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The Solvation of Polar Groups. I. A Study of Solvent Effects on Infrared Band Intensities

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The integrated intensities of the infrared bands of the nitrile group of several substituted benzonitriles, and the carbonyl group of acetone and of ethyl benzoate have been determined in a number of solvents and binary solvent mixtures. The data indicate specific solvent–solute complex formation in several cases. It appears that these complexes are formed between the polar groups of the solute and the solvent. The implications of these findings on the solvent dependence of substituent effects are discussed.

Introduction

In a recent study,[1] it was found that substituent effects on reactivity are not independent of solvent even in cases where steric and resonance effects are controlled. Two possible explanations for this observation were proposed. Either specific solvation of certain polar groups could occur, changing the effect of the group on a remote point of the molecule, or linear free energy correlations of structure and reactivity might be limited to certain solvents.

In order to investigate the possibility of specific solvation, we decided to study solvent effects on the infrared bands of some polar groups which showed anomalous effects in the previous study.

Infrared studies have been used extensively in the past in the investigation of hydrogen bonding,[2] and complex formation.[3] Our hope that infrared methods would be helpful in the present problem was strengthened by Brown's report[4] that the integrated intensity of the nitrile band of benzonitrile was increased by a factor of 1.4 by the addition of 10% of pyridine to a carbon tetrachloride solution of the nitrile. Brown's suggestion that this increase might be due to an interaction of the lone pair of electrons on the nitrogen of pyridine with the nitrile group was particularly leading.

This paper reports the results of a study of the intensities of the nitrile band of several substituted benzonitriles, and of the carbonyl bands of acetone and ethyl benzoate in various single solvents and binary solvent mixtures.

Experimental

The compounds used in this study were all reagent and spectro grade materials from commercial sources.

A Perkin-Elmer model 21 recording infrared spectrophotometer equipped with sodium chloride optics was used for the measurement of intensities. Frequencies were determined with a Perkin-Elmer model 112 single beam instrument equipped with lithium fluoride optics and calibrated with carbon monoxide and carbon dioxide.

Measurements of the intensities of the nitrile band were carried out using a mechanical slit width of 0.040 mm., corresponding to a spectral slit width of 7 cm.$^{-1}$. For the carbonyl band measurements, the mechanical slit width was 0.051 mm., corresponding to 4 cm.$^{-1}$ spectral slit width.

Beer's law plots of each solute in each solvent were constructed, and all intensity measurements were carried out using concentrations within the linear portion of these plots.

Fixed path cells, 0.26-mm. length, were employed throughout.

Binary solvent mixtures were prepared by introducing a known volume of one of the solvents into a volumetric flask, and then diluting to the mark with the second solvent. Thus, X volume per cent. of solvent A in carbon tetrachloride means X volumes of solvent A in a total volume of one hundred.

Methods and Results

Integrated intensities of the bands were calculated from Ramsay's equation[5]

TABLE I

INFRARED BANDS OF SOLUTES IN SINGLE SOLVENTS

Solute	Solvent	ν_{max}, cm.$^{-1}$ Found	Lit.[a]	O.D.[b]	$\Delta\nu^{1/2}$, cm.$^{-1}$	$A^c \times 10^{-4}$ Found	Lit.[a]
Benzonitrile	CCl_4	2231	2232	47.2	13.6	0.22	0.20
	n-Hexane	2232		..	..	..	0.15
	Pyridine	2228		64.4	14.7	0.32	..
	DMSO[d]	2226		62.7	15.0	.32	
	DMF[e]	2228		71.4	14.2	.34	
	Acetone	2229		69.7	13.8	.32	
	CS_2	2228		46.3	14.2	.22	
	i-PrOH[f]	2232		68.4	17.3	.40	
p-Tolunitrile	CCl_4	2230	2231	72.0	12.7	.31	0.28
m-Tolunitrile	CCl_4	2231	2231	55.7	12.7	.24	.20
p-Cl-Benzonitrile	CCl_4	2233	2233	54.3	12.6	.23	.20
	CS_2	..	..	55.8	12.5	.24	
	Pyridine	2230		78.9	13.4	.36	
	DMSO[d]	2230		73.8	13.2	.33	
p-NO_2-Benzonitrile	Pyridine	2234		31.3	13.3	.14	
	DMSO[d]	2232		35.1	14.3	.17	
m-NO_2-Benzonitrile	Pyridine	2233		38.6	13.4	.17	
	DMSO[d]	2235		42.7	14.2	.20	
Acetone	$CHCl_3$	1712[g]	1712	423	15.2	2.3	
	CCl_4	1719[g]	1719	308	17.0	1.9	
	CH_3CN	1713[g]	1713	386	14.5	2.0	
	DMSO[d]	1711[g]		437	14.0	2.2	
	Pyridine	1713[g]	1712	416	14.0	2.1	
	Benzene	1717[g]	1716	308	16.0	1.8	
Ethyl benzoate	$CHCl_3$	1715[g]		538	24.2	4.7	
	CCl_4	1722[g]		652	15.0	3.6	
	CH_3CN	1719[g]		560	17.5	3.6	
	DMSO[d]	1711[g]		517	17.5	3.3	
	Pyridine	1718[g]		559	17.6	3.6	
	Benzene	1723[g]		673	13.8	3.4	

