation, it is desirable to have at least one gas-phase enthalpy.

As an immediate application, we had earlier predicted,[12] and this prediction is borne out by the magnitude of the E parameters,[4] that triethylamine would be a weaker donor than diethylamine toward an acid where the electrostatic interaction dominated. Chloroform is such an acid and this reversal in donor order is predicted from a consideration of the E and C factors and does not invoke any consideration of the steric factors often employed to account for such reversals.

Data for the interaction of boron trifluoride with ethyl acetate are also presented. The incorporation of BF_3 into our correlation is discussed.

Experimental Section

A. Apparatus.—The manometer illustrated in Figure 1 was attached to the reactor bulb and to a vacuum line. The reactor bulb and manometer were contained in an insulated vapor jacket. Constant temperature was maintained by refluxing a suitable pure liquid at a preset, subatmospheric pressure in the gas-tight vapor jacket surrounding the reactor. For temperatures below about 70°, carbon tetrachloride was quite suitable, chlorobenzene was satisfactory from 70 to 125°, and *o*-dichlorobenzene was used for temperatures up to about 170°. The jacket and pressure regulator are similar to those described by McLaughlin and Tamres[13] except that O-ring joints are used instead of ball and socket joints for connecting the dome and boiling pot to the jacket and through-tubes rather than ring seals are used to obtain entry through the dome.

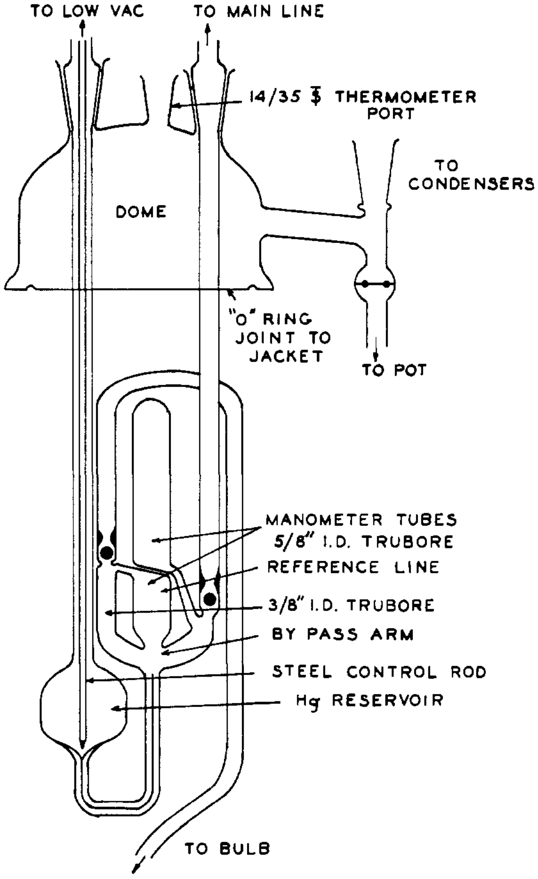

Figure 1.—Schematic of reactor manometer unit.

The manometer design of Brown and Gerstein[14] appeared to offer greatest accuracy by allowing a single, vertical measurement, avoiding the error incurred in our system (*ca.* 0.04 mm) when the cathetometer was swung from one manometer arm to the other. A major limitation of their instrument is the large unusable region (20 mm) at the top of the lower bulb and bottom of the upper bulb where the side arms are joined. By using a by-pass system, we have been able to reduce this unusable region to less than 10 mm, greatly extending the usefulness of the apparatus without reducing transfer times appreciably. Another advantage of this design is the single mercury reservoir which not only regulates the mercury for the manometer but also operates two check valves, one to the reactor bulb (to prevent accidental blow-over) and the other to the vacuum line (to maintain a saturated mercury vapor over both arms of the manometer). Precision-bore tubing of $^5/_8$-in. i.d. was used to minimize distortion and simplify corrections for meniscus height variation.[15] A modification of the unit shown provides a side-arm manometer for (less precise) measurements at pressures below 10 torr.

It was estimated that pressure readings could be reproduced within an error of 0.01 torr. Since the thermostat required reflux for effective temperature control, operation was limited at the lower end of the scale to about 5° above ambient. The

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[4] R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

[5] J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949). A dipole–dipole interaction for chloroform of 860 cal/mol is based on second virial coefficient interpretation of *P–T* data. However, at room temperature, the interaction, even if real, would not cause appreciable deviation from ideal gas behavior.

