

$$\frac{1}{6.5} = \frac{1.5 \times 0.7}{R_{\text{H}_2\text{O}^A} \times 1.4}$$

or

$$R_{\text{H}_2\text{O}^A} = 5$$

This value is in good agreement with the fact that weak acids ROH are normally stronger than ROD by factor of from 3 to 6 and also with the experimental conclusion of Pocker that in 50-50 H₂O-D₂O, neutralization of an anion by H₂O is roughly 6-fold faster than by D₂O.¹¹ This result implies

that for a reaction subject only to general acid catalysis the rate of the "solvent" reaction should be five-fold faster for H₂O than for D₂O.

All of the above *R* ratios derive from data for reaction with particular acidic and basic species and their values can be expected to vary somewhat as strengths of these reference species change. However, these variations should not be large, probably no larger than the uncertainty in the present ratios themselves.

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The Relative Acidities of Iodine Monochloride, Bromine and Sulfur Dioxide toward *N,N*-Dimethylacetamide

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The relative acidities of ICl, Br₂ and SO₂ are compared by evaluating the heats of formation of the adducts formed with *N,N*-dimethylacetamide. This series of acids, and iodine, provides an interesting variation in dipole moment and polarizability. The relative order of acidity obtained is: ICl > I₂ > SO₂ > Br₂. The dipole moments of the compounds in this series are: SO₂, 1.6 Debye; ICl, 1.3 Debye; Br₂ and I₂, zero Debye. The observed order of acidity cannot be explained by simply considering the dipole moment of the acid. It is concluded that polarizability must be a very important factor contributing to acidity. The structure of the complexes and a description of the bonding is discussed qualitatively.

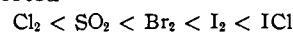
Introduction

In a previous article the thermodynamic data for the formation of an addition compound between *N,N*-dimethylacetamide (DMA) and iodine were reported.² In an attempt to gain information concerning the nature of such interactions, free energies and enthalpies of formation were measured for the 1:1 adducts formed by DMA with ICl, Br₂ and SO₂. These acids all react with DMA to form compounds whose solubilities permit use of the solvent carbon tetrachloride. This feature simplifies the interpretation of the enthalpy data obtained.

Since the bonding in the adduct depends upon contributions from covalency, dispersion forces and electrostatic interactions, the heat of formation of the adduct should be enhanced by an acid with a large polarizability and a high dipole moment. The polarizabilities³ decrease in the order I₂ > ICl > Br₂ >> SO₂. The dipole moments of I₂ and Br₂ are zero while the moments of ICl and SO₂ are 1.2 and 1.6 Debye,⁴ respectively. An interesting variation in these two parameters is provided by this series of acids. Information on the relative acid strengths should provide an insight into the nature of the bonding forces in these complexes.

This study represents the first evaluation of the enthalpy of formation of adducts of all three of these acids with a single reference base. The following order of acidity⁵ derived from the magnitude of

the equilibrium constant for the benzene complexes has been reported



Iodine monochloride has been studied extensively. The equilibrium constants with benzene,⁶⁻⁸ substituted benzenes,⁷⁻⁸ acetic acid,^{9,10} propionitrile,^{9,10} dioxane,^{11,12} pentamethylenetetrazole¹³ and acetonitrile¹⁴ have been reported. In all instances *K* and ΔH values for the formation of the ICl adducts were found to be larger than those for the corresponding iodine addition compound. Enthalpy measurements were carried out only on some substituted benzene donors.⁸ The data available on bromine are limited to equilibrium constant determinations of the complexes formed with some benzene derivatives^{15,16} and *t*-butyl alcohol.¹⁶ Again, enthalpy data are lacking.

Sulfur dioxide has been investigated as a Lewis acid toward a number of aromatics,^{5,17,18} olefins¹⁸ and ethyl alcohol.¹⁹ A large discrepancy exists in the heat of formation reported for the benzene complex^{17,18} ($-\Delta H = 7.8$ or 1.0 kcal./mole).

It was of interest to evaluate the acidity as indicated by enthalpy measurements of these Lewis

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acids toward a polar reference base. N,N-Dimethylacetamide was selected.

