A spectroscopic study of charge-transfer complexes of aniline and N-alkylanilines with nitromethane

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Formation of yellow coloured charge-transfer complexes of aniline, N-methylaniline, N,N-dimethylaniline and N,N-diethylaniline with nitromethane (NM) in carbon tetrachloride solution has been investigated by UV-vis spectrophotometry and $^{1}HNMR$ spectrometry. The $\lambda_{CT}$ of the resulting 1:1 molecular complexes have been isolated. The molar absorptivities and association constants have been determined. The stabilities of these complexes vary in the order: aniline-NM > N-methylaniline-NM > N,N-dimethylaniline-NM > N,N-diethylaniline-NM. The study shows that hydrogen bonding contributes significantly to the stabilities of the complexes of aniline and N-methylaniline.

Both nitromethane$^1$ and aromatic amines$^{2,3}$ are reported to form charge-transfer complexes. However, there is no report on the charge-transfer complexes of nitromethane with aromatic amines. Qureshi$^4$ had earlier proposed that the interaction of aromatic amines and dinitrobenzenes was due to charge-transfer and not hydrogen bonding. This was at variance to the studies of Thorne and Koop$^5$ whose conclusions were based solely on phase diagrams. A further study$^6$ reported that both the interactions are important. With increasing awareness that many hydrogen bonded systems are predominantly charge-transfer complexes and vice versa$^7$ it was found worthwhile to investigate the complexes of aniline and N-alkylanilines with nitromethane because nitromethane is a simple non-aromatic molecule, contains single nitro and methyl groups, gives a sharp singlet in the $^{1}HNMR$ spectrum and can behave as an electron acceptor as well as a proton acceptor.

Experimental

Nitromethane, N,N-dimethylaniline and N,N-diethylaniline were from BDH Poole England and aniline and N-methylaniline were from Riedel. All were Analytical Grade reagents. Aniline and N-methylaniline were freshly distilled over zinc dust prior to use. The solvent used was CCl$_4$ (BDH, Analar). Nitromethane and CCl$_4$ were used as received. The UV-vis spectral data was obtained on ELICO SL 151 UV-vis spectrophotometer and the $^{1}HNMR$ spectral data was recorded on Hitachi R-600 FTNMR spectrometer, working at 60 MHz with TMS as the reference.

In the UV-vis spectrum, nitromethane was found to be transparent throughout the region of interest. The small absorption of aniline/N-alkylaniline was compensated by taking an equal concentration of aniline/N-alkylaniline in the reference cell as present in the complex. The procedure followed a method developed by Mulliken$^8$. For isolation of absorption maxima of the nitromethane-aromatic amine complexes equal volumes of 0.1 M solutions of nitromethane and aromatic amine in CCl$_4$ were mixed and the spectra recorded against a blank containing an equal concentration of aromatic amine.

Association constants of nitromethane-aromatic amine complexes were evaluated by optical spectroscopy using the well known Benesi-Hildebrand equation$^9$ at the respective $\lambda_{CT}$ of the complexes under the condition $[D]_0 >> |A|_o$.

$$[A]_k = \frac{1}{A} \frac{1}{K \epsilon_h} \frac{1}{[D]_0} + \frac{1}{\epsilon_h}$$

where $[A]_0$ is the initial concentration of the acceptor, $[D]_0$ is the initial concentration of the donor, $K$ is the association constant of the complex, $A$ is the absorbance of the complex at $\lambda_{CT}$ and $\epsilon_h$ is the molar absorptivity of the complex at $\lambda_{CT}$. $|A|_o$ was kept constant and $[D]_0$ was varied and kept in large excess over the acceptor. On plotting $|A|_o/A$ vs $1/[D]_0$ for a series of solutions under the condition $[D]_0 >> |A|_0$ a linear graph was obtained with intercept $1/\epsilon_h$ and the slope $1/K\epsilon_h$.

Results and discussion

The UV-vis spectra of nitromethane, aromatic amines and the mixture in CCl$_4$ were recorded. On mixing the two components, a stable yellow colour was obtained. The appearance of a new band in the mixture indicated the formation of a CT complex. The straight line obtained in the Benesi-Hildebrand plot indicates a 1:1 stoichiometry of the complexes. The CT-bands, the molar absorptivities and the association
Table 1—CT-bands, association constants and molar absorptivities of the nitromethane-aromatic amine complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{CT}$ (nm)</th>
<th>$\nu_{CT}$ (cm$^{-1}$)</th>
<th>$K$ (25°C) (1 mol$^{-1}$)</th>
<th>$\epsilon_{CT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$—Aniline</td>
<td>365</td>
<td>27397</td>
<td>0.99</td>
<td>8.77</td>
</tr>
<tr>
<td>CH$_3$NO$_2$—N-Methylaniline</td>
<td>364</td>
<td>27473</td>
<td>0.95</td>
<td>38.46</td>
</tr>
<tr>
<td>CH$_3$NO$_2$—N,N-Dimethylaniline</td>
<td>373</td>
<td>26809</td>
<td>0.70</td>
<td>15.38</td>
</tr>
<tr>
<td>CH$_3$NO$_2$—N,N-Diethylaniline</td>
<td>377</td>
<td>26525</td>
<td>0.31</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Fig. 1—$^1$HNMR spectrum of nitromethane—aniline complex in CCl$_4$

