in a one to one ratio to give an absorbing product in the latter solvent also. Water is also a participant in the reaction and the stoichiometry appears to be

$$I_2 + HSCN + 2H_2O \rightleftharpoons HI_2SCN{\cdot}2H_2O$$

It is notable, however, that the plot of log A *vs.* log C_{HSCN} has a slope which is somewhat less than unity and that the experimentally determined equilibrium constant in ether is not entirely independent of the thiocyanic acid concentration. Enough careful measurements were made in determining the slope to convince us that the value obtained 0.84 was not the consequence of a systematic error in the measurement or of impurities in the reagents employed but rather was due to some other equilibrium operating in the solution. One possible reaction which would lead to the observed slopes would involve dimerization of the HSCN. Distribution studies of thiocyanic acid between water and ether eliminated this, however. In the HSCN concentration range studied such a system was found to closely obey the relationship

$$K_D = \frac{(HSCN)_{ether}}{(a_{H^+})_{H_2O}(a_{SCN^-})_{H_2O}}$$

Here the quantity in the numerator is the analytical concentration of HSCN in the ether and the quantities in the denominator are the activities of the two ions in the aqueous solvent.

A possible competing equilibrium which could lead to the experimentally observed slopes for water and iodine and which would also give a HSCN slope of less than unity is

$$HSCN + 2I_2 + 4H_2O \rightleftharpoons ISCN{\cdot}2H_2O + HI_3{\cdot}2H_2O$$

Here the ratio of the concentration of $ISCN{\cdot}2H_2O$ to $HI_2SCN{\cdot}2H_2O$ would be independent of the concentration of I_2 and H_2O but dependent upon that for HSCN. High concentration of HSCN would favor formation of the $HI_2SCN{\cdot}2H_2O$ and a more constant value for the experimentally determined K.

The similarity between the absorption spectrum of the iodine–thiocyanic acid complex and those of the 1:1 complexes of iodine and organic sulfides, disulfides and N,N-dimethylaniline derivatives is striking.[9] In various organic solvents, these exhibit strong charge transfer bands with maxima in the region of 300–310 mμ; they also show a similar shift in the visible iodine absorption peak toward shorter wave lengths. It should perhaps be mentioned that because of interaction of the solvent with iodine the values for K and ΔH^0 reported in this paper are not directly comparable with those for the sulfide, and N,N-dimethylaniline with those for the sulfide, disulfide and N,N-dimethylaniline complexes which have all been measured in non-polar solvents.

In contrast to the behavior of thiocyanic acid, *n*-butyl sulfide was found to complex with iodine in the absence of water to give a strong absorption peak. It is also of interest that neither ethyl thiocyanate nor ethyl isothiocyanate form an absorbing product regardless of whether or not moisture is present. These observations suggest that the role of water in the thiocyanic acid–iodine reaction may, in part, involve the formation of an ion pair in which form the thiocyanate is a better electron donor.

Acknowledgment.—The authors wish to thank Mr. Calvin Long for his assistance in making some of the spectral measurements reported in this paper.

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[9] S. H. Hastings, *Anal. Chem.*, **25**, 420 (1953); H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961); H. Tsubomura, *ibid.*, **82**, 40 (1960).

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

Thermodynamic Data for Iodine Adducts with a Series of Substituted N,N-Dimethylamides

BY RUSSELL S. DRAGO, DONALD A. WENZ[1] AND ROBERT L. CARLSON[1]

RECEIVED SEPTEMBER 13, 1961

Thermodynamic data for the formation of adducts of iodine with a series of amides of the type $R\overset{O}{\overset{/\!/}{C}}N(CH_3)_2$ are reported. Compounds investigated include those in which R is either a –H, $–C_2H_5$, $–CH_2Cl$ or $–CCl_3$ group. The enthalpies of formation agree well with those expected from the inductive effect of the R group as measured by the σ^* values. Deviations are encountered when the equilibrium constants are compared with the σ^* values. These deviations are explained by considering the entropy effects that can arise from the rotational isomers that probably exist for some of these amides.

Introduction

In a recent publication[2] the thermodynamic data for the formation of the adduct between N,N-dimethylacetamide (DMA) and iodine are reported. In conjunction with our program of evaluating basicity of non-aqueous solvents, a systematic study of the basicity of a series of amides of general formula $R\overset{O}{\overset{/\!/}{C}}{-}N(CH_3)_2$ was undertaken using iodine as the reference acid. The amides in which R is $-CH_3$, $-H$, $-C_2H_5$, $-CH_2Cl$ and $-CCl_3$ have now been investigated. This series of compounds provides a set of solvents of varying basicity. N,N-Dimethyl propionamide (DMP) and DMA are more basic toward iodine than N,N-dimethylformamide (DMF); while N,N-

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[1] Abstracted in part from the Ph.D. theses of Donald A. Wenz, University of Illinois (1961) and Robert L. Carlson, University of Illinois (1962).

