and a values to curve c, Fig. 1 (hydrolysis of $Ir(OH_2)Cl_5^{-2}$ in water at 50°), suggesting that hydrolysis of $Ir(OH_2)Cl_5^{-2}$ in water at 50° is aquation and not base hydrolysis and further implying that the aquation rates in water and in 2.5 F $HClO_4$ are not grossly different. It was not feasible to carry out measurements of spectra on $K_2Ir(OH_2)Cl_5$ in solutions such as those of Tables I and II, owing to the limited solubility of this salt in 1–2.5 F $HClO_4$.

[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Thermodynamic Data for the Association of Phenol with N,N-Dimethylacetamide and N,N-Dimethylmonochloroacetamide

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Equilibrium constants and enthalpies for the formation of adducts of phenol with N,N-dimethylacetamide, DMA, and N,N-dimethylmonochloroacetamide, DMMCA, are reported. A procedure is indicated for the accurate determination of enthalpies. The heat of formation obtained for the DMA-phenol adduct is compared with enthalpies of formation for the adducts of ICl, I_2, SO_2 and Br_2 with the donor DMA. These acids are a series with widely differing polarizabilities and dipole moments. The effect of these parameters on the enthalpies of adduct formation is discussed qualitatively.

Introduction

In connection with research in this Laboratory concerning the acidity of ICl,[2] I_2,[3] SO_2[2] and Br_2,[2] it was of interest to extend the range of acids studied to include hydrogen bonding types. Phenol was selected because of its ease of handling and convenient ultraviolet absorption.

A large number of equilibrium constants for phenol–base interactions have been summarized by Pimentel and McClellan,[4] but very little reliable enthalpy data are available. In this article a general procedure for obtaining accurate enthalpy data is outlined. The results obtained with phenol as the acid are compared with the enthalpies obtained for some halogen acids and sulfur dioxide.

Experimental

Materials.—Fisher Spectranalyzed carbon tetrachloride was used without further purification. Purification of DMA has been described previously.[5] DMMCA, $ClCH_2CON(CH_3)_2$, was prepared from the corresponding chloroacetylchloride. The amide was fractionally distilled at about 2 mm. pressure, and the fraction boiling at 85° was collected.

Anal. Calcd. for $ClCH_2CON(CH_3)_2$: C, 39.52; H, 6.63; N, 11.52. Found: C, 39.62; H, 6.68; N, 11.47.

Baker and Adamson Reagent Grade phenol was distilled at atmospheric pressure. The fraction boiling at 182° was collected.

Apparatus.—Preliminary spectra were recorded with a Cary model 14M spectrophotometer. After selection of an appropriate wave length, a Beckman D.U. spectrophotometer equipped with a temperature controlled, forced air, heating system was employed for all measurements. The temperature of the solution was measured directly with a thermistor located in a well in the sample cell.

Sample Preparation.—Phenol and amide master solutions were prepared by weighing these materials in volumetric flasks and diluting with carbon tetrachloride. The sample solutions were prepared from aliquots of these stock solutions. Concentrations were corrected for volume changes at various temperatures. To avoid formation of polymeric species, phenol concentrations of $4 \times 10^{-3}M$ or less were used.

Procedure.—The following equation was derived[6] and employed for equilibrium constant calculations

$$K^{-1} = \frac{A - A^0 - A_D}{\epsilon_C - \epsilon_A - \epsilon_D} - C_A - C_D + \frac{C_A C_D(\epsilon_C - \epsilon_A - \epsilon_D)}{A - A^0 - A_D} \quad (1)$$

A, absorbance of system at a given wave length; A^0, absorbance due to initial phenol concentration; A_D, absorbance due to initial amide concentration; ϵ_C, molar absorptivity of complex; ϵ_A, molar absorptivity of phenol; ϵ_D, molar absorptivity of amide; C_A, initial concentration of phenol; C_D, initial concentration of amide. Its derivation is similar to that reported[7] for the case where A_D and ϵ_D are zero.

The quantity A–A^0 is obtained directly by measuring the absorbance difference of a carbon tetrachloride solution of phenol in the reference cell and a phenol–amide solution of similar total phenol concentration in the sample cell. The entire spectrum was traced in the ultraviolet region in order to find the optimum wave length for study, *i.e.*, the region of largest absorbance change. The phenol adduct absorbs in the same region as free phenol but the adduct has a higher molar absorptivity. Both donor systems exhibit the largest difference in absorbance at 284 and 277 mμ. Equilibrium constant and enthalpy measurements were made at 284, 277 and 288 mμ. Agreement in the values measured at all three wave lengths is obtained.

