Kinetics and Mechanism between Chloranil and s-Butylamine in Cyclohexane Solution

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The interaction of chloranil (CA) with s-butylamine (A), in cyclohexane solution has been studied by measuring visible and ultraviolet absorption spectra at various temperatures in the range 279—308 K. Kinetic and thermodynamic parameters have been derived and a mechanism has been proposed for this reaction. The results indicate the existence of a charge-transfer complex in the presence of an excess of s-butylamine, which decomposes to give a final product (D: the disubstituted product of CA). The reaction path has been found to be autocatalysed by the presence of the amine.

The nucleophilic substitution of quinones by aromatic or aliphatic amines has been extensively studied.[1–7] However if the acceptor reagent is chloranil (CA), some unsolved problems still remain,[3–5,8] (most of which are the consequence of the rapid reaction rate) as well as the assignation and identification of intermediate reactions.

Previous studies of the nucleophilic substitution of CA by aliphatic amines (A), considering the nature of the solvent and the nature of the amines employed, resulted in the following suggested mechanisms: (*a*) direct electron transfer to the electrophilic species CA, to form a radical ion, in polar solvents [7–9] with primary and secondary aliphatic amines and (*b*) charge-transfer complex formation in non polar solvents [3–4] with primary and secondary amines. In both (*a*) and (*b*) the disubstituted product of CA was obtained, in which the substituted group was -NHR. A third mechanism involving the dehydrogenation of tertiary aliphatic amines (type RR′NEt) by CA either neat [9] or in benzene [2,10] was also proposed.

In all cases it was necessary for the concentration of amine to be in considerable excess with respect to CA, in order for the reaction to proceed rapidly.

We focused our attention on the reactions of CA with aliphatic amines in non-polar solvents, which have analytical applications [11–13] principally the use of CA as a fungicide,[14] and we observed the mono- and di-substituted products that primary and secondary aliphatic amines in non-polar solvents are known to form with CA.

Lautenberger *et al.*[3] and Dwivedi *et al.*[4] have studied the interactions of some aliphatic amines with CA in cyclohexane solution, and have found that the rate of disappearance of a monosubstituted product (M) was similar to the rate of formation of the disubstituted product (D), under limited conditions of only one concentration and temperature. They proposed a mechanism in which the first step was the formation of a electron donor–acceptor complex between the amine and CA, with further decomposition leading to a monosubstituted derivative as an intermediate in the reaction. In the literature this intermediate (M) was not synthesized nor isolated.[1] However, upon further investigation, Dwivedi *et al.*[5] concluded that by using conductimetric techniques, the stoicheiometry was 2:1 (D:A) if the acceptor was CA and the donor s-butylamine.

The aim of the present work is to establish and verify the mechanism and the kinetic parameters of the chloranil–s-butylamine system in cyclohexane solution.

Experimental

Materials.—Chloranil (CA) (Fluka puriss. p.a.) was recrystallized twice from acetone and resublimed under vacuum. The melting point observed was 290.0 °C.

s-Butylamine (A) (Merck p.a.) was distillled twice over KOH, with a slow stream of inert nitrogen being passed through the system to protect the amine from atmospheric oxygen. The distillate was stored over 4 Å molecular sieves.

Cyclohexane, of spectrosol grade, was commercially available (Scharlau) and was used without further purification. Sodium wire was used as the drying agent.[15]

The last product in the reaction was the disubstituted derivative of CA [(D): 3,6-dichloro-2,5-bis-(s-butylamino)cyclohexa-2,5-diene-1,4-dione], obtained by synthesis, following the method of Buckley *et al.*,[1] and further purified by crystallization from a mixture of 1,4-dioxane and ethyl acetate. The last melting point obtained was 195—196 °C. This product (D) was characterized spectroscopically. U.v.–vis spectroscopy in cyclohexane [16] gave two absorption maxima at 353 (ε 27 068) and 518 nm (ε 250). The i.r. spectrum (Perkin-Elmer 281; KBr disc.[17,18]) showed two bands and 1 370 and 1 385 cm^{-1} of different intensity corresponding to the bending mode of the methyl groups, a strong band at 1 580 cm^{-1} corresponding to an associated C=O group, and a weak band at 1 650 assigned to the non-associated carbonyl group.[17] A sharp band at 3 224 cm^{-1} is attributed to the N–H stretching mode. The n.m.r. spectrum (Varian 90 MHz; $CDCl_3$) showed the following signals: an asymmetric triplet at 0.9 p.p.m. (Me terminal), a doublet at 1.25 p.p.m. (Me), quartets at 1.55 p.p.m. ($-CH_2-$), and multiplets at 4.65 (–CH–) the last of which had relative intensities of 1:3:1:3:3:1:3:1, corresponding to two quartets of similar chemical shift, arising from the tertiary protons adjacent to the nitrogen.[19,20] Finally, a broad singlet at 7.8 p.p.m. (NH) confirming the substitution of the amino group.

