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Molecular Addition Compounds of Iodine. III. An Infrared Investigation of the Interaction Between Dimethylacetamide and Iodine[1]

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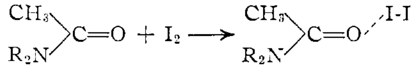
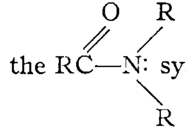
The infrared spectra of carbon tetrachloride solutions of dimethyl acetamide and iodine indicate that complexation occurs through the oxygen. Thermodynamic data for the formation of the molecular addition compound have been determined by using infrared spectroscopy to follow changes in the carbonyl absorption. The method of calculation is described and a comparison is made between the infrared and ultraviolet methods. The values obtained for the reaction were



$$K_{298} = 9.5 \pm 0.4;\quad -\Delta F_{298} = 1.33 \pm 0.4 \text{ kcal./mole}$$
$$-\Delta H = 5.1 \pm 0.1 \text{ kcal./mole}$$
$$-\Delta S = 12.6 \pm 0.2 \text{ e.u.}$$

These data indicate that the amide is a much better base toward iodine than acetone.

Introduction

The unusual solvent properties of dimethyl formamide have attracted considerable attention but little is known of the mechanism of solvent action. The high solubility of many Lewis acids in amides indicates that the basicity as well as the dielectric constant is an important factor. Since there is a lack of quantitative information on the basicity of amides, it was felt that a systematic study of the donor properties as a function of substituents in the  system would be valuable. Such information could aid in the understanding of solvent action and possibly lead to the design of better solvents.

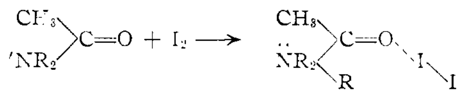
Since amides have two basic centers the mechanism of donor action is of added interest. It is shown that iodine coördinates preferentially to the oxygen. The increased basicity of the carbonyl which accompanies the substitution of a CH_3 group by a $N(CH_3)_2$ group is determined by a quantitative comparison of the basicity of acetone and dimethyl acetamide toward iodine.

Iodine was selected as the Lewis acid in this study for the following reasons:

(1) The addition compounds formed with iodine are soluble in carbon tetrachloride. Thus, the heats of formation are free of the large contributions from heats of solvation encountered in polar solvents and are also free of the lattice energies encountered with solids.

(2) There are considerable data available on donor-iodine systems[3] and on the nature of these interactions.[4] The amide–iodine system is an ideal one for obtaining further information. The heat of formation of the complex can be measured by following the changes in the iodine molecule upon coordination by using visible and ultraviolet spectroscopy.[5,6] A check can be obtained by following the changes in the donor molecule upon coördination by using infrared spectroscopy.

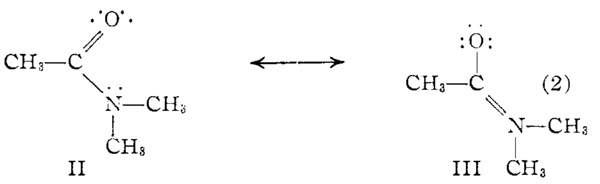
In this article an infrared method used for obtaining thermodynamic data on the complex between N–N dimethylacetamide and iodine will be described and compared with the ultraviolet method. Thermodynamic data (ΔF, ΔH and ΔS) are presented for the reaction

 (1)

In subsequent papers data obtained by both infrared and ultraviolet spectroscopy will be presented for a series of amides.

Discussion

The structure of N,N-dimethylacetamide (DMA) is best described as a resonance hydrid of the primary structures



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The same structure is described using molecular orbital terminology by delocalizing the pi-electrons in the O–C–N system. Since this molecule has two basic centers, our first concern was with the position of coördination. The structure of the amide indicates that the carbonyl oxygen should be more basic than that in acetone while the nitrogen should be less basic than that in an aliphatic amine. A reported[7] infrared investigation of the solid addition compound formed between amide and BF_3 was interpreted to indicate bonding to the nitrogen for no change in the carbonyl frequency was observed. This is by no means conclusive in view of possible lattice effects on the spectrum, so the coördination with BF_3 is still uncertain. The infrared spectrum of the carbonyl group[8] in the DMA complex

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[1] Presented at the Fall Meeting of the American Chemical Society at Chicago, Ill., 1958.

