Charge-transfer Interaction between *N,N*-Dimethylaniline and Aromatic Sulphonyl Chlorides

Harimoorthi Kothandaraman and Narayanan Arumugasamy
Department of Polymer Science, University of Madras, Madras-600 025, India

The donor–acceptor interactions of *N,N*-dimethylaniline with toluene-*p*-sulphonyl chloride, toluene-*o*-sulphonyl chloride, and benzenesulphonyl chloride have been investigated by u.v.–visible spectroscopy. New charge-transfer bands were observed in acetonitrile medium. Equilibrium constants and thermodynamic parameters were determined.

The work of Benesi and Hildebrand[1] on the interaction of iodine with aromatic hydrocarbons has led to an increasing number of investigations on charge-transfer complexes. Molecular orbital techniques have been applied to such molecular interactions, based on Mulliken's theory[2] of intermolecular charge-transfer. Experimentally the structures and physical properties of charge-transfer complexes have been studied by u.v.,[3,4] i.r.,[5,6] and n.m.r.[7] methods. Association constants have been evaluated for a large number of donor–acceptor complexes, and in many cases the corresponding heats and entropies of formation have also been determined.

It has also been shown that during the interaction of *N,N*-dimethylaniline (DMA) with anhydrides and acid chlorides of carboxylic acids[8,9] charge-transfer complexes are formed, which may initiate the polymerization of unsaturated compounds. Despite the interesting possibilities raised by the variable valency of sulphur, few studies[10,11] have been done on the donor–acceptor interactions of sulphur compounds (as 'acceptors'). In the present paper, a detailed study of the charge-transfer interactions of DMA with toluene-*p*-sulphonyl chloride (TsCl), toluene-*o*-sulphonyl chloride (*o*-TsCl), and benzenesulphonyl chloride (BsCl) is reported.

Experimental

Reagents.—DMA Was purified as described by Vogel[12a] (b.p. 193 °C). TsCl was prepared[12b] from toluene and chlorosulphonic acid, and twice recrystallized from light petroleum (b.p. 40—60 °C) (m.p. 69 °C). *o*-TsCl was also prepared[12b] from toluene and chlorosulphonic acid, and purified and then distilled under vacuum (b.p. 154 °C at 36 mmHg). BsCl was twice distilled under reduced pressure (b.p. 120 °C at 10 mmHg).

Spectroscopic Measurements.—The spectroscopic measurements were carried out with a Carl-Zeiss UV-VIS spectrophotometer. In general, measured volumes of acetonitrile solutions of known concentration of DMA (0.158—1.420 mol l^{-1}) were mixed with measured volumes of standard solutions of aromatic sulphonyl chlorides in acetonitrile. The optical densities of the resulting solutions were measured immediately in 1 cm quartz cells. The measurements were made against blanks which were identical with the reaction mixtures except that they contained no acceptor. Temperature control was accurate to within ±0.1 °C.

Results and Discussion

Determination of Equilibrium Constants.—The results of the absorption measurements on the mixtures are presented in the Figure together with spectra of the starting materials. The Figure shows the appearance of new bands in the visible region corresponding to the charge-transfer absorptions. The individual components do not absorb in these regions at the concentrations used. On increasing the concentration of DMA, the optical density of the charge-transfer complexes increased, showing that these bands could be directly correlated with the donor action of DMA.

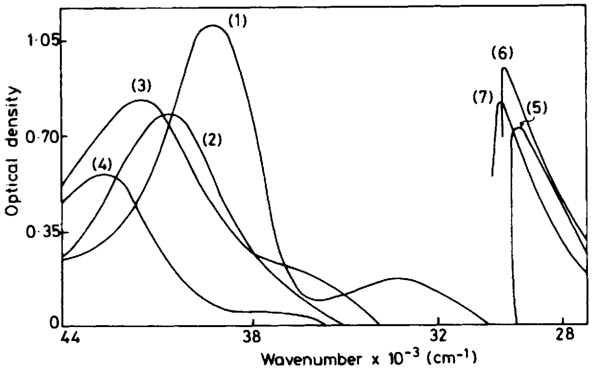

Figure. U.v. spectra of (1) DMA (5×10^{-5} mol l^{-1}), (2) TsCl (1×10^{-4} mol l^{-1}), (3) *o*-TsCl (1×10^{-4} mol l^{-1}), (4) BsCl (7.5×10^{-5} mol l^{-1}), (5) DMA–TsCl ([DMA] = 0.789 mol l^{-1}; [TsCl] = 1.53×10^{-2} mol l^{-1}), (6) DMA–*o*-TsCl ([DMA] = 1.341 mol l^{-1}; [*o*-TsCl] = 1.05×10^{-2} mol l^{-1}), (7) DMA–BsCl ([DMA] = 0.868 mol l^{-1}; [BsCl] = 1.18×10^{-2} mol l^{-1}).

