TABLE III

THE EFFECT OF SOLVENT ON THE 2500 Å. BAND OF DIETHYL DISULFIDE

Solvent	$\bar{\nu}_{max}$(cm.$^{-1}$)	ϵ
Cyclohexane	39990	455
Acetonitrile	39990	455
Alcohol	40310	436
Water[a]	40803	..
Vapor	40473	..

[a] Solubility was too low to permit measurement of ϵ.

in this work does seem to indicate that the genesis orbital is $\phi_\pm$, and the ability to account for so many diverse aspects of the –S—S– absorption band using the designation $\phi_\pm \rightarrow \sigma^*$ is taken as support for this assignment. Under no circumstances, however, should this work be considered as "*proving*" such an assignment; for example, the terminal state σ(4s) is equally probable.

If all of the foregoing assumptions are correct, a calculable red shift of the characteristic –S—S– absorption band will occur upon electron transfer from the disulfide bond region. A concomitant opening or closing of the dihedral angle θ will occur; the authors presume that the increase of θ is more probable from steric considerations (using molecular models), but at least for smaller alkyl groups this is not an overriding conclusion, and in this case θ may very well decrease.

The experimental basis for the 2000 cm.$^{-1}$ red shift must now be questioned. At best, any attempt to resolve a composite two peak curve (Fig. 4a) into three contributing curves may be questioned. However, in the present instance the detailed shapes of curves b and d are known experimentally, and but for the doubt about absolute extinction values for curve b, this resolution would be straightforward. The slight shift of the 40,000 cm.$^{-1}$ peak cannot be accounted for by an additive contribution from curve b, and because of this a red shift such as shown in Fig. 4 is considered the more probable.

Acknowledgment.—The authors wish to thank the sponsors of this work. They are also grateful to Mr. Harold Barnes who carried out much of the absorption work reported herein.

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN]

Solvent Effects on the Energy Barrier for Hindered Internal Rotation in Some N,N-Disubstituted Amides[1,2]

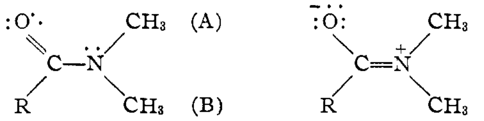
BY JAMES C. WOODBREY[3] AND MAX T. ROGERS

RECEIVED MAY 2, 1961

From the temperature dependence of the proton magnetic resonance (p.m.r.) spectra of some substituted amides we have obtained values for the energy barriers restricting internal rotation about the central C–N bond. It has been found that the barrier height E_a is strongly dependent on the nature of the solvent, and on the concentration, when these substances are studied in solution. Measurements were made on N,N-dibenzylacetamide (DBA) at a single concentration and on both N,N-dimethylpropionamide (DMP) and N,N-dimethylcarbamyl chloride (DMCC) over a range of concentrations. The barrier height appears to decrease monotonically with increasing dilution in carbon tetrachloride whereas it increases initially but passes through a maximum, with increasing dilution in dibromomethane. A possible explanation for these results is suggested.

Introduction

At sufficiently low temperatures most N,N-dimethylamides (I) show a doublet in the p.m.r. spectrum of the —N(CH$_3$)$_2$ group. It was proved



I II

by Phillips[4] that this doublet was the result of a chemical-shift difference between the resonances for the methyl groups at A and B (I) and becomes apparent when the mean lifetime of a methyl group at one or the other of the sites is sufficiently long. Gutowsky and Holm[5] developed a method for obtaining the mean lifetime 2 τ of a methyl group at each of the sites from the line shapes of the –N(CH$_3$)$_2$ chemical-shift doublet. Earlier methods of analyzing the data have been reviewed.[6] Recently a method similar to that proposed by Loewenstein and Meiboom[7] has been shown to yield more precise values of τ for the N,N-dimethylamides. The energy barriers for a series of substituted N,N-dimethylamides have been determined with fair precision by Rogers and Woodbrey[8] from the temperature dependence of τ by use of this method.

