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Kinetic & Spectroscopic Studies on Interactions of Primary Aliphatic Amines with Chloranil

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Kinetics of interactions of some primary aliphatic amines, namely *s*-butyl-, isobutyl-, isopropyl-, allyl- and cyclohexyl-amines with chloranil have been investigated by UV spectroscopy. The monosubstituted product formed in a fast step immediately on mixing the amine and chloranil solutions, decomposes to give a disubstituted product in a slow step. Pseudo-first order rate constants for the disappearance of the monosubstituted product as well as for the formation of the disubstituted product have been evaluated and found to be the same. Possible participation of an electron donor-acceptor complex formed between the amine and chloranil in the reaction is indicated.

The interaction of *n*-alkylamines with chloranil (CA), earlier investigated in our laboratory[1], indicated the possible participation of an electron donor-acceptor (EDA) complex formed between the primary aliphatic amine and CA in the reaction to give mono- and di-substituted products. In continuation of this work, the kinetics of interactions of *s*-butylamine, isobutyl-amine, isopropylamine, allylamine and cyclohexyl-amine with CA have now been investigated and the results are presented in this paper.

Materials and Methods

Cyclohexane was purified by standard methods, dried over anhydrous calcium chloride for several hours, refluxed and distilled over sodium metal. Chloroform (S Merck, GR) and dichloromethane (E Merck, LR) were fractionally distilled before use. All the amines were purified by distillation over potassium hydroxide. Chloranil was recrystallised repeatedly from benzene to give yellow platelets; m.p. 289°. The spectral measurements were made on a Beckman DU spectrophotometer fitted with variable temperature cell compartment, using glass stoppered silica cells of 1 cm path length. Pseudo-first order rate constants (k) (in the presence of a large excess of donor) of the formation of the mono- and di-substituted products were evaluated employing Eqs (1) and (2), respectively.

$$k = \frac{2.303}{t} \log \frac{D_0}{D_t} \qquad \ldots (1)$$

$$k = \frac{2.303}{t} \log \frac{D_\infty - D_0}{D_\infty - D_t} \qquad \ldots (2)$$

Here, D_0, D_t and D_∞ are the absorbances at time zero (initial), t and at the end of reaction, respectively. A typical plot for calculating k for the system isobutylamine + CA in cyclohexane is shown in Fig. 1. In all the kinetic studies, the rate data were recorded for the first 10 min only.

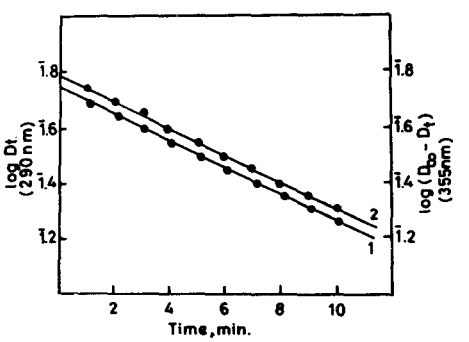

Fig. 1—Pseudo-first order rate plots for isobutylamine (6.7×10^{-2} mol dm^{-3}) + CA (2.9×10^{-5} mol dm^{-3}) in cyclohexane at 308 K [1 at 290 nm and 2 at 355 nm]

Results and Discussion

Spectral data

The UV spectra of CA and amine + CA were recorded in cyclohexane medium. All the primary aliphatic amines used in this study showed negligible absorbance above 250 nm. Identical spectra were obtained in all the cases. Some typical spectra are shown in Fig. 2 for the allylamine + CA system at 308 K. As the absorbances of the solutions containing amine and CA change rapidly during measurements, the spectra are not shown to the scale in Fig. 2. An absorption band around 290 nm appears immediately on mixing the amine and CA solutions. The intensity of this band diminishes rapidly with concomitant appearance of a new band around 355 nm. These spectral changes are similar to those reported by

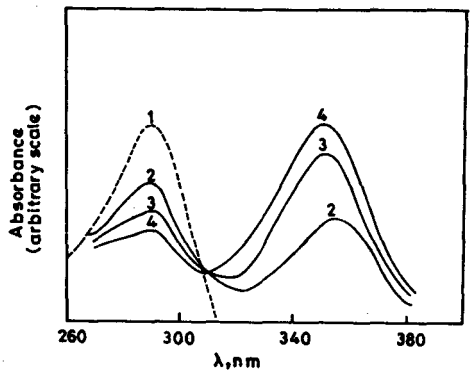

Fig. 2—UV absorption spectra of CA (2.9×10^{-5} mol dm^{-3}) (curve 1) and a mixture of allylamine (6.7×10^{-2} mol dm^{-3}) and CA (2.9×10^{-5} mol dm^{-3}) in cyclohexane at 308 K [curve 2 for fresh solution; curves 3 and 4 after 6 and 12 min respectively]