Fig. 2—$^1$HNMR spectrum of nitromethane—N,N-dimethylaniline complex in CCl$_4$
constants are listed in Table 1. The charge-transfer chemistry of these complexes has been studied by $^1$H NMR spectrometry.

$^1$H NMR spectra of the two components and the mixture in CCl$_4$ were recorded. The spectrum of the mixture is a summation of the spectra of the two components. However, the shifts in the peaks are clearly visible. In the spectrum of nitromethane, the CH$_3$NO$_2$ resonance appears as a sharp singlet at 4.17 ppm. In the spectra of anilines, the NH protons of aniline and N-methylaniline appear as sharp singlets at 3.32 ppm and 2.39 ppm respectively. The aromatic protons of aromatic amines give very complex patterns and are difficult to decipher. On complexation the CH$_3$NO$_2$ singlet moves upfield while the NH protons of aniline and N-methylaniline move downfield (Fig. 1). The downfield shift of NH protons is not very diagnostic because the electron density around NH protons would decrease both in charge-transfer as well as hydrogen bonding. An upfield shift of CH$_3$NO$_2$ singlet in all the four complexes is an indication of higher charge density on the methyl hydrogens of nitromethane which in turn is an indication of charge-transfer (CH$_3$NO$_2$ being an acceptor). The alkyl protons of N,N-dimethylaniline and N,N-diethylamine do not show any appreciable shifts (Fig. 2). This indicates that the alkyl protons are not involved in hydrogen bonding and that the complexation of N,N-dimethylaniline and N,N-diethylamine with nitromethane is due to charge-transfer.

The small values of the association constants (Table 1) indicate the weak nature of these complexes. The ionization potential of the aromatic amines are in the following order: aniline > N,N-dimethylaniline > N,N-diethylamine. A high ionization potential signifies a low tendency towards charge-transfer (i.e., weak donor). If charge-transfer was the only mode of interaction, then aniline would form the weakest charge-transfer complex and N,N-diethylamine would form the strongest charge-transfer complex with nitromethane in the present series and the association constants obtained would be in the following order: N,N-diethylamine > N,N-dimethylaniline > aniline. However, a reverse trend is obtained here. The greater stability of the aniline and N-methylaniline complexes (higher K values) than N,N-dimethylaniline and N,N-diethylamine complexes is probably because aniline and N-methylaniline are capable of forming hydrogen bonding in addition to charge-transfer and both the forces reinforce each other.

A glance at the nitromethane molecule shows that nitromethane can behave as an electron acceptor as well as a proton acceptor. The aromatic amines are n-donors. Besides, both aniline and N-methylaniline possess amino protons and are capable of hydrogen bonding too. The greater stability of aniline and N-methylaniline complexes is because of complex formation by simultaneous charge-transfer and hydrogen bonding (Structure I).

The complex formation of N,N-dimethylaniline and N,N-diethylamine with nitromethane takes place by charge-transfer alone; they cannot form hydrogen bonded complexes as the protons are attached to carbon and not nitrogen. This is confirmed by the absence of any appreciable shifts in the alkyl protons of the N-alkylanilines. For coherent interaction between the donor and the acceptor, the acceptor molecule must approach the donor site (N atom) as closely as possible which is hindered by the bulky alkyl groups around the N atoms (Structure II). This steric effect is more in N,N-diethylamine than in N,N-dimethylaniline as ethyl groups are more bulky than the methyl groups. This explains the higher value of K for N,N-dimethylaniline than for N,N-diethylamine against the Ip values.

The $v_{CT}$ values for these CH$_3$NO$_2$ - aromatic amine complexes are given in Table 1. The trend in ionization potential of these aromatic amines is aniline > N-methylaniline > N,N-dimethylaniline > N,N-diethylamine. McConnell et al. have shown that the relationship between Ip and $v_{CT}$ for
complexes of iodine with a wide range of donors is almost linear. Since then, linear relationship between $I_p$ and $v_{CT}$ for various donors with a common acceptor has been obtained by various workers. Although there is no theoretical explanation for such a linear relationship, it is taken as a confirmation of charge-transfer chemistry of the complexes. However, in the present study charge-transfer does not seem to be the only mode of interaction between aromatic amines and nitromethane; hydrogen bonding also seems to be significant in the present system. No linearity is therefore, expected.

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References