

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

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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<sup>1-6</sup> and aliphatic<sup>7-13</sup> amines or proteins<sup>14</sup> has been widely studied. However, in the case of aliphatic amines, the literature is not extensive in spite of the analytical applications.<sup>15,16</sup>

Primary and secondary aliphatic amines are known to form the disubstituted products (D) of CA (substituted group NHR),<sup>7</sup> but some tertiary aliphatic amines (type R<sup>1</sup>R<sup>2</sup>NET) give a monosubstituted product (substituted group CH=CHNR<sup>1</sup>R<sup>2</sup>).<sup>7,17</sup>

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<sup>12-14</sup> and in non-polar solvents charge-transfer complexes or monosubstituted (M) intermediates are formed.<sup>8,9</sup> Finally, with tertiary amines in non-polar solvents, the formation of a disubstituted product does not occur, and instead, charge-transfer complexes are obtained.<sup>18</sup>

Dwivedi and Banga<sup>9</sup> 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.*<sup>10</sup> concluded that the stoichiometry 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.<sup>19</sup>

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.*<sup>7</sup> 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 ( $\epsilon$  27 344), and 520 nm (240). The i.r. spectrum (Perkin-Elmer 281 spectrometer; KBr disc,<sup>20,21</sup>) showed a strong band at 1 590 cm<sup>-1</sup> corresponding to an associated C=O group, and a weak band at 1 660 cm<sup>-1</sup> assigned to the non-associated carbonyl group.<sup>19</sup> At 3 230 cm<sup>-1</sup> a sharp band is attributed to the N-H stretching mode. The <sup>1</sup>H n.m.r. spectrum (Varian 90 MHz spectrometer; CDCl<sub>3</sub>) showed  $\delta$  0.9 (t, Me), 1.55 (m, CH<sub>2</sub>), 3.8 (q, CH<sub>2</sub>N), and 7.3 (br, NH). The <sup>13</sup>C n.m.r. spectrum (Bruker AC-200 MHz spectrometer; CDCl<sub>3</sub>) showed  $\delta$  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<sup>7</sup>) and confirmed that from equimolecular amounts of CA and amine the disubstituted derivative was obtained together with unchanged CA,<sup>7</sup> 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.<sup>19</sup>

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 ( $4.5 \times 10^{-5}$  and  $8.5 \times 10^{-5}$  M). At 25 °C, five initial concentrations were used:  $4.5 \times 10^{-5}$ ,  $6.4 \times 10^{-5}$ ,  $7.4 \times 10^{-5}$ ,  $8.5 \times 10^{-5}$ , and  $10.5 \times 10^{-5}$  M. In all cases ten different excesses of amine were performed, the selected concentration range being 0.03–0.20 M.

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

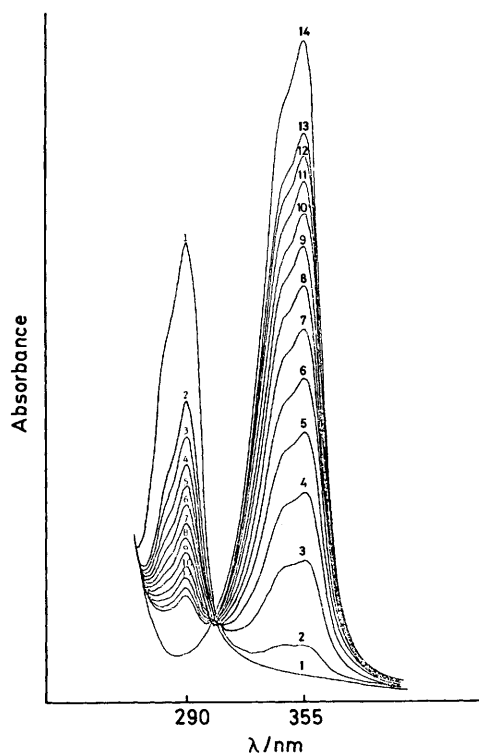


Figure 1. Spectrum 1: chloranil solution in cyclohexane ( $[CA]_0$   $6.4 \times 10^{-5}M$ ). Spectra 2—14: time variation of the absorption bands for the n-butylamine-chloranil reaction in cyclohexane ( $[CA]_0$   $6.4 \times 10^{-5}M$ ;  $[A]$   $0.15M$ ) in which the time intervals were kept constant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

