Kinetics and Mechanism of the Reactions between Chloranil and n-Butylamine in Cyclohexane Solution

Isidro S. Monzó, Juan Palou, Jose Roca, and Rosa Valero *
Departamento de Química Física, Facultad de Químicas, Universidad de Valencia, Burjassot (Valencia), Spain

Interaction between chloranil (CA) and n-butylamine (A) at several temperatures has been studied by u.v.–visible spectroscopy. Kinetic and thermodynamic parameters, as well as a mechanism, have been proposed for this reaction. The results indicate the initial formation of charge-transfer complexes between CA and A, in the presence of an excess of amine, which decomposes to give a final product (D) (disubstituted product of CA). The reaction path is autocatalysed by the presence of amine.

The kinetics of nucleophilic substitution on chloranil (CA) by aromatic[1–6] and aliphatic[7–13] amines or proteins[14] has been widely studied. However, in the case of aliphatic amines, the literature is not extensive in spite of the analytical applications.[15,16]

Primary and secondary aliphatic amines are known to form the disubstituted products (D) of CA (substituted group NHR),[7] but some tertiary aliphatic amines (type R^1R^2NEt) give a monosubstituted product (substituted group $CH=CHNR^1R^2$).[7,17]

The nature of the intermediates in these reactions changes with the polarity of the solvent, in such a manner that in polar solvents they become ionic species[12–14] and in non-polar solvents charge-transfer complexes or monosubstituted (M) intermediates are formed.[8,9] Finally, with tertiary amines in non-polar solvents, the formation of a disubstituted product does not occur, and instead, charge-transfer complexes are obtained.[18]

Dwivedi and Banga[9] studied the interaction of some aliphatic amines with CA in cyclohexane solution, under limited experimental conditions. They proposed a mechanism in which the first step was the formation of an electron donor–acceptor complex between the amine and CA, with further decomposition leading to a monosubstituted derivative as an intermediate in this reaction. This complex was previously unknown. However, upon further investigation, Dwivedi *et al.*[10] concluded that the stoicheiometry of the charge-transfer complex was 1:1, or 2:1 if the acceptor was CA and the donor n-butyl- or s-butyl-amine, respectively.

In order to establish and extend the general mechanism of interaction between aliphatic amines and CA, as well as to determine all the kinetic rate constants involved, the reaction between n-butylamine and chloranil has been examined by means of a spectroscopic method and by using statistical methodology.

Experimental

Materials.—Details of the purification of chloranil, amine, and solvent have been reported previously.[19]

The last product in this reaction was the disubstituted derivative (D) of CA [2,5-bis(butylamino)-3,6-dichlorocyclohexa-2,5-diene-1,4-dione], obtained by synthesis (m.p. 200 °C; yield 52%) following the method of Buckley *et al.*[7] and purified by crystallization from 1,4-dioxane–ethyl acetate. A secondary product, n-butylamine chlorohydrate was also obtained (m.p. 151 °C). The final product (D) was characterized by spectroscopy: u.v.–visible spectroscopy (Cary 219 spectrometer) in cyclohexane gave three absorption maxima at 240 (difficult to observe in this solvent), 354 (ε 27 344), and 520 nm (240). The i.r. spectrum (Perkin-Elmer 281 spectrometer; KBr disc,[20,21]) showed a strong band at 1 590 cm^{-1} corresponding to an associated C=O group, and a weak band at 1 660 cm^{-1} assigned to the non-associated carbonyl group.[19] At 3 230 cm^{-1} a sharp band is attributed to the N–H stretching mode. The ^1H n.m.r. spectrum (Varian 90 MHz spectrometer; $CDCl_3$) showed δ 0.9 (t, Me), 1.55 (m, CH_2), 3.8 (q, CH_2N), and 7.3 (br, NH). The ^{13}C n.m.r. spectrum (Bruker AC-200 MHz spectrometer; $CDCl_3$) showed δ 190 (s, C=O), 149 (s, CCl), and 129 p.p.m. (CN). These signals are in accord with a 2,5-disubstituted product.