[2] Abstracted in part from the Ph.D. Thesis of C. D. Schmulbach

[3] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[4] S. P. McGlynn, *ibid.*, **58**, 1113 (1958).

[5] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[6] N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

[7] E. L. Muetterties and E. G. Rochow, *ibid.*, **75**, 490 (1953).

[8] The assignment of this frequency to the carbonyl group is not intended to imply that the absorption is localized in the C–O bond. There are probably significant contributions from the C–N bond.

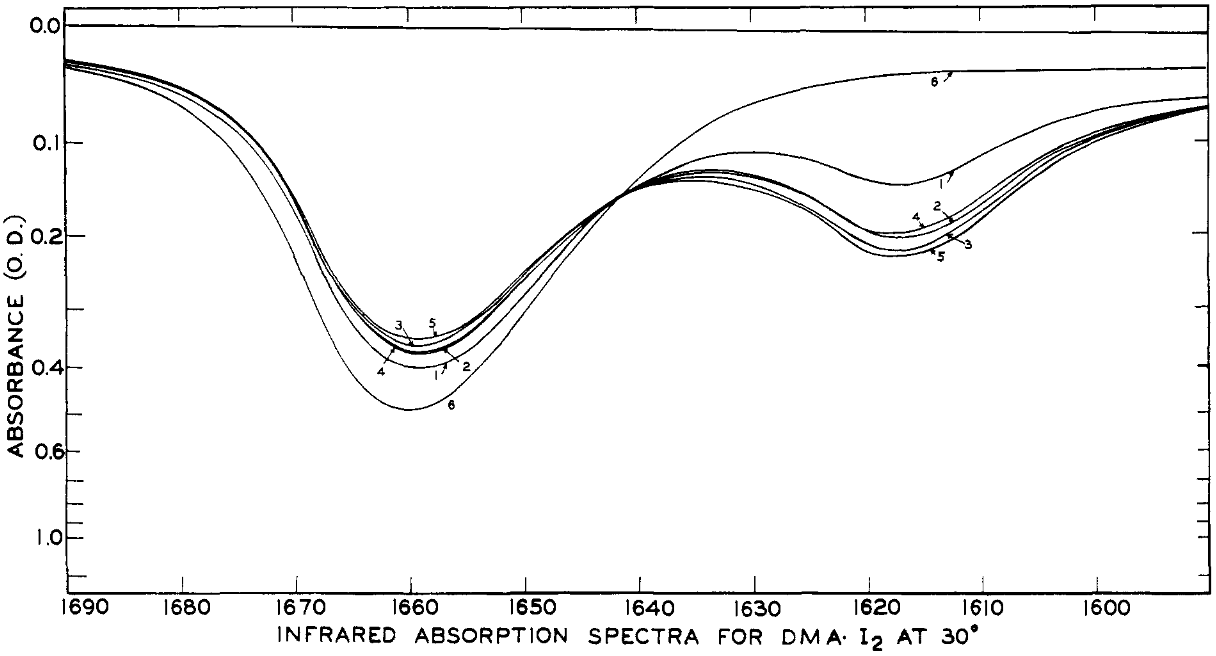

Fig. 1.

with iodine is shifted 43 cm.$^{-1}$ lower than the absorption for the free amide. This indicates a decrease in the stretching force constant and favors coördination to the oxygen. Coördination to nitrogen would decrease the contribution of structure II to the ground state of the complex and cause an increase in the carbonyl frequency.

