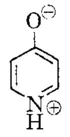
charge cannot be delocalized on oxygen. The difference in stabilization energies between *12* and *13* cannot be fixed other than that it must exceed 1.8 kcal./mole to account for the observed predominance of *12*.

The ketamine resonance is formally similar to that of aliphatic amides for which the resonance energy has been estimated as 16–21 kcal./mole.[32,33] Additionally, 4-pyridone, *9*, is related to *12* in that they both may be considered vinylogous amides. To account for the stability of the keto form, its acidity and aromatic character, contribution from *14* has been given considerable weight.[22,23]

Using an acid–base argument the ketamine stability is reasonable. In water acetylacetone enol has $pK_a \approx 9$,[34] form *2* (R′ = aryl) 13–14[11] and 2:1 condensate of acetylacetone and cyclohexanediamine > 14.[35] A proton on an enolic



14

oxygen is more acidic in these cases than a proton on nitrogen by a factor > 10^4 (or $\sim 5^1/_2$ kcal.). It is thus not surprising that substituent variation has no effect on the observable equilibrium composition of the solutions.

Acknowledgments.—Financial support by the National Science Foundation and the Milton Fund of Harvard University is gratefully acknowledged.

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(32) L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, 1960, p. 197.

(33) Ref. 30, p. 99; see also pp. 109–110.

(34) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(35) M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957).

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Thermodynamic Data for the Association of Phenol with a Series of Amides

BY MELVIN D. JOESTEN[1] AND RUSSELL S. DRAGO

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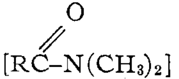
Thermodynamic data for the formation of addition compounds of phenol with N,N-dimethylformamide (DMF), N,N-dimethylpropionamide (DMP) and N,N-dimethyltrichloroacetamide (DMTCA) are reported. The equilibrium constants can be combined with those previously reported for N,N-dimethylacetamide (DMA) and N,N-dimethylmonochloroacetamide (DMMCA) to give the following series: DMA > DMP > DMF > DMMCA > DMTCA. The heats of formation of the phenol adducts are: −6.4 ± 0.3; −6.4 ± 0.2; −6.1 ± 0.4; −4.7 ± 0.5; −3.8 ± 0.5 kcal. mole^{-1}, respectively. The equilibrium constants obtained do not correlate with the σ^* values of the R substituents in the series  $RC(=O)-N(CH_3)_2$. An explanation is proposed.

Introduction

In earlier articles we have reported[2,3] equilibrium constants and heats of formation for the adducts of iodine with N,N-dimethylformamide (DMF); N,N-dimethylacetamide (DMA); N,N-dimethylpropionamide (DMP); N,N-dimethylmonochloroacetamide (DMMCA); and N,N-dimethyltrichloroacetamide (DMTCA). It was found that the equilibrium constants for this series of amides  $[RC(=O)-N(CH_3)_2]$ deviated from that predicted from the σ^* value of the R substituent. The DMP value is too low and the DMTCA value is too high. Even though DMP and DMMCA have similar shapes, a low value was not obtained for DMMCA. These results were explained by considering the rotamers that can exist for these amides. An interaction of the acid with both the oxygen and the chlorine of the rotamer in which the carbonyl oxygen and chlorine have a *cis* configuration[3] was proposed. An entropy effect reduces *K* for DMP by preferential coördination with the gauche rotamer requiring a rearrangement of amide molecules for coördination.

Since the proposed explanation for the deviation from expected behavior was attributed to the amide, it was felt that the proposal should be tested by utilizing a Lewis acid other than iodine. Phenol was selected because its steric requirements and structure are quite different from those of iodine.

Phenol-amide equilibrium constants deviate from the σ^* plot just as the iodine–amide equilibrium constants do. This is additional support for our proposed explanation.

Experimental

The preparation and purification of the amides has been previously described.[3]

Apparatus.—Preliminary spectra were recorded with a Bausch and Lomb Spectronic 505 recording 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.

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

(3) R. S. Drago, D. A. Wenz and R. L. Carlson, *ibid.*, **84**, 1106 (1962).

Procedure.—The procedure employed to carry out these measurements and the method employed to calculate the data has been described previously.[4] As indicated,[4] it is necessary to know the temperature dependence of the molar absorptivity of the amide, ϵ_D, when its absorbance overlaps the complex. Overlap does not occur with DMF and DMP. The values calculated for ϵ_D for DMTCA at 284 mμ are: $\epsilon_D = 18.9$ at 25°; $\epsilon_D = 19.6$ at 30.0°; and $\epsilon_D = 19.9$ at 35.0°. Equilibrium constants for DMF and DMP were measured at 284, 288 and 277 mμ. DMTCA was investigated only at 284 mμ. The term $\epsilon_C - \epsilon_A - \epsilon_D$ changed appreciably with temperature for DMTCA. Accurate determination of this quantity at several temperatures was necessary.