All attempts at synthesizing the monosubstituted derivative of CA [(M): 3,5,6-trichloro-2-s-butylaminocyclohexa-2,5-diene-1,4-dione] were unproductive, (in agreement with Buckley [1]) and confirmed that from the equimolar amounts of CA and amine, the disubstituted derivative was obtained together with unchanged CA.

Measurements.—Absorption spectra and absorbance measurements from data displays were obtained with a Cary Model 219 spectrophotometer, with a double-beam system and a temperature-regulated cell holder adapted for a 1 cm cell. Circulating water maintained the holder temperature constant to an an accuracy of ±0.1 °C. The temperature was monitored with a thermocouple attached to the reference cell. Matched, stoppered quartz cells of path length 1 cm were used.

The chosen wavelengths were 290 and 353 nm, in which CA and D have the maximum absorbance values, respectively, and we verify that Beer's law were obeyed.

The four temperatures selected were 6 (temperatures lower than this froze the solution), 10, 25, and 35 °C. At each

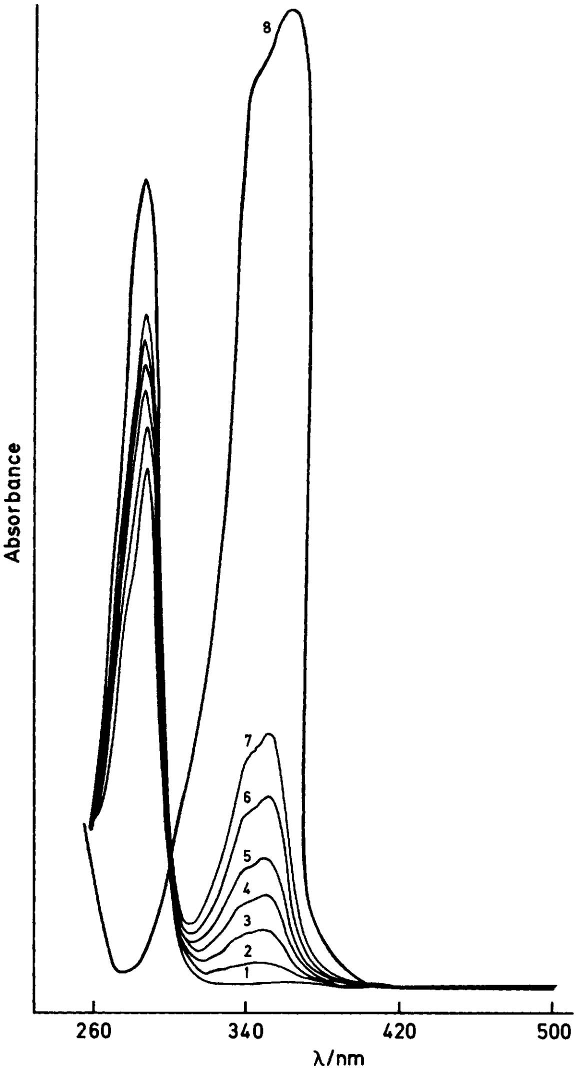

Figure 1. Absorbance–time spectra at 290 and 353 nm at 25 °C for the s-butylamine–chloranil system in cyclohexane. $[CA]_0 = 4.5 \times 10^{-5}$; $[A] = 0.11$ mol l^{-1}

temperature the concentration ranges used were: 4.5 ± 0.2—$8.5 \pm 0.4 \times 10^{-5}$ mol l^{-1} ($[CA]_0$) and 0.30 ± 0.02—$2.0 \pm 0.1 \times 10^{-1}$ mol l^{-1} ($[A]_0$).