There is another principal change that occurs in the spectrum of dimethylacetamide upon coördination to iodine. The absorption frequency assigned to the C—N stretch at 1460 cm.$^{-1}$ is shifted to higher frequencies (about 1530 cm.$^{-1}$). This is expected if oxygen is the donor atom. (See resonance hybrid II.) The intensity of the absorption at 1000 cm.$^{-1}$ has undergone a noticeable increase but the frequency remains unchanged.

The infrared spectra of several other carbonyl containing compounds (acetone, cyclopentanone, cyclohexanone and ethylacetate) were investigated. A lowering of the carbonyl frequency upon coördination was characteristic of all these compounds supporting our interpretation of the amide shift. Similar changes in the infrared spectra of the donor upon coördination have also been reported for other carbonyl compounds.[9]

The proposed structure of the complex is indicated in equation 1. There is no direct evidence to support a linear arrangement of oxygen and iodine atoms but X-ray data on the acetone–bromine system suggests a linear arrangement.[10] The possible existence of isomers of these compounds in solution has been previously discussed.[11]

The frequency shift of the carbonyl upon coordination to iodine is large enough to produce two fairly well resolved peaks for the free amide and the complex. An expanded spectrum is illustrated in Fig. 1. The amide concentration is kept constant in the series of curves illustrated but the iodine concentration is varied. As the concentration of iodine increases, a decrease is observed in the intensity of the free amide peak (on the left at 1662 cm.$^{-1}$) while the intensity of the complex peak (1619 cm.$^{-1}$) increases. An isosbestic point is obtained indicating that only two principal species (the free amide and the complex) are present. Equilibrium constants can be calculated from these curves by the procedure described below.

Experimental

Purification of Materials.—Baker and Adamson resublimed iodine was ground together with 25% by weight of potassium iodide. About 10% barium oxide was added and thoroughly blended. The mixture was sublimed under reduced pressure. The iodine obtained was resublimed and stored in a desiccator over phosphorus pentoxide.

Carbon tetrachloride was purified using the method described by deMaine.[12]

Vapor phase chromatography indicated that Eastman Kodak White Label DMA contained two impurities. The amide was shaken over BaO for several days, refluxed over BaO for 1 hr. and fractionally distilled under reduced pressure through a 20 mm. × 40 cm. vacuum-jacketed Podbielniak column. The constant boiling center fraction was retained (b.p. = 58.0–58.5° at 11.4 mm.). Chromatography indicated that the two impurities present in the original amide were reduced to a level below 0.01% by this treatment.

Procedure.—Amide stock solutions were prepared by weighing dimethylacetamide into 100-ml. volumetric flasks. A portion of carbon tetrachloride was added to the flask and the solution permitted to attain thermal equilibrium. Carbon tetrachloride was then added to the mark. The stock solutions used in this study were prepared no earlier than 4 hr. prior to making the curve traces in order to avoid serious error due to solvent evaporation. Five milliliter aliquots of the amide stock solutions were introduced into 10-ml. volumetric flasks containing weighed amounts of iodine in carbon tetrachloride. Carbon tetrachloride was added to the mark. Iodine concentrations were determined by titration with sodium thiosulfate using a micro burette.

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[9] G. D. L. Glusker, H. W. Thompson and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1407 (1953).

[10] O. Hassel, *et al.*, *Acta Chem. Scand.*, **13**, 275 (1959).

[11] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957).

[12] P. A. D. deMaine, *J. Chem. Phys.*, **26**, 1192 (1957).

