

The Complex Formation of Dibenzyl Sulfoxide with Various Proton Donors

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The complex formation of dibenzyl sulfoxide with phenol, 1-naphthol, 2-naphthol, 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol, 2,2,2-tribromoethanol, pyrrole, indole and carbazole has been studied by near infrared spectrophotometry in carbon tetrachloride at 288.15, 298.15, 308.15 and 318.15 K.

The results show the proton-accepting ability of dibenzyl sulfoxide to be smaller than that of dimethyl sulfoxide and greater than that of diphenyl sulfoxide toward all the OH and NH proton donors studied.

This paper is a part of our attempt to clarify systematically the complex formation ability of sulfonyl and sulfinyl compounds. The earlier results suggest a close similarity in the proton accepting behaviours of sulfones and sulfonamides and, correspondingly, of sulfoxides and sulfenamides. On the other hand, the complex formation ability of dimethyl sulfoxide is known to be relatively strong and that of diphenyl sulfoxide has been found to be half as great, as measured by the K values.^{1,2} We have now extended our studies to the complex formation of dibenzyl sulfoxide with various OH and NH proton donors in carbon tetrachloride.

EXPERIMENTAL

Dibenzyl sulfoxide (a *purum* reagent from Fluka AG) was crystallized several times from absolute ethanol. Carbon tetrachloride for IR-spectroscopy (Fluka AG, Buchs, Switzerland) was dried and preserved above Union Carbide molecular sieves, Type 4 A, from Fluka AG.

The proton donors were commercial products, purified as described earlier.^{1–6}

All spectra were recorded with a Beckman ACTA MIV spectrophotometer at 288.15, 298.15, 308.15 and 318.15 K in carbon tetrachloride solution. A

quartz cell of 10-mm path length was used. The temperature of the measuring and reference cells was kept constant to within $\pm 0.2^\circ\text{C}$. The concentration of the proton donors was between 0.002 and 0.004 mol dm⁻³ and the dibenzylsulfoxide was used in various amounts of excess depending on the proton donor. The cell in the reference beam contained the base in carbon tetrachloride at the same initial concentration as in the sample cell. Details of the apparatus and the methods have been reported previously.¹

RESULTS

The equilibrium constants at different temperatures for the complex formation of dibenzyl sulfoxide with various proton donors are presented in Table 1. The K values were calculated from the absorbance values of the free OH/NH group stretching band of the proton donor observed before (A°) and after (A) the complex formation, using eqn. (1), where

$$K_{11} = \frac{1 - A/A^\circ}{A/A^\circ [C_B^\circ - C_A^\circ (1 - A/A^\circ)]} \quad (1)$$

C_B° and C_A° are the initial concentrations of proton acceptor and proton donor, respectively. The K values, as well as the ΔH values and other quantities presented in Table 2, are mean values of 3–5 independent measurements. The standard error of the mean values is also given in Tables 1 and 2. The ΔH values were obtained from the temperature dependence of the K values and other thermodynamic quantities according to the normal thermodynamic relations.

For comparison Tables 3 and 4 contain the equilibrium constants (K) at 298.15 K, the complexation enthalpies (ΔH), and the wavenumber shifts ($\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$) for the complexes of dimethyl sulfoxide

Table 1. Values of $K_{11}/\text{dm}^3 \text{ mol}^{-1}$ for the complex formation of dibenzyl sulfoxide with various proton donors in carbon tetrachloride at different temperatures.

Proton donor	288.15 K	298.15 K	308.15 K	318.15 K
Phenol	205 ± 15	145 ± 12	106 ± 8	78.7 ± 5.5
1-Naphthol	272 ± 20	190 ± 16	135 ± 10	97.1 ± 6.0
2-Naphthol	307 ± 16	213 ± 13	151 ± 10	110 ± 7
2,2,2-Tribromoethanol	53.9 ± 4.2	41.3 ± 3.3	33.4 ± 2.7	26.1 ± 1.9
2,2,2-Trichloroethanol	63.4 ± 5.2	46.9 ± 4.0	35.3 ± 3.1	25.9 ± 2.2
2,2,2-Trifluoroethanol	141 ± 12	104 ± 9	77.0 ± 7.0	59.1 ± 5.6
Pyrrole	12.7 ± 1.0	10.5 ± 0.9	8.76 ± 0.80	7.17 ± 0.62
Indole	21.3 ± 2.0	17.2 ± 1.7	14.1 ± 1.3	12.1 ± 1.1
Carbazole	30.9 ± 2.3	24.8 ± 1.9	19.8 ± 1.4	16.3 ± 1.2

Table 2. Values of thermodynamic quantities ΔH , ΔG° and ΔS° and the wavenumber shifts $\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ for the complex formation between dibenzyl sulfoxide and various proton donors in carbon tetrachloride.