In view of the volatile nature of the amine and the solvent employed, all kinetic runs were carried out in triplicate, and averaged absorbance values were used.

Results and Discussion

In Figure 1 the typical absorption bands for CA and D, curves 1 and 8 respectively are shown; together with the changes in absorbance with time of a mixture chloranil–s-butylamine (lines 2 to 7), in which the time intervals were kept constant at 1 min. A discontinuous initial relationship between the decrease of the band at 290 nm (lines 1 and 2) and the corresponding increase at 353 nm is observed; although a definite isosbestic point between these bands does not exist there are indications that the mechanism might involve a reaction intermediate. The absorbance of s-butylamine in cyclohexane was negligible above 250 nm and the absorbance observed at 353 nm was attributed solely to the final product (D).

Taking into account the aforementioned facts, we followed the developing absorbances at 353 nm. Using a program in FORTRAN V, it was verified that the disubstituted formation rates lead to the following expression:

$$d[D]/dt = k_{exp.}\{[CA]_0 - [D]\} \quad (1)$$

where $[CA]_0$ is the initial concentration of CA and [D] is the instantaneous concentration of the disubstituted product, obtained from Beer's law calibration.[21–23]

Integrating equation (1) gives

$$-\ln([CA]_0\varepsilon_D - A_b) = -\ln([CA]_0\varepsilon_D) + k_{exp.}t \quad (2)$$

where ε_D is the molar extinction coefficient of D and A_b represents the averaged absorbance values recorded at 353 nm. In order to determine the influence of $[CA]_0$ and [A] and the values of the experimental constant, $k_{exp.}$, several runs were performed and the results, at 25 °C, are shown in Figure 2. The difference between Figures 2a and b is the initial concentration of CA. In all cases, for each of the ten excesses of concentration of A, the developing pseudo-first-order equation is shown, with respect to the appearance of the final product,[3,4] at constant temperature. As can be seen, the initial concentration of CA does not influence the slope (superimposed graphs, Figures 2a and b) within the same excess of concentration of amine, as was found previously in another similar system.[15] However, the slopes rise considerably as the amine concentration is increased. A small induction period was noted at the start of most of the reactions before the final pseudo-first-order rate was attained. This may be an effect resulting from possible intermediate formation, leading to the disubstituted product, D.

Good straight lines were found at all the temperatures studied, and the corresponding parameters, obtained using the Lagrange multiplier method,[24] are shown in Table 1.

In all cases mentioned, the value of ε_D at 353 nm, used in equation (2) to determine $k_{exp.}$, was $27\,068 \pm 122$ l mol^{-1} cm^{-1}, which corresponds to a visible $\pi \longrightarrow \pi^*$ band.[1,25] From this point on, $k_{exp.}$ values represent the corresponding weighted average for varying $[CA]_0$ but with constant [A] and temperature.

Of all the quantitative relations between $k_{exp.}$ and amine concentrations considered, at each of the temperatures studied, that which adapted best was found through the following expression:

$$\ln\frac{[A]}{k_{exp.}} = a_0 + \sum_{n=1}^{2} a_n \frac{1}{[A]^n} \quad (3)$$

in which the exponents $n \geqslant 3$ have no significance.

Typical plots of equation (3) are shown in Figure 3. As expected at higher amine concentrations, the plot of $\ln [A]/k_{exp.}$ is almost linear at each temperature. As shown in Table 2, the three absolute values of the fitted coefficients obtained, increase as the temperature increases. Because equation (3) was found to be quantitatively adjusted for all experimental runs in the present work, it can be considered that the rate $[A]/k_{exp.}$ approximates to the following Fourier series:

$$\frac{[A]}{k_{exp.}} = \exp\left\{a_0 + \sum_{n=1}^{2} a_n \frac{1}{[A]^n}\right\} \quad (4)$$