[2] R. S. Drago, R. L. Carlson, N. J. Rose and D. A. Wenz, *J. Am. Chem. Soc.*, **83**, 3572 (1961).

dimethyltrichloroacetamide (DMTCA) is the least basic of this series. Thermodynamic data for the formation of these adducts are reported.

The data obtained for the heat of formation of the complexes correlate fairly well (within experimental error) with the σ^* values[3] for the substituents. This represents the first such correlation reported for iodine adducts and enables predictions to be made concerning the basicity of several other substituted aliphatic amides. A tentative explanation is proposed for the deviations observed in the attempted correlation of the equilibrium constants of these adducts with σ^*.

Experimental

The procedures for carrying out the spectrophotometric measurements[2] and calculating the equilibrium constants[4] have been described. In all experiments $A - A^0$ values (*i.e.* the difference in absorbance of an amide–iodine solution A and the absorbance of an iodine solution of similar concentration A^0) were read directly by using a solution of iodine in CCl_4 as the reference and a CCl_4 solution of amide plus iodine in the sample cell. The same total concentration of iodine was employed in the reference and sample. All values for K are reported with reasonable error limits.

Preparation and Purification of Compounds.—N,N-Dimethylpropionamide (DMP).—Eastman white label amide was shaken over barium oxide for one to two days and then distilled through a packed column at reduced pressure. The middle fraction was collected and its purity checked by vapor phase chromatography.

N,N-Dimethyltrichloroacetamide (DMTCA).—This amide was prepared by a reported procedure.[5] The amide was distilled from barium oxide at 70° and 2 mm. pressure.

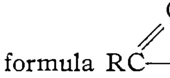
Anal. Calcd. for $Cl_3C_4H_6ON$: C, 25.22; H, 3.18; N, 7.35. Found: C, 25.59; H, 3.23; N, 7.39.

N,N-Dimethylformamide (DMF).—A 10% solution of duPont technical grade N,N-dimethylformamide in spectrograde benzene was distilled at atmospheric pressure to remove the water–benzene azeotrope and the remaining benzene. The residue was shaken over barium oxide for one day, the amide was decanted and distilled at 50° and 10–15 mm. pressure. The purity was checked with vapor phase chromatography.

N,N-Dimethylmonochloroacetamide (DMMCA).—This amide was prepared from monochloroacetyl chloride. The compound was purified by distillation at 85° and 1 to 3 mm. pressure.

Anal. Calcd. for ClC_4H_8ON: C, 39.52; H, 6.63; N, 11.52. Found: C, 39.62; H, 6.68; N, 11.47.

Results and Discussion

The amides investigated all have the general formula  $RC(=O)—N(CH_3)_2$. Upon coördination to an iodine molecule, the carbonyl oxygen in all the amides serves as the basic center. A tentative structure is proposed in Fig. 1. This structure is indicated[6] by the shift in the infrared spectra of the carbonyl stretching mode to lower wave numbers in the complex than in the free amide.

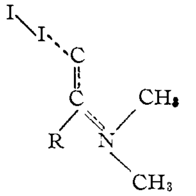
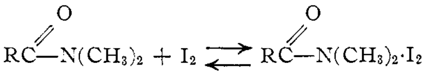


Fig. 1.—Tentative structure of the amide–iodine complexes.

The strength of the interaction of the carbonyl oxygen with the iodine is markedly affected by the inductive properties of the —R group. The magnitude of this interaction is measured by the heat of formation of adduct formed between amide and iodine in carbon tetrachloride solution.



$$RC(=O)—N(CH_3)_2 + I_2 \rightleftharpoons RC(=O)—N(CH_3)_2\cdot I_2 \quad (1)$$

The experimental results are obtained from two types of experiments: (1) Determination of K[4] and (2) determination of ΔH.[2] The results of the equilibrium constant studies are summarized in Table I.

