Interaction of 2,3-dichloro-1,4-naphthoquinone with *n*-butylamine in halocarbon solvents

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Abstract

The rapid interaction between 2,3-dichloro-1,4-naphthoquinone (DClNQ) and *n*-butylamine results in the formation of 2N(*n*-butylamino)-3-chloro-1,4-naphthoquinone as the final product. The reaction is found to proceed through the initial formation of charge-transfer (CT) complex as an intermediate. The final product of the reaction has been isolated and characterized using FTIR, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The rate of formation of product has been measured as a function of time in different halocarbon solvents, viz., chloroform, dichloromethane and 1:1 (v/v) mixture of two solvents. The pseudo first order and second order rate constants at various temperatures for the transformation process were evaluated from the absorbance time data. The activation parameters (E_a, $\Delta S^\#$, $\Delta H^\#$, and $\Delta G^\#$) were obtained from temperature dependence of rate constants. The influence of dielectric constant on the properties of reaction was discussed and the probable course of reaction is presented.

Keywords: 2,3-Dichloro-1,4-naphthoquinone (DClNQ); *n*-Butylamine; Charge-transfer complex; Spectroscopic; Kinetics

1. Introduction

Since the publication of Mulliken's [1,2] novel theory of charge-transfer interactions (CT interactions), also called as molecular complexes, between electron donor and an electron acceptor, it has been successfully applied to many interesting studies [3,4] amongst them is the possible role of CT-complexes in chemical reactions [5]. Charge-transfer complexes (CT-complexes) are known to take part in many chemical reactions like addition, substitution and condensation. These complexes are of current interest due to their potential nonlinear optical activity [6]. Formation of such complexes is currently being studied in micelles and micro-emulsions [7–9].

The survey of the literature reveals an enormous study on the spectroscopic and other physico-chemical aspects [4,10–16], however, reports on detailed kinetic studies of reactions proceeding through the ground state of such complexes are quite a few in number [5,17–19]. Both aliphatic and aromatic amines form such complexes, several such reactions have been deliberated fairly recently [20–29]. Aliphatic amines are known to act as strong electron donors and forms electron donor–acceptor (EDA) complexes with number of electron acceptors [30]. The EDA complexes (outer complexes) lead to the formation of σ-complexes (inner complexes) which finally led to the formation of the final product(s) of the reaction [30,31]. The primary and secondary amines are known to form both mono- and di-substituted products with chloranil [32–34]. The results have indicated the possible participation of π and σ (outer and inner) complexes in the substitution reactions. A major part of the evidence for the participation of outer complexes as intermediates in these reactions has been based on kinetic measurements. The previously reported kinetic and spectrophotometric studies on the interaction of *n*-butylamine with chloranil have provided the valuable information towards the existence of CT-complex in solution, which can act as an intermediate in the substitution reactions [30,31,35]. However, such studies on the interaction of *n*-butylamine with naphthoquinone derivatives, as acceptors are quite sparse.

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The present article describes about kinetic and spectroscopic study of interaction between 2,3-dichloro-1,4-naphthoquinone (DClNQ) (E_A = 0.98 eV) [36] and *n*-butylamine (I_p = 8.71 eV) [37] in different halocarbon solvents, viz., chloroform, dichloromethane and 1:1 (v/v) mixture of the two solvents. The detailed kinetic study, including isolation, characterization and identification of the final product was carried out. The observed results afford evidence concerning the critical role of dielectric constant on the kinetic behaviour of the reaction.

2. Experimental

2.1. Materials and methods

The DClNQ (Fluka AG) was purified by repeated crystallization from chloroform, to get bright yellow needles having m.p. of 196 °C (uncorrected), whereas *n*-butylamine (BDH) was dried over caustic potash and distilled twice just before use. The spectroscopic grade chloroform (BDH) and dichloromethane (Ranbaxy) were used as received. Benzene was purified by reported methods [12] and was used as eluent for column chromatography to purify the product. The column was packed with 60–120 mesh silica gel (Fischer).

Absorbance measurements were made using Cary-50 double beam Bio UV–vis Spectrophotometer. The temperature of the solutions was varied by the use of peltier accessory. A matched pair of quartz cuvetts (10 mm path length) with Teflon airtight stoppers was used for absorbance measurements. The FTIR spectrum of the reaction product was recorded using Nicolet Impact 410 spectrometer. The ^{1}H and ^{13}C NMR spectra of the compound were recorded using Brucker, 300 MHz NMR spectrometer. The mass spectrum of the compound was recorded in Autospec mass spectrometer. The elemental analysis data of the product was carried out with ThermoQuest elemental analyzer.