Taking into account the development of the e^x series and applying it to the terms $\exp a_1/[A]$ and $\exp a_2/[A]^2$, expression (4) can be rearranged as:

$$\frac{[A]}{k_{exp.}} = e^{a_0}\{1 + (a_1/[A]) + 1/2!\,(a_1/[A])^2\} \times \{1 + (a_2/[A]^2) + 1/2!\,(a_2/[A]^2)^2\} \quad (5)$$

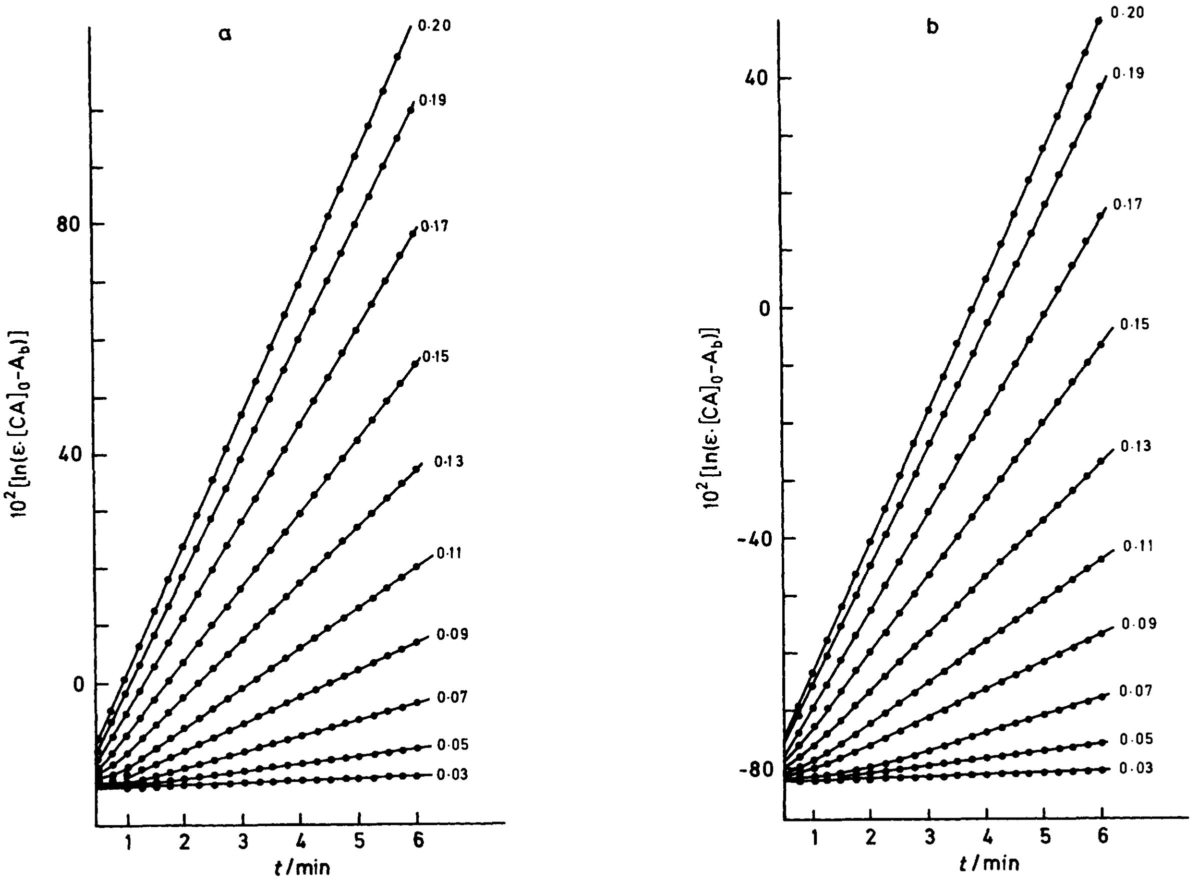

Figure 2. Typical plots from equation (2) at 353 nm at 35 °C: (*a*) $[CA]_0 = 4.5$; (*b*) $[CA]_0 = 8.5 \times 10^{-5}$ mol l^{-1} at the indicated amine concentration ($[A] = 0.03$—0.20 mol l^{-1})

which leads to the following expression, if it is assumed that third-order terms can be neglected:

$$\frac{[A]}{k_{\text{exp.}}} = e^{a0}\left\{1 + \frac{a_1}{[A]} + \left(\frac{a_1^2}{2} + a_2\right)\frac{1}{[A]^2}\right\} \qquad (6)$$