The rather large energy barriers observed[8] for internal rotation about the central C–N bond of amides appear to be the result of some partial double-bond character acquired by this bond through resonance between structures I and II in the ground states of the amides. Since the more polar form II should be stabilized more in polar solvents than the less polar form I, we might expect the barrier height to depend on the nature and

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(1) Research supported by a grant from the National Science Foundation.

(2) Abstracted in part from a thesis submitted by J. C. Woodbrey, in partial fulfillment of the requirements for the Ph.D. degree, June, 1960.

(3) W. R. Grace and Co., Washington Research Center, Clarksville, Maryland.

(4) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955).

(5) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(6) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(7) A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

(8) M. T. Rogers and J. C. Woodbrey, unpublished results.

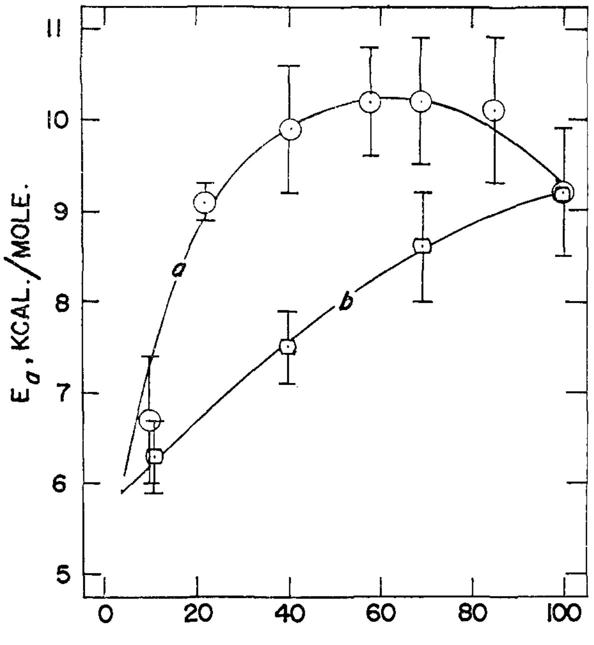

Fig. 1.—The concentration dependence of E_a for N,N-dimethylpropionamide in (a) CH_2Br_2 and (b) CCl_4.

concentration of the solvent when solutions are studied. We have therefore measured the barrier height for three N,N-disubstituted amides in both a polar and a non-polar solvent and have determined the dependence of E_a on concentration for two of them.

Experimental

A Varian Associates High-resolution NMR Spectrometer operating at ν_0 = 60.000 Mc. was used. Measurements above and below room temperature were made with a vacuum-jacketed receiver-coil insert[9] which provided control of the sample temperature to better than ± 0.1° in the range 0 to 100° and to better than ± 0.5° in the ranges −100 to 0° and 100 to 220°. Precision drawn sample tubes[9] were employed (0.192 ± 0.002″ o.d., straight to 0.003″ over an 8″ length).

The sources, methods of purification and some physical constants for DMP and DMCC have been given.[8] The DBA was prepared in this Laboratory: b.p. 194.2° at 1 mm. Carbon tetrachloride and dibromomethane were reagent chemicals dried over anhydrous sodium sulfate and purified by fractional distillation. The concentrations of solutions were calculated from the weights of pure components, and care was taken to prevent changes in concentration due to volatilization. Each sample was thoroughly degassed and sealed *in vacuo*.

Proton magnetic resonance spectra were obtained for each sample at several temperatures. At a given temperature the mean lifetime 2τ was found by a method similar[8] to that of Loewenstein and Meiboom[7] from the ratio r of maximum to central minimum v-mode intensities for the chemical-shift doublet arising from the protons *alpha* to nitrogen in the $-NR_2$ groups. Each value of r was the mean of five to ten measurements. The barrier height E_a and frequency factor A were obtained from the slope and intercept, respectively, of a plot of log $(1/2\tau)$ *versus* $10^3/2.3026RT$, using the method of least squares. The limits of 90% confidence in E_a and A were computed by standard statistical procedures.[8,10] The experimental technique and method of calculation have been described in detail.[8]