Results

The results obtained in these experiments are of two types: (1) equilibrium constant and molar absorptivity determinations calculated from the absorbance values of several solutions of differing concentration at constant temperature; (2) enthalpy determinations calculated by employing the above determined molar absorptivities and the absorbance of a single solution at several temperatures.

TABLE I

EQUILIBRIUM CONSTANT DETERMINATIONS FOR PHENOL–AMIDE ADDUCTS

Amide	$C_D \times 10^3$, M	$C_A \times 10^3$, M	$A - A^0$	$\epsilon_C - \epsilon_A$	λ, mμ	T, °C.	K
DMP	3.09	0.935	0.355	1582	284	25.1	110
	12.37	0.935	.837				
DMP	4.75	1.09	.560	1550	284	25.1	113
	9.50	1.09	.850				
DMP	4.75	1.09	.361	1020	288	25.1	109
	9.50	1.09	.550				
DMP	3.09	0.935	.231	1022	288	25.1	111
	12.37	0.935	.544				

$K_{25^0} = 107 \pm 2$ l. mole^{-1}; $\epsilon_C - \epsilon_A$ (284 mμ) $= 1579 \pm 47$

Amide	$C_D \times 10^3$, M	$C_A \times 10^3$, M	$A - A^0$	$\epsilon_C - \epsilon_A$	λ, mμ	T, °C.	K
DMF	4.77	1.40	0.442	1432	284	24.9	63.5
	9.53	1.40	0.730	1405			65
	19.06	1.40	1.070	1400			66
DMF	3.59	1.28	0.315	1440	284	25.0	61
	7.18	1.28	.542	1405			63
	14.36	1.28	.837	1390			64
DMF	3.58	1.28	.126	560	278	25.0	60
	7.18	1.28	.216	530			63
	14.36	1.28	.327	512			68

$K_{25^0} = 64 \pm 1$ l. mole^{-1}; $\epsilon_C - \epsilon_A$ (284 mμ) $= 1412 \pm 20$

Amide	$C_D \times 10^3$, M	$C_A \times 10^3$, M	$A - A_0$	A_D	$\epsilon_C - \epsilon_A - \epsilon_D$	λ, mμ	T, °C.	K, l. mole$^-$
DMTCA	8.32	3.86	0.312	0.155	205	284	25.2	32
	33.27	3.86	1.025	.628				
DMTCA	17.03	3.72	0.563	.322	200	284	25.3	30
	34.06	3.72	1.013	.644				
DMTCA	9.54	3.61	0.329	.181	207	284	25.1	28
	38.18	3.61	1.100	.724				
DMTCA	8.74	3.81	0.344	.164	210	284	25.0	36
	34.96	3.81	1.090	.656				

$K_{25^0} = 32 \pm 3$ l. mole^{-1}; $\epsilon_C - \epsilon_A - \epsilon_{D25^0}$ (284 mμ) $= 209 \pm 10$

Representative data obtained from enthalpy measurements are given in Table II.

TABLE II

ENTHALPY RESULTS FOR THE FORMATION OF ADDUCTS OF PHENOL WITH SOME AMIDES

Amide	$C_D \times 10^3$, M	$C_A \times 10^3$, M	$A - A^0$	λ, mμ	T, °C.	K, l. mole^{-1}
DMF	7.18	1.28	0.542	284	25.0	63.2
	7.13	1.28	.481		29.8	54.0
	7.11	1.27	.447		32.4	49.1
	7.09	1.27	.424		34.6	46.0
	7.05	1.26	.387		38.3	41.1

Equilibrium constants were calculated using an $\epsilon_C - \epsilon_A$ of 1410. Least squares treatment of the data gives a ΔH^0 of -6.2 ± 0.5 kcal. mole.$^{-1}$ Statistical treatment of the data from four determinations at 284 mμ, three determinations at 278 mμ, three determinations at 278 mμ and one determination at 288 mμ give: $-\Delta H^0 = 6.1 \pm 0.4$ kcal. mole^{-1}.