[a] Ref. 4 and H. W. Thompson and D. J. Jewell, *Spectrochim. Acta*, **13**, 254 (1958). [b] Optical density as $\log_{10}(I_0/I)$ in units of liters-moles^{-1}-cm.$^{-1}$, measured at wave length of maximum absorbance. [c] Units of liters moles^{-1}-cm.$^{-1}$. [d] Dimethyl sulfoxide. [e] Dimethylformamide. [f] Isopropyl alcohol. [g] Frequencies measured with model 21 spectrophotometer calibrated with acetone in carbon tetrachloride; these values may not be as reliable as those reported for the nitriles.

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[1] C. D. Ritchie and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 591 (1962).

[2] L. J. Bellamy and co-workers, *Trans. Faraday Soc.*, **55**, 220 (1959); *Spectrochim. Acta*, **14**, 192 (1959); *Trans. Faraday Soc.*, **54**, 1120 (1958); K. B. Whetsel and R. E. Kagarise, *Spectrochim. Acta*, **18**, 315 (1962).

[3] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Am. Chem. Soc.*, **82**, 29 (1960), and earlier references cited there.

[4] T. L. Brown, *ibid.*, **80**, 794 (1960).

[5] D. A. Ramsay, *ibid.*, **74**, 72 (1952).

TABLE II

INTENSITIES OF THE NITRILE BAND OF X-SUBSTITUTED BENZONITRILES IN CCl_4–DMSO SOLVENTS[a]

Vol. % DMSO	X = H			*p*-Cl			*p*-NO_2			*m*-NO_2		
	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$
0	47.2	13.7	2.17	54.3	12.5	2.27	..	..	..	..	..	..
2	51.0	14.2	2.43	59.6	12.5	2.50	..	..	..	..	..	..
4	53.7	14.2	2.56	62.0	12.7	2.64	23.0	13.2	1.04	28.8	13.2	1.28
6	55.7	14.5	2.71	63.8	12.5	2.67	25.0	13.5	1.13	31.4	13.0	1.37
8	56.0	14.2	2.67	65.3	12.7	2.78	..	..	..	..	..	..
10	57.9	14.2	2.76	66.2	12.7	2.82	27.6	13.0	1.20	34.7	12.5	1.45
15	59.4	13.8	2.75	69.1	12.5	2.90	..	..	..	..	..	..
20	61.5	14.0	2.89	..	..	..	30.2	13.2	1.34	38.6	14.0	1.81
25	64.8	14.0	3.05	72.0	12.7	3.07	..	..	..	..	..	..
30	..	..	..	..	..	..	32.8	13.5	1.48	41.3	13.5	1.87
50	63.8	14.2	3.04	73.5	12.7	3.13	33.4	13.0	1.45	45.1	13.0	1.97
75	65.2	14.5	3.17	76.1	13.0	3.32	36.0	14.5	1.75	44.5	14.0	2.09
100	62.7	15.0	3.16	76.1	13.5	3.45	35.0	14.5	1.70	42.7	14.7	2.10

[a] All units and abbreviations are those used and defined in Table I.

$$A = \frac{K}{cl}\left(\log_e \frac{I_0}{I}\right)_{\nu_{\max}} \Delta\nu^1/_2 \qquad (1)$$

where A is the integrated intensity of the band, K is a function of the band width, optical density and spectral slit width, c is the concentration of the solute, l is the path length, and the other symbols have their usual meanings. Use of this equation, which assumes a Lorenzian band, takes account of the wing correction. Values for K were taken from the tables given in Ramsay's article.