3. Results and discussion

3.1. Isolation of the final product

One mole of DClNQ and 3 mol of *n*-butylamine were mixed in 75 ml of chloroform. Then the reaction was allowed to proceed for about 80 h in room temperature with constant stirring under dry conditions. Afterwards by subjecting the reaction mixture to column chromatography on silica gel. A red colored compound was collected using benzene as eluent (64% yield). The characterization and identification of this unknown product is as follows.

3.2. Characterization of the final product

The obtained product has the m.p. of 112 °C (uncorrected) and FTIR spectrum in KBr shows the following important

absorption bands. The one at 3308 cm^{-1} which seems to be sharp and is assigned to $\bar{v}_{N-H}$ stretching, the second rather strong and sharp band that appeared at 1678 cm^{-1} is attributed to $\bar{v}_{C=O}$. The third band which seems to be sharp, appeared at 1641 cm^{-1} (weak) and is due to the $\bar{v}_{C=O}$ and the fourth sharp and strong band is observed at 721 cm^{-1} which is due to $\bar{v}_{C-Cl}$ stretching.

The ^{1}H NMR spectrum of the product in CDCl$_3$ displayed distinct signals with appropriate multiplets. The triplet (J = 7.3 Hz) accounting for three protons centered at 0.99δ is assigned to the protons of methyl group. The multiplet in the region of 1.39–1.51δ accounting for two protons is assigned to the methylene protons adjacent to the methyl group. The multiplet in the region of 1.64–1.74δ accounting for two protons is assignable to methylene protons, β to the −NH grouping. The two methylene protons of −NH−CH$_2$ grouping resonated as a quartet centered at 3.86δ. The broad singlet at 6.08δ was D$_2$O exchangeable and is therefore assignable to −NH proton. The aromatic region corresponds to four protons. The triplet (J = 7.5 Hz) centered at 7.63δ is assigned to