DMP	4.75	1.09	0.560	284	25.0	109
	4.73	1.09	.510		28.7	95.7
	4.72	1.08	.480		31.1	88.3
	4.70	1.08	.448		33.6	80.5

Equilibrium constants were calculated using an $\epsilon_C - \epsilon_A$ of 1580. Least squares treatment of the data gives a ΔH^0 of -6.4 ± 0.2 kcal. mole^{-1}. Statistical treatment of the data from two determinations at 284 mμ and two determinations at 288 mμ give: $-\Delta H^0 = 6.4 \pm 0.2$ kcal. mole^{-1}.

Amide	$C_D \times 10^3$, M	$C_A \times 10^3$, M	$A - A^0$	A_D	λ, mμ	$\epsilon_C - \epsilon_A - \epsilon_D$	T, °C.	K, mole^{-1}
DMTCA	17.68	4.06	0.661	0.336	284	210	24.9	38.25
	17.58	4.03	.628	.339		198	29.7	35.2
	17.51	4.01	.608	.344		190	33.0	22.85
	17.44	4.00	.589	.347		182	36.2	30.9

Least squares analysis of this data gives a ΔH^0 of -3.5 ± 0.4 kcal. mole^{-1}. After considering the errors limits of $\epsilon_C - \epsilon_A - \epsilon_D$, a value of -3.8 ± 0.5 kcal. mole^{-1} was obtained.

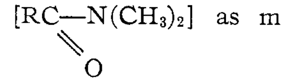
Discussion

A summary of the thermodynamic data obtained for the phenol–amide adducts is given in Table III. The iodine–amide equilibrium constants[3] are much smaller but give the same relative order.

TABLE III

SUMMARY OF THERMODYNAMIC DATA FOR SOME PHENOL–AMIDE ADDUCTS

Adduct	K_{25^0}, l. mole^{-1}	$-\Delta H^0$, kcal. mole^{-1}	$-\Delta S_{25^0}$, e.u.
DMA–phenol	134 ± 3	6.4 ± 0.3	11.7 ± 0.6
DMP–phenol	107 ± 2	6.4 ± .2	12.1 ± .6
DMF–phenol	64 ± 1	6.1 ± .4	12.1 ± .7
DMMCA–phenol	38 ± 2	4.7 ± .5	8.5 ± 1.6
DMTCA–phenol	32 ± 3	3.8 ± .5	5.5 ± 1.8

The heat of formation of the complex is that expected from the inductive effect of the R substituent  $[\mathrm{RC(=O)—N(CH_3)_2}]$ as measured by the σ^*

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[4] M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2037 (1962).

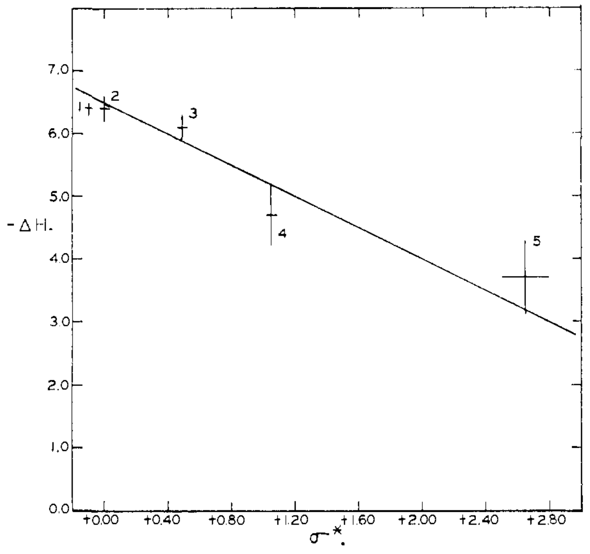

Fig. 1.—A plot of σ^* *versus* the heat of formation for the adducts formed between phenol and a series of amides. 1, DMP; 2, DMA; 3, DMF; 4, DMMCA; 5, DMTCA. Error limits are indicated by the size of the mark on the graph.

value.[5] A linear plot (within experimental error) is obtained when ΔH^0 is plotted against σ^* (Fig. 1). Some interesting variations are encountered in the plot of log K vs. σ^* (Fig. 2). The deviations are similar to those encountered for the iodine adducts but since both ΔF^0 and ΔH^0 are larger for phenol, the deviations are also larger.