[6] C. J. Creswell and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1723 (1963).

[7] J. H. P. Fox and J. D. Lambert, *Proc. Roy. Soc.* (London), **A210**, 557 (1951).

[8] J. D. Lambert, J. S. Clarke, J. F. Duke, C. L. Hicks, S. D. Lawrence, D. M. Morris, and M. G. T. Stone, *ibid.*, **A249**, 414 (1956).

[9] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

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[11] R. E. Kagarise, *Spectrochim. Acta*, **19**, 629 (1963).

[12] R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

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

[14] H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

[15] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

weakness of the chloroform–dimethylamine interaction restricted the higher temperature limit so that only about a 20° range was accessible. Operation of the apparatus was similar to that described previously.[13] Equilibrium dissociation constants were calculated from the expression

$$K_p = \frac{(P_T - P^0_A)(P_T - P^0_B)}{P^0_A + P^0_B - P_T} \tag{2}$$

where P_T is the total experimental pressure for the mixture, and P^0_A and P^0_B are the pressures of the acceptor and donor at each temperature as calculated from the isochores. Enthalpies were calculated from the van't Hoff equation using a least-squares computer program.

B. Purification of Materials.—All materials were prepurified before transfer to the high-vacuum lines. Liquids were distilled in an all-Pyrex still consisting of a 12-in. vacuum-jacketed 6-mm o.d. column, fitted with a tungsten spiral, and a four-arm collector. Materials were introduced through a purification train to the storage part of the high-vacuum line. Final traces of volatiles were removed in all cases through the vacuum line until a static pressure over the frozen material (−196°) below 10^{-5} torr was obtained.

Boron trifluoride was purified *via* the benzonitrile adduct[16] which was made in a preparative vacuum line. The sample was sealed off and transferred to the vacuum line purification train and fractionated (vapor pressure 306 torr at −111°; lit. values: 300 torr,[16] 306.2 torr[17]).

Ethyl acetate was distilled and a fraction boiling at 76.2° (749 torr) (uncorrected) (lit.[18] 77.15° (760 torr)) was collected in a break-tip bulb. The sample was transferred to the purification train and the tip broken with the sample frozen out (−196°). After several freezing–thawing cycles for removal of gases, the material was purified by vacuum fractionation until isotenically homogeneous.

Reagent grade phosphoryl chloride (J. T. Baker) was evacuated before distillation under dry nitrogen and collected in a break-tip bulb [bp 104° (744 torr) (uncorrected)]. The sample was thawed, pumped, and refrozen twice to remove dissolved gases before transferal to the vacuum line.

Chloroform was shaken with Merck reagent grade (chromatographic) alumina; a portion was decanted and distilled into a break-tip bulb [bp 59.4° (734 torr); lit.[18] 61.3° (760 torr)]. The material was twice thawed, refrozen, and pumped to expel gases and then fractionated in the purification train. Before use, about the first 10% of the material (vapor pressure 61 torr at 0°) was transferred to another storage bulb and the next fraction was used (all remaining material had a vapor pressure of 60.5 torr at 0°; lit.[18] 61.0 torr at 0°).

Dimethylamine was transferred from a cylinder directly to the purification train. It was fractionated several times and the center cut of each fractionation was retained (vapor pressure 2 torr at −78°, 125 torr at −30.7°, 565 torr at 0°; lit.[19] 561 torr at 0°).

Results

(1) **Boron Trifluoride–Phosphoryl Chloride.**—The isochore for a sample of boron trifluoride sufficient to produce a pressure of about 15 torr at 25° was obtained. A slightly larger portion of phosphoryl chloride was similarly measured and the mixture was examined at 83 and 34°. No significant pressure decrease (0.01 torr) over that calculated for the mixture was found.

(2) **Boron Trifluoride–Ethyl Acetate.**—The BF_3 isochore was measured at four temperatures over the range 80–100°. The P/T ratio was (2.408 ± 0.003) × 10^{-2} torr/deg, corresponding to a pressure of 6.577 torr at 0°. The ethyl acetate isochore was measured at four temperatures over the range 70–100°. The P/T ratio was (2.3340 ± 0.005) × 10^{-2} torr/deg, corresponding to pressure of 6.376 torr at 0°.