Considering the facts presented [Figures 1—3 and equation (4)] and assuming the stationary state[26] we suggest the following as the most appropriate mechanism:

$$CA + 2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1$$

$$C_1 \xrightarrow[A]{k_2} D + 2HCl$$

in which the first step is a reversible complex formation supported by (i) the appearance of a weak visible band at 750 nm, (ii) the disappearance of this band as the temperature increased, and (iii) the fact that it was not possible to assign this particular absorption to either CA or D. These facts are in agreement with other, similar systems reported in the literature.[27]

The irreversibility of the last step was confirmed by carrying out two further runs which differed only in that a disubstituted product, previously obtained by synthesis,[1] was incorporated into the reaction mixture. The velocity of the formation of D was found to be the same within the range of experimental error. The evidence of elimination HCl was obtained by shaking the mixture with water and testing the aqueous layer for the presence of chloride ion. Blank tests were also performed. This phenomenon has been demonstrated previously, using a different solvent.[28] In the synthesis of D and in presence of an excess of the amine, the s-butylamine hydrochloride was obtained, which was dried and purified, and gave a melting point of 145—146 °C.

The fitted parameters a_0, a_1, and a_2 from equations (3) or (7) are related to the equilibrium constant ($K_1 = k_1/k_{-1}$) and the kinetic rate (k_1 or k_2). Let us apply the stationary-state asumption to the concentration of C_1 as:

$$[C_1] = \frac{k_1[A]^2[CA]}{k_{-1} + k_2[A]} \qquad (7)$$

Taking into account the mass balance for [CA] equation (1) is transformed into

$$d[D]/dt = k_{\text{exp.}}([CA] + [C_1]) \qquad (8)$$

However, the disubstituted formation rate was

$$d[D]/dt = k_2[A][C_1] \qquad (9)$$

From equations (7)—(9) we can conclude:

$$\frac{[A]}{k_{\text{exp.}}} = \frac{1}{k_2} + \frac{1}{k_1}\frac{1}{[A]} + \frac{1}{K_1 k_2}\frac{1}{[A]^2} \qquad (10)$$

Now, if we identify the coefficients of equations (6) and (10), we attain the following equations

$$K_1 = \{(a_1^2/2) + a_2\}^{-1} \qquad (11)$$

Table 1. Rate constants[a] from equation (2) for the chloranil–s-butylamine system in cyclohexane

10[A]/	*T*/K	279		283		298		308	
mol l^{-1}	[CA]$_0$[b]	1	2	1	2	1	2	1	2
0.30 ± 0.02		0.0015 ±0.000 04	0.0013 ±0.000 03	0.0016 ±0.000 04	0.0018 ±0.0001	0.0022 ±0.0001	0.0026 ±0.0001	0.0395 ±0.0001	0.0401 ±0.0001
0.50 ± 0.03		0.0065 ±0.000 01	0.0062 ±0.0001	0.0068 ±0.000 01	0.0079 ±0.0001	0.0093 ±0.0001	0.0107 ±0.0002	0.0139 ±0.0002	0.0142 ±0.0002
0.70 ± 0.04		0.0160 ±0.0002	0.0150 ±0.0002	0.0180 ±0.0002	0.0200 ±0.0002	0.0220 ±0.0002	0.0250 ±0.0002	0.0306 ±0.0003	0.0301 ±0.0003
0.90 ± 0.05		0.0300 ±0.0001	0.0280 ±0.0001	0.0320 ±0.0002	0.0350 ±0.0002	0.0389 ±0.0002	0.0460 ±0.0002	0.0520 ±0.0002	0.0520 ±0.0002
1.10 ± 0.05		0.0480 ±0.0001	0.0440 ±0.0001	0.0500 ±0.0002	0.0623 ±0.0001	0.0580 ±0.0002	0.0690 ±0.0002	0.0770 ±0.0002	0.0780 ±0.0003
1.3 ± 0.1		0.0660 ±0.0002	0.0660 ±0.0002	0.0741 ±0.0001	0.0811 ±0.0002	0.0880 ±0.0002	0.0970 ±0.0002	0.1101 ±0.0004	0.1115 ±0.0004
1.5 ± 0.1		0.0840 ±0.0004	0.0810 ±0.0003	0.0935 ±0.0008	0.1062 ±0.0003	0.1100 ±0.0004	0.1310 ±0.0004	0.1470 ±0.0005	0.1519 ±0.0006
1.7 ± 0.1		0.1093 ±0.0006	0.1032 ±0.0004	0.1163 ±0.0001	0.1358 ±0.0006	0.1403 ±0.0003	0.1910 ±0.0004	0.1935 ±0.0008	0.1981 ±0.0010
1.9 ± 0.1		0.1300 ±0.0008	0.1225 ±0.0005	0.1574 ±0.0002	0.1763 ±0.0008	0.1800 ±0.0006	0.2100 ±0.0007	0.2388 ±0.0001	0.2458 ±0.0001
2.0 ± 0.1		0.1500 ±0.0010	0.1390 ±0.0050	0.1657 ±0.0003	0.1900 ±0.0009	0.1926 ±0.0006	0.2380 ±0.0001	0.2720 ±0.0010	0.2713 ±0.0020