The K value for the DMP complex is lower than that predicted from the σ^* plot. Since the steric requirements of $-Cl$ and $-CH_3$ are nearly alike, one might expect the K for DMMCA to be low. Instead, it falls near the line while the K for DMTCA is much larger than expected. A tentative explanation can be proposed for this data which is based upon the existence of rotamers in the amide. Since the existence of rotamers has been demonstrated in monochloroacetone,[6] it is safe to assume that they exist in the amide. Two of the three rotamers are indicated in Fig. 3. When X is a $-CH_3$ group, rotamer I does not coördinate as readily as the other rotamers. An unfavorable entropy term will arise leading to a small value for K. Since the hydrogen atom in phenol is small, the poor coördinating ability of rotamer I cannot be a steric effect between the methyl group and the acid. We propose that coördination of the oxygen causes a rehybridization of the orbitals accommodating the lone pairs and increases the steric interaction between the oxygen atom and the $-X$ group when X is methyl. The carbon–oxygen bond is more singly bonded and electron density is placed on oxygen in the complex *via* this mechanism. This steric effect causes preferential coördination with rotamer II.

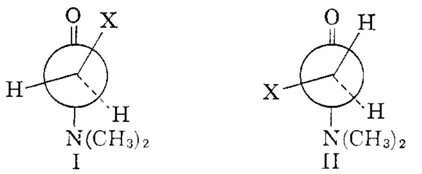

Fig. 3.—Possible rotamers in amides of the type $XCH_2CON(CH_3)_2$.

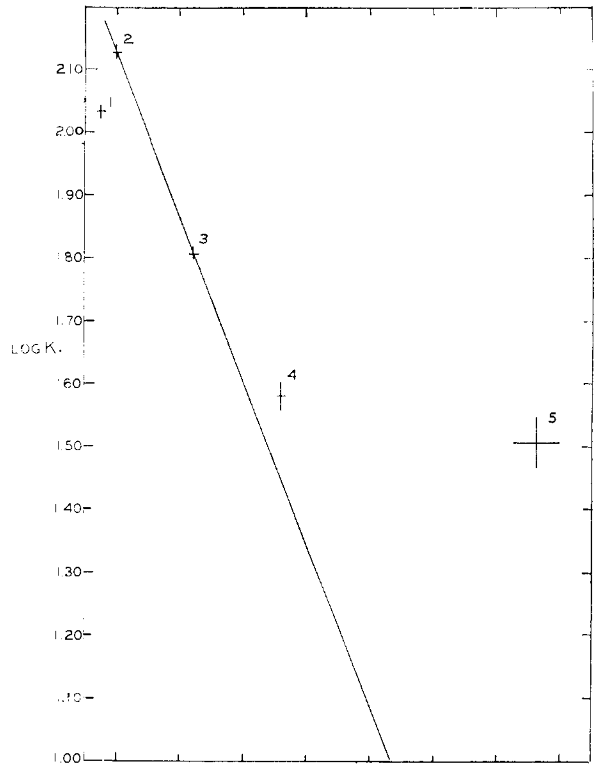

Fig. 2.—A plot of log K *versus* σ^* for a series of amides. 1, DMP; 2, DMA; 3, DMF; 4, DMMCA; 5, DMTCA. Error limits are indicated by the size of the mark on the graph.

The absence of this effect in DMMCA and the very large equilibrium constant for DMTCA indicates that when the chlorine is *cis* to the carbonyl, the chlorine interacts with the acid (through London dispersion forces or dipole–dipole attraction) in addition to the main interaction of the acid with the carbonyl oxygen donor. This chelate effect gives rise to an entropy term favoring complexation and increases the equilibrium constant. This interaction more than compensates for any steric interaction between the carbonyl oxygen and the chlorine. In the case of DMMCA coördination can occur to both rotamers, and any entropy effects favoring rotamer I would be partially counterbalanced by an unfavorable entropy of rearrangement. As a result, this point falls close to the σ^* plot. In DMTCA a chlorine is always *cis* to the carbonyl, and rearrangement is not necessary. Therefore, a large deviation is obtained in the log K *vs.* σ^* plot.

The interaction between the chlorine and the acid is not manifested by a large change in the heat of formation for this is a small enthalpy effect that is masked by experimental error. It is difficult

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(5) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–675.

(6) S. Mizushima, *et al.*, *J. Chem. Phys.*, **21**, 815 (1953).

to ascertain to what degree the above effects are manifested in the entropy or enthalpy terms. At lower confidence levels indications are that they both contribute. It should be further pointed out that other possible lines can be drawn (Fig. 2), but a consistent, reasonable explanation for the deviation of points from these lines is obtained only for the line drawn.

The similarity in the interaction of these amides with both iodine and phenol supports the above argument by demonstrating that the factors determining the basicity are inherent in the amide.