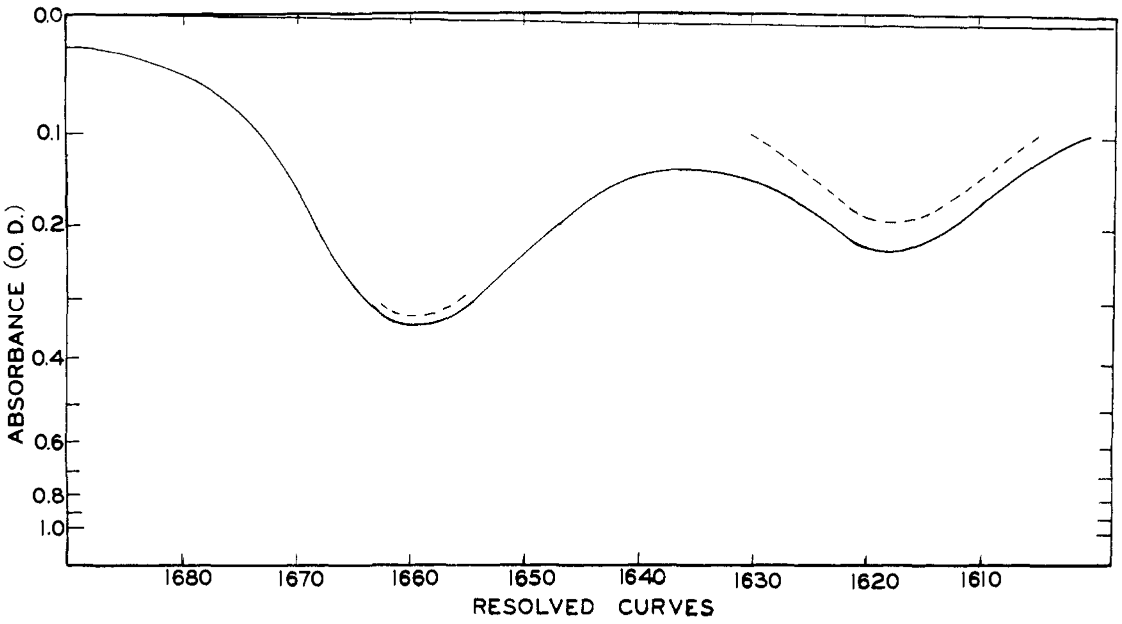

Fig. 2.

Solvent volume increases at elevated temperatures were calculated[13] and corrections made to the amide and iodine concentrations. Identical absorption curves can be obtained for an amide–iodine solution over a period of 7.5 hr. indicating the system has come to a measurable equilibrium.

The spectra were measured with a Perkin–Elmer Model 21 spectrometer employing sodium chloride optics. The cell thickness was 0.985 mm. The slit program dial was set at 940 and the "slit opening" counter reading was checked during each run to insure that at any fixed wave length the slit opening was constant. This programming results in a spectral slit width of 11 cm.$^{-1}$ ±1 over the short wave length interval studied. The spectrometer was frequency calibrated in the carbonyl region using water vapor absorption as the standard. The reproducibility of the absorbance is ±1%. The spectra were obtained at constant temperature using the thermostat, cell and temperature measuring device described elsewhere.[14]

It has been reported that iodine addition compounds undergo a reaction leading to the formation of I_3^- in concentrated base solution. The absence of I_3^- in our system was verified by the absence of the characteristic absorption of the ion in the ultraviolet spectra of diluted samples.

Calculation of the Equilibrium Constant.—The data corresponding to the infrared curves of Fig. 1 are presented in Table I. The top curve on this figure represents a background trace with carbon tetrachloride in both cells. At 1662 cm.$^{-1}$, the curves represent the experiments 6, 1, 4, 2, 3 and 5 in the order of decreasing absorbance. At 1619 cm.$^{-1}$ this order represents increasing absorbance values. In order to use this data for quantitative work, it is necessary to demonstrate that solutions of pure DMA obey Beer's Law in the concentration range studied. A Beer's Law plot was obtained for each temperature at which equilibrium constants were evaluated. The concentration of DMA at equilibrium is obtained from the Beer's Law curve and curves similar to those in Fig. 1 after the complex and free DMA peaks are resolved. Curve 5 is used to demonstrate the procedure employed on all traces to resolve the peaks and thus correct for overlap.