Band widths could only be determined to ±1 cm.$^{-1}$, and this is probably the largest single source of experimental error in the determinations. We estimate the error in A to be *ca.* ± 10%.

The band characteristics are reported in Tables I–VI. In those cases where comparison is possible, the results agree well with previously determined values.

TABLE III

INTENSITIES OF THE NITRILE BAND OF BENZONITRILE IN CCl_4–DMF AND CCl_4–PYRIDINE SOLVENTS[a]

Vol. % DMF	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$	Vol. % pyridine	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-3}$
0	47.2	13.5	2.14	0	47.2	14.5	2.29
2	50.3	13.5	2.28	2	47.5	14.2	2.26
4	51.5	13.2	2.28	4	48.5	14.2	2.31
6	53.5	13.2	2.37	6	48.0	14.2	2.29
8	54.4	13.7	2.50	8	49.5	14.2	2.36
10	56.6	14.0	2.66	10	50.1	14.2	2.39
15	57.9	13.7	2.67	15	51.5	14.0	2.42
20	60.5	13.7	2.78	20	53.6	14.0	2.52
25	60.7	13.5	2.80	25	52.1	14.5	2.53
50	65.7	13.5	2.97	50	58.1	14.5	2.83
75	67.7	13.2	3.00	75	60.1	14.7	2.96
100	70.2	13.2	3.11	100	61.5	14.7	3.04

[a] All units and abbreviations are those used and defined in Table I.

The frequency measurements reported in the tables were made in order to determine the possibility of detecting band splitting in the binary solvents.[6] The frequency shifts from one solvent to another are so small that resolution of two bands would be impossible with the instrumentation used in this study.

TABLE IV

INTENSITIES OF THE CARBONYL BAND OF ACETONE IN CCl_4–DMSO AND CCl_4–PYRIDINE SOLVENTS[a]

Vol. % DMSO	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-4}$	Vol. % pyridine	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-4}$
0	315	17.0	1.93	0	315	17.0	1.93
5	340	16.0	1.96	5	..	..	..
10	361	15.2	1.98	10	321	16.2	1.88
15	378	14.7	2.00	15	..	..	..
20	391	14.5	2.05	20	325	16.2	1.90
30	407	13.7	2.01	30	342	15.7	1.93
40	413	13.2	1.97	40	345	15.2	1.89
50	435	13.0	2.04	50	369	13.7	1.82
60	..	..	..	60	387	13.2	1.85
75	438	13.5	2.14	75	..	..	..
90	..	..	..	90	397	12.7	1.82
100	437	14.5	2.28	100	416	14.0	2.10

[a] All units and abbreviations are those used and defined in Table I.

TABLE V

INTENSITIES OF THE CARBONYL BAND OF ETHYL BENZOATE IN CCl_4–DMSO SOLVENTS[a]

Vol. % DMSO	O.D.	$\Delta\nu^1/_2$	$A \times 10^{-4}$
0	652	15.2	3.58
5	606	17.2	3.76
10	609	18.5	4.06
15	578	18.5	3.86
20	559	19.5	3.93
30	569	19.2	3.94
40	574	19.0	3.94
50	568	18.5	3.80
60	565	18.5	3.78
70	566	18.2	3.72
90	570	18.0	3.71
100	502	17.5	3.17

[a] All units and abbreviations are those used and defined in Table I.

Discussion

Many previous workers have noted the difficulties in interpreting the frequency shifts and intensity changes caused by a change in solvent.[7]

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[6] This has been accomplished in hydrogen bonding studies; *cf.* ref. 2.

[7] T. L. Brown, *Spectrochim. Acta*, **10**, 149 (1957); H. W. Thompson, *ibid.*, **14**, 145 (1959); C. A. Coulson, *ibid.*, **14**, 161 (1959); C. LaLau, *ibid.*, **14**, 181 (1959); J. P. Jesson and H. W. Thompson, *ibid.*, **13**, 217 (1958).