Experimental

Procedure.—The apparatus employed for spectral measurements was a Beckman D.U. spectrophotometer equipped with a temperature controlled, forced air heating system.² The temperature of the solution was measured directly with a thermistor located in a well in the sample cell. Except for the specific precautions described below, the general procedure is similar to that previously described.² Infrared spectra were obtained with a Perkin Elmer Model 21 spectrometer employing sodium chloride optics. The spectrometer was frequency calibrated in the carbonyl region using water vapor absorption as the standard.

The concentrations of the bromine and iodine monochloride solutions were calculated using the molar absorptivities reported in the literature.^{9,10} [$\epsilon_{\text{Br}_2} = 203 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ and $\epsilon_{\text{ICl}} = 152 \text{ l. mole}^{-1} \text{ cm.}^{-1}$]. These values were reproduced in our Laboratory by weighing out samples of Br_2 and ICl in a volumetric flask, freezing with Dry Ice and diluting to volume with CCl_4 under a nitrogen stream.

In our procedure for making up samples, the concentration of the stock solution is determined and aliquots are taken for sample solutions. The volatility of SO_2 caused difficulty in transfer. An automatic pipet was constructed by attaching a pipet to a 50 ml. reservoir through a three way Teflon stopcock. This provided a closed system for pipetting the stock solution. The sample cells were filled by attaching a device to the volumetric flask that in effect converted it to a wash bottle. Nitrogen gas was used to push the liquid into the cell. It was demonstrated that the solutions could be transferred without appreciable loss of SO_2 in this system. A value of $\epsilon_{\text{SO}_2} = 298 \text{ l. mole}^{-1} \text{ cm.}^{-1}$ at $290 \text{ m}\mu$ ¹⁹ was employed to determine the concentration of SO_2 in solution.

Flasks wrapped with black tape were used for the bromine-DMA solutions because light was found to catalyze a side reaction with bromine. The operations required to make up solutions and obtain their spectra were performed in subdued light.

The procedure employed to calculate equilibrium constants and enthalpies has been described previously.²⁰ All errors are reported at the 95% confidence level in accordance with the statistical procedure already described.²

Purification of Compounds.—The purification of carbon tetrachloride, iodine and DMA have been described previously.²

Iodine Monochloride.—Eastman, practical grade iodine monochloride was purified by gradual cooling of the liquid until about 80% solidified, followed by decanting and discarding of the liquid portion.²¹ The purified material was divided and sealed in a number of small vials to prevent decomposition. Each vial contained a sufficient quantity for one stock solution and was opened when required.

Sulfur Dioxide.—Matheson anhydrous sulfur dioxide was used without further purification. Specifications indicate a purity of at least 99.98%.

Bromine.—Mallinckrodt analytical reagent grade bromine was employed without purification. The material was stored in a glass stoppered flask in a desiccator.

Results

The equilibrium constants obtained in this research are summarized in Tables I to III. In addition, results from experiments on heats of formation are described. In these experiments the absorbance of a single sample solution is examined as a function of temperature. The ϵ values determined from a series of equilibrium constant determinations (Tables I to III) are employed to calculate K and hence ΔH from this type of experiment.

A least squares treatment of the data in Table I produces a $-\Delta H$ of $9.2 \pm 0.2 \text{ kcal./mole}$. Four heat of formation experiments were carried out using the

