Photochemical Reactions of Primary Aromatic Amines with Chloromethanes in Solution. I. Spectrochemical Studies

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Interactions were studied of aniline, 4-methoxyaniline and 4-ethoxyaniline with tetrachloromethane, chloroform and dichloromethane in their ground and first excited singlet states. Stability constants of the complexes of these amines with the chloromethanes in cyclohexane were determined as well as their quantum yields of fluorescence in this solvent. The quenching of fluorescence of aniline and its derivatives by the chloromethanes was ascertained and characterized. Quantum yields of the formation of hydrogen chloride, φ_{HCl}, were measured during photochemically induced reaction of the amines in tetrachloromethane, chloroform and dichloromethane.

Introduction

Chloromethanes (tetrachloromethane, chloroform and dichloromethane), owing to their specific physico-chemical properties, have found widespread use in organic chemistry and spectroscopy as well as in photochemistry. Owing to their high electron affinity they cannot be considered as inert solvents. For instance, solutions of aromatic amines in these solvents exhibit photochemical activity. As yet, photochemical transformations of tertiary aromatic amines in CCl_4, $CHCl_3$ and CH_2Cl_2 have been most extensively studied [1−6]. There are no reports, however, on the photochemistry of aniline and its derivatives in these solvents. Spectrochemical studies of N,N-dimethylaniline (DMA) and other tertiary aromatic amines in chloromethane solvents revealed electron-donor-acceptor interactions to have taken place in the ground state [1, 7]. The complexation occurring in these systems was detected on the basis of the shapes of the fluorescence quenching curves of DMA [1]. The preponderance of the mechanism involving electron transfer from the amine molecule to that of chloromethane was subsequently confirmed by identification of products of the primary photoreaction which included a radical cation of the amine, a radical of the chloromethane and the chloride ion [8−13]. Both the variable composition of the polychloromethyl radical and the extreme instability of the radical cation of the amine give rise to a variety of reaction pathways in each of the systems studied, as evidenced by a great number of photoproducts of DMA and other tertiary aromatic amines found in these solvents [1−6].

We found that the aniline solutions in these solvents were also photochemically active. On this basis an attempt was made to evaluate the nature of interactions of aniline and its derivatives with chloromethanes in solution. The higher ionization potential of aniline (7.70 eV) [14] as compared to that of DMA (7.10 eV) [14] is indicative of poorer electron-donor capability this amine which is likely to manifest itself in much weaker CT interactions in the systems considered.

Land and Porter [15], who used the flash photolysis technique, detected the aniline radical ($C_6H_5\dot{N}H$) among the primary products of the photolysis of aniline. The primary process of photolysis of aniline in aqueous solution was also studied by Zechner and co-workers [16]. They also were able to detected the aniline radical in weakly alkaline solutions. Both reports suggest the formation of the radical rather than the radical cation during the photochemical reaction of aniline.

Experimental

Aniline (analytical-reagent grade; POCh, Gliwice), 4-methoxyaniline (Fluka AG) and 4-ethoxyaniline (BDH Chemicals Ltd) were purified by repeated distillation over zinc dust under reduced pressure. Tetrachloromethane, chloroform and dichloromethane were purified as described elsewhere [2, 3]. The absorption spectra and measurements of the fluorescence quenching were taken on a Specord

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M-40 spectrophotometer equipped with an attachment. The luminescence spectra were measured on a modular spectrofluorimeter according to Jasny [17]. The quantum yield, φ, was measured with 2-aminopyridine as a standard ($\varphi = 0.74$) [18]. Stability constants of the complexes were determined by a modified Benesi-Hildebrand method [19] and by that of Rose and Drago [20]. Quantum yield of the formation of hydrogen chloride was measured as previously described [1, 2], using a Hatchard and Parker actinometer [21] for measuring radiation intensity.