All attempts at synthesizing the monosubstituted derivative (M) of CA (2-butylamino-3,5,6-trichlorocyclohexa-2,5-diene-1,4-dione) were unproductive (in agreement with Buckley[7]) and confirmed that from equimolecular amounts of CA and amine the disubstituted derivative was obtained together with unchanged CA,[7] and if a deficit of amine was used, reaction did not occur.

U.v.–Visible Measurements.—The details of the spectrophotometer (Cary model 219) and the thermostat unit have been reported previously.[19]

The chosen wavelengths were 6, 10, 25, and 35 °C. At each temperature (except for 25 °C) two different initial concentrations of CA were used (4.5 × 10^{-5} and 8.5 × 10^{-5}M). At 25 °C, five initial concentrations were used: 4.5 × 10^{-5}, 6.4 × 10^{-5}, 7.4 × 10^{-5}, 8.5 × 10^{-5}, and 10.5 × 10^{-5}M. In all cases ten different excesses of amine were performed, the selected concentration range being 0.03—0.20M.

Kinetic runs were in triplicate, and the values of absorbances are averages. Several programs were written to determine the kinetic and thermodynamic parameters. The calculations were performed on an Eclipse C/350 computer.

Results and Discussion

In Figure 1 typical absorption bands for CA and the disubstituted product, noted as 1 and 14 respectively, are shown together with the changes in absorbance with time of n-butylamine–chloranil mixtures (2—13), in which the intervals were 2 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. The absorbance of amine was negligible above 250 nm.

Given the rapid decrease of the band at 290 nm we followed the evolution of absorbance at 354 nm. Using a FORTRAN V

Figure 1. Spectrum 1: chloranil solution in cyclohexane ($[CA]_0$ 6.4×10^{-5}M). Spectra 2—14: time variation of the absorption bands for the n-butylamine–chloranil reaction in cyclohexane ($[CA]_0$ 6.4×10^{-5}M; [A] 0.15M) in which the time intervals were kept constant at 1 min

program, it was shown that the formations of disubstituted product follows the rate law (1), where $[CA]_0$ is the initial

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

concentration of CA and [D] is the instantaneous concentration of the disubstituted product, obtained from Beer's law.[22–24]

Integrating equation (1) gives (2) where ε_D is the molar extinction coefficient of D and A_D represents the average absorbance at 354 nm. In order to determinate the influence of $[CA]_0$ and [A] and the values of the experimental constant k_{exp}, several runs were performed.[25] Upon plotting the left-hand side of equation (2) against time, good straight lines were found at

$$-\ln([CA]_0\varepsilon_D - A_D) = -\ln([CA]_0\varepsilon_D + k_{exp}t) \qquad (2)$$

all temperatures studied. A small induction period was noted at the start of most reactions before pseudo-first-order rate conditions were attained. This may be an effect of intermediate formation, leading to the disubstituted product, D.

In Table 1 the corresponding parameters, derived from equation (2) by the application of Lagrange's multiplier method,[26] are shown. In all cases, the value of ε_D at 354 nm used to determine k_{exp} was 27 344 ± 50 mol^{-1} cm^{-1}. The initial concentration of CA does not influence the slope when there is a constant excess of amine. However, the slopes rise considerably as the amine concentration increases. From this point on, k_{exp} values are the weighted average when varying $[CA]_0$ but with constant [A] and temperature.

Of all the quantitative relations between k_{exp} and amine concentrations considered, at each temperature studied, the best

Table 1. Rate constants* from equation (2) for n-butylamine–CA system in cyclohexane solution