[a] $k_{exp.}$/min^{-1}. [b] The numbers 1 and 2 correspond to $[CA]_0$ (4.5 ± 0.2) × 10^{-5} and (8.5 ± 0.4) × 10^{-5} mol l^{-1}, respectively.

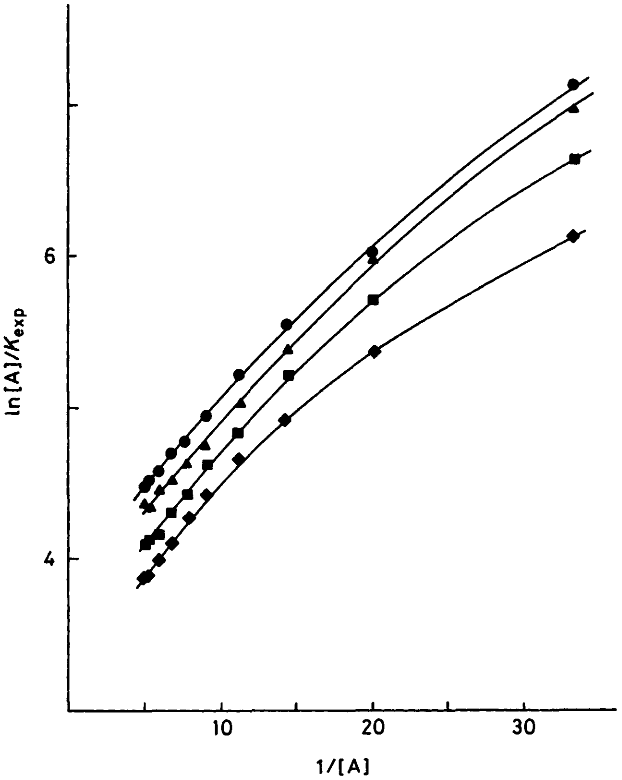

Figure 3. ln $[A]/k_{exp.}$ as a function of 1/[A] from equation (3) for the s-butylamine–chloranil system at varying temperature: (●), 6; (▲), 10; (■), 25; ◆, 35 °C

$$k_1 = (e^{a}o a_1)^{-1} \quad (12)$$

$$k_2 = e^{-a}o \quad (13)$$

which can be shown from the equations (1), (3), (4), and (7). These results are presented in Table 2.

As is expected, the development of K_1 with respect to the temperature indicates the typical equilibrium formation of a charge-transfer complex between CA and A at the commencement of the reaction. On the other hand, k_1 and k_2 increase as the temperature is increased—typical behaviour of kinetic rate constants. Because $k_2 \ll k_1$ the rate-determining step is the formation of disubstituted product.