Table VI

Dissociation Constants for Various Solvent–Solute Complexes

Solute	Solvent	$K_{\text{diss.}}$, moles-l.$^{-1}$
Benzonitrile	DMSO	1.1
p-Chlorobenzonitrile	DMSO	1.1
p-Nitrobenzonitrile	DMSO	1.1
m-Nitrobenzonitrile	DMSO	1.1
Benzonitrile	DMF	1.6
Benzonitrile	Pyridine	6.2
Acetone	DMSO	2.7

The data reported in Table I illustrate the type of anomalies frequently found. For example, the nitrile band frequency is hardly affected by a change in solvent from *n*-hexane to isopropyl alcohol even though the intensity is doubled in the latter solvent. The same situation is noted in the solvents carbon disulfide and dimethylformamide. On the other hand, a 3-cm.$^{-1}$ frequency shift is caused by a change from acetone to dimethyl sulfoxide solvent while the intensity is not affected. Even more confusing, the change of solvent from pyridine to dimethyl sulfoxide lowers the frequency of the nitrile band of *p*-nitrobenzonitrile by 2 cm.$^{-1}$, while the same solvent change *raises* the frequency for *m*-nitrobenzonitrile by the same amount.

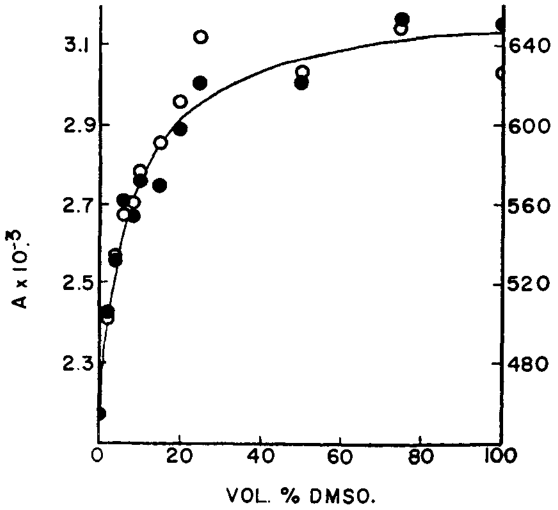

Fig. 1.—Benzonitrile in CCl_4–DMSO solvents; solid line calculated from K = 1.1.

Figs. 1–9.—Integrated intensities and optical densities of the nitrile groups of benzonitriles and the carbonyl groups of acetone and ethyl benzoate in carbon tetrachloride–polar solvent binary mixtures: ●, integrated intensity; O, optical density; DMSO = dimethyl sulfoxide; DMF = dimethylformamide.

The frequencies of the carbonyl bands are extremely solvent sensitive, but the integrated intensities are hardly affected. The insensitivity of the integrated intensity is caused by compensation of the increase in optical density by a decrease in band width.

Another interesting observation, which we cannot explain, is that the optical density of the carbonyl bands of acetone and ethyl benzoate are affected in a dissimilar manner by solvent changes even though the frequency shifts appear to be similar. These data raise many interesting questions. We feel, however, that any interpretation must await further knowledge of specific solvent–solute interactions as discussed below.

The integrated intensities and optical densities of the nitrile bands of the substituted benzonitriles are plotted against volume per cent. of polar solvent in the binary solvents in Figs. 1–6. The shape of these plots strongly suggest equilibrium reactions between the solute and polar solvent. This suggestion is confirmed by calculation.

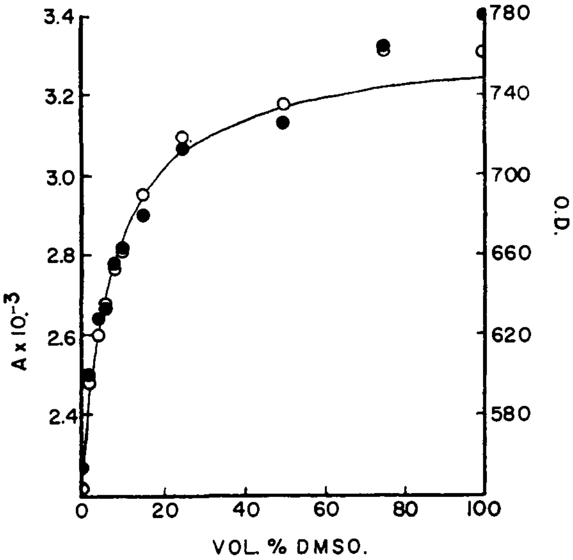

Fig. 2.—*p*-Chlorobenzonitrile in CCl_4–DMSO solvents; solid line calculated from K = 1.1.

