

The Complex Formation of 2-Naphthol with Some Sulfur – Oxygen Electron Donors

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A near infrared spectrophotometric method was used to obtain the equilibrium constant K_{11} for the complex formation of 2-naphthol with some aliphatic and aromatic sulfinyl and sulfonyl compounds, at 288.15, 298.15, 308.15 and 318.15 K. The thermodynamic quantities, ΔH , ΔG° and ΔS° , and the values of wave number shifts, $\Delta\nu_{\text{OH}}$, were also determined. Measurements were made in carbon tetrachloride solution. On the basis of the obtained data, the proton donor strength of 2-naphthol was found to be of about the same magnitude as that of 1-naphthol. Furthermore, the results show that the association properties of sulfoxides and sulfinamides and, correspondingly, those of sulfones and sulfonamides resemble each other.

Sulfonamides are interesting compounds biologically, and their electronic and spectral properties have been thoroughly studied. The studies have shown that sulfonamides are weaker proton acceptors than carboxamides,^{1,2} for example. Moreover, the hydrogen bonding abilities of *N,N*-dimethylmethanesulfonamide and *N,N*-dimethylacetamide have been found to be about the same.^{2,3} Taken together, these studies strongly indicate that sulfinyl compounds are stronger proton acceptors than the corresponding sulfonyl compounds.

In an earlier paper, results were reported for the complex formation of 1-naphthol with some sulfur – oxygen proton acceptors.⁴ To obtain further information concerning the proton acceptor properties of sulfinyl and sulfonyl compounds, the association of 2-naphthol with the same aliphatic and aromatic sulfoxides (R_2SO), sulfinamides ($\text{RSON}(\text{CH}_3)_2$), sulfones (R_2SO_2) and sulfonamides ($\text{RSO}_2\text{N}(\text{CH}_3)_2$) was studied in carbon tetrachloride by a near infrared spectroscopic method. To our

knowledge, the proton donor properties of 2-naphthol towards sulfur – oxygen proton acceptors have not been studied previously.

EXPERIMENTAL

2-Naphthol, a *puriss.* reagent from Merck AG, Darmstadt, BRD, was crystallized from carbon tetrachloride and dried over phosphorus pentoxide in a desiccator.⁵

Dimethylsulfoxide and diphenylsulfone were commercial products, purified as reported earlier.^{6,7} Sulfonamides and sulfinamides as well as diphenylsulfoxide were prepared according to known methods as described earlier.⁷ Sulfinamides were purified by distillation and sulfonamides and diphenylsulfoxide were crystallized several times from absolute ethanol. Physical and spectral properties were consistent with the literature values.

Carbon tetrachloride for IR-spectroscopy was obtained from Fluka AG, Buchs, Switzerland, and was dried and preserved above Union Carbide Molecular Sieves, Type 4A, from British Drug Houses Ltd., Poole, England.

Infrared spectra were recorded on a Beckman Acta MIV spectrophotometer equipped with a thermostated cell compartment. Quartz cells (Hellma No. 110, QI) of 10 mm path length were used. The spectrum of the 2-naphthol – base mixture was scanned against a carbon tetrachloride solution containing the same initial concentration of the base as in the experimental mixture. The spectra were recorded within 2 h after preparation of the solutions and the temperature in the measuring cell was found to be constant within $\pm 0.1^\circ$. The time allowed for temperature equilibration of the solutions was about 25 min.

The stock solution of 2-naphthol prepared was about $0.008 \text{ mol dm}^{-3}$. Five milliliter amounts of

Table 1. Values of $K_{11}/\text{dm}^3 \text{ mol}^{-1}$ for the complex formation between 2-naphthol and some sulfur – oxygen proton acceptors in carbon tetrachloride at different temperatures.

Proton acceptor	288.15 K	298.15 K	308.15 K	318.15 K
Dimethylsulfoxide	421 ± 12	288 ± 3	203 ± 5	145 ± 3
<i>N,N</i> -Dimethylmethanesulfinamide	281 ± 17	198 ± 13	144 ± 11	107 ± 7
Diphenylsulfoxide	124 ± 7	89.8 ± 6.4	66.2 ± 5.5	49.6 ± 4.0
<i>N,N</i> -Dimethylbenzenesulfinamide	157 ± 5	110 ± 4	81.3 ± 4.1	60.6 ± 3.5
<i>N,N</i> -Dimethylmethanesulfonamide	28.1 ± 1.7	21.6 ± 1.2	16.9 ± 0.7	13.8 ± 1.1
Diphenylsulfone	22.5 ± 2.3	17.4 ± 1.8	14.0 ± 1.4	11.2 ± 1.6
<i>N,N</i> -Dimethylbenzenesulfonamide	22.2 ± 1.6	17.2 ± 1.1	13.8 ± 0.8	11.3 ± 1.0

this solution were used together with carbon tetrachloride and different weighed quantities of base to give 10 ml in a volumetric flask. As earlier, no systematic difference was found between the K values when the solutions were prepared by weighing all the components.⁴

RESULTS

The equilibrium constants K_{11} for the 1:1 complexes were calculated from the equation

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

where A° and A are the absorbances at the stretching frequency of the free hydroxyl group of 2-naphthol before and after the complex formation, C_A° is the total concentration of 2-naphthol and C_B° that of the proton acceptor. For each system, the values of equilibrium constants were determined in at least four separate experiments.