the C−6H, while the triplet (J = 7.4 Hz) centered at 7.73δ is assigned to C−7H. C−8H protons resonated as a doublet at 8.04δ (J = 7.4 Hz), while the downfield doublet (J = 7.5 Hz) centered at 8.16δ is assigned to C−5H. Based on these observations the following structure may be assigned for the obtained product:
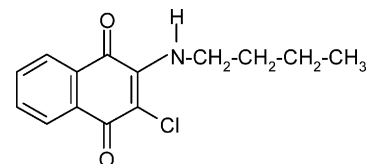
Additional evidences for the assigned structure are the ^{13}C NMR spectrum of the compound shows 13 signals corresponding to 14 carbon atoms of the molecule. The signals at 3.88, 19.93, 33.10 and 44.73δ are characteristic of the carbon atoms of the *n*-butyl chain. The assignments for the aromatic carbon atoms and quaternary carbon atoms could be made as follows:
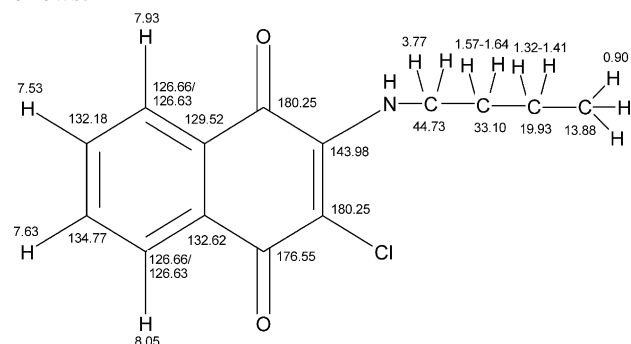
The EI mass spectrum of the product displayed molecular ion peaks M^+ at m/z (%) 263 (39) and at 265 (13) due to $(M + 2)^+$ suggesting the molecular weight of the assigned product and also the presence of chlorine in the molecule. Auxiliary, the following fragments observed in the mass spectrum of the compound confirm the assigned structure for the compound:
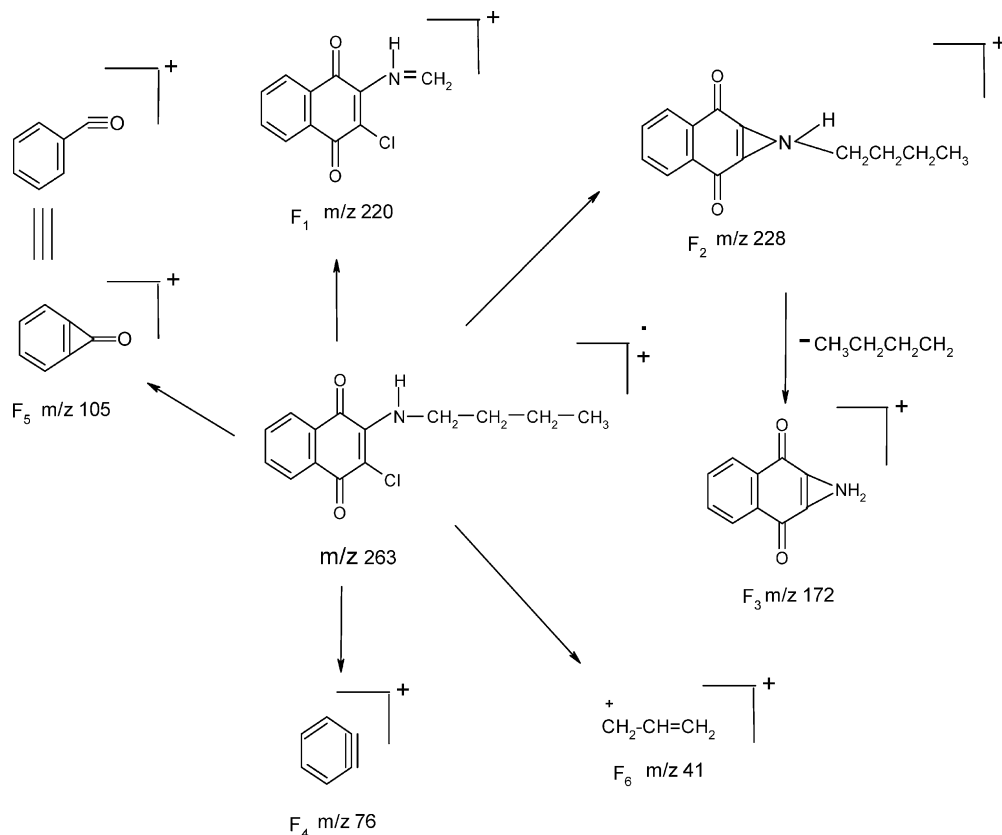
The cleavage of propyl radical from the $>N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ of the molecular ion gives rise to fragment F_1 at $m/z\,(\%)$ 220 (100) which is the base peak. The peak at $m/z\,(\%)$ 228 (5) is due to F_2 fragment obtained from the molecular ion by the loss of a chlorine free radical. The peaks at 105, 76, 41 are characteristic peaks corresponding to fragments F_5, F_4, and F_6, respectively. Thus, the structure of the compound is in agreement with the observed spectral data. Moreover, the proposed structure for the product is consistent with elemental analysis data i.e. $C_{14}H_{14}O_2NCl$ requires C 63.74%, H 5.35%, and N 5.31%; found C 63.71%, H 5.37%, and N 5.29%.