TABLE I

SPECTROPHOTOMETRIC DATA EMPLOYED FOR EQUILIBRIUM CONSTANT CALCULATIONS

Amide	Wave length, mμ	Temp., °C.	$C_D \times 10^2$	$C_{I_2} \times 10^3$	$-(A - A^0)$
DMF	520	25.2	4.97	1.60	0.175
DMF	520	25.2	9.94	1.60	.313
DMF	520	25.2	19.89	1.60	.509
DMF	520	25.3	5.08	1.54	.173
DMF	520	25.3	10.16	1.54	.308
DMF	520	25.3	20.33	1.54	.495
$K = 2.9 \pm 0.2$ $\epsilon_C - \epsilon_{I_2} = -860 \pm 40$					
DMP	520	25.0	7.85	1.26	0.209
DMP	520	25.0	9.81	1.26	.245
DMP	520	25.0	19.61	1.26	.385
DMP	520	25.0	32.23	1.26	.537
$K = 3.9 \pm 0.2$ $\epsilon_C - \epsilon_I = -704 \pm 40$					
DMTCA	450	25.0	9.34	4.61	0.134
DMTCA	450	25.0	18.68	4.61	.267
DMTCA	450	25.0	28.02	4.61	.395
DMTCA	450	25.0	11.24	6.95	.249
DMTCA	450	25.0	22.48	6.95	.471
$K = 0.3 \pm 0.1$ $\epsilon_C - \epsilon_I = 1100 \pm 60$					
DMMCA	520	25.0	8.03	1.75	0.131
DMMCA	520	25.0	10.04	1.75	.159
DMMCA	520	25.0	20.08	1.75	.293
DMMCA	520	25.0	40.16	1.75	.478
$K = 1.3 \pm 0.2$ $\epsilon_C - \epsilon_I = -700 \pm 60$					

The heats of formation of the amide–iodine adducts were obtained by measuring the $A - A^0$ values for individual amide–iodine solutions as a function of temperature. Readings were taken every 4 or 5°. These results are reported in Table II. The two temperature extremes investigated for each solution are reported. The $A - A^0$ values corresponding to the two temperature extremes are reported under the column Range $A - A^0$.

The thermodynamic data obtained on the series of amides and that reported for DMA[2] are summarized in Table III.

In Fig. 2 the σ^* value for the substituent group is plotted against ΔH. A fairly good relationship is obtained. Those groups which are most electron withdrawing, $-CCl_3$, form the weakest complexes. This correlation permits prediction of the

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(3) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 556–675.

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

(5) H. Brintzinger, K. Pfannsteil and H. Koddebusch, *Chem. Ber.*, **82**, 389 (1949).

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

TABLE II

SPECTROPHOTOMETRIC DATA EMPLOYED FOR HEAT OF FORMATION CALCULATIONS

Amide	Wave length, mμ	Range of temp., °C.	$C_D \times 10^3$ 25°	$C_{I_2} \times 10^3$ 25°	Range of $-(A - A^0)$	$-\Delta H^0$, kcal./mole
DMF	450	8.6 to 28.2	4.94	5.47	0.159 to 0.099	3.7 ± 0.3
DMP	450	23.1 to 43.6	4.99	4.87	.108 to .066	4.0 ± .3
DMP	450	16.3 to 38.3	8.60	3.74	.175 to .105	4.0 ± .3
DMTCA	450	23.4 to 38.2	42.8	7.50	.102 to .080	2.5 ± .3
	450	14.4 to 38.3	49.3	7.28	.143 to .098	2.5 ± .3
	476	25.0 to 43.3	182.8	3.32	.173 to .132	2.5 ± .3
DMMCA	470	24.9 to 43.3	100.4	1.66	.200 to .116	3.4 ± .2
	470	25.0 to 43.1	200.8	1.75	.355 to .268	3.3 ± .3

basicity of other amides whose σ^* values are known.[7]

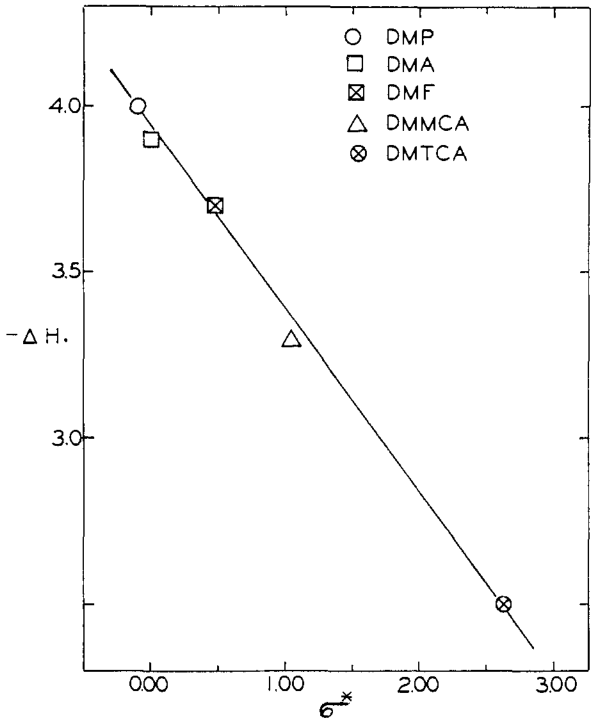
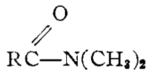


Fig. 2.—Plot of the heat of association of the iodine adducts of a series of amides *vs.* σ^*.