In a second experiment the isochore for a new sample of BF_3 was measured at four temperatures over the range 50–70°. The P/T ratio was (2.539 ± 0.003) × 10^{-2} torr/deg, corresponding to a pressure of 6.936 torr at 0°. The ethyl acetate isochore, measured at four temperatures over the range 50–70°, gave the P/T ratio (2.371 ± 0.006) × 10^{-2} torr/deg, corresponding to a pressure of 6.477 torr at 0°. Isochores for the mixture are on file with the ADI.[20] The results are presented in Figure 2. From a least-squares treatment, $\Delta H_D = 12.8 \pm 0.7$ kcal/mol at the 90% confidence level and $\Delta S_{D,298} = 37$ eu, from which arises

$$\log K_D = \frac{2798.9}{T} + 10.923$$

(K_D in torr), corresponding to $K_D(25°) = 34.8$ torr (4.6×10^{-2} atm).

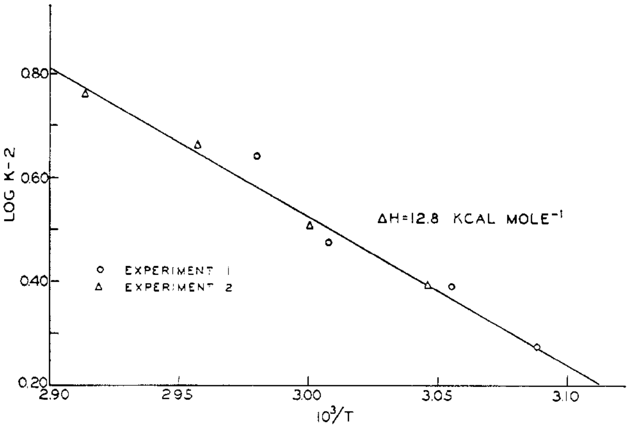

Figure 2.—Interaction of boron trifluoride with ethyl acetate.

(3) **Chloroform–Dimethylamine.**—The isochore for a chloroform sample was obtained at five temperatures over the range 19–49°; $P/T = (14.389 \pm 0.020) \times 10^{-2}$ torr/deg, corresponding to a pressure of 39.304 torr at 0°. The dimethylamine isochore was obtained at 11 temperatures over the range 10–64°; $P/T = (15.364 \pm 0.015) \times 10^{-2}$ torr/deg, corresponding to a pressure of 41.968 torr at 0°. The P–T data for the mixture of the two samples are filed with the ADI.[20] A least-squares treatment of K_D *vs.* $1/T$ (Figure 3) gives $\Delta H_D = 6.36 \pm 0.5$ kcal/mol at the 90% confidence level and $\Delta S_D = 24$ eu, from which arises

$$\log K_D = \frac{1390}{T} + 8.22$$

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

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

(18) H. R. Raikes and E. J. Bowen, "International Critical Tables," Vol. III, National Research Council, McGraw-Hill Book Co., Inc., New York, N. Y., 1933, p 214.

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(20) Material supplementary to this article has been deposited as Document No. 10016 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

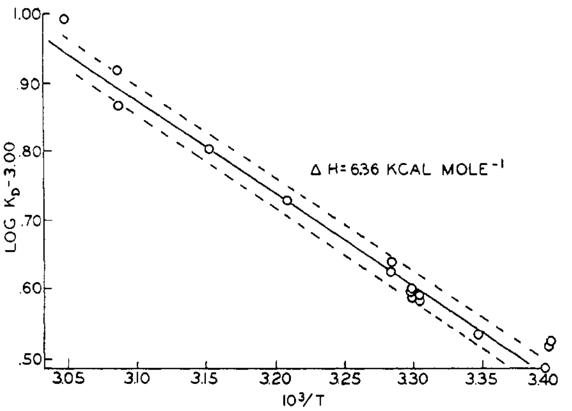

Figure 3.—Interaction of dimethylamine with chloroform.

(K_D in torr), corresponding to $K_D(25°) = 3.50 \times 10^3$ torr (4.6 atm).

In a second experiment, the isochore for a second chloroform sample was obtained at two temperatures, 29 and 44°. The mean P/T ratio for several measurements at each temperature was $(10.408 \pm 0.006) \times 10^{-2}$ torr/deg, corresponding to a pressure of 28.430 torr at 0°. The dimethylamine isochlore was obtained at five temperatures in the range 30–49°. The mean P/T ratio was $(10.413 \pm 0.006) \times 10^{-2}$ torr/deg, corresponding to 28.444 torr at 0°. The mixture of reactants was measured at ten temperatures in the range 21.7–54.1°. The least-squares treatment of K_D *vs.* $1/T$ gives $\Delta H_D = 5.2 \pm 0.7$ kcal/mol at the 90% confidence level and $\Delta S_D = 21$ eu, from which arises

$$\log K_D = \frac{1136}{T} + 7.43$$

(K_D in torr), corresponding to $K_D(25°) = 4.16 \times 10^3$ torr (3.7 atm).