Two types of experiments were performed to obtain the thermodynamic data. In one, referred to hereafter as an equilibrium constant determination, the absorbance of each of several solutions was measured at constant temperature. The equilibrium constants and the values for $\epsilon_C - \epsilon_A - \epsilon_D$ were calculated from data obtained at several temperatures by use of equation 1.[7] In the other procedure, referred to as an enthalpy determination, very precise enthalpy results are obtained by measuring the absorbance change of a single solution as a function of temperature. The values for $\epsilon_C - \epsilon_A - \epsilon_D$ obtained at various temperatures from the equilibrium constant experiment are used in equation 1 for the calculation of the values of K in the enthalpy experiment.

The quantities A_D and ϵ_D were determined for the free amide at various temperatures.

In employing equation 1, one subtracts A_D from the $A - A^0$ readings and obtains the quantity $\epsilon_C - \epsilon_A - \epsilon_D$ from the K^{-1} *vs.* ϵ plot.[7]

Table I contains data on the temperature dependence of the molar absorptivities of DMMCA and phenol.

A negligible amount of error is introduced in the enthalpy calculations by neglecting variation in A_D with temperature at 284 and 288 mμ. This change cannot be neglected at 276 mμ.

The temperature dependence of the term $\epsilon_C - \epsilon_A - \epsilon_D$ was determined from equilibrium constant determinations at

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(1) Eastman Kodak Fellow, 1960–1961. Abstracted in part from the Ph.D. thesis of M. D. Joesten, University of Illinois (1962).

(2) R. S. Drago and D. A. Wenz, *J. Am. Chem. Soc.*, **84**, 526 (1962).

(3) R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, *ibid.*, **83**, 3572 (1961).

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, California, 1960.

(5) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(6) N. J. Rose, Ph.D. Thesis, University of Illinois (1960).

(7) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

TABLE I

TEMPERATURE DEPENDENCE OF ϵ_D AND ϵ_A

Compound	Wave length (mμ)	25.0°	εValues 31.9°	37.5°
Phenol	273	2100	2072	2056
	276	1482	1485	1480
	279	1840	1814	1795
	284	475	474	473
	288	51	62	67
		25.0°	30.9°	35.2°
DMMCA	276	18.4	19.0	19.3
	284	3.65	3.75	3.89
	288	1.51	1.60	1.70

three different temperatures. No change in this quantity was encountered in the DMA system (within experimental error). For DMMCA a linear decrease in $\epsilon_C - \epsilon_A - \epsilon_D$ was observed as the temperature was increased (Table III). In calculating the enthalpy for the DMMCA system from an enthalpy experiment, a linear interpolation was employed to obtain values of $\epsilon_C - \epsilon_A - \epsilon_D$ at intermediate temperatures.

If the changes in $\epsilon_C - \epsilon_A - \epsilon_D$ are neglected, the ΔH value obtained for DMMCA is about 1.5 kcal. too high. For example, a value of -4.70 ± 0.15 kcal. mole^{-1} is reported (Table IV) for DMMCA. If no correction is applied to the quantity $\epsilon_C - \epsilon_A - \epsilon_D$, a value of -6.2 kcal. mole^{-1} is obtained. Since the change in $\epsilon_C - \epsilon_A - \epsilon_D$ with temperature is important, the error in determining the change in $\epsilon_C - \epsilon_A - \epsilon_D$ must be taken into consideration when imposing the errors limits. For example, $\epsilon_C - \epsilon_A - \epsilon_D$ is determined to be 1230 ± 30 at 25° and 1100 ± 30 at 39.5° for DMMCA. If the values 1230 and 1100 are employed, an enthalpy of -4.70 ± 0.15 kcal. mole^{-1} is obtained. If the two extremes are employed (1200 and 1130), a value of -5.5 ± 0.5 k cal. mole^{-1} results. Therefore, the error limit reported for DMMCA is larger than that calculated at the 95% confidence level using the method previously described.[8]

Results

The data obtained in the equilibrium constant determinations are summarized in Table II.

TABLE II

EQUILIBRIUM CONSTANTS FOR PHENOL–AMIDE ADDUCTS

Amide	$C_D \times 10^3$, mole l.$^{-1}$	$C_A \times 10^3$, mole l.$^{-1}$	$A - A^0$	$\epsilon_C - \epsilon_A$	λmμ	T, °C.	K, l. mole^{-1}
DMA	2.99	0.51	0.211	1518	284	25.0	133
	5.98	0.51	.333				
DMA	2.87	1.02	.403	1529	284	24.7	135
	11.47	1.02	.922				
DMA	3.23	1.02	.428	1490	284	24.9	133
	12.91	1.02	.943				
DMA	3.23	1.02	.252	865	277	24.9	138
	6.46	1.02	.396				
DMA	2.98	1.33	.395	1020	288	25.0	129
	11.94	1.33	.990				

$K_{25°} = 134 \pm 3$ l. mole^{-1}; $\epsilon_C - \epsilon_A$ (284 mμ) $= 1502 \pm 22$