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

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

concentration of CA and  $[D]$  is the instantaneous concentration of the disubstituted product, obtained from Beer's law.<sup>22-24</sup>

Integrating equation (1) gives (2) where  $\epsilon_D$  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.<sup>25</sup> Upon plotting the left-hand side of equation (2) against time, good straight lines were found at

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

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,<sup>26</sup> are shown. In all cases, the value of  $\epsilon_D$  at 354 nm used to determine  $k_{exp}$  was  $27344 \pm 50 \text{ mol}^{-1} \text{ cm}^{-1}$ . 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
$0.30 \pm 0.02$		$0.46 \pm 0.001$	$0.517 \pm 0.001$	$0.517 \pm 0.001$	$0.517 \pm 0.002$	$0.883 \pm 0.005$	$0.860 \pm 0.005$	$1.067 \pm 0.005$	$1.067 \pm 0.005$
$0.50 \pm 0.03$		$0.78 \pm 0.01$	$0.883 \pm 0.005$	$0.097 \pm 0.003$	$0.102 \pm 0.003$	$2.010 \pm 0.002$	$2.050 \pm 0.003$	$2.70 \pm 0.003$	$2.78 \pm 0.005$
$0.70 \pm 0.04$		$1.02 \pm 0.01$	$1.15 \pm 0.01$	$1.40 \pm 0.01$	$1.38 \pm 0.01$	$3.02 \pm 0.003$	$3.16 \pm 0.002$	$4.62 \pm 0.01$	$4.73 \pm 0.01$
$0.90 \pm 0.05$		$1.25 \pm 0.02$	$1.35 \pm 0.01$	$1.77 \pm 0.02$	$1.80 \pm 0.01$	$3.88 \pm 0.05$	$4.30 \pm 0.06$	$6.55 \pm 0.02$	$6.75 \pm 0.04$
$1.10 \pm 0.05$		$1.47 \pm 0.03$	$1.58 \pm 0.12$	$2.30 \pm 0.02$	$2.08 \pm 0.02$	$5.00 \pm 0.02$	$5.50 \pm 0.02$	$8.24 \pm 0.04$	$8.66 \pm 0.02$
$1.3 \pm 0.1$		$1.72 \pm 0.03$	$1.79 \pm 0.02$	$2.42 \pm 0.03$	$2.46 \pm 0.02$	$5.90 \pm 0.02$	$6.00 \pm 0.02$	$9.53 \pm 0.05$	$10.0 \pm 0.2$
$1.5 \pm 0.1$		$1.95 \pm 0.03$	$2.00 \pm 0.02$	$2.67 \pm 0.03$	$2.40 \pm 0.02$	$6.02 \pm 0.02$	$6.90 \pm 0.04$	$10.4 \pm 0.1$	$11.5 \pm 0.2$
$1.7 \pm 0.1$		$2.10 \pm 0.03$	$2.44 \pm 0.02$	$2.95 \pm 0.03$	$2.75 \pm 0.02$	$6.73 \pm 0.04$	$7.50 \pm 0.04$	$12.1 \pm 0.1$	$12.6 \pm 0.2$
$1.9 \pm 0.1$		$2.50 \pm 0.03$	$2.60 \pm 0.03$	$3.18 \pm 0.03$	$3.20 \pm 0.03$	$7.59 \pm 0.04$	$8.44 \pm 0.05$	$12.5 \pm 0.1$	$14.0 \pm 0.4$
$2.0 \pm 0.1$		$1.99 \pm 0.03$	$2.83 \pm 0.03$	$3.35 \pm 0.03$	$3.36 \pm 0.03$	$7.9 \pm 0.04$	$8.50 \pm 0.02$	$13.0 \pm 0.3$	$15.5 \pm 0.4$