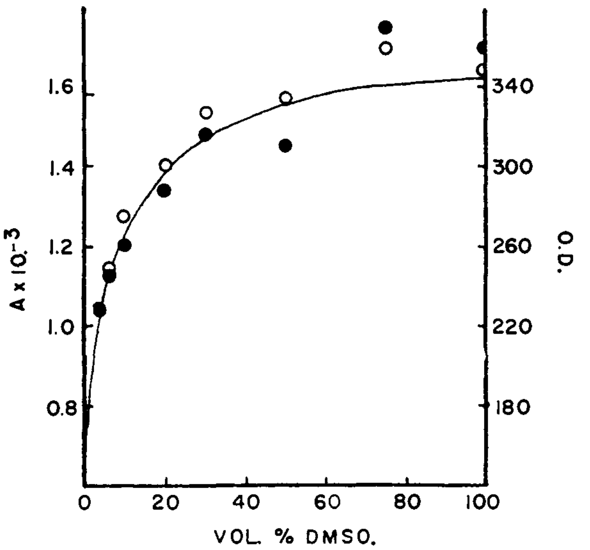

Fig. 3.—*p*-Nitrobenzonitrile in CCl_4–DMSO solvents; solid line calculated from K = 1.1.

For the purpose of calculation, we assume that activity coefficients of all individual species remain constant throughout the concentration range studied. Concentration is expressed in moles per liter, and standard states are taken as one molar solutions in carbon tetrachloride. Although,

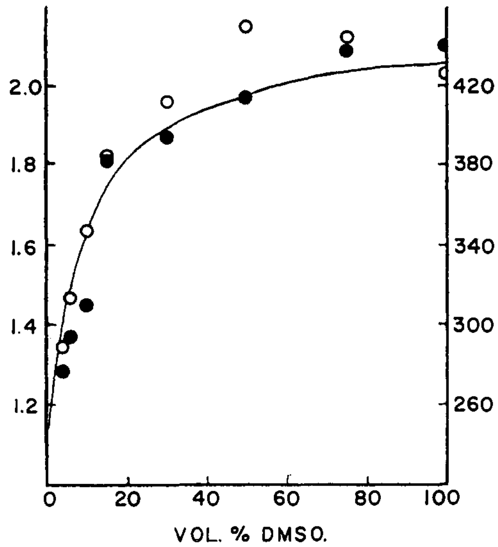

Fig. 4.—*m*-Nitrobenzonitrile in CCl_4–DMSO solvents; solid line calculated from $K = 1.1$.

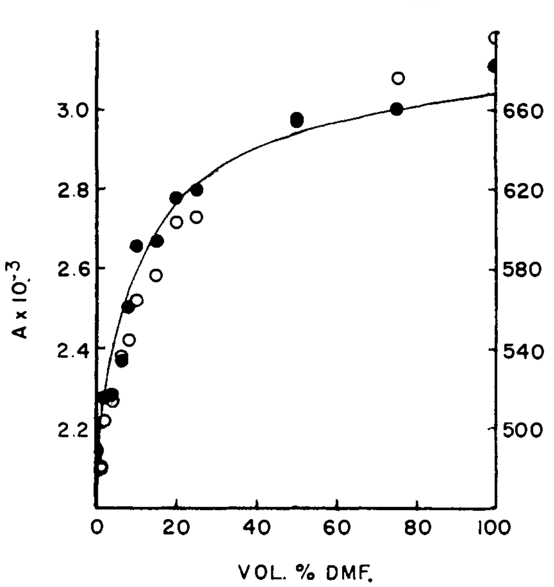

Fig. 5.—Benzonitrile in CCl_4–DMF solvents; solid line calculated from $K = 1.6$.

strictly, equilibrium constants should be expressed in terms of mole fraction, appreciable deviations from the proportionality of the two constants would only occur at concentrations of polar solvent greater than 40 volume per cent.[8] Within this range, the experimental data is insensitive to the chosen value of K, and, therefore, nothing is lost by using the more convenient molar units. Serious deviations from the other assumptions above would also be expected in this high concentration range, and cannot be detected by our data.