Proton donor	$-\Delta H$ kJ mol ⁻¹	$-\Delta G^\circ$ kJ mol ⁻¹	$-\Delta S^\circ$ J mol ⁻¹ K ⁻¹	$\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ cm ⁻¹
Phenol	24.3 ± 1.9	12.34 ± 0.20	42.0 ± 5.2	342 ± 2
1-Naphthol	26.2 ± 1.2	13.00 ± 0.21	44.3 ± 4.8	369 ± 2
2-Naphthol	26.1 ± 1.3	13.29 ± 0.15	43.0 ± 5.0	359 ± 2
2,2,2-Tribromoethanol	18.1 ± 0.9	9.22 ± 0.11	29.9 ± 3.3	277 ± 2
2,2,2-Trichloroethanol	22.6 ± 0.8	9.54 ± 0.20	43.8 ± 3.4	283 ± 2
2,2,2-Trifluoroethanol	23.2 ± 0.7	11.50 ± 0.25	39.2 ± 3.3	285 ± 2
Pyrrole	14.4 ± 0.9	5.82 ± 0.21	28.7 ± 3.8	167 ± 2
Indole	14.5 ± 0.8	7.05 ± 0.26	24.9 ± 3.6	186 ± 2
Carbazole	16.4 ± 1.2	7.96 ± 0.18	28.2 ± 4.6	190 ± 2

Table 3. Values of K^{298} , ΔH and $\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ for the complex formation of dimethyl sulfoxide with various proton donors in carbon tetrachloride.

Proton donor	K^{298} dm ³ mol ⁻¹	$-\Delta H$ kJ mol ⁻¹	$\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ cm ⁻¹	Ref.
Phenol	220	24.3	362	1
1-Naphthol	254	27.1	389	3
2-Naphthol	288	27.1	376	4
2,2,2-Tribromoethanol	48.1	21.3	296	7
2,2,2-Trichloroethanol	68.4	21.3	301	7
2,2,2-Trifluoroethanol	148	23.1	306	5
Pyrrole	16.5	15.6	185	6
Indole	21.9	16.9	203	6
Carbazole	31.2	17.4	210	6

with the same proton donors.¹⁻⁷ The complex formation of dibenzyl sulfoxide with naphthols has earlier been studied under quite different conditions⁸ and some isolated values have been published for phenol⁹ and indole.¹⁰

DISCUSSION

It is well known that sulfoxides act as electron donors in hydrogen bond formation and that their electron donating ability is much greater than that of sulfones.^{3,4,11-13} Among sulfoxides, the

Table 4. Values of K^{298} , ΔH and $\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ for the complex formation of diphenyl sulfoxide with various proton donors in carbon tetrachloride.

Proton donor	K^{298} $\text{dm}^3 \text{mol}^{-1}$	$-\Delta H$ kJ mol^{-1}	$\Delta\bar{\nu}_{\text{OH}}/\Delta\bar{\nu}_{\text{NH}}$ cm^{-1}	Ref.
Phenol	61.4	20.3	298	2
1-Naphthol	77.9	23.1	321	3
2-Naphthol	89.8	23.4	315	4
2,2,2-Tribromoethanol	17.6	18.8	243	7
2,2,2-Trichloroethanol	22.1	18.8	247	7
2,2,2-Trifluoroethanol	48.6	21.0	250	5
Pyrrole	9.05	13.5	153	6
Indole	11.6	14.8	172	6
Carbazole	15.8	13.5	174	6

complex formation of dimethyl sulfoxide^{14,15} with various proton donors has been extensively studied, and to a lesser extent the complex formation of diphenyl sulfoxide.¹⁶⁻¹⁸ These studies have shown that the complex formation ability of dimethyl sulfoxide is greater than that of diphenyl sulfoxide, as do the results gathered from our earlier studies collected in Tables 3 and 4.

The results obtained here for the complex formation of dibenzyl sulfoxide with various proton donors seem to be in agreement with those reported earlier in the literature,^{9,10} i.e. the tendency of dibenzyl sulfoxide to form hydrogen-bonded complexes is a little smaller than that of dimethyl sulfoxide (Table 3). This finding is consistent with the tendency of the phenyl group to withdraw electrons, in contrast to the methyl group in dimethyl sulfoxide. Steric factors may further help to lower the ability of dibenzyl sulfoxide to form hydrogen-bonded complexes. Taken together the results presented in Tables 1-4 show the relative basicities of the sulfoxides to be as follows:

diphenyl sulfoxide < dibenzyl sulfoxide < dimethyl sulfoxide

It may also be noted that there is no possibility of direct interaction between the phenyl ring and the sulfur atom in dibenzyl sulfoxide, a fact which is consistent with the sequence of the proton accepting ability found for diphenyl sulfoxide $[(\text{C}_6\text{H}_5)_2\text{SO}]$ and dibenzyl sulfoxide $[(\text{C}_6\text{H}_5-\text{CH}_2)_2\text{SO}]$.