3.3. Kinetic study of the reaction

The kinetics of the reaction between *n*-butylamine and DClNQ was studied in chloroform, dichloromethane and in a binary mixture of chloroform and dichloromethane at different temperatures. Hence, the reaction is carried under the psuedo first order condition, i.e. $C_D^0 \gg C_A^0$, where C_D^0 and C_A^0 are the initial molar concentrations of the donor and acceptor, respectively.

On mixing the *n*-butylamine and DClNQ, there was an instantaneous formation of orange color with an absorption maximum centered around 470 nm. The intensity of this band goes on increasing with time, consequently the change in absorbance of the solution was measured as a function of time. The typical spectra recorded in chloroform at 25 °C at different time of intervals, are shown in Fig. 1. The continuous

increase in absorbance at 470 nm is indicative of formation of the final reaction product, because at this wavelength neither the acceptor nor the donor absorbs. Additional support for this conclusion is the electronic absorption spectra of final product in chloroform, shown in Fig. 2, which has the identical absorption maxima as that of the solution of *n*-butylamine and
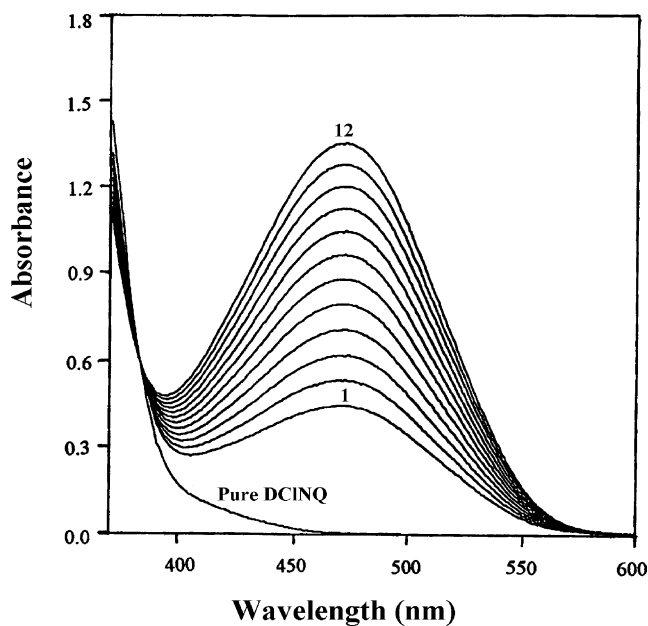

Fig. 1. Absorption spectra of 2,3-dichloro-1,4-naphthoquinone and *n*-butylamine in chloroform at 25 °C, where $C_A^0 = 8.3016 \times 10^{-4}$ M and $C_D^0 = 0.2028$ M.
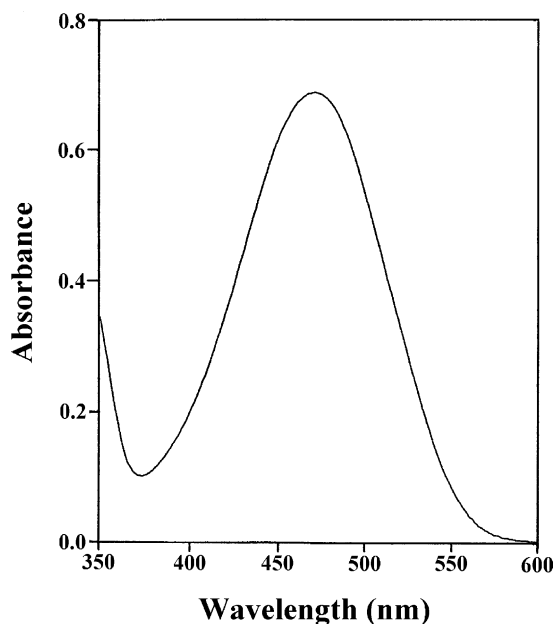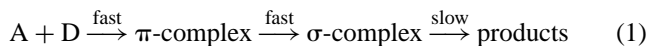
Fig. 2. UV–vis absorption spectrum of the product, 2N(*n*-butylamino)-3-chloro-1,4-naphthoquinone in chloroform at 25 °C.

DClNQ mixture. At the same time the observed band cannot be characteristic absorption band of EDA complex because: (i) the formation of EDA complex is an instantaneous process; and (ii) the concentration of the EDA complex may be very low, so immediately it converts to the σ-complex and forms the final products of the reaction.

Hence, the title reaction appears to proceed through the initial formation of the π-complex (outer complex), which might be transformed into the σ-complex that ultimately breaks down into the final products [26,37]. In the present case, it was observed that the formation of the π- and σ-complexes were extremely fast irrespective of maintaining a very low temperature. Whereas the formation of the final product takes place at a measurable velocity, thus, the reaction may be formulated as

$$A + D \xrightarrow{\text{fast}} \pi\text{-complex} \xrightarrow{\text{fast}} \sigma\text{-complex} \xrightarrow{\text{slow}} \text{products} \quad (1)$$

The recorded band was found to be slightly solvent-dependent in such a way that it has λ_{max} at 471 nm in CHCl$_3$, 469 nm in CH$_2$Cl$_2$ and 470 nm in 1:1 (v/v) mixture of the two, which agrees very well with the values of the final product in respective solvents. The observed increase in the absorption band intensity of the *n*-butylamine–DClNQ complex with elapse of time, further it supports the fact that the EDA complex formed is of the dative type structure [D$^+$−A$^-$] which consequently converts to an ionic intermediate [D$^+$A$^-$] [38]. Thus, the obtained data for one of the runs as a function of time is given in Table 1.