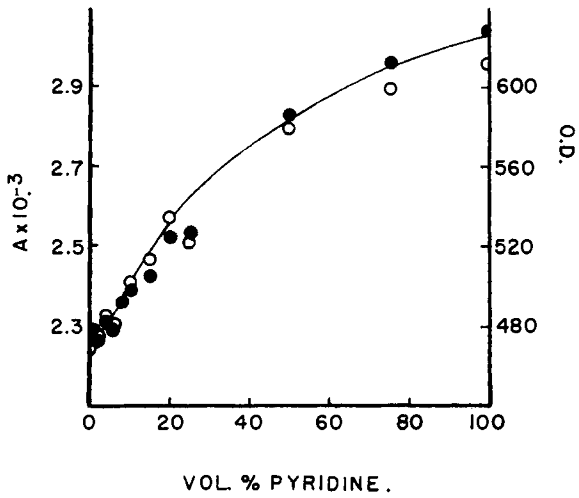

Fig. 6.—Benzonitrile in CCl_4-pyridine solvents; solid line calculated from $K = 6.2$.

We also assume that the intensity of the band caused by a single solute species is not dependent on the solvent. With this assumption, it is possible to calculate equilibrium constants for complex formation between the solute and polar solvent for various stoichiometries from the reported data. The integrated intensity of the band arising from the complex is taken as the integrated intensity observed in 100% polar solvent; that of the uncomplexed species is the observed value in pure carbon tetrachloride. A rough curve was then drawn through the experimental points. The concentration of polar solvent at the point on this curve half-way between initial and final intensity was used to calculate an equilibrium constant. Since the shapes of the experimental curves are consistent only with a 1:1 complex, the concentration of solvent at the point where half of the solute is complexed is equal to the dissociation constant of the complex.

The equilibrium constant calculated in this manner was then used to calculate the degree of dissociation of the complex at 100% polar solvent. This value was used to calculate a refined value for the intensity of the complexed species, and the process was reiterated until successive calculations showed agreement. Usually, the second iteration was satisfactory.

The calculated equilibrium constants and intensities were then used to calculate the theoretical intensity at any solvent composition. The solid lines of Figs. 1–6 show these calculated intensities. The calculated and observed values show agreement well within the estimated experimental error. Values of the equilibrium constants are reported in Table VI. These values are probably not accurate to better than ±50%.

The integrated intensity of the carbonyl band of acetone does not change greatly with solvent. We have, therefore, used the optical density to calculate equilibrium constants in the same manner as outlined above.

In the CCl_4–pyridine binary solvents, the complexing of the carbonyl group, if any, is slight, and no effort to calculate an equilibrium constant was

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(8) The volumes of the mixed solvents are the sums of the volumes of the components—to better than 1%. It can then be shown that $K_x = K_m \Big/ \left[10V_a\left(\frac{D_a}{M_a} - \frac{D_d}{M_a}\right) + 1000\,\frac{D_d}{M_d}\right]$, when K_x is the equilibrium constant expressed in mole fraction, K_m that expressed in molarities, V_a is the volume per cent. of polar solvent, D_a is the density of the polar solvent, D_d is the density of carbon tetrachloride and the M's are the molecular weights of the solvents. Therefore, for the present system: $K_x = K_m/10.40 \pm 20\%$.

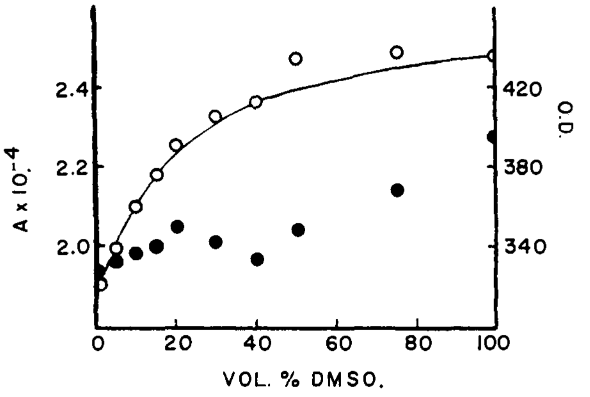

Fig. 7.—Acetone in CCl_4–DMSO solvents; solid line calculated from $K = 2.7$.

made. Plots of the data for the acetone studies are shown in Figs. 7 and 8. The equilibrium constant for the acetone–dimethyl sulfoxide complex is reported in Table VI.

The integrated intensities and optical densities of the carbonyl band of ethyl benzoate in carbon tetrachloride–DMSO solvents are shown in Fig. 9. The points do not fall on a smooth curve, and obviously no equilibrium constant can give agreement with the observed data. Perhaps in this case the bulky ethoxyl group prevents close approach of the solvent to the carbonyl group.