Results and Discussion

The chemical shifts of the principal lines in the p.m.r. spectra of DMP in solutions of dibromomethane and in solutions of carbon tetrachloride are shown in Table I. The shifts in p.p.m. δ are defined as

$$\delta \equiv \frac{(H - H_{\text{ref}})10^6}{H_{\text{ref}}} \tag{1}$$

The resonance of the ring protons of toluene was used as the external reference. The two values of δ for the $-N(CH_3)_2$ group indicate the positions of the components of the chemical-shift doublet for this group at the temperature where internal rotation about the central C–N bond is very slow. The corresponding results for solutions of DMCC in the same solvents are shown in Table II. For 38.0$_9$ mole % DBA in bromomethane the proton chemical shifts are $\delta_{C_6H_5}$ = −0.70$_5$, $\delta_{CH_2Br_2}$ = 1.66$_8$, δ_{CH_2} = 1.95$_0$ and 2.15$_0$, and δ_{CH_3} = 4.44$_0$ p.p.m. at −5.2°. For 38.2$_9$ mole % DBA in carbon tetrachloride the proton chemical shifts are $\delta_{C_6H_5}$ = −0.57$_0$, δ_{CH_2} = 2.11$_8$ and 2.28$_1$, and δ_{CH_3} = 4.60$_0$ p.p.m. The solution effects on the chemical shifts of the $-NH_2$ groups observed here are qualitatively the same as those reported[11] for N,N-dimethylformamide and N,N-dimethylacetamide in non-aromatic solvents.

TABLE I

PROTON CHEMICAL SHIFTS FOR SOME SOLUTIONS OF N,N-DIMETHYLPROPIONAMIDE[a,b]

Amide, mole %	Solvent	δ_{solvent}, p.p.m.	$\delta_{N(CH_3)_2}$, p.p.m.		δ_{CH_2}, p.p.m.	δ_{CH_3}, p.p.m.	Temp., °C.
100			3.75$_4$	3.90$_7$	4.36$_2$	5.68$_3$	−27.5
84.7$_1$	CH_2Br_2	1.21$_3$	3.64$_3$	3.79$_1$	4.31$_7$	5.60$_0$	−26.8
68.8$_8$	CH_2Br_2	1.19$_7$	3.46$_2$	3.60$_5$	4.21$_7$	5.49$_7$	−26.8
58.0$_9$	CH_2Br_2	1.17$_5$	3.44$_0$	3.57$_7$	4.15$_8$	5.42$_7$	−23.4
40.5$_7$	CH_2Br_2	1.09$_7$	3.26$_5$	3.38$_9$	3.99$_5$	5.23$_8$	−26.4
22.1$_7$	CH_2Br_2	0.98$_0$	3.11$_0$	3.21$_7$	3.79$_3$	5.04$_7$	−24.0
10.1$_4$	CH_2Br_2	0.91$_3$	2.99$_9$	3.09$_4$	3.66$_7$	4.92$_5$	−23.8
69.3$_4$	CCl_4		3.83$_0$	4.31$_8$	4.31$_8$	5.59$_2$	−24.0
39.9$_4$	CCl_4		3.68$_7$	4.20$_8$	4.20$_8$	5.48$_3$	−24.0
11.0$_7$	CCl_4		3.59$_7$	4.17$_5$	4.17$_5$	5.40$_0$	−23.8

[a] Chemical shifts, $\delta \equiv 10^6 (H - H_{\text{ref.}})/H_{\text{ref.}}$, are relative to the ring protons of toluene as an external reference. Reference tubes were 1 mm. Pyrex capillaries concentric with the sample tubes. [b] The value of the proton spin–spin coupling constant for the ethyl group, $J_{CH_3CH_2}$, was about 7.2 c.p.s. in each solution studied.

