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Complex Formation of Pyrrole, Indole and Carbazole with Some Sulfur–Oxygen Electron Donors

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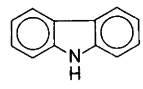
Thermodynamic data and the NH stretching wave number shifts, $\Delta\nu_{NH}$, were determined for the 1:1 hydrogen-bonded complexes of pyrrole, indole and carbazole with dimethyl sulfoxide, *N*,*N*-dimethylmethanesulfinamide, diphenyl sulfoxide and *N*,*N*-dimethylbenzenesulfinamide. The measurements were performed by near infrared spectrophotometric method at 288.15, 298.15, 308.15 and 318.15 K in carbon tetrachloride solution.

The results clearly show that three NH proton donors form relatively weak molecular complexes with the sulfinyl compounds. The proton accepting power of the sulfinyl compounds decreases in the order dimethyl sulfoxide > *N*,*N*-dimethylmethanesulfinamide > *N*,*N*-dimethylbenzenesulfinamide ~ diphenyl sulfoxide, and the proton donating power of the NH proton donors increases in the order pyrrole < indole < carbazole.

I

II



III

In earlier studies sulfinamides were prepared[1,2] and their hydrogen bonding ability towards phenols, 1-naphthol and 2-naphthol studied in carbon tetrachloride solution.[3–6] Further, the complex formation of pyrrole (I), indole (II) and carbazole (III) with substituted 1-phenyl-2-pyrrolidinones has previously been studied in our laboratory.[7] According to these studies, the proton acceptor properties of sulfoxides (R_2SO) and sulfinamides ($RSON(CH_3)_2$) closely resemble each other and the proton donating power of the NH proton donors increases in the order pyrrole < indole < carbazole.

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Wishing to clarify further the proton acceptor properties of sulfinyl compounds, and bearing in mind the importance of indole and indole derivatives and their ability to form hydrogen bonds in biological systems,[8] we have investigated the complex formation of the above-mentioned NH proton donors with some aliphatic and aromatic sulfoxides and sulfinamides in carbon tetrachloride solution. As far as we know, studies on the complex formation of these NH proton donors with sulfinyl compounds have so far been restricted to the pyrrole or indole dimethyl sulfoxide and diphenyl sulfoxide complexes.[9–11]

EXPERIMENTAL

Dimethyl sulfoxide, *N*,*N*-dimethylmethanesulfinamide, *N*,*N*-dimethylbenzenesulfinamide and diphenyl sulfoxide were available from our earlier studies.[5,6]

Pyrrole, a *purum* product from Fluka AG, Buchs, Switzerland, was distilled twice, shortly before use, above barium oxide, and preserved above Union Carbide Molecular Sieves, Type 4A, from British Drug Houses Ltd., Poole, England.[7]

Indole, a *p.a.* product from E. Merck AG, Darmstadt, BRD, was used as received.

Carbazole, a *purissimum* reagent from Fluka AG, was recrystallized three times from absolute ethanol and thereafter once from light petroleum – ethanol mixture.

Carbon tetrachloride, a product for IR-spectroscopy from Fluka AG, was dried and preserved above Molecular Sieves, 4A.

Spectrophotometric measurements were carried out with a Beckman Acta MIV spectrophotometer equipped with a thermostatted cell compartment, which maintained the temperature constant within

Table 1. The values of K, ΔH, $\Delta G°$, $\Delta S°$ and $\Delta\nu_{NH}$ for the complex formation of pyrrole with various proton acceptors in carbon tetrachloride.

		Dimethyl sulfoxide	*N*,*N*-Dimethyl-methanesulfin-amide	Diphenyl sulfoxide	*N*,*N*-Dimethyl-benzenesulfin-amide
K/dm^3 mol^{-1}	288.15 K	20.4±2.9	16.1±2.2	10.9±1.2	11.7±1.0
	298.15 K	16.5±2.5	13.2±1.8	9.05±0.92	9.58±0.90
	308.15 K	13.5±2.3	10.9±1.5	7.53±0.85	8.02±0.75
	318.15 K	11.2±1.8	9.28±1.3	6.42±0.56	7.00±0.50
$-\Delta H$/kJ mol^{-1}		15.6±0.9	14.1±0.3	13.5±0.9	13.4±1.5
$-\Delta G°$/kJ mol^{-1}		6.92±0.43	6.37±0.45	5.45±0.26	5.59±0.25
$-\Delta S°$/J mol^{-1} K^{-1}		29.2±3.2	26.0±1.7	26.9±2.9	26.1±5.0
$\Delta\nu_{NH}$/cm^{-1}		185	173	153	161

±0.1 °C. Quartz cells (Hellma, No. 110-QI) of 10 mm path length were used. The spectra of each solution were recorded at 288.15, 298.15, 308.15 and 318.15 K and after a change in temperature an equilibrium period of about 25 min was allowed.