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Iodine Monochloride

TABLE I^a

EQUILIBRIUM CONSTANT DETERMINATIONS AT $460 \text{ m}\mu$ FOR DMA-ICl

Temp., °C.	$C_{\text{DMA}} \times 10^3$, mole/l.	$C_{\text{ICl}} \times 10^3$, mole/l.	$(A - A^0)$	K
28.6	5.21	4.92	0.389	854
28.6	10.41	4.92	.513	854
28.6	20.82	4.92	.568	854
28.6	4.45	4.91	.355	893
28.6	8.90	4.91	.500	833
28.6	17.80	4.91	.566	775
Average $K = 840 \pm 40$ $\epsilon_c - \epsilon_{\text{ICl}} = -125 \pm 2$				
36.8	4.53	4.89	0.316	556
36.8	9.06	4.89	.454	546
36.8	18.13	4.89	.536	532
36.8	5.46	5.64	.397	571
36.8	10.92	5.64	.553	564
36.8	21.84	5.64	.637	559
Average $K = 560 \pm 20$ $\epsilon_c - \epsilon_{\text{ICl}} = -125 \pm 1$				
46.2	4.47	5.33	0.292	357
46.2	8.45	5.33	.443	357
46.2	17.40	5.33	.556	357
46.2	4.73	4.40	.288	362
46.2	9.46	4.40	.423	362
46.2	18.42	4.40	.518	362
Average $K = 360 \pm 10$ $\epsilon_c - \epsilon_{\text{ICl}} = -126 \pm 1$				

^a The K values reported are intersections taken from plots²² of K vs. $\epsilon_c - \epsilon_{\text{ICl}}$ for three sets of base concentrations.

following sets of base and iodine monochloride concentrations

$$C_{\text{DMA}} = 3.8 \times 10^{-3}, C_{\text{ICl}} = 5.6 \times 10^{-3};$$

$$C_{\text{DMA}} = 25 \times 10^{-3}, C_{\text{ICl}} = 4.5 \times 10^{-3}$$

$$C_{\text{DMA}} = 2.5 \times 10^{-3}, C_{\text{ICl}} = 6.5 \times 10^{-3};$$

$$C_{\text{DMA}} = 1 \times 10^{-3}, C_{\text{ICl}} = 5.4 \times 10^{-3}$$

The value obtained for $-\Delta H$ is $9.7 \pm 0.7 \text{ kcal./mole}$ in agreement with the value obtained from Table I. The value we report for $-\Delta H$ on this system is $9.5 \pm 0.5 \text{ kcal./mole}$.

Sulfur Dioxide

TABLE II

EQUILIBRIUM CONSTANT DETERMINATION FOR DMA- SO_2 AT 21.9° AND $290 \text{ m}\mu$

$C_{\text{DMA}} \times 10^3$, mole/l.	$C_{\text{SO}_2} \times 10^3$, mole/l.	$A - A^0$
4.22	3.54	0.366
8.44	3.54	0.659
16.88	3.51	1.143
2.84	2.88	0.205
5.68	2.88	.371
11.35	2.88	.660
3.55	2.88	.236
7.11	2.88	.465
14.21	2.88	.799

In the sulfur dioxide system, difficulties were encountered because of the volatility of SO_2 . As a result poor crossings were obtained in the K^{-1} vs. ϵ_c plots. This makes averaging more difficult, so the data were calculated by the Ketelaar-Van de Stolpe procedure.²² A value of $\epsilon_c - \epsilon_{\text{SO}_2}$ of 1200 ± 80 and a K value of $2.2 \pm 0.3 \text{ l. mole}^{-1}$ were ob-

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tained at 21.9°. Several ΔH experiments were carried out on this system over the temperature range from 8 to 35°. The concentration range employed for C_{DMA} was from 9×10^{-2} to 9×10^{-3} , while a range for C_{SO_2} from 2×10^{-3} to 4×10^{-3} was employed. A value for $-\Delta H$ of 3.3 ± 0.8 kcal./mole was obtained. The value for the heat of formation is insensitive to the value of $\epsilon_c - \epsilon_{SO_2}$ since a similar ΔH is obtained using $\epsilon_c - \epsilon_{SO_2} = 1500$. Experimental difficulties prohibit one from obtaining the heat of formation more accurately.

Bromine.—The main difficulty encountered in the bromine series was the reactivity of the solutions. Thirty seven different solutions were examined in an attempt to determine K and $\epsilon_c - \epsilon_{Br_2}$. Statistical treatment of the data indicate a value for $\epsilon_c - \epsilon_{Br_2}$ of 100 at 405 $m\mu$. The K values are summarized in Table III.