It should be emphasized that the magnitude of the equilibrium constants reported are not very accurate. Values differing by 50% from those reported can be made to give agreement with the experimental data. The significance of our observations can be summarized as: (1) The assumption of other than a 1:1 solvent–solute complex leads to appreciable deviations from the data. (2) The simple assumption of complex formation accounts quantitatively for the variations in band intensities within experimental error. Although other factors certainly influence intensities, they are minor in comparison to the effect of complexing.

Several interesting conclusions regarding the nature of the complexes formed appear to be justified by the above data. First, the equilibrium constant for the benzonitrile–dimethyl sulfoxide complex does not appear to be affected by substituents on the benzene ring. If simple dipolar attractions involving the entire molecule were responsible for complex formation, we would expect a very large substituent effect. Likewise, large substituent effects would be expected if the interaction took place through the π-system of the benzene ring. We therefore feel that complex formation involves the nitrile group specifically. Small substituent effects which would be expected in this case might well be within the limits of errors in the reported dissociation constants.

In the previous study of substituent effects on acidity,[1] it was noted that dimethyl sulfoxide caused a lowering of the electron-withdrawing ability of the nitrile group relative to the bromo substituent. This effect would appear to indicate that the sulfoxide group has its dipole oriented opposite to that of the nitrile group in the complex. Thus, the negative oxygen of the sulfoxide acts as an electron-donating group.

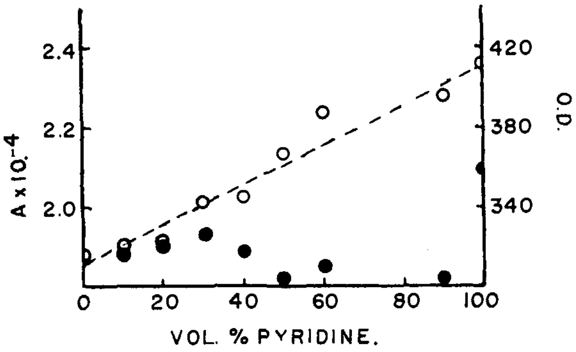

Fig. 8.—Acetone in CCl_4–pyridine solvents.

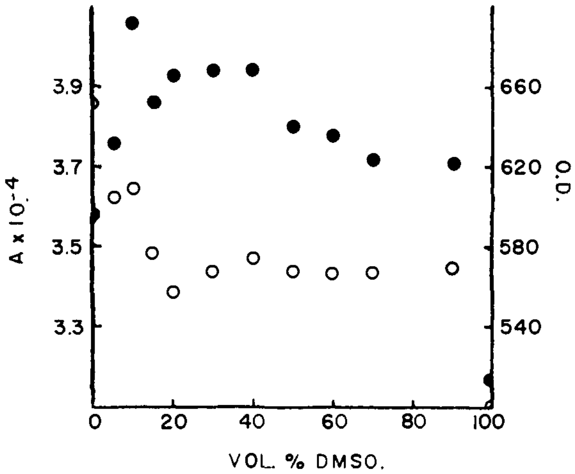

Fig. 9.—Ethyl benzoate in CCl_4–DMSO solvents.

The simplest picture of the complex which appears to be consistent with all of the data is one in which the dipole of the sulfoxide group lies on the dipole of the nitrile group. Analogous complexes are envisioned in the cases of the carbonyl group and other solvents.

Whether the forces of attraction within the complex are simple electrostatic forces, or chemical forces resulting from overlap, cannot be decided from our data. Since, however, the frequencies of the groups are changed only slightly, we tend to favor an electrostatic description at the present time. Further studies of electronic and steric requirements for complex formation are underway, and may well shed further light on the precise nature of the complexes.

The implications of the results reported here are clearly of interest in the problem of solvent effects on reactivity of organic compounds. The effect produced by this type of complex formation would be completely analogous to the case of hydrogen bonding of solute and solvent.

From the results of this and the previous study,[1] it would appear that specific interactions will be quite important in the interpretation of solvent effects on structure–reactivity correlations. We would like to emphasize, however, that we do not yet feel confident in placing all of the deviations noted in the acidity study as being due to complex formation. The present results are strongly indicative that specific interactions are at least partly responsible for the deviations, but further studies of the solvent dependence of substituent effects are necessary to determine if other effects are also important. Work along those lines is continuing.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIF.]