After background absorption is subtracted from all readings, the next step involves subtraction of the free amide absorption from that of the complex. Values for the absorbance of 5a are read off at various frequencies in the region 1635 to 1605 cm.$^{-1}$. The absorption due to the amide at equilibrium is estimated by multiplying the absorption in the 1635 to 1605 cm.$^{-1}$ region due to the initial amide concentration (*i.e.*, curve 6a) by the ratio equilibrium/initial concentration of amide. The equilibrium concentration of free amide is calculated by estimating[15] a value for the equilibrium constant for a 1:1 complex. Subtraction of the calculated free amide absorption at equilibrium from the total absorbance gives values for the absorption due to the complex in the region 1605 to 1635 cm.$^{-1}$. The resolved curves are illustrated by the dotted lines in Fig. 2

Since the complex curve is symmetrical in the region 1635 to 1605 cm.$^{-1}$, the Ramsay equation[16] is used to calculate the absorbance of the complex under the free amide peak (1662 cm.$^{-1}$). ϵ_c is determined by using the concentration of complex calculated from the assumed K.[17]

Once the curves are resolved, the equilibrium constant is calculated using the absorption at the free carbonyl peak and the equation[6]:

$$K^{-1} = \frac{A - A^0}{\epsilon_c - \epsilon_A} - C_D - C_I + \frac{C_D C_I}{A - A^0}(\epsilon_c - \epsilon_A) \qquad (2)$$

where A = total absorbance, A° = absorbance of the initial concentration of amide, ϵ_c = molar absorptivity of the complex at 1662 cm.$^{-1}$, ϵ_A = molar absorptivity of the amide, at 1662 cm.$^{-1}$, C_D = initial molarity of DMA, C_I = initial molarity of iodine and where l, the path length, is 1 mm. Both A and ϵ values are calculated for a 1 mm. path length. ϵ_A is calculated from the data used to obtain the Beer's Law curve. ϵ_c is obtained for each curve by dividing the absorbance calculated from the Ramsay equation by the concentration of the complex calculated from the assumed equilibrium constant. These quantities are substituted into equation 2 and K is calculated. If this K does not agree with the assumed K, the entire procedure is repeated using the calculated K in place of the assumed K. The procedure is repeated until agreement is obtained.

Results and Conclusions

The data and equilibrium constant values obtained at 30° are presented in Table I. Values of ϵ_A = 68.7 and ϵ_c = 7.5 were employed.

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(13) International Critical Tables, Vol. III, p. 28.

(14) C. D. Schmulbach and R. S. Drago to be published.

(15) A rough value for K can be obtained by using the free amide peak neglecting overlap.

(16) A. Weissberger, "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 280.

(17) An alternate procedure would involve determination of the complex absorption under the free carbonyl peak by assuming a symmetrical complex peak and using the value for the absorption 43 cm.$^{-1}$ to the right of the complex maxima. However, solvent absorption is appreciable in this region and use of the Ramsay equation is preferred.

TABLE I

DATA AND EQUILIBRIUM CONSTANTS OBTAINED FOR DMA–I_2 AT 30°

C_D × 10^3	C_I × 10^2	A, 1662 cm.$^{-1}$	A, 1619 cm.$^{-1}$	K_{eq}, 1662 cm.$^{-1}$	K_{eq}, 1619 cm.$^{-1}$
7.20	2.61	0.407	0.140	..	8.24
7.20	4.52	.374	.201	8.16	8.47
7.20	5.08	.364	.217	8.24	8.57
7.20	4.35	.376	.195	8.22	8.38
7.20	5.40	.354	.224	8.49	8.54
7.20	..	.490(A^0)	.033	..	..
6.42	..	.441(A^0)	.030	..	..
6.42	3.57	.360	.159	7.56	8.76
6.42	2.49	.378	.123	7.99	8.34
6.42	4.88	.328	.183	8.59	8.03
6.42	5.64	.316	.206	8.57	8.47
6.42	5.40	.316	.189	8.98	7.85
			Av.	8.3 ± 0.3	8.3 ± 0.1

The equilibrium constant was also calculated using the absorbance of the complex (*i.e.*, 1619 cm.$^{-1}$). ϵ_c was calculated by dividing the resolved complex absorbance by the complex concentration calculated from the equilibrium constant[18] obtained at 1662 cm.$^{-1}$ (*i.e.*, 8.2). The significance of this calculation lies in the constancy of the K values and not in the magnitude of the number for this is assumed by the method of calculation. Constancy indicates that all of the amide disappearing is converted to a 1:1 complex.