Lautenberger and coworkers[2] and Dwivedi and coworkers[1] and may be explained by the formation of an electron donor-acceptor (EDA) complex between the amine and CA, which gives rise to a monosubstituted product (λ_{max} 290 nm) in a very fast step. The 355 nm band attains its maximum intensity in about 10 min and thereafter there is no change in intensity on keeping the solution for a long time. The 355 nm band may, therefore, be assigned to the formation of a disubstituted product (final product) in a slow step. The spectra do not exhibit charge-transfer bands characteristic of the EDA complexes because of their fast conversion into the monosubstituted product. The 290 nm band cannot be due to the EDA complex on the basis of the conclusion drawn for the triethylamine + CA system[3]. The formation of an EDA complex between these primary aliphatic amines and CA has been established by conductance measurements[4]. Although, a solution of CA in cyclohexane exhibits an absorption band around 290 nm, this band in the mixed solution is assigned to the monosubstituted product due to the following reasons:

(i) The zero time absorbance of the mixed solution at 290 nm (obtained by extrapolation of the log D_t versus time plot) is greater than that of CA itself in all the cases and since amines do not absorb at 290 nm, this band should be assigned to the monosubstituted product which has an extinction coefficient larger than that of CA.

(ii) In the presence of large excess of donor (i.e. amine), most of CA will be converted into an EDA complex. Hence free CA will have negligible contribution to this absorption at 290 nm of the mixed solution.

Kinetic data

The pseudo-first order rate constants, k, were evaluated employing both the 290 nm and 355 nm bands. The results are given in Table 1 alongwith the energies of activation, E_a, and the entropies of activation, $\Delta S\ddagger$. The k values follow the order: isobutylamine > isopropylamine > allylamine > *s*-butylamine > cyclohexylamine in all the solvents studied. The k values depend on the donor strengths of structurally similar electron donors, e.g. isopropylamine and isobutylamine (Table 1). A similar dependence of the kinetic data on donor strength has been reported recently by Dwivedi and Banga[1] for the *n*-alkylamine + CA systems. However, such a

Table 1—Kinetic Data† for Reaction of Chloranil with Primary Aliphatic Amines at 308K

Amine	Ionization potential	Solvent	Dielectric constant	Values at 290 nm (mono-substituted product)			Values at 355 nm (di-substituted product)		
				$k \times 10^3$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S\ddagger$ (JK^{-1} mol^{-1})	$k \times 10^3$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S\ddagger$ (JK^{-1} mol^{-1})
Cyclohexylamine	8.38	Cyclohexane	2.02	0.38	72	−63	0.38	72	−63
		$CHCl_3$	4.5	0.57	52	−124	0.57	52	−124
		CH_2Cl_2	9.1	1.12	43	−149	1.12	44	−153
s-Butylamine	8.70	Cyclohexane	2.02	0.65	53	−118	0.61	54	−115
		$CHCl_3$	4.5	0.97	38	−166	0.94	40	−160
		CH_2Cl_2	9.1	1.6	28	−194	1.63	30	−188
Allylamine	9.6	Cyclohexane	2.02	1.15	30	−190	0.96	31	−181
		$CHCl_3$	4.5	1.53	23	−213	1.39	25	−206
		CH_2Cl_2	9.1	1.92	19	−223	1.74	21	−216
Isopropylamine	8.72	Cyclohexane	2.02	1.8	28	−195	1.75	27	−199
		$CHCl_3$	4.5	2.42	20	−219	2.37	19	−222
		CH_2Cl_2	9.1	2.83	12	−243	2.75	11	−246
Isobutylamine	8.70	Cyclohexane	2.02	1.85	19	−222	1.82	22	−212
		$CHCl_3$	4.5	2.6	11	−246	2.47	13	−240
		CH_2Cl_2	9.1	3.83	8	−254	3.53	8	−254

†Concentrations of amines and CA were 0.067 mol dm^{-3} and 2.9×10^{-5} mol dm^{-3} respectively in all the cases.

dependence is not observed for structurally dissimilar electron donors such as cyclohexylamine, *s*-butylamine and allylamine. The E_a values decrease with increase in k values as expected. The rate constants as well as the E_a values, at (290 and 355 nm are nearly equal, indicating that no intermediate of appreciable stability exists during the conversion of monosubstituted product to a disubstituted one in a slow step. Thus, unlike for the aniline + CA system[5], the formation of final products in the aliphatic amine + CA systems do not involve σ-complexes as reaction intermediates. Further the k values increase and E_a values decrease with increase in solvent polarity. This solvent dependence of k values suggests that there may be some charge separation in the transformation of the EDA complex to the final product. The $\Delta S^{\ddagger}$ values are large and negative, the magnitude being higher in more polar solvents. These $\Delta S^{\ddagger}$ values indicate that the transition state in the slow step is more polar than the initial state (which is likely to be the monosubstituted product). The dependence of the k, E_a and $\Delta S^{\ddagger}$ values upon the donor strength of structurally related aliphatic amines supports the assumption that the reaction of the primary aliphatic amines with CA proceeds through an EDA complex.

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