In Fig. 3 we have attempted a correlation of log K *vs.* σ^* for the amides studied. In contrast to the ΔH *vs.* σ^* plot, it is found that the equilibrium constant for DMP is less than that expected from σ^* and the K obtained for DMTCA is greater than expected. A similar effect is observed for the adducts formed between phenol and this series of amides.[8]

TABLE III

SUMMARY OF THERMODYNAMIC DATA FOR THE ADDUCTS OF IODINE WITH VARIOUS SUBSTITUTED AMIDES OF THE TYPE



$\mathrm{RC(=O)—N(CH_3)_2}$

R	$K_{25°}$	$\Delta F^0_{25°}$	$-\Delta H^0$	$-\Delta S^0$
$-C_2H_5$	3.9 ± 0.2	−0.81 ± 0.03	4.0 ± 0.3	10.7 ± 1.0
$-CH_3$	6.8 ± .2	−1.14 ± .04	3.9 ± .1	9.3 ± 0.6
-H	2.9 ± .2	−0.63 ± .04	3.7 ± .3	10.4 ± 1.0
$-CH_2Cl$	1.3 ± .2	− .15 ± .09	3.3 ± .3	10.5 ± 1.0
$-CCl_3$	0.3 ± .1	+ .71 ± .20	2.5 ± .3	10.7 ± 1.7

A tentative explanation can be offered to explain the deviations encountered in K. The proposal is consistent with all of the data obtained on the iodine and phenol systems.

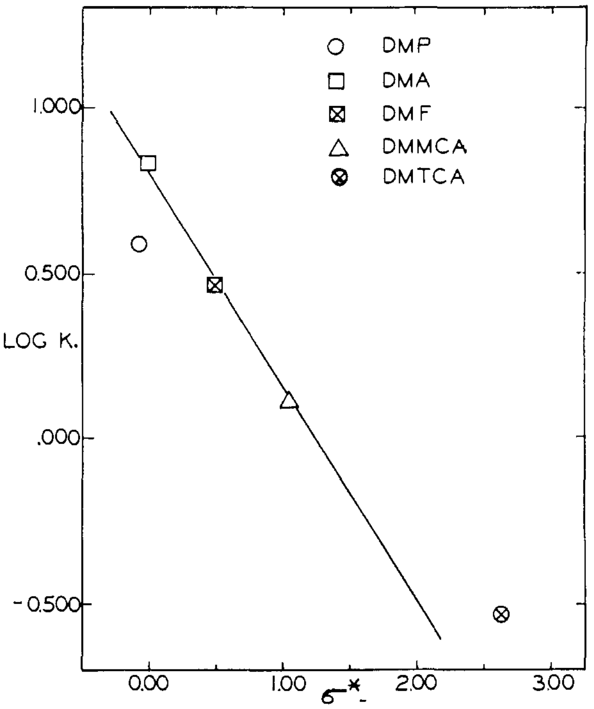


Fig. 3.—Plot of log K *vs.* σ^* for a series of amide–iodine addition compounds.

It has been demonstrated that in solution monochloroacetone is a mixture of the two rotational isomers in which the chlorine is gauche and cis to the carbonyl group.[9] It is reasonable to expect that in aliphatic amides of the type $\mathrm{XCH_2C(=O)—N(CH_3)_2}$ rotational isomers will also exist. Two of the three conformations are illustrated, (Fig. 4). When X is a $—CH_3$ group, isomer I does not coördinate as readily as isomer II (or an isomer III similar to II). This could be due to steric interaction between the $—CH_3$ group and the carbonyl oxygen.[10] Since coördination is favored with isomer II, an unfavorable entropy term arises leading to a

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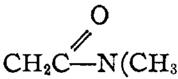
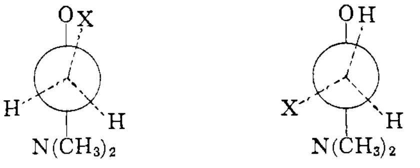
[7] Ref. 3., p. 619.

[8] M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, May (1962).

[9] S. Mizushima, *et al.*, *J. Chem. Phys.*, **21**, 815 (1953).