The values of K_{11} at different temperatures, presented in Table 1, are the mean values of the independent measurements. The values of ΔH were

calculated from the temperature dependence of the K_{11} values, using plots of $\ln K_{11}$ against $1/T$ and the method of least mean squares. The thermodynamic quantities ΔG° and ΔS° were obtained according to usual thermodynamic relations:

$$\Delta G^\circ = -RT \ln K_{11}^{298} \quad (2)$$

$$\Delta S^\circ = \frac{\Delta H - \Delta G^\circ}{T} \quad (3)$$

The quantities ΔH , ΔG° and ΔS° presented in Table 2 are also mean values and all the errors in Tables 1–3 are standard errors.

The wave number shifts, $\Delta\nu_{\text{OH}}$ at 298.15 K, of the 2-naphthol OH-stretching band for base – 2-naphthol complexes are also given in Table 2. The errors of these values were within $\pm 1 \text{ cm}^{-1}$.

DISCUSSION

As mentioned earlier, very few experimental data exist on the complex formation of naphthols.⁴ In Table 1 values of K_{11} for the 2-naphthol complexes are given.

Inspection of the above K_{11}^{298} values shows that

Table 2. Values of thermodynamic quantities ΔH , ΔG° and ΔS° both the wave number shifts, $\Delta\nu_{\text{OH}}$, for the complex formation between 2-naphthol and various bases in carbon tetrachloride at 298.15 K.

Proton acceptor	$-\Delta H$	$-\Delta G^\circ$	$-\Delta S^\circ$	$\Delta\nu_{\text{OH}}$
	kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	cm^{-1}
Dimethylsulfoxide	27.1 ± 1.2	14.04 ± 0.03	43.9 ± 3.9	376
<i>N,N</i> -Dimethylmethanesulfinamide	24.7 ± 0.9	13.10 ± 0.17	38.8 ± 3.3	354
Diphenylsulfoxide	23.4 ± 0.9	11.14 ± 0.17	41.1 ± 3.4	315
<i>N,N</i> -Dimethylbenzenesulfinamide	24.2 ± 0.8	11.66 ± 0.09	41.9 ± 2.9	331
<i>N,N</i> -Dimethylmethanesulfonamide	18.1 ± 0.9	7.61 ± 0.14	35.0 ± 3.0	149
Diphenylsulfone	17.6 ± 0.9	7.08 ± 0.26	35.4 ± 3.9	140
<i>N,N</i> -Dimethylbenzenesulfonamide	17.1 ± 0.9	6.94 ± 0.30	34.0 ± 2.8	136

Table 3. Values of K_{11}^{298} , ΔH and $\Delta\nu_{OH}$ for the complex formation of 1-naphthol and various proton acceptors in carbon tetrachloride. From Ref. 4.

Proton acceptor	K_{11} $\text{dm}^3 \text{mol}^{-1}$	$-\Delta H$ kJ mol^{-1}	$\Delta\nu_{OH}$ cm^{-1}
Dimethylsulfoxide	254 ± 7	27.1 ± 1.1	389
<i>N,N</i> -Dimethylmethanesulfinamide	172 ± 9	25.4 ± 1.1	362
Diphenylsulfoxide	77.9 ± 3.7	23.1 ± 0.9	321
<i>N,N</i> -Dimethylbenzenesulfinamide	95.8 ± 3.4	23.5 ± 0.9	336
<i>N,N</i> -Dimethylmethanesulfonamide	16.0 ± 0.9	17.2 ± 1.0	152
Diphenylsulfone	12.8 ± 0.7	16.0 ± 1.4	143
<i>N,N</i> -Dimethylbenzenesulfonamide	12.9 ± 1.0	16.4 ± 0.4	139

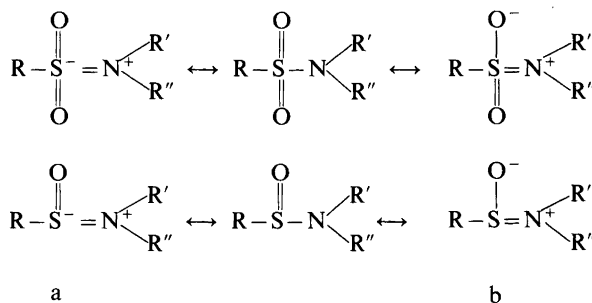
the equilibrium constant is larger for the dimethylsulfoxide–2-naphthol complex than for the *N,N*-dimethylmethanesulfinamide–2-naphthol complex, whereas in the corresponding aromatic compounds the K values are about the same. The differences between the K values for the aliphatic and aromatic sulfoxides and sulfinamides may be due to the tendency of the phenyl group to withdraw electrons from the sulfur atom and thus to decrease the electron density of the oxygen atom of the sulfinyl group. The greater steric hindrance of the two phenyl groups of diphenyl sulfoxide than the one of *N,N*-dimethylbenzenesulfinamide may also affect the sequence of the equilibrium constants for these compounds.