Results and Discussion

Fig. 1 shows a portion of the UV spectrum of aniline in cyclohexane at various concentrations of tetrachloromethane.
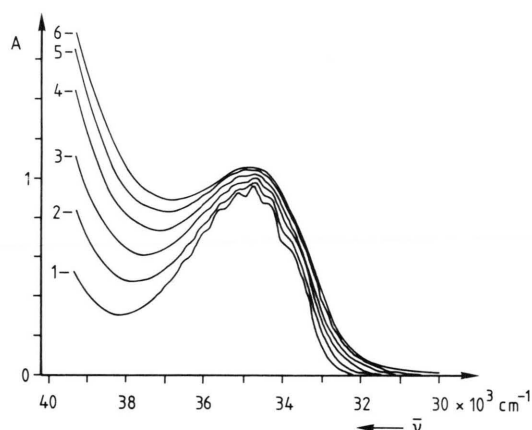

Fig. 1. Absorption spectra of aniline in cyclohexane taken at various CCl$_4$ concentration (in % vol.): 1−0% CCl$_4$; 2−10% CCl$_4$; 3−20% CCl$_4$; 4−30% CCl$_4$; 5−40% CCl$_4$; 6−50% CCl$_4$.

There is distinct change in the shape of the spectrum with increasing CCl$_4$ concentration. The spacing between the absorption bands ($39,000-36,000$ cm^{-1}) fills up in a similar way as for N,N-dimethylaniline [1], thus suggesting the appearance of new absorbing species, aniline-CCl$_4$ complexes. Similar, though not so clear changes were observed in the UV spectra

of aniline upon raising CHCl$_3$ concentrations, and still minor with those of CH$_2$Cl$_2$. Analogous spectral patterns were obtained for 4-methoxyaniline and 4-ethoxyaniline in cyclohexane solutions with the chloromethanes.

Table I lists stability constants of the complexes of the primary aromatic amines with chloromethanes calculated from the modified Benesi−Hildebrand equation [19]. Appropriate concentration range of the chloromethanes during determination of the stability constants was chosen on the basis of the criteria suggested by Person [22]. Negative values of the stability constants were obtained for systems involving a primary aromatic amine and CH$_2$Cl$_2$. Similar results were obtained by employing the Rose−Drago method [20].

The higher stability constant values of 4-methoxyaniline and 4-ethoxyaniline as compared to those of aniline are obviously due to enhanced electron density within the benzene ring of the amine (positive mesomeric effect of the methoxyl and ethoxyl groups).

The results of Table I show that neither the Benesi−Hildebrand equation nor the Rose−Drago method give satisfactory results for stability constants of weak complexes. Even though the stability constant is positive, the probability that it is actual one, is unfortunately low.

For such cases Carter and co-authors [23] suggest the following equation for the complex formation:

$$AS_n + DS_m \leftrightharpoons (AD)S_p + qS \tag{1}$$

where n, m and p are the numbers of the solvent molecules associated with A, D and AD respectively, and $n + m - p = q$. Considering these relationships they obtained two equations:

$$\begin{aligned} K_{BH} &= K_{true} - \frac{q(m+1)}{S_o} \\ \varepsilon_{BH} &= \varepsilon_{true} \times \frac{K_{true}}{K_{BH}} \end{aligned} \tag{2}$$

where K_{BH} is the stability constant obtained from the Benesi−Hildebrand equation, K_{true} is that calculated from eq. (1) and S_o is the solvent concentration in

Table I. Stability constants of the complexes of aniline and its *para*-substituted derivatives with CCl$_4$ and CHCl$_3$.

Amine	CCl$_4$ 15 °C	25 °C	CHCl$_3$ 15 °C	25 °C
Aniline	.014±.004	~0	~0	negative
4-Methoxyaniline	.092±.013	.085±.006	.089±.023	.081±.014
4-Ethoxyaniline	.074±.019	.070±.021	.066±.013	.059±.013