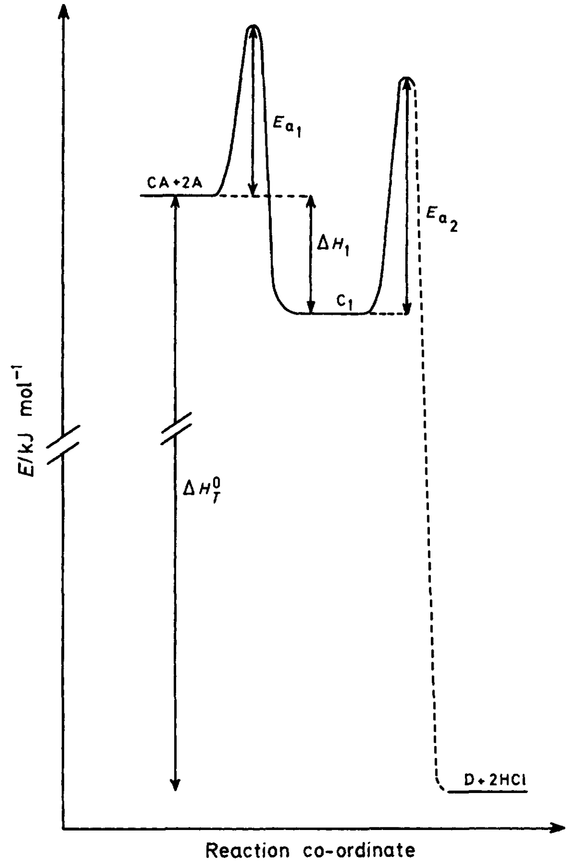

Figure 4. Experimentally determined potential curves and the relative energy levels for the chloranil–s-butylamine system in cyclohexane

Table 2. Fitted coefficients from equation (3), kinetic data, and thermodynamic parameters (kJ mol^{-1}) from the chloroanil–s-butylamine system in cyclohexane

T/K	279	283	298	308	$-\Delta H^\circ_1$	E_{a_1}	E_{a_2}
R	0.9998	0.9990	0.9996	0.9990			
a_0	3.74 ± 0.02	3.65 ± 0.06	3.39 ± 0.03	3.21 ± 0.05			
$10a_1/l\ mol^{-1}$	1.35 ± 0.03	1.39 ± 0.09	1.47 ± 0.05	1.58 ± 0.08			
$-10^3\ a_2/l^2\ mol^{-2}$	1.08 ± 0.09	1.18 ± 0.25	1.54 ± 0.12	1.76 ± 0.21			
$K_1/l^2\ mol^{-2}$	124 ± 8	117 ± 18	106 ± 8	94 ± 10	6.37 ± 0.75		
$10^3k_1/l^2\ mol^{-2}\ s^{-1}$	176 ± 6	187 ± 15	227 ± 8	255 ± 15		9.13 ± 0.42	
$10^3k_2/s^{-1}$	24 ± 1	26 ± 2	34 ± 1	40 ± 2			12.67 ± 0.52

From the data listed in Table 2, the thermodynamic parameters ΔH°_1, E_{a_1}, and E_{a_2} were derived by standard methods. The change on the integral enthalpy for the kinetic reaction between CA and 2 A, to lead to D + 2 HCl, has been estimated from the additive contributions from the individual atoms or bonds in the corresponding molecules,[29] since the nature of solvent was non-polar. This was found to be -77.7 kJ mol^{-1}.

Figure 4 shows schematically the potential curves and the relative energy levels for the different steps of the chloranil–s-butylamine system. These results suggest that, the molecular complex is an intermediate which has a relatively small difference in enthalpy from the reactants with respect to the final products. In agreement with previous results for similar systems[30] the activation energy in the first steps of the nucleophilic substitution is similar to the ones for later steps. These values (E_{a_1}, E_{a_2}) together with the aforementioned results (Figure 4) mean that it is impossible to synthesize or isolate this intermediate complex, as is found in the literature for other similar systems.[1,3,8]

However, from thermodynamic considerations for this complex, C_1, it is possible to demonstrate that the value of the entropic term, $T\Delta S^\circ_1$, is of the same order of magnitude as the enthalpic one, ΔH°_1, which infers that there are no covalent bonds involved, as is the case with the charge-transfer complex formation.[31]

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