The concentrations of pyrrole and indole were between 0.002 and 0.004 mol dm^{-3} and the concentration of carbazole was about 0.002 mol dm^{-3}. The base was used in excess and the concentration varied. The spectrum of the NH proton donor – base mixture was scanned within two hours after preparation of the solution against a carbon tetrachloride solution containing the same initial concentration of the base as in the NH proton donor – base mixture.

RESULTS

The experimental results are summarized in Tables 1, 2 and 3 for pyrrole, indole and carbazole, respectively. The equilibrium constants at each temperature were evaluated from the free NH group stretching band of pyrrole, indole or carbazole via the equation

$$K_{11} = \frac{1 - A/A°}{A/A° \left[C°_B - C°_A(1 - A/A°)\right]} \quad (1)$$

where A and $A°$ are the absorbances at the above-mentioned stretching frequency before and after the complex formation, and $C°_A$ and $C°_B$ are the initial concentrations of NH proton donor and proton acceptor, respectively. The K values presented in Tables 1 – 3 are the mean values from 4 – 6 separate experiments. The thermodynamic quantities ΔH, $\Delta G°$ and $\Delta S°$ listed in Tables 1 – 3 are also mean values obtained from the temperature dependence of the equilibrium constants and according to normal thermodynamic relations.[7] All the errors in Tables 1 – 3 are standard errors. The values of $\Delta\nu_{NH}$, the wave number difference between the free and complexed NH-groups, were accurate within ±(1 – 2) cm^{-1} and are also given in Tables 1 – 3.

The hydrogen-bond formation of pyrrole with

Table 2. The values of K, ΔH, $\Delta S°$ and $\Delta\nu_{NH}$ for the complex formation of indole with various proton acceptors in carbon tetrachloride.

		Dimethyl sulfoxide	*N*,*N*-Dimethyl-methanesulfin-amide	Diphenyl sulfoxide	*N*,*N*-Dimethyl-benzenesulfin-amide
K/dm^3 mol^{-1}	288.15 K	27.8±1.5	19.7±2.1	14.2±1.4	13.2±1.5
	298.15 K	21.9±1.2	15.6±1.4	11.6±1.0	10.8±1.2
	308.15 K	17.5±1.0	12.8±1.2	9.53±0.86	8.91±1.09
	318.15 K	14.3±0.9	10.7±0.6	7.87±0.60	7.58±0.87
$-\Delta H$/kJ mol^{-1}		16.9±0.7	15.6±1.2	14.8±1.5	14.4±1.0
$-\Delta G°$/kJ mol^{-1}		7.65±0.14	6.81±0.20	6.06±0.20	5.88±0.30
$-\Delta S°$/J mol^{-1} K^{-1}		31.0±2.6	28.9±3.8	31.2±2.4	28.6±3.5
$\Delta\nu_{NH}$/cm^{-1}		203	188	172	178

Table 3. The values of K, ΔH, $\Delta G°$, ΔS and $\Delta\nu_{NH}$ for the complex formation of carbazole with various proton acceptors in carbon tetrachloride.

		Dimethyl sulfoxide	*N,N*-Dimethyl-methanesulfin-amide	Diphenyl sulfoxide	*N,N*-Dimethyl-benzenesulfin-amide
K/dm^3 mol^{-1}	288.15 K	39.7±3.4	26.5±1.5	18.6±0.7	18.4±2.1
	298.15 K	31.2±2.8	21.3±1.5	15.8±0.6	15.2±1.8
	308.15 K	24.6±2.4	17.6±1.4	13.0±0.5	13.1±1.6
	318.15 K	20.1±2.1	14.2±1.3	11.2±0.5	11.3±1.4
$-\Delta H$/kJ mol^{-1}		17.4±0.7	15.4±1.3	13.5±0.9	12.4±0.6
$-\Delta G°$/kJ mol^{-1}		8.52±0.23	7.58±0.17	6.84±0.08	6.73±0.27
$-\Delta S°$/J mol^{-1} K^{-1}		29.8±2.9	27.7±4.4	23.2±2.8	18.9±2.8
$\Delta\nu_{NH}$/cm^{-1}		210	194	174	181

dimethyl sulfoxide has been investigated earlier by some researchers. Nozari and Drago[10] obtained by calorimetric method the K value 11.3 dm^3 mol^{-1} at 298.15 K for the dimethyl sulfoxide – pyrrole and the value -4.2 ± 0.1 kcal mol^{-1} (17.6 ± 0.4 kJ mol^{-1}) for the complexation enthalpy in carbon tetrachloride solution. Porter and Brey[9] found $K=8.69$ (in mol fraction units) at 306 K and $-\Delta H=3.0\pm0.5$ kcal mol^{-1} (12.6 ± 2.1 kJ mol^{-1}) for the same complex in dimethyl sulfoxide solution, using ^{1}H NMR spectroscopy.