the absence of donor. According to Carter *et al.*, the term $q(m+1)/S_o$ is the order $1-3$ dm^3 mol^{-1} and the error due to it for weak complexes ($K = 1$) is *ca.* 100% or more. Further, for weak complexes $q(m+1)/S_o = K_{true}$ or $q(m+1) > K_{true}$ to give $K_{BH} = 0$ or negative. Emslie and co-workers [24] present an opposite opinion postulating that if K_{BH} is dependent on the solvent used, the ε_{BH} shouldn't. Abnormal K_{BH} values are due to deviations from the Beer's law for the complex being formed. However, the deviations would have been quite large to justify the zero or negative K_{BH} values. Again, Orgel and Mulliken [25] argue that the zero values of the Benesi−Hildebrand constant can be interpreted in terms of the so-called contact charge-transfer between the donor and the acceptor molecules. Whetsel and Lady [26] determined stability constants of the aniline-$CHCl_3$ complex ($K = 0.51$) from the IR spectra. By comparison with appropriate constant for the benzene-$CHCl_3$ complex, they concluded that aniline formed rather a $C-H\cdots N$ hydrogen bonding with $CHCl_3$ than with π electrons of the aromatic ring. Desphande and Pandya [27] determined stability constant of the aniline-CCl_4 complex by the microcalorimetric method to obtain a values of the order of $1-2$ dm^3 mol^{-1}. As it is seen, numerical values of the stability constants strongly depend on the method of their determination. However, all of them reveal interactions of aniline with chloromethanes in the ground state.

Quantum yields of the fluorescence of aniline, 4-methoxyaniline and 4-ethoxyaniline in cyclohexane are 0.13, 0.10 and 0.10 respectively. The chloromethanes do quench the fluorescence of the amines (Fig. 2). The quenching of the fluorescence of these amines in cyclohexane does not obey the Stern−Volmer relation, thus confirming the predicted contribution of the static component. The K_{SV} constants, determined for the concentration range over which the Stern−Volmer relation is satisfied (up to approx. 0.075 M for CCl_4 and $CHCl_3$), are shown in Table II.
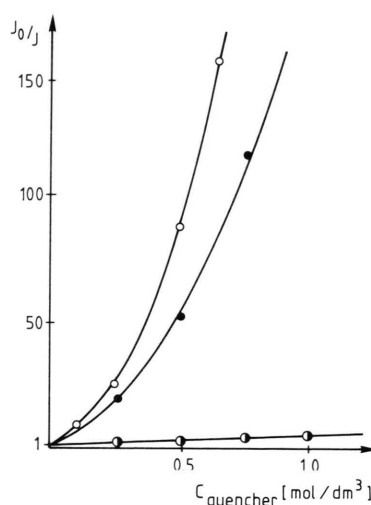

Fig. 2. Fluorescence quenching curves of aniline by CCl_4 —○—○—, $CHCl_3$ —●—●— and CH_2Cl_2 —◑—◑— in cyclohexane.

Prolonged refluxing of aniline with chloromethanes did not induce any detectable transformations. On the other hand, exposition of the aniline solutions in CCl_4, $CHCl_3$ and CH_2Cl_2 to the UV radiation revealed photoactivity of these systems. Quantum yields of the formation of hydrogen chloride, which is at least in part the product of the primary photoreaction, are shown in Table III.

Table III. Quantum yields of the formation of hydrogen chloride, φ_{HCl}, during photochemical reactions of the amines in chloromethanes; $c_{amine} = 0.05$ M; $\lambda = 313$ nm; at 20 °C.

Amine/Chloromethane	CH_2Cl_2	$CHCl_3$	CCl_4
Aniline	1.48	1.53	1.62
4-Methoxyaniline	1.62	1.67	1.91
4-Ethoxyaniline	1.55	1.61	1.77

The higher than unity quantum yields of the formation of hydrogen chloride are probably due to the contribution of the dark reaction. It is worth noting that in spite of the differences in the reaction media (polarity, electron affinity), the φ_{HCl} values are comparable. This suggests alike mechanisms of the primary and secondary photoreactions in each of the systems studied. In the presence of chloromethanes

Table II. Quenching constants, K_{SV} [dm^3 mol^{-1}], of aniline and its *para*-substituted derivatives in cyclohexane.