TABLE III
EQUILIBRIUM CONSTANTS FOR THE FORMATION OF THE
DMA- Br_2 ADDITION COMPOUND AT 405 $m\mu$

Temp., °C.	K
20.4	1.8 ± 0.1
27.0	$1.7 \pm .1$
31.7	$1.4 \pm .1$
40.5	$1.4 \pm .2$
5.10	$1.2 \pm .1$

The heat of formation of the complex calculated from the data in Table III is -2.0 ± 0.4 kcal./mole. Two ΔH experiments were performed. These produced values for the heat of formation of -1.6 ± 0.3 kcal./mole.

Discussion

The thermodynamic data obtained in this study on the DMA adducts of the above three acids and data obtained on the iodine² addition compound are summarized in Table IV.

TABLE IV
THERMODYNAMIC DATA ON THE FORMATION OF SOME DMA
ADDITION COMPOUNDS

Lewis acid	K_{250} , l. mole ⁻¹	$-\Delta H^0$, kcal. mole ⁻¹	$-\Delta S^0_{250}$, e.u.
I_2	6.9 ± 0.2	4.0 ± 0.1	9.6 ± 1
ICl	1100 ± 100	$9.5 \pm .5$	17 ± 2
SO_2	2.6 ± 0.3	$3.3 \pm .8$	9 ± 2
Br_2	1.8 ± 0.4	$1.6 \pm .3$	4 ± 1

The data in Table IV clearly demonstrate the importance of both polarizability and dipole moment in determining the order of acidity. Due to a high dipole moment and a large polarizability, iodine monochloride is the strongest acid. Although iodine has no dipole moment, it is a stronger acid than SO_2 ($\mu = 1.6$ Debye) because iodine is more polarizable. Bromine is more polarizable than SO_2 but is much less polarizable than iodine, has no dipole moment and is the weakest acid.

The interaction of SO_2 with the amide is essentially electrostatic (dipole-dipole). The infrared

spectrum indicates that complexation of SO_2 by the amide has no effect upon the frequency of the S-O stretching vibration. Complexation of I_2 , ICl and Br_2 all have been reported²³ to produce a change in the $I \leftrightarrow I$, $Br \leftrightarrow Br$ and $I \leftrightarrow Cl$ stretching mode. Very little polarization of SO_2 occurs, and the interaction is essentially electrostatic. The relative position of SO_2 as an acid toward benzene⁵ type donors further supports this description. Bromine is a stronger acid than SO_2 toward benzene for benzene has no dipole moment. Since bromine is more polarizable and has a smaller dipole moment than SO_2 , the relative acidities are interchanged toward a polar and non-polar donor.

The infrared spectra of carbon tetrachloride solutions of DMA and the various acids employed in this study indicate that the oxygen atom of the amide is the donor in all the addition compounds. The structures are probably similar to that proposed for the iodine-amide adduct.²⁴ The lowering of the frequency for the carbonyl band upon complexation crudely parallels the heat of formation of the adduct. The carbonyl stretching vibration at 1662 cm^{-1} in the free amide is lowered 62 cm^{-1} in the ICl complex. A lowering of 43 cm^{-1} occurs in the iodine complex,²² while the complexed carbonyl absorbs 25 cm^{-1} lower in the SO_2 complex than in the free amide. Bromine also coordinates with the oxygen of the amide. Difficulty is encountered in obtaining an accurate frequency shift for the bromine complex. Reaction occurs in the system as evidenced by formation of solid in the infrared cell.

To complete the description of the bonding for these adducts, it should be mentioned that the total strength of the interaction with each of the above acids is extremely weak. Upon coordination, there is a slight change in the carbonyl stretching frequency which is crudely related to the heat of formation of the complex. However, even with the most polarizable acid, I_2 , it has been demonstrated that there is little change in the electron distribution of the amide upon complexation. Nuclear magnetic resonance experiments²⁵ did not show a change in any of the C-H proton chemical shifts on comparing the spectra of the free and complexed amide molecules. The weakness of the interaction should not be attributed to pure electrostatic interactions as demonstrated by the series obtained above for acid strengths. The relative acidities of ICl and SO_2 demonstrate that the polarizability of the acid is a most important consideration.

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