T/K		279		283		298‡		308	
10[A]/M	$[CA]_0$†	1	2	1	2	1	2	1	2
0.30 ± 0.02		0.46 ± 0.001	0.517 ± 0.001	0.517 ± 0.001	0.517 ± 0.002	0.883 ± 0.005	0.860 ± 0.005	1.067 ± 0.005	1.067 ± 0.005
0.50 ± 0.03		0.78 ± 0.01	0.883 ± 0.005	0.097 ± 0.003	0.102 ± 0.003	2.010 ± 0.002	2.050 ± 0.003	2.70 ± 0.003	2.78 ± 0.005
0.70 ± 0.04		1.02 ± 0.01	1.15 ± 0.01	1.40 ± 0.01	1.38 ± 0.01	3.02 ± 0.003	3.16 ± 0.002	4.62 ± 0.01	4.73 ± 0.01
0.90 ± 0.05		1.25 ± 0.02	1.35 ± 0.01	1.77 ± 0.02	1.80 ± 0.01	3.88 ± 0.05	4.30 ± 0.06	6.55 ± 0.02	6.75 ± 0.04
1.10 ± 0.05		1.47 ± 0.03	1.58 ± 0.12	2.30 ± 0.02	2.08 ± 0.02	5.00 ± 0.02	5.50 ± 0.02	8.24 ± 0.04	8.66 ± 0.02
1.3 ± 0.1		1.72 ± 0.03	1.79 ± 0.02	2.42 ± 0.03	2.46 ± 0.02	5.90 ± 0.02	6.00 ± 0.02	9.53 ± 0.05	10.0 ± 0.2
1.5 ± 0.1		1.95 ± 0.03	2.00 ± 0.02	2.67 ± 0.03	2.40 ± 0.02	6.02 ± 0.02	6.90 ± 0.04	10.4 ± 0.1	11.5 ± 0.2
1.7 ± 0.1		2.10 ± 0.03	2.44 ± 0.02	2.95 ± 0.03	2.75 ± 0.02	6.73 ± 0.04	7.50 ± 0.04	12.1 ± 0.1	12.6 ± 0.2
1.9 ± 0.1		2.50 ± 0.03	2.60 ± 0.03	3.18 ± 0.03	3.20 ± 0.03	7.59 ± 0.04	8.44 ± 0.05	12.5 ± 0.1	14.0 ± 0.4
2.0 ± 0.1		1.99 ± 0.03	2.83 ± 0.03	3.35 ± 0.03	3.36 ± 0.03	7.9 ± 0.04	8.50 ± 0.02	13.0 ± 0.3	15.5 ± 0.4

* $k_{exp} \times 10^3$ (s^{-1}). † The numbers 1 and 2 correspond to (4.5 ± 0.2) × 10^{-5} and (8.5 ± 0.4) × 10^{-5}M $[CA]_0$. ‡ At 298 K the k_{exp} values for three $[CA]_0$ (6.4×10^{-5}, 7.4×10^{-5}, and 10.5×10^{-5}M) have been omitted.

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

T/K	279	283	298	308	$-\Delta H_1^\circ$	$-\Delta H_2^\circ$	$\vec{E}_{a_3}$
r	0.9990	0.9990	0.9997	0.9998			
a_0	5.46 ± 0.05	5.23 ± 0.05	4.16 ± 0.002	3.49 ± 0.02			
10 a_1/M	1.06 ± 0.08	1.11 ± 0.08	1.27 ± 0.03	1.53 ± 0.03			
-10^3 a_2/M^2	1.25 ± 0.21	1.17 ± 0.21	1.30 ± 0.08	1.57 ± 0.09			
K_1/dm^3 mol^{-1}	24 ± 1	23 ± 1	18.7 ± 0.5	15.1 ± 0.2	11.2 ± 0.3		
K_2/dm^3 mol^{-1}	9.5 ± 0.7	9.1 ± 0.6	7.8 ± 0.2	6.5 ± 0.1		8.7 ± 1	
10^3 k_3/s^{-1}	4.3 ± 0.2	5.3 ± 0.3	15.6 ± 0.3	30.4 ± 0.5			49 ± 1