As the experimental data in Tables 1 and 2 show, the proton donor ability of various proton donors towards dibenzyl sulfoxide, as displayed in the K and $-\Delta H$ values, decreases in the order:

2-naphthol > 1-naphthol > phenol > 2,2,2-trifluoroethanol > 2,2,2-trichloroethanol > 2,2,2-tribromoethanol > carbazole > indole > pyrrole

The $\Delta\bar{\nu}_{\text{OH}}$ and $\Delta\bar{\nu}_{\text{NH}}$ values also follow this same sequence, except in naphthols, where the $\Delta\bar{\nu}_{\text{OH}}$ is greater (369 cm^{-1}) for the 1-naphthol-dibenzyl sulfoxide complex than for the 2-naphthol-dibenzyl sulfoxide complex (359 cm^{-1}). It is unnecessary therefore to consider the possibility of specific interactions between dibenzyl sulfoxide and the various proton donors studied.

The presented complex formation ability of phenol, 1-naphthol and 2-naphthol towards sulfur-oxygen electron donors follows the acidity order of the proton donors and that of 2,2,2-trifluoroethanol follows the proton donor ability of phenol.^{4,5,19} Among NH proton donors the proton donor ability is also in agreement with the acidity order between pyrrole and indole expressed as $\text{p}K_{\text{a}}$ values determined in water.^{6,20}

Finally, the recent studies by us and earlier studies by other investigators suggest that the complex formation ability of sulfoxides resembles that of sulfinamides.^{1-7,21} The complex formation ability of sulfinamides is, in turn, of about the same order of magnitude as that of carboxamides. The K values are $145 \text{ dm}^3 \text{mol}^{-1}$ for N,N -dimethylacetamide-phenol and $155 \text{ dm}^3 \text{mol}^{-1}$ for N,N -dimethylmethanesulfinamide-phenol complexes at 298.15 K in carbon tetrachloride.^{21,22} The sulfoxides are widely used as solvents, as well as extraction agents in liquid-liquid extraction or in extraction chromatography.²³ It may also be worth noticing that aromatic sulfoxides like dibenzyl sulfoxide seem to be more suitable than aliphatic sulfoxides

for the extraction of *e.g.* inorganic compounds due to their lower ability to form complexes as also the results presented in this paper clearly demonstrate.^{23,24}

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24. Vlacil, F. and Khanh, H. D. *Collect. Czech. Chem. Commun.* 44 (1979) 1918.

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REFERENCES

1. Ruostesuo, P. *Finn. Chem. Lett.* (1979) 202.
2. Ruostesuo, P. *Finn. Chem. Lett.* (1979) 206.
3. Ruostesuo, P. and Karjalainen, J. *Finn. Chem. Lett.* (1979) 210.
4. Ruostesuo, P. and Karjalainen, J. *Acta Chem. Scand. A* 33 (1979) 765.
5. Karjalainen, J. and Ruostesuo, P. *Finn. Chem. Lett.* (1980) 169.
6. Karjalainen, J. and Ruostesuo, P. *Acta Chem. Scand. A* 34 (1980) 573.
7. Ruostesuo, P. and Karjalainen, J. *Spectrochim. Acta A* 37 (1981) 535.
8. Saffioti, W., Nazario, G. and Gullo, I. M. de L. *Eletica Quim. I* (1976) 59.
9. Gramstad, T. *Spectrochim. Acta* 19 (1963) 829.
10. Hadzi, D., Klofutar, C. and Oblak, S. *J. Chem. Soc. A* (1968) 905.
11. Barnard, D., Fabian, J. M. and Koch, H. P. *J. Chem. Soc.* (1949) 2442.
12. Cairns, T., Eglinton, G. and Gibson, D. T. *Spectrochim. Acta* 20 (1964) 31.
13. Biscarini, P., Galloni, G. and Ghersetti, S. *Spectrochim. Acta* 20 (1964) 267.
14. Augdahl, E. and Klæboe, P. *Acta Chem. Scand.* 18 (1964) 18.
15. Drago, R. S., Wayland, B. and Carlson, R. L. *J. Am. Chem. Soc.* 85 (1963) 3125.
16. Figueroa, R. H., Roig, E. and Szmant, H. H. *Spectrochim. Acta* 22 (1966) 1107.
17. Kivinen, A., Murto, J. and Silvennoinen, B. *Acta Chem. Scand. A* 28 (1974) 697.
18. Kivinen, A., Murto, J., Liljequist, S. and Vaara, S. *Acta Chem. Scand. A* 29 (1975) 911.
19. Bhowmik, B. B. and Basu, S. *Trans. Faraday Soc.* 59 (1963) 813.
20. Yagil, G. *Tetrahedron* 23 (1967) 2855.
21. Møllendal, H., Grundnes, J. and Klæboe, P. *Spectrochim. A* 24 (1968) 1669.
22. Nakano, H., Nakano, N. I. and Higuchi, T. *J. Phys. Chem.* 71 (1967) 3954.
23. Vlacil, F. and Adamcova, E. *Collect. Czech. Chem. Commun.* 43 (1978) 1606.