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[CONTRIBUTION FROM THE PLASTICS LABORATORY, SCHOOL OF ENGINEERING, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Effects of High Pressure on Some Organic Semiconducting Polymers

BY HERBERT A. POHL, ALAN REMBAUM AND ARNOLD HENRY

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Certain organic polymers are shown to possess a very high piezo-resistive coefficient. Compared to metals which change up to two-fold in a given pressure range, these materials change by a factor of 100-fold or more. The results are explained in terms of the easily compressible intermolecular distances and energy barriers for electron transfer. A more quantitative theory in terms of an absolute reaction rate formalism is presented. Agreement in several respects with the theory by experiment is noted.

From what follows, it will be seen that certain organic polymers possess semiconducting properties which are quite pressure sensitive. The effects of high pressure on the conductivity of metals were studied intensely by Bridgman.[1] A majority of the metals examined showed an increase in conductivity as the pressure was increased, with the change in conductivity amounting to about two-fold as the external pressure attained some 100,000 atm. In these classic researches, samples of metal were imbedded in an insulating solid such that an approximately-uniform hydrostatic pressure was transmitted to the metal from an anvil arrangement.

The effects of hydrostatic pressure on the conductivity of germanium were studied by Paul and Brooks[2]; Paul and Pearson[3] studied effects on silicon. For pressures up to 30,000 atm., it was observed that the conductivity decreased as pressure increased.

Studies on the organic monomers have so far indicated that pressure has little effect upon the conductivity. Previous investigators have indicated the existence of a limiting pressure above which the electrical conductivity of organic materials does not change. Akamatsu and Inokuchi[4] found that the resistivity of iso-violanthrone powder decreases with pressure and then remains approximately constant above 80 atm. Eley, *et al.*,[5] reported that the effect of compression was to sharply lower the value of the activation energy for loose *versus* compacted powders of metal-free phthalocyanine by 50% and of iso-violanthrone by 25%. This change in energy of activation was attributed to packing effects upon the powders examined, an effect thought to be more marked in the needle-like crystals of phthalocyanine. It was concluded[6] on the basis of the above observations that pressurization serves only to remove macroscopic voids in the samples under investigation.

A study of the effect of pressure on the conductivity of an organic semiconducting polymer synthesized from 1-hydroxyanthraquinone and 1,8-naphthalic anhydride by condensation in the presence of $ZnCl_2$ at 306° by Pohl and Opp[7] showed that the conductivity increased quite reversibly. strongly and smoothly as pressure was increased up to about 60,000 atm.

The activation energy for the conduction process was also observed to change, falling as the pressure increased. Pohl and Engelhardt[8] noted a smooth change of conductivity with pressure on several similar polymers. In all cases, these organic polymers were observed to show an increase of conductivity with increase of temperature. It was conclusively demonstrated by Pohl and Engelhardt that conduction in these homogeneous polymers was electronic, and not ionic, as shown by the fact that (a) the conductivity did not change upon passage of many times more coulombs through the materials than was necessary to effect complete electrolysis of all atoms present and; (b) a rather large Hall effect could be measured. As a result of these preliminary studies, it was decided to examine more closely the effects of pressure on the electronic behavior of these polymers.

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(1) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **81**, 165 (1952).

(2) W. Paul and H. Brooks, *Phys. Rev.*, **94**, 1128 (1954).

(3) W. Paul and G. L. Pearson, *ibid.*, **98**, 1755 (1955).

(4) H. Akamatsu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).

(5) D. D. Eley, G. D. Parfitt, M. J. Perry and D. H. Taysum, *Trans. Faraday Soc.*, **49**, 79 (1953); D. D. Eley and G. D. Parfitt, *ibid.*, **51**, 1929 (1955).

(6) G. P. Brown and S. Aftergut, "Semiconduction in Molecular Solids," Proc. Princeton Univ. Conf., ed. by Herbert A. Pohl, Ivy-Curtis Press, 1960, p. 37.

(7) H. A. Pohl and D. A. Opp, Abstracts of Papers Presented at Chicago, Ill., Sept. 1961, Amer. Chem. Soc., Div. Phys. Chem., pp. 32–33, *cf.* Opp, D. A., Master's Thesis, Princeton Univ., 1961.

(8) H. A. Pohl and E. H. Engelhardt, Papers Presented at the Chicago Meeting, Sept. 1961, Amer. Chem. Soc., Div. Polymer Chem., Vol. II, 150–160, 1961, *cf.* E. H. Engelhardt, Master's Thesis, Princeton Univ., 1961.