TABLE II

PROTON CHEMICAL SHIFTS FOR SOME SOLUTIONS OF N,N-DIMETHYLCARBAMYL CHLORIDE[a]

Amide, mole %	Solvent	δ_{solvent}, p.p.m.	$\delta_{N(CH_3)_2}$, p.p.m.		Temp., °C.
100			3.496	3.603	−24.2
90.03	CH_2Br_2	1.388	3.415	3.522	−24.5
63.44	CH_2Br_2	1.253	3.209	3.314	−24.5
40.92	CH_2Br_2	1.107	3.048	3.152	−23.7
10.72	CH_2Br_2	0.903	2.804	2.906	−22.2
71.35	CCl_4		3.499	3.518	−20.2
40.08	CCl_4		3.322	3.444	−20.2
10.98	CCl_4		3.219	3.341	−19.7

[a] Chemical shifts, $\delta \equiv 10^6 (H - H_{\text{ref.}})/H_{\text{ref.}}$, are relative to the ring protons of toluene as an external reference. Reference tubes were 1 mm. Pyrex capillaries concentric with the sample tubes.

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(9) The Wilmad Glass Co., Vineland, N. J.

(10) J. F. Kenney and E. S. Keeping, "Mathematics of Statistics," part two, 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1951, pp. 207-211, 416-417.

(11) J. V. Hatton and R. E. Richards, *Molecular Phys.*, **3**, 253 (1960).

TABLE III

VALUES OF E_a, LOG A, $\Delta F^*_{298.2}$, AND T_c FOR INTERNAL ROTATION ABOUT THE CENTRAL C–N BOND OF SOME N,N-DISUBSTITUTED AMIDES IN CARBON TETRACHLORIDE SOLUTIONS AND IN DIBROMOMETHANE SOLUTIONS[a]

Amide	Amide, mole %	Solvent	E_a, kcal./mole	Log A	$\Delta F^*_{298.2}$, kcal./mole	T_c, °K.
N,N-Dibenzylacetamide	38.09	CH_2Br_2	7.3 0.5	6.1 ± 0.3	16.5	343.7
	38.29	CCl_4	6.4 .6	5.5 ± .4	16.3	334.5
N,N-Dimethylpropionamide	100		9.2 ± .7	7.3 ± .5	16.7	334.4
	84.71	CH_2Br_2	10.1 ± .8	7.9 ± .5	16.7	333.2
	68.88	CH_2Br_2	10.2 ± .7	8.0 ± .5	16.8	333.2
	58.00	CH_2Br_2	10.2 ± .6	8.0 ± .4	16.8	333.3
	40.57	CH_2Br_2	9.9 ± .7	7.7 ± .5	16.8	332.6
	22.17	CH_2Br_2	9.1 ± .2	7.1 ± .1	16.8	332.4
	10.15	CH_2Br_2	6.7 ± .7	5.4 ± .5	16.7	338.3
	69.34	CCl_4	8.6 ± .6	7.0 ± .4	16.5	330.3
	39.94	CCl_4	7.5 ± .4	6.6 ± .3	16.0	311.3
	11.07	CCl_4	6.3 ± .4	5.7 ± .3	16.0	316.4
N,N-Dimethylcarbamyl chloride	100		7.3 ± .5	6.1 ± .3	16.5	326.0
	90.03	CH_2Br_2	8.2 ± .3	6.6 ± .2	16.6	325.6
	63.44	CH_2Br_2	9.1 ± .6	7.2 ± .4	16.6	325.2
	40.92	CH_2Br_2	8.6 ± .6	6.9 ± .4	16.6	325.5
	10.72	CH_2Br_2	7.3 ± .6	6.0 ± .4	16.5	325.9
	71.34	CCl_4	6.9 ± .5	5.8 ± .4	16.5	326.5
	40.08	CCl_4	6.6 ± .5	6.6 ± .3	16.3	323.8
	10.98	CCl_4	6.8 ± .2	5.9 ± .2	16.2	317.4

[a] The values and errors given for E_a and log A include the limits of 90% confidence. The methods of calculation of $\Delta F^*_{298.2}$ and T_c were the same as described in ref. 8. The values of T_c are for ν_0 = 60.000 Mc.