The observation that the experimental results are nearly the same for corresponding sulfoxides and sulfinamides and the same, within experimental errors, for diphenylsulfone and *N,N*-dimethylbenzenesulfonamide are in agreement with the results found earlier in sulfinyl and sulfonyl compounds, that inductive effects of substituents attached to sulfur predominate over resonance effects in determining the sulfur–oxygen bond polarity.⁸ Accordingly, the results obtained by us support the conclusion, that resonance like that in carboxamides

(b) does not significantly affect the electronic structure of sulfon- and sulfinamides.⁹ The resonance structure (a), however, where the sulfur atom carries a partial charge, may explain the observations that hydrogen-bonding abilities of sulfoxides and sulfinamides and, correspondingly, those of sulfones and sulfonamides resemble each other.

The $\text{p}K_a$ values are 9.85, 9.93 and 9.95 for 1-naphthol, 2-naphthol and phenol, respectively.¹⁰ When we earlier studied the complex formation of 1-naphthol and phenol with the same sulfur–oxygen proton acceptors, we found the equilibrium constants to be greater for 1-naphthol systems than the corresponding phenol systems.^{4,7,11} This sequence follows the acidity order of the proton donors.

As Tables 1 and 3 show, the equilibrium constants are smaller for 1-naphthol complexes than for the corresponding 2-naphthol complexes. This trend is contrary to the acidity order, as represented by the above-mentioned $\text{p}K_a$ values. Similar sequences of equilibrium constants were obtained by Kubota,¹² who studied the complex formation of trimethylamine *N*-oxide with phenol, 1-naphthol and 2-naphthol in dichloromethane solution.



The values of $\Delta\nu_{\text{OH}}$ obtained for the 2-naphthol complexes of the various bases are presented in Table 2. Comparison of these values with the $\Delta\nu_{\text{OH}}$ values (Table 3) for the corresponding 1-naphthol complexes shows the value of $\Delta\nu_{\text{OH}}$ to be a little greater for the 1-naphthol complex in all cases. The wave number shift, $\Delta\nu_{\text{OH}}$, upon complexation with the same sulfur-oxygen proton acceptor is greater for both naphthols than for phenol, however.^{4,7,11}

On the other hand, it may be noted that the values of ΔH (Tables 2 and 3) are, within experimental error, the same and the $\Delta\nu_{\text{OH}}$ values nearly the same for the complexation of both 1-naphthol and 2-naphthol with these sulfinyl and sulfonyl compounds. Accordingly, we may conclude that the strengths of the hydrogen bonding of 1-naphthol and 2-naphthol complexes with the bases presented in Table 1 are similar both in regard to the wave number shifts, $\Delta\nu_{\text{OH}}$, of the free OH-stretching bands for the naphthol complexes and in regard to the values of complexation enthalpy.

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REFERENCES

1. Jarva, M., Saastamoinen, M. and Virtanen, P. O. I. *Finn. Chem. Lett.* (1974) 169.
2. Nakano, M., Nakano, N. I. and Higuchi, T. *J. Phys. Chem.* 71 (1967) 3954.
3. Møllendal, H., Grundnes, J. and Klæboe, P. *Spectrochim. Acta Part A* 24 (1968) 1669.
4. Ruostesuo, P. and Karjalainen, J. *Finn. Chem. Lett.* (1979). *In press.*
5. Perrin, D. D., Armarego, W. L. F. and Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Elmsford-Oxford 1966, p. 218.
6. Drago, R. S., Wayland, B. and Carlson, R. L. *J. Am. Chem. Soc.* 85 (1963) 3125.
7. Ruostesuo, P. *Finn. Chem. Lett.* (1979). *In press.*
8. Engberts, J. B. F. N. and Zuidema, G. *Recl. Trav. Chim. Pays-Bas* 89 (1970) 1202.
9. Hovius, K., Zuidema, G., Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* 90 (1971) 633.
10. Bhowmik, B. B. and Basu, S. *Trans. Faraday Soc.* 59 (1963) 813.
11. Ruostesuo, P. *Finn. Chem. Lett.* (1979). *In press.*
12. Kubota, T. *J. Am. Chem. Soc.* 88 (1966) 211.

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