The psuedo first order rate constants, k_1, were obtained by the least squares method as the slope of the correlation ln *d* against time, where '*d*' is the measured optical density of the reaction mixture at its λ_{max}. Then the second order rate

Time (min)	Optical density, *d*				
	0.05439[a]	0.1087[a]	0.1631[a]	0.2175[a]	0.2719[a]
6	0.1364	0.2942	0.4213	0.6087	0.8328
7	0.1449	0.314	0.4578	0.6618	0.9088
8	0.1529	0.3335	0.4933	0.7139	0.9808
9	0.1616	0.3531	0.5284	0.7638	1.0502
10	0.1698	0.3719	0.5628	0.8133	1.1171
11	0.1780	0.3908	0.5967	0.8608	1.1832
12	0.1865	0.4098	0.6302	0.9081	1.2450
13	0.1944	0.4282	0.6632	0.9538	1.3060
14	0.2029	0.4468	0.6958	0.9981	1.3649
15	0.2110	0.4650	0.7275	1.0418	1.4219

$\lambda_{max} = 471$ nm; $C_A^0 = 8.3016 \times 10^{-4}$ M.

[a] Concentration of donor, C_D^0 (M).

constants, k_2, were obtained by dividing k_1 with the amine concentrations, i.e.

$$k_1 = \text{slope} \quad (2)$$

and

$$k_2 = \frac{k_1}{C_D^0} \quad (3)$$

The acquired plots are shown in Fig. 3 and the corresponding values of rate constants are given in Table 2 . The data given in the table indicate that the pseudo first order rate constant increase with increasing temperature, the influence of temperature on the k_1 values being much more pronounced than that of the k_2 values. Hence, the second order rate constants strongly depends on the concentration of the *n*-butylamine, in such a way that, values of k_2, decrease with increase in amine concentration.

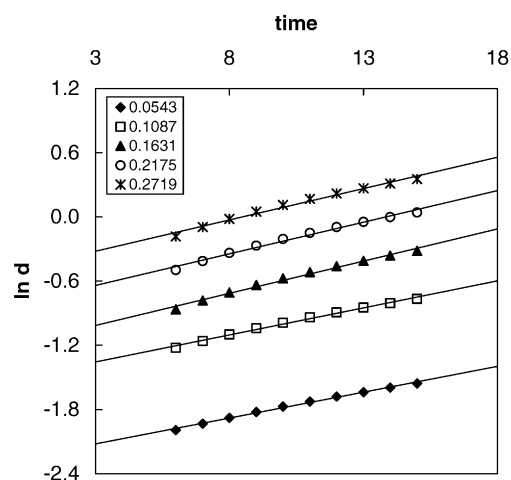Fig. 3. Plot of ln *d* vs. time for the formation of the product between 2,3-dichloro-1,4-naphthoquinone and *n*-butylamine in chloroform at 25 °C, where the concentration of acceptor, C_A^0 (M), was held constant while the concentration of the donor, C_D^0 (M), was varied by maintaining the condition that $C_A^0 \ll C_D^0$ (the numbers in the inset indicate the concentration of the donor).

Table 2
First order (k_1) and second order (k_2) rate constants for the reaction between 2,3-dichloro-1,4-naphthoquinone and n-butylamine in different solvents at different temperatures