The Kinetics of Dissociation of the Dichlorides of Iodomethyl Sulfones

BY J. L. COTTER, L. J. ANDREWS AND R. M. KEEFER

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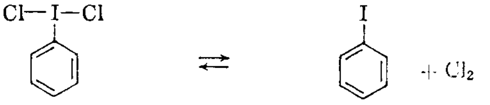
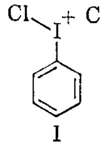
A number of iodomethyl sulfones have been prepared and converted to the corresponding iodoso chlorides ($R'SO_2CH_2ICl_2$). The rates of equilibration of these dichlorides with their components in a variety of polar solvents (acetic acid, acetonitrile and nitomethane) have been investigated by procedures used in earlier studies of iodobenzene dichloride and some of its ring substitution products. Like the iodobenzene dichlorides the iodomethyl sulfone derivatives come to equilibrium with the free iodo compounds and chlorine at easily measurable rates at room temperature, and the formation and dissociation rate constants for the two types of dichlorides are very similar. The insensitivity of these constants to changes in the nature of the organic substituent on iodine is ascribed to the high polarizability of this halogen.

Aliphatic iodides and chlorine normally form crystalline adducts[1] only at temperatures well below 0°. At higher temperatures a displacement reaction to form an alkyl chloride takes place.[2] Aromatic iodides form iodoso chlorides which can be isolated in crystalline form at room temperature. In polar organic solvents these come to equilibrium with their component iodobenzenes and chlorine (eq. 1) at easily measurable rates.[3] It has been established with reasonable certainty that the activated complexes which separate the dichlorides



(1)

from their dissociation products are polarized as indicated in structure I. The positions of the three halogen atoms in these complexes have not



I

been established unequivocally, although the proposed arrangement is favored by the authors.

The fact that the alkyliodoso chlorides are so unstable relative to their aryl analogs can be ascribed to the differences in susceptibilities of aliphatic and aromatic systems to attack by nucleophilic reagents. Exner[4] has discussed two alternate mechanisms (eq. 2 and eq. 3) for the decomposition of alkyliodoso chlorides to form alkyl chlorides, in which the substitution of a chlorine atom for an iodine atom on carbon occurs by processes to which he assigns, respectively, S_N2 and S_N1 character. The observation[2c,d] that reactions

$$RICl_2 \longrightarrow R\overset{+}{I}Cl\ Cl^- \longrightarrow ClR + ICl \qquad (2)$$
$$RICl_2 \longrightarrow R^+ICl_2^- \longrightarrow RCl + ICl \qquad (3)$$

of this kind occur with predominant inversion is interesting in this regard, but it should not be cited as evidence that one of these reaction paths is unequivocally to be preferred to the other. It should be noted that, unlike the intermediate in eq. 3, $R\overset{+}{I}Cl\ Cl^-$ could serve adequately as a common type of intermediate in reactions leading to the formation and decomposition of aryliodoso chlorides as well as to the formation and decomposition (either to an alkyl iodide or alkyl chloride) of alkyliodoso chlorides.

The iodomethyl sulfones, $R'SO_2CH_2I$, constitute one class of alkyl iodides which form crystalline iodoso chlorides at room temperature.[4] Exner attributes the unusual stability of these dichlorides to one of two possible influences of the sulfonyl function. Either the $R'SO_2$– group offers sufficient steric protection[5] to the methylene carbon so that S_N2 type decomposition (eq. 2) does not occur or, because of its unfavorable inductive effect, it retards S_N1 type decomposition (eq. 3).

In the earlier investigations concerning the equilibration of aryliodoso chlorides with their components in polar media,[3] it was observed that the rate constants for dissociation of the dichlorides were relatively insensitive to the effects of ring substituents located *meta* or *para* to the reaction site. That is, the reactions to form the free iodo compounds do not appear to be markedly influenced by the organic substituents on iodine. In this connection it has seemed worthwhile to determine the effects of changes in substituents R'– on the stabilities of dichlorides of iodomethyl sulfones ($R'SO_2CH_2ICl_2$). Several new dichlorides of this type have now been prepared, and the kinetics of their equilibration reactions with the free iodo compounds and chlorine have been investigated using acetonitrile, acetic acid and nitromethane as solvents.

Experimental

The Iodomethyl Sulfones.—In general, the sulfones were prepared by the reaction of the appropriate alkane- or arenesulfinic acid sodium salts with methylene iodide. The procedures used in the preparation of iodomethyl *p*-tolyl

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