The barrier heights E_a, frequency factors A, free energies of activation ΔF^* based on the absolute reaction rate theory (transmission coefficients taken as unity), and coalescence temperatures T_c for internal rotation about the central C–N bond of the amides studied are shown in Table III. The concentration dependence of E_a for DMP in dibromomethane and in carbon tetrachloride is plotted in Fig. 1 with the limits of 90% confidence in E_a indicated by the vertical lines through the least-squared points. The corresponding results for DMCC are plotted in Fig. 2. The standard deviations are smaller than the limits of 90% confidence, but we use the more severe criterion in order to show clearly how much confidence may be placed in the observed trends.

The barrier restricting internal rotation about the C–N bond of methylamine is 1.976 kcal./mole.[12] It seems reasonable to attribute the major portion of the much higher value (9.2 ± 0.7 kcal./mole) in pure DMP to the partial double-bond character of the central C–N bond acquired through resonance between structures I and II. The observed changes in barrier height in DMP with solvent and concentration may be associated with the effect of solvent on the stability of the ground state relative to that of the excited state.[13] It is known that amides are approximately planar, hence in the ground state an appreciable contribution from resonance structure II is possible; the polar structure is also favored by dipolar interactions of the type indicated in Fig. 3. The transition state for the process of internal rotation, however, must be non-planar, and its electronic structure probably is closely represented by resonance structure I. A slight amount of dimerization, as the result of the dipolar-type interactions shown in Fig. 3, would tend to favor the contribution of resonance structure II to the ground state in the pure liquid. These interactions have been proposed previously for pure liquid N,N-disubstituted amides,[11,14] and similar interactions in N-nitrosodialkylamines[15] have been suggested. The dielectric constants of DMP, carbon tetrachloride and dibromomethane are approximately 28, 2.2 and 7, respectively, at room temperature. Solutions of DMP in carbon tetrachloride, a non-polar solvent, should show a

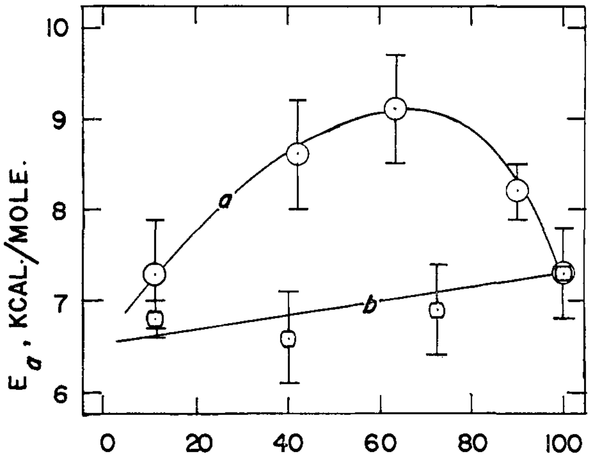

Fig. 2.—Concentration dependence of E_a for N,N-dimethylcarbamyl chloride in (a) CH_2Br_2 and (b) CCl_4.

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[12] C. C. Lin and J. D. Swalen, *Revs. Modern Phys.*, **31**, 841 (1959).

[13] We are indebted to Prof. Gideon Fraenkel of the Ohio State University for this suggestion.

[14] "Catalogue of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and Their Derivatives," Humble Oil and Refining Co., Baytown, Texas.

[15] C. E. Looney, W. D. Phillips and E. L. Reilly, *J. Am. Chem. Soc.*, **79**, 6136 (1957).

progressive decrease in stability of the more polar ground state relative to the less polar excited state with increasing dilution. The barrier height would therefore be expected to decrease monotonically with dilution as is indeed found.