Temperature (°C)	$C_A^0 \times 10^4$ (M)	C_D^0 (M)	$k_1 \times 10^3$ (s^{-1})	$k_2 \times 10^2$ (dm^3 mol^{-1} s^{-1})
Chloroform: $\lambda_{max} = 471$ nm				
20	8.3016	0.0815	0.67 ± 0.03	0.82 ± 0.05
	8.3016	0.1087	0.74 ± 0.06	0.68 ± 0.06
	8.3016	0.1359	0.75 ± 0.06	0.55 ± 0.07
	8.3016	0.1631	0.85 ± 0.03	0.52 ± 0.04
	8.3016	0.1903	0.93 ± 0.02	0.49 ± 0.03
25	8.3016	0.0543	0.80 ± 0.05	1.48 ± 0.08
	8.3016	0.1087	0.84 ± 0.07	0.77 ± 0.06
	8.3016	0.1631	1.00 ± 0.06	0.61 ± 0.05
	8.3016	0.2175	0.98 ± 0.03	0.45 ± 0.02
	8.3016	0.2719	0.97 ± 0.05	0.36 ± 0.03
30	8.0507	0.2185	0.97 ± 0.04	1.65 ± 0.03
	8.0507	0.3110	1.06 ± 0.08	0.89 ± 0.03
	8.0507	0.4575	1.02 ± 0.08	0.70 ± 0.06
	8.0507	0.5754	1.02 ± 0.06	0.50 ± 0.04
	8.0507	0.7116	0.99 ± 0.05	0.43 ± 0.03
35	8.3016	0.0543	1.13 ± 0.06	2.08 ± 0.09
	8.3016	0.1087	1.17 ± 0.06	1.08 ± 0.06
	8.3016	0.1631	1.16 ± 0.07	0.71 ± 0.04
	8.3016	0.2175	1.12 ± 0.08	0.51 ± 0.04
	8.3016	0.2719	1.03 ± 0.04	0.38 ± 0.03
Dichloromethane: $\lambda_{max} = 469$ nm				
20	7.7800	0.0869	0.44 ± 0.02	0.51 ± 0.05
	7.7800	0.1159	0.38 ± 0.01	0.33 ± 0.06
	7.7800	0.1449	0.29 ± 0.01	0.20 ± 0.03
	7.7800	0.1739	0.24 ± 0.01	0.14 ± 0.02
	7.7800	0.2029	0.19 ± 0.01	0.09 ± 0.02
25	8.5469	0.0579	0.56 ± 0.05	0.96 ± 0.09
	8.5469	0.1159	0.78 ± 0.06	0.67 ± 0.05
	8.5469	0.1739	0.73 ± 0.04	0.42 ± 0.03
	8.5469	0.2319	0.63 ± 0.04	0.27 ± 0.03
	8.5469	0.2899	0.61 ± 0.03	0.21 ± 0.04
30	8.5517	0.1104	0.79 ± 0.02	0.71 ± 0.06
	8.5517	0.2758	0.93 ± 0.03	0.80 ± 0.03
	8.5517	0.4592	0.88 ± 0.05	0.51 ± 0.03
	8.5517	0.6884	0.82 ± 0.06	0.35 ± 0.04
	8.5517	0.9301	0.77 ± 0.06	0.26 ± 0.04
35	8.5517	0.0579	0.97 ± 0.09	1.67 ± 0.08
	8.5517	0.0869	1.08 ± 0.08	1.24 ± 0.06
	8.5517	0.1159	1.13 ± 0.06	0.97 ± 0.05
	8.5517	0.1449	0.91 ± 0.05	0.63 ± 0.03
	8.5517	0.1739	0.72 ± 0.05	0.41 ± 0.03
1:1 (v/v) mixture of chloroform and dichloromethane: $\lambda_{max} = 470$ nm				
20	8.1534	0.0725	0.52 ± 0.02	0.69 ± 0.02
	8.1534	0.1087	0.61 ± 0.06	0.56 ± 0.02
	8.1534	0.1450	0.74 ± 0.05	0.51 ± 0.01
	8.1534	0.1812	0.78 ± 0.01	0.43 ± 0.03
	8.1534	0.2175	0.51 ± 0.08	0.24 ± 0.05
25	9.0451	0.0536	0.67 ± 0.06	1.59 ± 0.08
	9.0451	0.1073	0.80 ± 0.04	0.75 ± 0.05
	9.0451	0.1610	0.81 ± 0.05	0.50 ± 0.03
	9.0451	0.2147	0.85 ± 0.03	0.39 ± 0.03
	9.0451	0.2684	0.75 ± 0.05	0.28 ± 0.01

Table 2
(Continued)

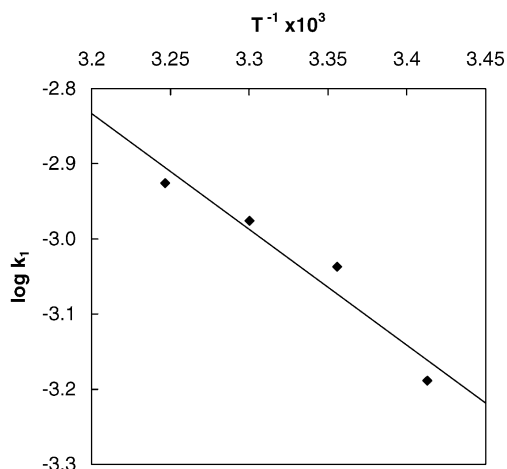| Temperature (°C)	$C_A^0 \times 10^4$ (M)	C_D^0 (M)	$k_1 \times 10^3$ (s^{-1})	$k_2 \times 10^2$ (dm^3 mol^{-1} s^{-1})
30	9.0451	0.0536	0.84 ± 0.04	1.57 ± 0.06
	9.0451	0.1073	0.98 ± 0.08	0.91 ± 0.05
	9.0451	0.1610	0.94 ± 0.05	0.58 ± 0.04
	9.0451	0.2147	0.89 ± 0.01	0.41 ± 0.03
	9.0451	0.2684	0.83 ± 0.06	0.31 ± 0.05
35	9.0451	0.0536	1.05 ± 0.07	1.97 ± 0.01
	9.0451	0.1073	1.15 ± 0.09	1.07 ± 0.06
	9.0451	0.1610	1.14 ± 0.03	0.71 ± 0.05
	9.0451	0.2147	0.95 ± 0.01	0.44 ± 0.02
	9.0451	0.2684	0.87 ± 0.06	0.32 ± 0.05