Amide	$C_D \times 10^3$, mole l.$^{-1}$	$C_A \times 10^3$, mole l.$^{-1}$	$A - A^0$	A_D	$\epsilon_C - \epsilon_A - \epsilon_D$	λmμ	T, °C.	K, l. mole^{-1}
DMMCA	9.91	1.43	0.502	0.036	1225	284	25.0	38.5
	19.82	1.43	.810	.072				
DMMCA	3.26	1.54	.212	.012	1230	284	25.0	38
	13.04	1.54	.659	.047				
DMMCA	5.05	1.69	.340	.018	1220	284	25.0	39
	15.14	1.69	.798	.055				
DMMCA	3.26	1.54	.116	.005	720	288	25.0	36
	13.04	1.54	.365	.021				

$K_{25°} = 38 \pm 2$ l. mole^{-1}; $\epsilon_C - \epsilon_A - \epsilon_D$ 25° (284 mμ) $= 1231 \pm 30$

Enthalpy results were obtained by studying the absorbance of a single solution as a function of temperature. Representative data are given in Table III.

TABLE III

HEATS OF FORMATION FOR PHENOL–AMIDE ADDUCTS

Amide	$C_D \times 10^3$, mole l.$^{-1}$	$C_A \times 10^3$, mole l.$^{-1}$	$A - A^\circ$	λ(mμ)	T, °C.	K, l. mole^{-1}
DMA	2.87	1.02	0.403	284	24.7	135
	11.47	1.02	.922		24.6	134
	2.86	1.01	.368		27.9	119
	2.83	1.00	.308		34.3	95.4
	2.82	1.00	.285		37.0	86.8
	5.62	0.99	.432		41.3	73.8

Equilibrium constants were calculated using an $\epsilon_C - \epsilon_A$ value of 1500. From the least squares treatment of the above data a ΔH of -6.7 ± 0.2 kcal. mole^{-1} is obtained. From the statistical treatment of the data from six determinations at 284 mμ, one determination at 277 mμ and one determination at 288 mμ a ΔH of -6.4 ± 0.2 kcal. mole^{-1} results.

TABLE IV

Amide	$C_D \times 10^3$, mole l.$^{-1}$	$C_A \times 10^3$, mole l.$^{-1}$	$A - A^0$	A_D	λ (mμ)	$\epsilon_C - \epsilon_A - \epsilon_D$	T, °C.	K, l. mole^{-1}
DMMCA	1.64	1.36	0.100	0.006	284	1230	25.0	38.0
	1.64	1.36	.094	.006		1215	26.8	36.0
	1.63	1.35	.085	.006		1186	30.1	33.1
	1.62	1.35	.079	.006		1165	32.5	31.2
	1.62	1.35	.076	.006		1153	33.9	30.2
	1.62	1.34	.070	.006		1131	36.5	28.2
	1.61	1.34	.066	.007		1109	39.1	26.6

From the least squares analysis of these data a ΔH of -4.70 ± 0.15 kcal. mole^{-1} results. After considering the error limits of the quantity $\epsilon_C - \epsilon_A - \epsilon_D$, a value of -4.7 ± 0.5 kcal. mole^{-1} is reported.

Discussion

The equilibrium constants and heats of formation for the addition compounds formed by DMA with ICl, C_6H_5OH, I_2, SO_2 and Br_2 are summarized in Table V. The interpretation of the data for the interaction of the acids ICl, I_2, SO_2 and Br_2 with DMA has been discussed previously.[2] Since a correlation between the dipole moment of the acids and the enthalpy was not found, it was proposed that polarizability of the acid was important.

TABLE V

THERMODYANIC DATA FOR DMA-ADDUCTS

Acid	$K^{25°}$ l./mole	$-\Delta H$ kcal./mole	μ(D)[9]
ICl	1100 ± 100	9.5 ± 0.5	0.65 to 1.5[a]
C_6H_5OH	134 ± 3	6.4 ± .2	1.45
I_2	6.9 ± 0.2	4.0 ± .1	0
SO_2	2.6 ± .3	3.4 ± .8	1.61
Br_2	1.8 ± .4	1.6 ± .3	0

[a] Reported dipole moments for ICl vary from 0.65 in the gas phase to 1.5 in CCl_4 and cyclohexane solution.

The bonding in these adducts consists of interactions of the type: (1) dipole–dipole (2) London dispersion (3) covalent or charge transfer and (4)

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(8) The calculated enthalpy is not affected by an appreciable amount of error in the magnitude of the molar absorptivities but is very sensitive to the magnitude of the change in this quantity with temperature.