Further comparison with the literature shows that a value of $\Delta\nu_{NH}$ 184 cm^{-1} for the dimethyl sulfoxide – pyrrole complex found by Nozari and Drago[10] in carbon tetrachloride supports our value of 185 cm^{-1}. The $\Delta\nu_{NH}$ value 172 cm^{-1} obtained here for diphenyl sulfoxide – indole complex is exactly the same, but 203 cm^{-1} for dimethyl sulfoxide – indole complex is a little lower than 212 cm^{-1} reported by Hadzi *et al.*[11]

Tables 1 – 3 show that the values of equilibrium constants K_{11}^{298} for the complex formation of pyrrole, indole and carbazole with dimethyl sulfoxide are 16.5, 21.9 and 31.2 dm^3 mol^{-1}, respectively. The corresponding values 13.2, 15.6 and 21.3 dm^3 mol^{-1} for *N,N*-dimethylmethane-sulfinamide complexes are a little lower. Further comparison of the values of K_{11} shows the complex formation ability of the aliphatic sulfinyl compounds to be clearly greater than that of the aromatic compounds. The equilibrium constants for diphenyl sulfoxide – and *N,N*-dimethyl-benzenesulfinamide – NH proton donor complexes are about the same.

Our value 16.5 dm^3 mol^{-1} at 298.15 K for the equilibrium constant of the pyrrole – dimethyl sulfoxide complex, determined by infrared spectrophotometric method, is a little greater than the value obtained by Nozari and Drago[10] by a different method. Moreover our $-\Delta H$ value of 15.6 ±0.9 kJ mol^{-1} for the same complex falls between the values (12.6 ± 2.1) and (17.6 ± 0.4) kJ mol^{-1} noted above. Since the experimental conditions and methods in the present work were not the same as those of Nozari and Drago[10] nor as those of Porter and Brey,[9] however, our results can be considered consistent with their values.

DISCUSSION

As can be seen from Tables 1 – 3, the accuracy of the results varies somewhat with the NH-proton donor – base system and the errors are a little greater than for the corresponding phenol, 1-naphthol and 2-naphthol systems.[1-4] Other studies of pyrroles, indoles and carbazole and related proton donors indicate that the self-association of the solutes in nonpolar solvents does not proceed to any considerable extent in the concentration range used in this work.[12-17] The probability of self-association of the sulfinyl compounds is also insignificant according to the work of Figueroa *et al.*[18] with dimethyl sulfoxide.

As the data in Tables 1 – 3 show, the hydrogen bonding ability of pyrrole, indole and carbazole towards sulfinyl compounds is very similar. In addition, the results show that these NH proton donors form relatively weak hydrogen-bonded complexes with sulfoxides and sulfinamides, $-\Delta H$ being about 13 – 17 kJ mol^{-1} and $\Delta\nu_{NH}$ varying in the range 153 – 210 cm^{-1}. The values seem to be somewhat smaller for the pyrrole – base

complexes than for the corresponding indole and carbazole complexes. Careful examination of the data presented in Tables 1 – 3 indicates the proton donating power of pyrrole, indole and carbazole to be as follows: pyrrole < indole < carbazole.

The pK_a values 16.97 for indole and 17.51 for pyrrole show that pyrrole is a weaker acid than indole.[19] Thus the proton donor ability order towards sulfinyl compounds found in this work: pyrrole < indole < carbazole, follows the acidity order of pyrrole and indole. The same finding was made earlier in our laboratory for the complex formation of substituted 1-phenyl-2-pyrrolidinones with these NH proton donors.[7] The sequence of the proton donating ability of NH proton donors also follows the order of the N – H stretching frequencies, 3496, 3491 and 3485 cm^{-1} for pyrrole, indole and carbazole, respectively, in carbon tetrachloride.[20] Hence the equilibrium constants and thermodynamic quantities presented in Tables 1 – 3 also probably express the relative acidities of the NH proton donors.