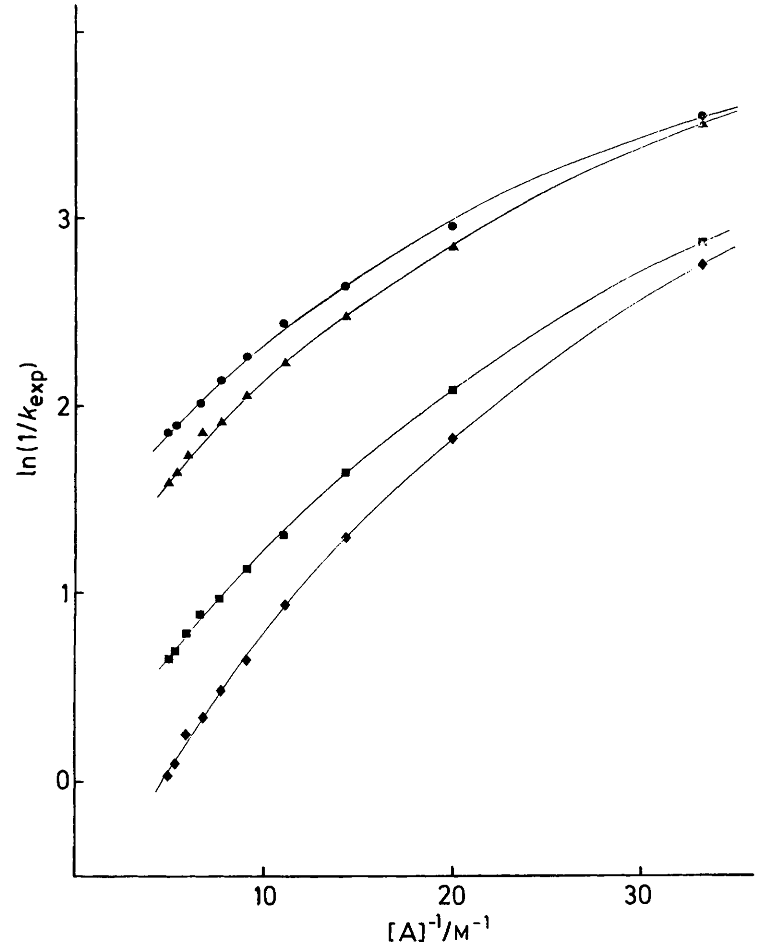


Figure 2. Variations of ln $(1/k_{exp})$ with $1/[A]$ from equation (3) for the n-butylamine–chloranil system at, (●) 6 °C; (▲) 10 °C; (■) 25 °C; (◆) 35 °C

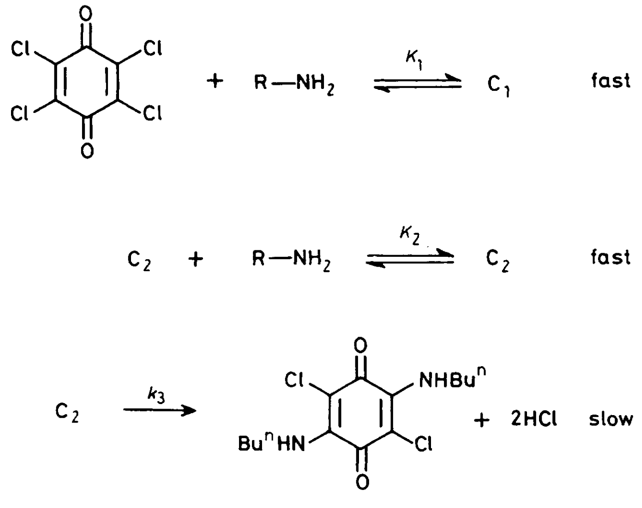
fit was given by (3) for which exponents $n \geq 3$ have no significance.

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

Typical plots of equation (3) are shown in Figure 2. At high concentrations of amine, the divergence of the curves seems to indicate that at least one step of the mechanism must be endothermic and rate determining. The coefficients of equation (3) are listed in Table 2. The alternating signs of the coefficients, as well as the shape of equation (3), seem to indicate that the function $1/k_{exp}$ can approximate to a Fourier series. By means of the procedure developed in ref. 19, one obtains expression (4).

$$1/k_{exp} = e^{a_0} \,.\, \{1 + a_1/[A] + |(a_1^2/2) + a_2|1/[A]^2\} \qquad (4)$$

From equation (4) and taking into account the conclusions of Figures 1 and 2 we selected the mechanism shown in the Scheme. The evidence for elimination of HCl was confirmed by shaking the mixture with water and testing the aqueous layer for chloride ion.[27]



Scheme.