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

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

T/K	279	283	298	308	$-\Delta H_1^\circ$	$-\Delta H_2^\circ$	$\bar{E}_{a3}$
$r$	0.9990	0.9990	0.9997	0.9998			
$a_0$	$5.46 \pm 0.05$	$5.23 \pm 0.05$	$4.16 \pm 0.002$	$3.49 \pm 0.02$			
$10 a_1/M$	$1.06 \pm 0.08$	$1.11 \pm 0.08$	$1.27 \pm 0.03$	$1.53 \pm 0.03$			
$-10^3 a_2/M^2$	$1.25 \pm 0.21$	$1.17 \pm 0.21$	$1.30 \pm 0.08$	$1.57 \pm 0.09$			
$K_1/\text{dm}^3 \text{ mol}^{-1}$	$24 \pm 1$	$23 \pm 1$	$18.7 \pm 0.5$	$15.1 \pm 0.2$	$11.2 \pm 0.3$		
$K_2/\text{dm}^3 \text{ mol}^{-1}$	$9.5 \pm 0.7$	$9.1 \pm 0.6$	$7.8 \pm 0.2$	$6.5 \pm 0.1$		$8.7 \pm 1$	
$10^3 k_3/s^{-1}$	$4.3 \pm 0.2$	$5.3 \pm 0.3$	$15.6 \pm 0.3$	$30.4 \pm 0.5$			$49 \pm 1$

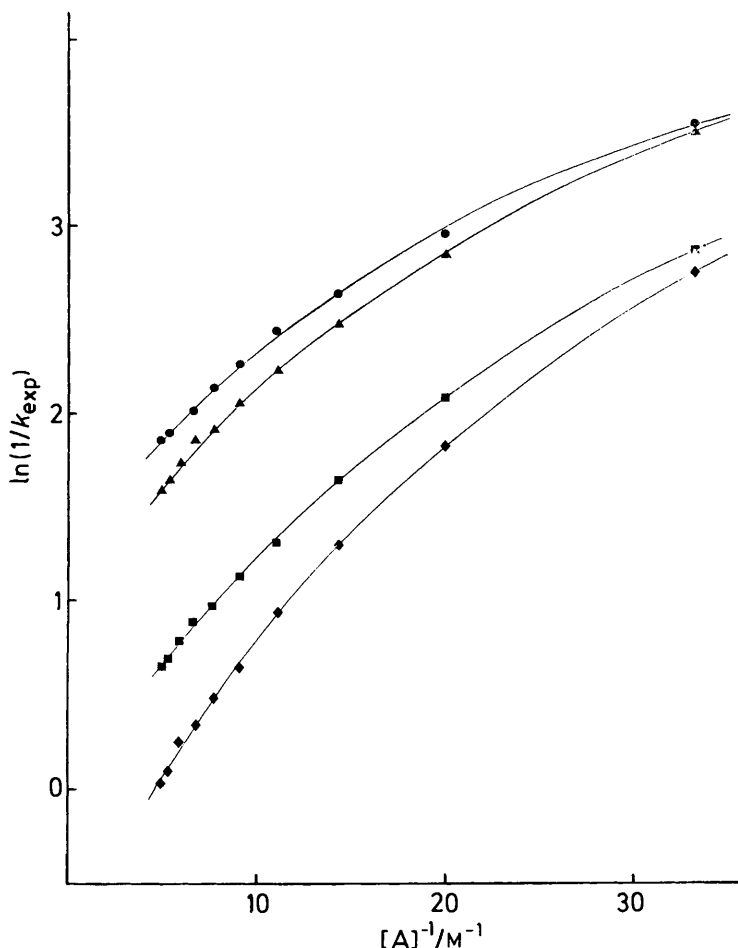


Figure 2. Variations of  $\ln(1/k_{\text{exp}})$  with  $1/[A]$  from equation (3) for the n-butylamine-chloranil system at, (●) 6 °C; (▲) 10 °C; (■) 25 °C; (◆) 35 °C

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

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

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  $1/k_{\text{exp}}$  can approximate to a Fourier series. By means of the procedure developed in ref. 19, one obtains expression (4).