TABLE II

DATA AND EQUILIBRIUM CONSTANTS OBTAINED FOR DMA I_2 AT 40 AND 45°

40°

ϵ_A = 67.4 C_D × 10^3	C_I × 10^2	A, 1662 cm.$^{-1}$	ϵ_c = 7.8 K_{eq}, 1662 cm.$^{-1}$
6.30	2.77	0.375	5.72
6.30	4.55	.342	6.39
6.30	2.87	.370	6.19
6.30	3.78	.356	6.17
6.30	..	.425	..
		Av.	6.1 ± 0.3

45°

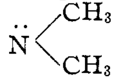
ϵ_A = 67.0 C_D × 10^3	C_I × 10^2	A, 1662 cm.$^{-1}$	ϵ_c = 8.1 K_{eq}, 1662 cm.$^{-1}$
5.97	3.50	0.344	5.21
5.97	6.00	.316	5.10
5.97	4.11	.339	4.95
5.97	5.58	.318	5.32
5.97	..	.397	..
		Av.	5.1 ± 0.2

50°

E_A = C_D × 10^3	C_I × 10^2	E_c = A at 1662 cm.$^{-1}$	K_{eq} at 1662 cm.$^{-1}$
6.07	3.50	0.340	5.44
6.07	4.61	.334	4.65
6.07	2 23	.355	5.48
6.07	..	.396	..
6.68	3.94	.378	4.61
6.68	5.46	.350	5.36
6.68	3.03	.383	5.42
6.68	..	.431	..
		Av.	5.1 ± .3

The data at 40 and 45° are presented in Table II. A least squares curve is fitted to a plot of the equilibrium constant values at 30, 40 and 45° and the value for ΔH is obtained. Each equilibrium constant is given unit weight. The following results are obtained at 298°K.:

$$K_{298} = 9.5 \pm 0.4;\ -\Delta F_{298} = 1.3 \pm 0.4 \text{ kcal./mole};\ -\Delta H = 5.1 \pm 0.1 \text{ kcal./mole};\ -\Delta S = 12.6 \pm 0.2 \text{ e.u.}$$

An attempt was made to calculate the equilibrium constant for the acetone–iodine system by this method. A slight shift in the carbonyl band from 1717 to 1701 cm.$^{-1}$ is observed. On long standing there is evidence for reaction of iodine with acetone but the spectra are unchanged over a period of 45 minutes. The weak basicity resulted in a relative insensitivity of the carbonyl band intensity to iodine concentration making evaluation of the equilibrium constant difficult. By reducing the acetone concentration to a low value (1.28 × 10^{-3} M) and working with iodine–acetone ratios of 93 to 1 a very crude value of 0.8 l./mole was obtained for the formation constant of the addition compound at room temperature. This result clearly indicates that the  $\ddot{N}<^{CH_3}_{CH_3}$ group is more effective than a methyl group by a factor of about ten in increasing the basicity of carbonyl oxygen toward iodine.

Acknowledgment.—The authors wish to express their thanks to the Research Corporation for financial assistance.

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[18] Theoretically the above system can be solved rigorously without resolving the two carbonyl peaks. The procedure has been described[5] for the evaluation of equilibrium constants using the "blue shift" iodine peak. Attempts to use this method on our infrared data were unsuccessful for changes in the absorbance values are smaller than those obtained in the ultraviolet spectra. The plot of K^{-1} *vs.* $\epsilon_C - \epsilon_A$ for the infrared data produces curves with very similar slopes. Thus a simultaneous solution for K^{-1} and ϵ_C is not feasible. This is definite indication of poorer accuracy for the equilibrium constants obtained by the infrared method. The data obtained by this method are none-the-less significant for they enable a determination of the equilibrium constant by following changes in the base.