For the determination of the composition of the complex, in each case, Job's method[13] of continuous variation was applied. It was observed that the maximum optical density, and consequently the maximum concentration of the complex, was observed at equimolar proportions. In all three systems, the stoicheiometry of the charge-transfer complex was observed to be 1 : 1.

In order to obtain supplementary evidence for the formation of 1 : 1 complexes, the Benesi–Hildebrand method and the Scatchard method[14] were also applied. The spectra of the various sulphonyl chlorides and DMA at various concentrations did not show any change even after an hour.

It can be assumed that the complex C coexists in solution with the free components D (DMA) and S (the aromatic sulphonyl chloride). The equilibrium between the complex and the components may be represented as in equations (1)—(3),

$$D + S \xrightleftharpoons{K_C} C \tag{1}$$

$$K_C = [C]/[D][S] \tag{2}$$

Table. Thermodynamic parameters of the charge-transfer complexes of *N,N*-dimethylaniline with aromatic sulphonyl chlorides at 25 °C

Acceptor	$\lambda_{max.}$ nm	ε_λ l mol^{-1} cm^{-1}	K_N	$-\Delta H_N^\circ$ kJ mol^{-1}	$-\Delta G_N^\circ$ kJ mol^{-1}	$-\Delta S_N^\circ$ J mol^{-1} K^{-1}
TsCl	342	250	6.00 ± 0.29	5.36 ± 0.19	4.44 ± 0.12	3.09 ± 0.23
o-TsCl	338	500	3.11 ± 0.05	4.31 ± 0.11	2.80 ± 0.04	5.06 ± 0.19
BsCl	336	294	6.94 ± 0.12	6.19 ± 0.20	4.81 ± 0.07	4.64 ± 0.41

$$K_C = [C]/([D]_0 - [C])([S]_0 - [C]) \quad (3)$$

where $[D]_0$ and $[S]_0$ indicate the total (*i.e.* free and uncomplexed) concentrations of D and S, respectively. Under the conditions $[D]_0 \gg [S]_0$, the Benesi–Hildebrand equation can be written as (4), where ε_λ is the molar extinction coefficient

$$[S]_0 l/A = 1/K_C\varepsilon_\lambda[D]_0 + 1/\varepsilon_\lambda \quad (4)$$

of C at the wavelength of measurement (λ), l is the pathlength, and A is the experimental absorbance.

Many investigators[1,8,15] have chosen to express the concentration of the donor in terms of its mole fraction (N_D) rather than in moles per litre [equation (5)]. The plots of

$$[S]_0 l/A = 1/K_N\varepsilon_\lambda N_D + 1/\varepsilon_\lambda \quad (5)$$

$[S]_0 l/A$ *vs.* $1/N_D$ for the three systems were found to be linear, indicating the formation of 1 : 1 complexes. The values of ε_λ were obtained from the reciprocals of the ordinate intercepts of the plots. The slopes of these lines, which, according to equation (5), are equal to $1/K_N\varepsilon_\lambda$, were measured to evaluate K_N. For comparison, the Scatchard plots were also drawn; the values of K_N(DMA–TsCl 5.22; DMA–*o*-TsCl 2.64; DMA–BsCl 5.45) and ε_λ (DMA–TsCl 280; DMA–*o*-TsCl 578; DMA–BsCl 352 l mol^{-1} cm^{-1}) obtained were not very different from the values obtained by the Benesi–Hildebrand treatment (Table).

Effect of Temperature.—The association constant (K_N) was determined for a wide range of temperature, over which the extinction coefficients of the complexes studied were apparently invariant. The intercept of each plot (the reciprocal of the extinction coefficient of the complex) remained constant as the temperature was changed (from 25 to 50 °C).

The thermodynamic parameters were obtained from the optically determined values of K_N at different temperatures. The values of ΔH and ΔS were estimated by use of the relation ln $K = \Delta H/RT + \Delta S/R$ (Table)

The values of the equilibrium constant decreased in the order DMA–BsCl > DMA–TsCl > DMA–*o*-TSCl. The lower value of K_N for DMA–TsCl as compared with DMA–BsCl could be due to a decreased acceptor character of the aromatic sulphonyl chloride, caused by the electron-donating 4-methyl group. The much lower value of K_N for DMA–*o*-TsCl system may be due to the steric influence of the 2-methyl group.

Studies of vinyl polymerization using these charge-transfer complexes are in progress.

Acknowledgements

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