Discussion

As can be seen from the results of the $(CH_3)_2NH$–$CHCl_3$ system, the predicted[12] reversal in donor strength of secondary and tertiary amines toward an acid with which the interaction is predominantly electrostatic is borne out. From a statistical treatment of combined data sets, the enthalpy value found in this study for formation of the adduct $(CH_3)_2NH$–$HCCl_3$ is -5.8 ± 1.1 kcal/mol and that previously reported[6] for $(C_2H_5)_3N$–$HCCl_3$ is -4.2 ± 0.2 kcal/mol.

Table I contains a summary of the E and C numbers for donors that will be considered in the discussion.

TABLE I

REPORTED E AND C NUMBERS FOR VARIOUS DONORS

Donor	E_B	C_B	Donor	E_B	C_B
NH_3	1.34	3.42	$CH_3C(O)CH_3$	0.71	0.66
CH_3NH_2	1.19	6.14	$(CH_2)_4O$	0.61	4.69
$(CH_3)_2NH$	0.94	8.68	$(C_2H_5)_3N$	0.65	11.35
$(CH_3)_3N$	0.59	11.61	$(C_2H_5)_2NH$	0.94	8.76

The E parameters for the amines are seen to be consistent with the qualitative interpretation of the electrostatic order.

Substituting the appropriate E_B and C_B values reported in Table I and the corresponding enthalpies of adduct formation of chloroform with triethylamine,[9] dimethylamine, acetone,[11] and tetrahydrofuran[6] into eq 1, one can solve the simultaneous equations for the values of C_A and E_A for chloroform. Two enthalpies of formation provide checks and two are forced to fit, for there are two unknowns.[21] The resulting values are $E_A = 5.03$ and $C_A = 0.096$. The experimental and calculated enthalpies are compared in Table II.

TABLE II

ENTHALPIES OF CHLOROFORM ADDUCT FORMATION AND THOSE CALCULATED FROM EQ 1

Donor	$\Delta H°$, kcal/mol	
	Exptl	Calcd
$(CH_3)_2CO$	−3.5	−3.6
$(CH_3)_2NH$	−5.8	−5.6
$(C_2H_5)_3N$	−4.2	−4.3
$(CH_2)_4O$	−3.6	−3.5

The parameters for $CHCl_3$ are such that the E terms for the amine donors are most important in determining the donor order. In contrast to this acid, $E_A = C_A = 1$ for iodine and the trend in the C_B term dominates. Consequently, $(CH_3)_3N$ is the strongest donor of the methyl-substituted aliphatic amines and the enthalpy of adduct formation with iodine is greater for $(C_2H_5)_3N$ than for $(CH_3)_2NH$. Toward phenol, where both electrostatic and covalent[22] contributions are significant, the enthalpies of adduct formation are about the same. As discussed in our original article, the excellent agreement of calculated and experimental enthalpies precludes the existence of steric effects in these adducts. Thus, the weaker donor strength of triethylamine toward chloroform is rationalized by the E and C model without recourse to steric effects between the donor and acceptor.

The enthalpy for formation of the C_6H_6–$HCCl_3$ adduct calculated with previously reported E and C numbers for benzene ($C_B = 1.36$ and $E_B = 0.14$) is not in agreement with the measured enthalpy. The E and C numbers for benzene were determined with an uncertain enthalpy for formation of the benzene–phenol adduct and are probably incorrect. Using the measured enthalpies of formation of the iodine and chloroform[6] adducts, values of $C_B = 1.12$ and $E_B = 0.38$ are calculated for benzene and a predicted value of −2.4 kcal/mol results for the benzene–phenol adduct.[23] In view of the limitations of spectrophotometric procedures on weak donor systems,[24] an nmr investigation of this system is essential to the incorporation of the donor, benzene, into this correlation.

The acid BF_3 is very difficult to incorporate into the E and C correlation. As mentioned in the original article[4] the correlation does not hold when there are

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[21] A computer program is employed to minimize the error and find a best fit for the four systems.