According to the data presented in Tables 1 – 3, the wave number shift due to the hydrogen bonding of sulfinyl compounds decreases in the order dimethyl sulfoxide > *N,N*-dimethylmethanesulfinamide > *N,N*-dimethylbenzenesulfinamide ~ diphenyl sulfoxide for all the NH proton donors. This order of $\Delta\nu_{NH}$ values is exactly the same as the order of equilibrium constants given in Tables 1 – 3. Further inspection shows an increase in the values of $\Delta\nu_{NH}$ with $-\Delta H$ of the hydrogen-bonded complexes, and the same pattern of increasing values for $-\Delta G°$ and $-\Delta S°$, too. The same sequence of spectral and thermodynamic quantities found here for sulfinyl compounds was found earlier for phenols, 1-naphthol and 2-naphthol complexed with the same proton acceptors.[1-4] Therefore the results obtained in this work may also express the relative basicities of the sulfinyl compounds.

The wave number shifts $\Delta\nu_{NH}$ found by Thyagarajan and Rao[20] for the complex formation of pyrrole, indole and carbazole with tetrahydrofuran in carbon tetrachloride solution are 146, 156 and 170 cm^{-1}, and with 1-methyl-2-pyrrolidinone by Virtanen and Karjalainen[7] 161, 181 and 184 cm^{-1}, respectively. The $\Delta\nu_{NH}$ values for the sulfinyl compounds presented in Tables 1 – 3 follow the same sequence.

Finally, comparison of our earlier studies[1-4] shows, that the $-\Delta H$ values for phenol-, 1-naphthol- and 2-naphthol – sulfinyl complexes are about 10 kJ mol^{-1} greater than the $-\Delta H$ values found in this work. Correspondingly, the $\Delta\nu_{NH}$ values are much lower than the $\Delta\nu_{OH}$ values. Hence NH proton donors form clearly weaker hydrogen bonds with sulfinyl compounds than the above mentioned OH proton donors. On the other hand, it may be noted that the results obtained in this work support our earlier conclusions that inductive effects of substituents attached to sulfur atom predominate over resonance effects in determining the electron density of the oxygen atom in the sulfinyl group.

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REFERENCES

1. Ruostesuo, P. *Finn. Chem. Lett.* (1978) 163.
2. Ruostesuo, P. *Finn. Chem. Lett.* (1978) 166.
3. Ruostesuo, P. *Finn. Chem. Lett.* (1979) 202.
4. Ruostesuo, P. *Finn. Chem. Lett.* (1979) 206.
5. Ruostesuo, P. and Karjalainen, J. *Finn. Chem. Lett.* (1979) 210.
6. Ruostesuo, P. and Karjalainen, J. *Acta Chem. Scand. A 33* (1979) 765.
7. Karjalainen, J. and Virtanen, P. O. I. *Acta Chem. Scand. A 33* (1979) 76.
8. Spencer, J. N., Gleim, J. E., Blevins, C. H., Garrett, R. C., Mayer, F. J., Merkle, J. E., Smith, S. L. and Hackman, M. L. *J. Phys. Chem. 83* (1979) 2615.
9. Porter, D. M. and Brey, W. S., Jr. *J. Phys. Chem. 72* (1968) 650.
10. Nozari, M. S. and Drago, R. S. *J. Am. Chem. Soc. 92* (1970) 7086.
11. Hadzi, D., Klofutar, C. and Oblak, S. *J. Chem. Soc. A* (1968) 905.
12. Fuson, N., Josien, M. L., Powell, R. L. and Utterback, E. *J. Chem. Phys. 20* (1952) 145.
13. Dos Santos, J., Cruege, F. and Pineau, P. *J. Chim. Phys. Phys.-Chim. Biol. 67* (1970) 826.
14. Bernard-Houplain, M.-C. and Sandorfy, C. *Can. J. Chem. 51* (1973) 1075.
15. Josien, M. L., Pineau, P., Paty, M. and Fuson, N. *J. Chem. Phys. 24* (1956) 1261.
16. Vinogradov, S. N. and Linnell, R. H. *J. Chem. Phys. 23* (1955) 93.
17. Happe, J. A. *J. Phys. Chem. 65* (1961) 72.
18. Fiqueroa, R. H., Roig, E. and Szmant, H. H. *Spectrochim. Acta 22* (1966) 587.
19. Yagil, G. *Tetrahedron 23* (1967) 2855.
20. Thyagarajan, G. and Rao, D. S. R. *Z. Phys. Chem. (Leipzig) 255* (1974) 97.

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