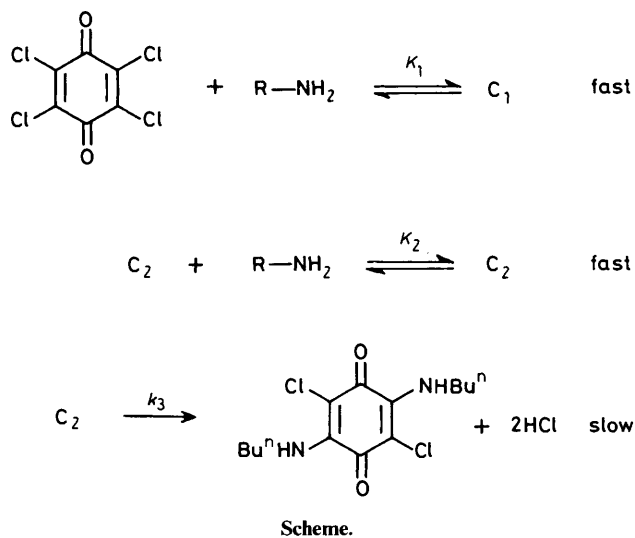
$$1/k_{\text{exp}} = e^{a_0} \cdot \{1 + a_1/[A] + [(a_1^2/2) + a_2]1/[A]^2\} \quad (4)$$

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.<sup>27</sup>

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<sup>28</sup> to the  $C_1$  and  $C_2$  we obtain equation (5). Taking

$$[C_2] = K_1 K_2 [A]^2 \cdot [CA] \quad (5)$$

into account equations (4) and (5) and the mass balance,



equation (1) was transformed into (6). Now, if we identify the

$$1/k_{\text{exp}} = 1/k_3 (1 + 1/K_2 \cdot 1/[A] + 1/K_1 K_2 \cdot 1/[A]^2) \quad (6)$$

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

$$K_1 = 2a_1 \cdot (a_1^2 + 2a_2)^{-1} \quad (7)$$

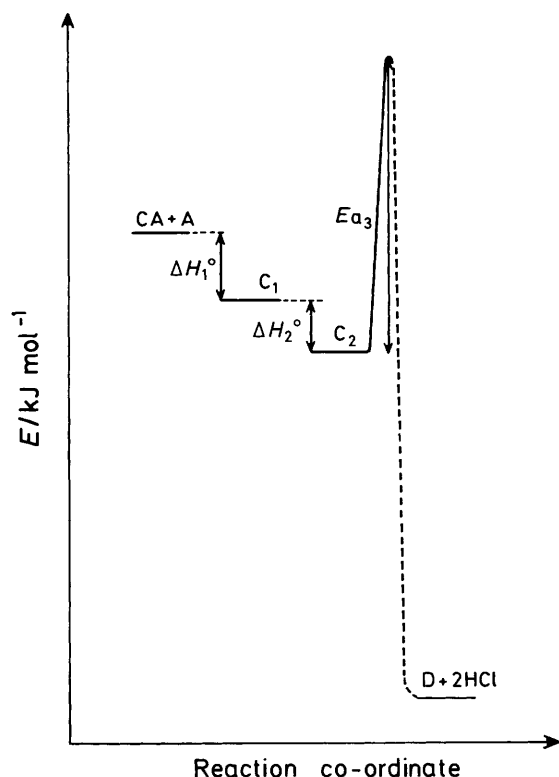


Figure 3. Relative energies of the reactives, intermediates, products, and barrier involved in the reaction between n-butylamine and chloranil (units  $\text{kJ mol}^{-1}$ )

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

$$k_3 = \exp(-a_0) \quad (9)$$

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 [ $\text{cov}(a_1, a_2) \approx 0$ ], i.e. the covariance between the parameters  $a_1$  and  $a_2$  is  $\sim 0$ .<sup>29</sup> 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.<sup>19</sup>