Fig. 4. Plot of $\log k_1$ vs. T^{-1} for the formation of the product of the reaction between 2,3-dichloro-1,4-naphthoquinone and n-butylamine system in 1:1 (v/v) mixture of chloroform and dichloromethane.

3.4. Activation parameters

The activation parameters for the reaction were calculated using the usual method by employing the data given in Table 2. The dependence of k_1 on the temperature was used to calculate the activation parameters. The energy of activation, E_a, of the reaction was obtained from the gradient of $\log k_1$ versus T^{-1} plots and such a plot is shown in Fig. 4. The entropy of activation was calculated by using the following relation [39]:

$$\frac{\Delta S^{\#}}{4.576} = \log k_1 - 10.753 - \log T + \frac{E_a}{4.576T} \qquad (4)$$

The results thus obtained are given in Table 3. The table reveals that the energy of activation, E_a, are positive while the entropy of activation, $\Delta S^{\#}$ values are negative, indicates that the studied reaction is spontaneous and the product of the reaction is stable. The other activation parameters, viz., $\Delta H^{\#}$ and $\Delta G^{\#}$ are all positive quantities.

3.5. Effect of solvent on the reaction

With increase in the dielectric constant, it was observed that λ_{max} value of the product shifts to shorter wavelengths though not appreciably. The values of the rate constant, k_1, were found to depend upon the dielectric constant of the medium in such a way that, with increase in dielectric constant of the medium, the first order rate constant (k_1) decreases as observed by Parker [40] and Roberts [41]. It is interesting to note that the observed solvent effect on the k_1 values supports EDA complex formed in this reaction is of the dative type structure. However, no distinct conclusion can be arrived at the dependence of second order rate constant on the dielectric constant of the medium. The activation parameters, viz., E_a, $\Delta S^{\#}$ and $\Delta H^{\#}$ were found to be solvent-dependent in such a way that the E_a and $\Delta H^{\#}$ values increase with the increase in dielectric constant of the medium whereas the reverse trend is observed for $\Delta S^{\#}$. Hence, the higher value of E_a and $\Delta H^{\#}$ in dichloromethane is due to its higher solvating ability and relative permittivity than chloroform [42]. Consequently, the rate of production of the EDA complex is expected to increase in dichloromethane solution, while the rate of its consumption to the final product should be decreased in this solvent.

3.6. Proposed mechanism for the course of reaction

In accordance to spectroscopic, analytical, and kinetic data, its confirmed that the product formed between the reaction of 2,3-dichloro-1,4-naphthoquinone (DClNQ) and *n*-butylamine is 2N(*n*-butylamino)-3-chloro-1,4-naphthoquinone. In view all above information, the following mechanism is proposed for the course of the studied reaction:

π-complex

σ-complex

-HCl

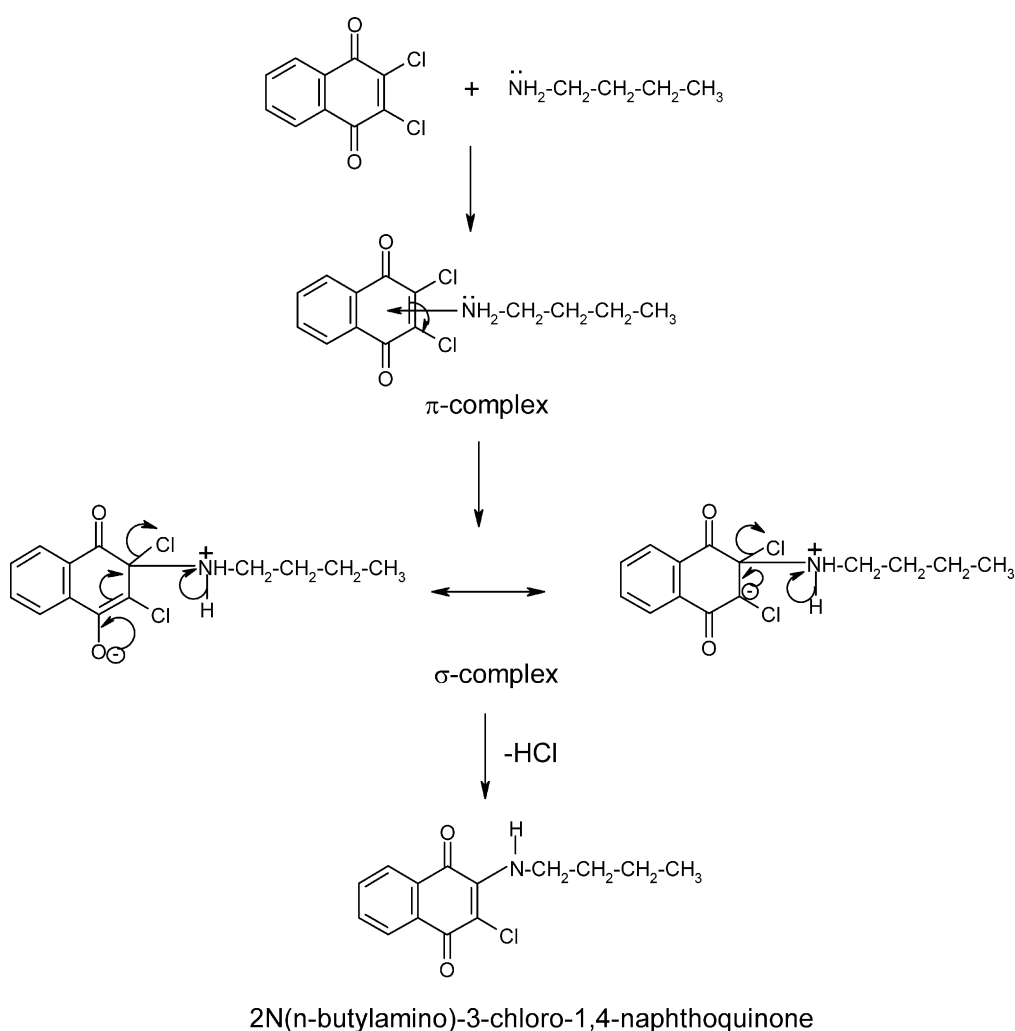2N(n-butylamino)-3-chloro-1,4-naphthoquinone

Table 3
Activation parameters for the reaction between 2,3-dichloro-1,4-naphthoquinone and *n*-butylamine in different solvents at different temperatures

Solvent	Temperature (K)	E_a (kJ mol^{-1})	$-\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
CHCl$_3$	293	17.40 ± 0.87	249.6 ± 7.5	15.0 ± 0.75	88.1 ± 2.5
	298		249.5 ± 6.6	14.9 ± 0.66	89.3 ± 3.0
	303		249.8 ± 4.6	14.9 ± 0.46	90.6 ± 2.1
	308		250.0 ± 7.9	14.8 ± 0.50	91.8 ± 2.2
CH$_2$Cl$_2$	293	61.07 ± 2.17	108.3 ± 3.3	58.6 ± 1.92	90.4 ± 2.3
	298		104.8 ± 3.7	58.6 ± 1.76	89.8 ± 2.0
	303		106.7 ± 3.3	58.6 ± 1.59	90.9 ± 2.5
	308		108.2 ± 2.9	58.5 ± 1.63	91.9 ± 2.1
1:1 (v/v) mixture of CHCl$_3$ and CH$_2$Cl$_2$	293	19.45 ± 1.08	243.2 ± 8.7	17.0 ± 0.62	84.1 ± 2.4
	298		243.6 ± 7.5	17.0 ± 0.66	89.5 ± 2.3
	303		243.6 ± 7.5	16.9 ± 0.54	90.7 ± 1.8
	308		243.6 ± 7.9	16.9 ± 0.46	91.9 ± 1.7

4. Conclusions

The interaction between 2,3-dichloro-1,4-naphthoquinone (DClNQ) and *n*-butylamine was found to be proceeded through three consecutive steps, out of these, the formation and conversion of reaction intermediates are extremely fast, whereas the formation of final product proceeds in a moderate velocity. The product formed in the reaction is of mono-substituted viz., 2N(*n*-butylamino)-3-chloro-1,4-naphthoquinone, but not the di-substituted product. The first order rate constant, k_1, and $\Delta S^{\#}$ are decreased with the increase in dielectric constant of the medium, whereas the reverse trend is observed for E_a and $\Delta H^{\#}$.

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