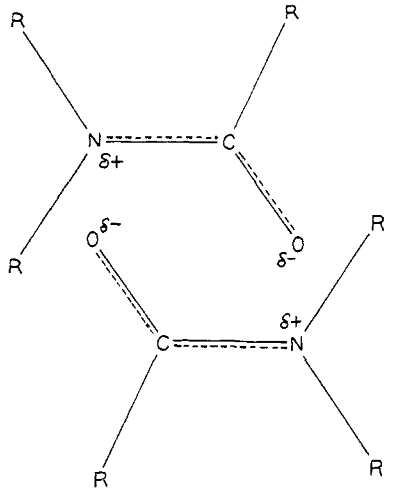
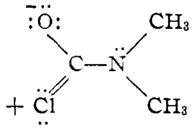


Fig. 3.—Structures favoring possible dimerization of N,N-disubstituted amides because of dipolar-type interactions.

When DMP is dissolved in the polar solvent dibromomethane, a similar decrease in barrier height with increasing dilution might be anticipated, but the formation of hydrogen bonds of the type $HBr_2C—H.....O = CR' - NR_2$ between solvent and solute may stabilize the more polar ground state relative to the transition state and increase the barrier height. At higher dilutions the low dielectric constant of the dibromomethane, compared to that of pure DMP, presumably leads to the observed decrease in the barrier, although the values are always higher than for carbon tetrachloride solutions of the same concentration. Another factor that might give rise to the maximum in the concentration dependence of E_a is the competition between hydrogen-bond formation between solvent and amide and dimer formation between the amide molecules.

A rather similar result is found for the potential barrier restricting internal rotation about the central C–N bond of DMCC. The barrier is lower for pure DMCC (7.3 ± 0.5 kcal./mole) than for pure DMP, and the difference has been attributed[8] to a decrease in the relative contribution of structures analogous to II as a result of competition from the cross-conjugation represented by III. It might be expected that dilution with a non-polar solvent would again decrease the barrier height but less markedly than for DMP. This apparently is true since the total variation of E_a for the solutions of DMCC in carbon tetrachloride is only 0.7 kcal./mole. Although the errors in E_a are of about the same order of magnitude, ±0.5 kcal./mole, as the total variation, we feel that the trend downward with dilution of the amide is significant. The barrier in DMCC shows an initial rise on adding dibromomethane followed by a decrease at greater dilutions just as was observed in DMP. It is interesting, but probably fortuitous, that the maximum value of E_a for both DMP and DMCC comes at a dilution corresponding to equal numbers of carbonyl oxygen atoms and of solvent hydrogen atoms available for hydrogen-bond formation. As suggested elsewhere,[8] the large free energies of activation ΔF^*, as compared to the activation energies E_a, probably are due to low transmission coefficients for the internal rotations involved. It is anticipated that more complex relationships will be observed with other solvents and other substituted amides, but the results should lead to further knowledge concerning intermolecular interactions in these mixtures.



III

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND, AND NORTHWESTERN UNIVERSITY, CHICAGO, ILLINOIS]

The Factors Determining Nucleophilic Reactivities

BY JOHN O. EDWARDS[1] AND RALPH G. PEARSON

RECEIVED MAY 17, 1961

Three important factors determining the reactivity of nucleophilic reagents are considered. These are basicity, polarizability and the presence of unshared pairs of electrons on the atom adjacent to the nucleophilic atom, the alpha effect. The theoretical bases for these three factors are discussed. Experimental data for a number of substrates are given which make it clear that the reactivities of some substrates depend almost entirely on basicity of the nucleophile, and some substrate reactivities depend entirely on the polarizability. Substrates which resemble the proton in having a high positive charge and a low number of electrons in the outer orbitals of the central atom depend on basicity. Substrates with a low positive charge and with many electrons in the outer orbitals of the central atom depend on polarizability. The alpha effect appears to be general for all substrates.

There is now available in the literature a large amount of data on the rates of the generalized bimolecular substitution reaction

$$N + SX \longrightarrow NS + X \qquad (1)$$

Here N is a nucleophilic reagent (ligand in inorganic chemistry) and SX is a substrate containing a replaceable group X and an electrophilic atom S. Other groups, of course, may be bound to S. The

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