From the data listed in Table 2, the thermodynamic parameters  $\Delta H_1^\circ$ ,  $\Delta H_2^\circ$ , 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.<sup>30</sup> It was found to be  $-77.7 \text{ kJ mol}^{-1}$ . 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,  $\Delta H_1^\circ$  or  $\Delta H_2^\circ$ , respectively. It can thus be inferred that there are no covalent bonds involved, as is the case with charge-transfer complex formation.<sup>31</sup>

## References

- 1 Z. Rappoport, *J. Chem. Soc.*, 1963, 4498.
- 2 A. V. Kerimbekova, *Tr. Soveshch. Org.*, 1968, 276.
- 3 D. C. Mukherjee and A. K. Chandra, *J. Phys. Chem.*, 1964, **68**, 477.
- 4 T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 355.
- 5 R. A. Dommissie, J. A. Lepoivre, and F. C. Alderweireldt, *Bull. Soc. Chim. Belg.*, 1977, **86**, 633.
- 6 T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 380.
- 7 D. Buckley, H. B. Henbest, and P. Slade, *J. Chem. Soc.*, 1957, 4891.
- 8 W. Lautenberger and J. G. Miller, *J. Phys. Chem.*, 1970, **74**, 2722.
- 9 P. C. Dwivedi and A. K. Banga, *J. Phys. Chem.*, 1981, **85**, 1768.
- 10 P. C. Dwivedi, A. K. Banga, and R. A. Garwal, *Electrochim. Acta*, 1982, **27**, 1697.
- 11 S. B. Shah and A. S. N. Murthy, *J. Phys. Chem.*, 1975, **79**, 322.
- 12 T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2971.
- 13 For a review of this subject, see O. Buttufei, *Rev. Chim.*, 1980, **30**, 140.
- 14 K. Hoffmann, *Naturwissenschaften*, 1965, **52**, 428.
- 15 S. Sass, J. J. Kaufman, A. A. Cardenas, and J. J. Martin, *Anal. Chem.*, 1958, **30**, 529.
- 16 R. E. Smith and W. R. Davis, *Anal. Chem.*, 1984, **56**, 2345.
- 17 R. Foster, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 711.
- 18 A. Nakajima and H. Akamatu, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 3030.
- 19 A. Codoñer, I. S. Monzó, J. Palou, and R. Valero, *J. Chem. Soc., Perkin Trans. 2*, 1988, 221.
- 20 J. F. Bagli, *J. Am. Chem. Soc.*, 1962, **84**, 177.
- 21 R. Valero, 'Tesis Doctoral,' Valencia 1985, pp. 26–28.
- 22 P. R. Bevington, 'Data Reduction and Error Analysis for the Physical Scientist,' McGraw-Hill, London, 1969, p. 73.
- 23 J. A. John and M. H. Quenouille, 'Experiments: Design and Analysis,' Griffin, London, 1977, 2nd edn., p. 12.
- 24 L. Sachs, 'Estadística Aplicada,' Labor, Barcelona, 1978, p. 69.
- 25 N. H. Nie, 'SPSS (Statistical Package for the Social Sciences), Manual,' McGraw-Hill, New York, 1975, 2nd edn., p. 320.
- 26 W. E. Deming, 'Statistical Adjustment of Data,' Dover, New York, 1964, p. 53.
- 27 B. K. Das and B. Majee, *J. Indian Chem. Soc.*, 1968, **45**, 1054.
- 28 D. H. McDaniel, *J. Phys. Chem.*, 1956, **60**, 968.
- 29 K. A. Brownlee, 'Statistical Theory and Methodology in Science and Engineering,' Wiley, New York, 1965, 2nd edn., p. 77.
- 30 S. W. Benson, 'Thermodynamical Kinetics,' Wiley, New York, 1976, p. 135.
- 31 R. S. Mulliken and W. B. Person, 'Molecular Complexes,' Wiley, New York, 1969.

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