(9) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, p. 86.

dipole-induced dipole. The latter two forces both result in an appreciable change in the electron distribution in the acid and are difficult to distinguish experimentally. As a result of contributions to the bonding from these two forces (3 and 4), the infrared stretching vibrations of the halogen molecules[10] undergo a pronounced decrease in frequency upon complexation. In contrast, the S-O stretching mode in the SO_2 adduct is not changed from that observed in SO_2. This evidence indicates that the interaction is essentially dipole–dipole in the SO_2 adduct.

There is general agreement that the electrostatic model does not provide an adequate description of the hydrogen bonding interaction. The inadequacies have been reviewed by Coulson.[11] As with the halogen acids, the O–H stretching vibration of phenol undergoes a marked decrease in frequency upon complexation. The heat of formation of the phenol adduct is much greater than that of the SO_2 adduct. Both of these observations are attributed to the fact that phenol is easily polarized and the phenol adduct has appreciable contributions from covalent and dipole-induced dipole interactions in addition to those of the dipole–dipole type. The enthalpies for this series of acids are interpreted qualitatively by considering the dipole moments and assigning the following order of decreasing polarizability and covalency toward DMA

$$\mathrm{ICl} > \mathrm{I_2}{}^{12} \gg \mathrm{C_6H_5OH} > \mathrm{Br_2} > \mathrm{SO_2}$$

Since phenol and ICl have dipole moments close to that of SO_2 and since the former are much more polarizable, it is expected that SO_2 will be a weaker acid than phenol or ICl toward most donors.

Acknowledgment.—The authors would like to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1) 758.

[10] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Am. Chem. Soc.*, **82**, 29 (1960), and papers referenced therein.

[11] C. A. Coulson, *Research* (London), **10**, 149–159 (1957), also (4) p. 233.

[12] The order for iodine and ICl cannot be distinguished with certainty but the very high heat of the ICl adduct (greater than the sum of I_2 plus SO_2) favors this sequence. The polarization of ICl surely increases its dipole moment in the adduct and results in greater dipole–dipole interaction.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Exchange of Deuterium with Solid Potassium Hydroborate

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Potassium deuterioborate has been prepared by reaction of deuterium gas with potassium hydroborate at temperatures near 500°. It is proposed that both the exchange reaction and the pyrolysis proceed through the following initial dissociation: $BH_4^- \rightarrow H^- + {}^1/_2B_2H_6$. The proportions of the anions BH_4^-, BH_3D^-, $BH_2D_2^-$, BHD_3^- and BD_4^- in partially deuteriated samples have been deduced from the composition of the hydrogen evolved upon hydrolysis, from proton magnetic resonance spectra and from the magnitude of the equilibrium constant for exchange. The proportions of these anions in partially deuteriated samples which have been equilibrated at *ca.* 500° correspond to a random distribution of deuterium atoms.

Introduction

In order to study kinetic isotope effects of reactions of the hydroborate ion (BH_4^-), we needed an alkali metal deuterioborate (*e.g.*, KBD_4). Sodium deuterioborate has been prepared[2] from B_2D_6 and $NaB(OCH_3)_4$ and could probably be prepared[3] by the reaction of NaD with methyl borate. However, because it has been shown that tritium gas undergoes exchange with the hydrogen in lithium and sodium hydroborates at elevated temperatures,[4] we concluded that an analogous exchange reaction of deuterium gas might serve for the preparation of an alkali deuterioborate. Indeed, the latter method has been found very convenient for preparing potassium deuterioborate, and we present here the details of the synthesis.

Three pieces of evidence lead to the conclusion that, in partially deuteriated samples of potassium hydroborate which are at equilibrium, the relative amounts of the various anions (BH_4^-, BH_3D^-, etc.) are governed chiefly by statistics. These pieces of evidence (discussed below) involve: (1) the amounts of H_2, HD and D_2 evolved upon hydrolysis of samples in aqueous acid, (2) the proton magnetic resonance spectra of aqueous solutions of partially deuteriated samples and (3) the measured equilibrium constants for the solid–gas exchange reaction.

Discussion of Results

Preparation of Potassium Deuterioborate.—Initially, attempts were made to carry out the exchange reaction by heating potassium hydroborate at 430° in 1/3 atm. of deuterium gas. Working with such a low pressure of hydrogen was unsatisfactory not only because of the necessity of handling large volumes of gas, but also because most of the sample decomposed to a dark solid and a mixture of boron hydrides. When deuterium gas pressures of 70–100 atm. were used, it was possible to work at temperatures as high as 538° with only slight decomposition in a three-day period. These results are in agreement with the findings of Ostroff

[1] Taken from a thesis presented by R. E. Mesmer for partial satisfaction of the requirements of the Ph.D. degree, University of California, Berkeley, 1962.

[2] R. E. Davis, C. L. Kibby and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5950 (1960).

[3] H. C. Brown, E. J. Mead and P. A. Tierney, *ibid.*, **79**, 5400 (1957).

[4] W. G. Brown, L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 1343 (1952).