[10] NOTE ADDED IN PROOF.—A similiar result is observed with phenol where steric interaction with the Lewis acid is not probable. The stearic effect proposed reduces the basicity of the oxygen by inhibiting the size increase that accompanies placing electron density on it.

small K. When X is a chloro group interaction between the donor chlorine atom and the iodine appears to occur in addition to interaction with the carbonyl. This interaction is probably best described as London dispersion and dipole-induced dipole interactions. Since the interaction is weak, it has a negligible effect on ΔH, but ring formation leads to a favorable entropy term enhancing the stability of the complex. The favorable entropy term is in part cancelled by the entropy of rearrangement. Coördination can also occur to a lesser extent with isomer II. As a result of all of these effects, Cl- $CH_2\overset{O}{C}—N(CH_3)_2$ falls on the σ^* plot. In the case of DMTCA, a chloro group most probably is always *cis* to the carbonyl. Fischer–Hirschfelder models indicate a pronounced steric effect between the Cl and $—N(CH_3)_2$ groups when they are both in the same plane. This steric effect requires the chloro group to be *cis* to the carbonyl. This chloro group interacts with the iodine and the equilibrium constant for the iodine complex of DMTCA is larger than that expected from the σ^* number. Since all molecules have a chloro-group *cis* to the carbonyl, rearrangement is not necessary and the absence of the unfavorable entropy term for complexation produces a large deviation from the σ^*–log K line. The interaction of the chloro group with the iodine is not manifested in the heats of association for this effect is smaller than the experimental error in the ΔH.



I II

Fig. 4.—Possible isomers in $XCH_2\overset{O}{C}—N(CH_3)_2$ compounds.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

The Chemisorption and Catalytic Decomposition of Ethylene on Nickel

BY DOUGLAS W. MCKEE

RECEIVED SEPTEMBER 20, 1961

The chemisorption and dissociation of ethylene on unsupported nickel catalysts has been studied by a volumetric technique over the temperature range −78 to 200°. The formation of ethane by self-hydrogenation was measureable even at the lowest temperature and the kinetics of the reaction were studied between −78° and 0°. The rate of ethane evolution was found to be proportional to the initial concentration of chemisorbed ethylene and the apparent activation energy for the self-hydrogenation reaction was 3 kcal./mole. Above 60°, methane began to appear in the gas phase and at 200° was the sole gaseous product. The mechanism of catalytic dissociation of ethylene and the nature of the adsorbed residues on the metal surface are discussed.

Introduction

In spite of the very considerable literature that exists on the catalytic addition reactions of olefins, there is still little general agreement as to the detailed mechanisms of these processes. The hydrogenation of ethylene on nickel has been studied intensively since the days of Sabatier, but the reaction kinetics and structure of the adsorbed complex on the surface remain highly controversial.[1] Almost every possible mechanism has been proposed for the hydrogenation reaction at one time or another and the activation energy has been assigned values ranging from 1.8 kcal./mole to 11 kcal./mole. However, a value of about 10.7 kcal./mole, based on Beeck's work on evaporated films,[2] is generally considered the most reliable.

Of crucial importance to the whole problem is the nature of the surface complex which is formed when ethylene is chemisorbed on a clean metal surface. Surprisingly, studies of the chemisorption and dissociation of ethylene on metals, in the absence of hydrogen, are rather sparse and often contradictory. Early exchange experiments by Horiuti and Polanyi[3] and by Twigg and Rideal,[4] suggested that adsorption of ethylene takes place by the "associative" mechanism in which opening of the double bond occurs, whereas, more recent work on ethylene chemisorption on evaporated nickel films by Jenkins and Rideal[5] and by Stephens[6] have supported the alternative "dissociative" mechanism involving fission of the carbon–hydrogen bond. It is probable that both mechanisms have some validity under different conditions and the infrared spectra of adsorbed ethylene on nickel, as determined by Eischens,[7] showed that adsorption could take place by either mechanism depending on the temperature and presence or absence of a pre-adsorbed hydrogen layer.

In view of the complexities of the published data on ethylene adsorption on nickel, it seemed desir-

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(1) *E.g.*, T. I. Taylor, "Catalysis," Vol. V, ed. P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, p. 257.

(2) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945); *Discussions Faraday Soc.*, **8**, 118 (1950).

(3) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(4) G. H. Twigg and E. Rideal, *Proc. Roy. Soc. (London)*, **A171**, 55 (1939).

(5) G. I. Jenkins and E. Rideal, *J. Chem. Soc.*, 2490 (1955).

(6) S. J. Stephens, *J. Phys. Chem.*, **62**, 714 (1958).

(7) R. P. Eischens, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 1.