Amine/Quencher	CH_2Cl_2	$CHCl_3$	CCl_4
Aniline	4.8	51.8	60.2
4-Methoxyaniline	4.7	35.3	38.5
4-Ethoxyaniline	4.7	34.5	38.5

electronic excitation of the aniline molecule may, apart from deactivation processes, lead to transfer of the hydrogen atom (or to successive electron and proton transfer) from the amine molecule to that of chloromethane. Consequently, products of the primary photoreaction would involve the aniline radi-

cal, the $\dot{C}H_{3-X}Cl_X$ ($X = 1, 2, 3$) radical and the HCl molecule.

We now expect confirmation of the suggested mechanism of the primary and secondary photoreactions from investigations of the products of photochemically induced transformations.

[1] T. Latowski and E. Sikorska, Roczniki Chem. **42**, 1063 (1968).
[2] T. Latowski and B. Zelent, Roczniki Chem. **48**, 831 (1974).
[3] T. Latowski, M. Przytarska, and B. Zelent, Roczniki Chem. **51**, 995 (1977).
[4] T. Latowski and B. Zelent, Roczniki Chem. **51**, 1405 (1977).
[5] T. Latowski and B. Zelent, Roczniki Chem. **51**, 1709 (1977).
[6] T. Latowski and B. Zelent, Roczniki Chem. **51**, 1883 (1977).
[7] K. M. C. Davis and M. F. Farmer, J. Chem. Soc. (B) **1967**, 28.
[8] R. F. C. Claridge and J. E. Willard, J. Am. Chem. Soc. **87**, 4992 (1965).
[9] O. D. Dmitrievskii, Opt. Spektrosk. **19**, 828 (1965).
[10] H. S. Bagdasaryan, B. S. Borowkowa, and W. F. Pikelni, DAN USSR **200**, 1126 (1971).
[11] K. Wyrzykowska, M. Grodowski, K. Weiss, and T. Latowski, Photochem. Photobiol. **28**, 311 (1978).
[12] T. Iwasaki, T. Sawada, M. Okuyama, and Kamada, Photogr. Sci. Eng. **22**, 312 (1979).
[13] T. Iwasaki, T. Sawada, M. Okuyama, and H. Kamada, J. Phys. Chem. **82**, 371 (1978).
[14] J. L. Franklin, J. G. Pillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, Ionization Potentials, Appearance Potentials and Heats of Formation

of Gaseous Positive Ions, NSRDS-NBS **26**, National Boreau of Standards, Washington, D.C. (1964).
[15] E. J. Land and G. Porter, Trans. Faraday Soc. **59**, 2027 (1963).
[16] J. Zechner, L. Prangova, and G. J. Grabner, Z. Phys. Chem. (B) **102**, 137 (1976).
[17] J. Jasny, J. Luminescence **17**, 149 (1978).
[18] National Bureau of Standards Special Publication 378, Accuracy in Spectrophotometry and Luminescence Measurements, Proc. Conf. NBS, Gaithersburg (1972) (Issued 1973), p. 183.
[19] H. A. Benesi and J. H. Hildebrand, J. Chem. Soc. **71**, 2703 (1949).
[20] N. J. Rose and R. S. Drago, J. Am. Chem. Soc. **81**, 6138 (1959); ibid. **81**, 6142 (1959).
[21] C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. (A) **235**, 518 (1956).
[22] W. B. Person, J. Am. Chem. Soc. **87**, 167 (1965).
[23] S. Carter, J. N. Murrell, and E. J. Rosch, J. Chem. Soc. **1965**, 2048.
[24] P. H. Emslie, R. Foster, C. A. Fyfe, and I. Horman, Tetrahedron **21**, 2843 (1965).
[25] L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. **79**, 1839 (1957).
[26] K. B. Whetsel and J. H. Lady, J. Phys. Chem. **68**, 1010 (1964); ibid. **69**, 1596 (1965).
[27] D. D. Desphande and M. V. Pandya, Trans. Faraday Soc. **61**, 1858 (1965).