[22] The electrostatic–covalent formalism of R. S. Mulliken (*J. Am. Chem. Soc.*, **74**, 811 (1952)) is being used because of its conceptual simplicity. The same phenomena can also be described by molecular orbital model.

[23] T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967).

[24] P. H. Emski, R. Forster, C. A. Fybe, and I. Horman, *Tetrahedron*, **21**, 2843 (1965).

steric repulsions in the adduct. The studies of Tamres, *et al.*,[25] indicate that steric effects are very common in BF_3 adducts. These authors believed F strain was minimal in tetrahydrofuran (THF), and it should also be small in the BF_3–$CH_3C(O)OC_2H_5$ adduct. Using the gas-phase enthalpies of adduct formation of BF_3 with the donors THF, ethyl acetate, and dimethyl ether, we calculate E_A and C_A parameters of 11.6 and 1.98, respectively. These should be regarded as tentative in view of the limited amount of enthalpy data on BF_3 systems in which steric effects can be assumed to be minor. Since two enthalpies are needed to calculate E and C, we have only one check. The parameters reported for diethyl ether were taken for dimethyl ether, since those for the latter have not been evaluated. This assumption is based on the similarity of the E and C values for the analogous methyl- and ethylamines. The reported enthalpy of formation of the BF_3 adduct of diethyl ether is 2 kcal/mol lower than that of dimethyl ether[24] suggesting the likelihood of steric problems in the diethyl ether adduct. The calculated and experimental values are listed in Table III.

TABLE III

CALCULATED AND EXPERIMENTAL ENTHALPIES OF FORMATION OF BF_3 ADDUCTS

Donor	E_B	C_B	$\Delta H°$, kcal/mol Calcd	$\Delta H°$, kcal/mol Exptl
$(CH_3)_2O$[a]	0.65	3.55	−14.6	−13.7
$CH_3C(O)OC_2H_5$	0.83	1.67	13.1	−12.8
$(CH_2)_4O$	0.61	4.69	−16.4	−16.8

[a] E_B and C_B are the $(C_2H_5)_2O$ parameters.

The E_B and C_B parameters for $(C_2H_5)_2S$ when combined with E_A and C_A for BF_3 lead to a calculated enthalpy of −15.2 kcal/mol. This is in contrast with an experimental enthalpy of −2.9 kcal/mol. A tentative explanation that can be offered at present is a steric repulsion of the large sulfur atom and fluorines of BF_3. More thermodynamic data on carefully designed systems are needed before the behavior of BF_3 as an acid can be understood and be incorporated into the correlation with confidence.

Acknowledgment.—The authors wish to thank the National Science Foundation for their generous support of this research through Grant GP-5498.

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Nucleophilicity of Thioethers toward Neutral Platinum(II) Complexes

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The kinetics of the nucleophilic displacement of the ligand X from complexes of the type Pt(bipy)(C)X (C, X = Cl, Cl; N_3, Cl; NO_2, Cl; NO_2, NO_2; NO_2, N_3) by thioethers (RSR′) have been measured in methanol at 25°. The results permit the discussion of the effect of the nature of the entering group, of the leaving group, and of the *cis* effect. The rates of these reactions are compared with those of the same substrates with other reagents under the same experimental conditions and the differences are discussed in terms of the different role of the bond-making and bond-breaking aspects of the substitution in the intimate mechanism.

Introduction

The kinetics of ligand displacement in planar complexes of d^8 transition metal ions, particularly platinum(II) derivatives, have been studied extensively in the past few years.[1,2] It was suggested[3] that the intimate mechanism of square-planar substitution corresponds to an association between the substrate and the entering group to produce a labile intermediate of higher coordination number which then dissociates to give the four-coordinate product. There has been indirect evidence to support this hypothesis[4–6] but the only direct kinetic evidence was obtained[7] with a peculiar planar rhodium(I) complex. Therefore, in the majority of the cases, it is still necessary to decide whether the formation of the new bond (increase of coordination) or the breaking of the old one (decrease of coordination) is more important in controlling the rate of the reaction.

In order to elucidate this point we decided to investigate the kinetic behavior of thioethers acting as nucleophiles toward planar complexes, since the sulfur donors are expected to be relatively soft[8] and could favor the formation of relatively stable intermediates when interacting with soft reaction centers, such as platinum(II) complexes. There are data in the literature concerning the reactions of complexes of the type Pt(bipy)(C)X with a variety of reagents, which enable one to discuss (a) the effect of the nature of the leaving

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