The parameters a_0, a_1, and a_2 have been related to the equilibrium constants (K_1 and K_2) and to the kinetic rate (k_3) as follows demonstration. Applying the equilibrium-state assumption[28] to the C_1 and C_2 we obtain equation (5). Taking

$$[C_2] = K_1K_2[A]^2 \,.\, [CA] \qquad (5)$$

into account equations (4) and (5) and the mass balance, equation (1) was transformed into (6). Now, if we identify the

$$1/k_{exp} = 1/k_3\,(1 + 1/K_2 \,.\, 1/[A] + 1/K_1K_2 \,.\, 1/[A]^2) \qquad (6)$$

coefficients of equations (4) and (6), we obtain (7)—(9).

$$K_1 = 2a_1 \,.\, (a_1^2 + 2a_2)^{-1} \qquad (7)$$

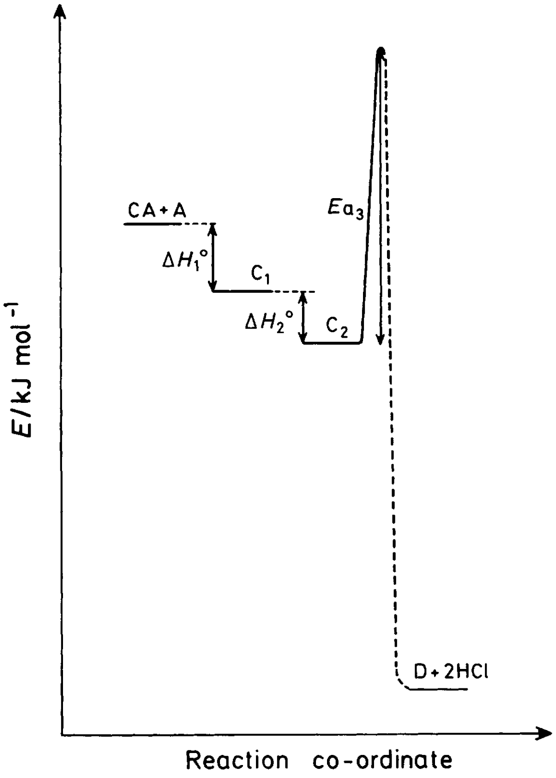


Figure 3. Relative energies of the reactives, intermediates, products, and barrier involved in the reaction between n-butylamine and chloranil (units kJ mol^{-1})

$$K_2 = (a_1)^{-1} \tag{8}$$

$$k_3 = \exp(-a_0) \tag{9}$$

The kinetic parameters as well as their corresponding standard errors are listed in Table 2. To calculate the K_1 errors we have assumed that the parameters a_1 and a_2 are uncorrelated [cov $(a_1,a_2) \simeq 0$], *i.e.* the covariance between the parameters a_1 and a_2 is ~ 0.[29] As observed, the values of the equilibrium constants (K_1 or K_2) decrease as the temperature increases. Thus the intermediates C_1 and C_2 could be of charge-transfer complex nature, in agreement with the results obtained for a similar system.[19]

From the data listed in Table 2, the thermodynamic parameters ΔH_1°, ΔH_2°, and E_{a_3} were derived by standard methods. The change in the integral enthalpy for the kinetic reaction between CA and 2A, leading to D + 2HCl, has been estimated from the additive contributions from the individual atoms or bonds in the corresponding molecules.[30] It was found to be −77.7 kJ mol^{-1}. From this result, the change of enthalpy for the latter step has been estimated.

Figure 3 shows the relative energy levels for the different steps of the n-butylamine–chloranil reaction. These results suggest that the molecular complexes C_1 and C_2 are intermediates with relatively small differences of enthalpy between the reactants and the final products. From thermodynamic considerations, it is possible to demonstrate that the values of the entropy terms, $T\Delta S_1^\circ$ and $T\Delta S_2^\circ$, are of the same order of magnitude as the enthalpy ones, ΔH_1° or ΔH_2°, respectively. It can thus be inferred that there are no covalent bonds involved, as is the case with charge-transfer complex formation.[31]

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