# Kinetic and Thermodynamic Studies on Molecular Interaction of Antipyrine Donor and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone as an Electron Acceptor in Different Solvents

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*Received 5 November 2010; revised 11 April 2012, 30 April 2012; accepted 30 April 2012*

*DOI 10.1002/kin.20745*
*Published online 18 December 2012 in Wiley Online Library (wileyonlinelibrary.com).*

ABSTRACT: The charge–transfer (CT) complex of donor antipyrine with Π-acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been investigated spectrophotometrically in different halocarbon and acetonitrile solvents. The results indicated immediate formation of an electron donor–acceptor complex (DA), which is followed by two relatively slow consecutive reactions. The pseudo–first-order rate constants for the formation of the ionic intermediate and the final product at various temperatures were evaluated from the absorbance–time data. The activation parameters, viz. activation energy, enthalpy, entropy, and free energy of activation, were computed from temperature dependence of rate constants. The stoichiometry of the complex was found to be 1:1 by Job's method of continuous variation. The formation constants of the resulting DA complexes were determined by the Benesi–Hildebrand equation at four different temperatures. The enthalpies and entropies of the complex formation reactions have been obtained by temperature dependence of the formation constants using Van't Hoff equation. The results indicate that DDQ complexes of antipyrine in all solvents are enthalpy stabilized but entropy destabilized. Both the kinetics of the interaction and the formation constants of the complexes are dependent upon the polarity of the solvents. © 2012 Wiley Periodicals, Inc. Int J Chem Kinet 45: 81–91, 2013

## INTRODUCTION

Intermolecular charge–transfer (CT) complexes are formed when electron donors (D) and electron

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acceptors (A) interact, a general phenomenon in organic chemistry [1]. Mulliken [2] considered such complexes to arise from a Lewis acid–Lewis base type of interaction, the bond between the components of the complex being postulated to arise from the partial transfer of an electron from the base (D) to orbital of the acid (A). One characteristic feature of a donor–acceptor (DA) complex is the appearance of a new absorption band in the spectrum of the complex, commonly attributed to an intermolecular CT transition, involving electron transfer from the donor to the acceptor.

Because of their wide application and use (ranging from chemistry, materials science, and medicine to biology), CT complexes have attracted considerable research interest, and over the years a very large number of CT complexes have been prepared and experimentally studied [3]. CT complexes are known to take part in many chemical reactions such as addition, substitution, and condensation. Molecular complexation and structural recognition are important process in biological systems. For example, drug action, enzyme catalysis, and ion transfer through lipophilic membranes all involves complexation.

Over the past few years, antipyrine and its derivatives have been widely used in different fields of medicine. They have been widely used as an effective analgesic and anti-inflammatory drug. Antipyrine is used to relieve pain, swelling, and congestion in ears and eyes associated with some infections [4]. New antipyrine derivatives such as amides of 4-aminoantipyrine and 9,10-substituted stearinic acids are effective pharmaceuticals for prophylactic and treatment of viral diseases.

The mechanism of action of drug is largely determined by its physicochemical properties in solution. Thus spectroscopic and thermodynamic studies on drug molecules are of great relevance in pharmacokinetics [5] and in developing analytical methods for detection and estimation of small quantities of specific drugs. The primary event in the action of many drugs is often a reversible association between a drug molecule and a receptor to form a complex. Spectroscopic and thermodynamic investigations lead to a measure of the strength of binding of the drug molecules to other substances present in living systems. DA complexes possibly have some role in binding [6]. An important parameter in this respect is the electron donor ability of a drug molecule to form CT complexes by electron transfer from an occupied orbital to an empty orbital of an acceptor molecule. The formation constant of a drug–protein complex is an important parameter in pharmaceutical science [7–9], particularly in the context of targeted drug delivery.

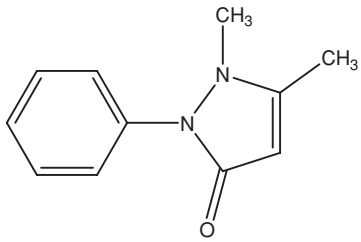


**Figure 1** Structure of antipyrine.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a quinone, which does not occur in natural systems, but its behavior may be considered indicative of that of other quinines, such as ubiquinone and menadion (2-methyl-1,4-naphthoquinone) which are of biological interest [10]. In view of biological significance of electron donor–acceptor (EDA) complexes and antipyrine as a drug on the one hand and usefulness of DDQ as a suitable model compound on the other hand, it is useful to obtain deeper insight into the CT interactions of antipyrine and DDQ. For this purpose, a detailed spectroscopic and thermodynamic study of CT complexation of the antipyrine with DDQ has been carried out in the present work.

## EXPERIMENTAL

Antipyrine (from Fluka; Fig. 1) and DDQ (Merck) were of the highest purity available and used without any further purification. Spectroscopic-grade chloroform, dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), and acetonitrile (AN) (all from Merck) were used as received. The selection of solvents is based on the solubility of the components and so as to have a wide range of relative permittivity. For purposes of UV–vis spectral determination of the formation constants ($K_{DA}$) and molar absorption coefficient ($\varepsilon_{DA}$) of the CT complexes, stock solutions of the donor and acceptor in proper solvents were freshly prepared prior to use by dissolving precisely weighed amounts of the components in the appropriate volume of solvent and spectra were collected after mixing solutions of the donor and acceptor. Computations for such $K_{DA}$ and $\varepsilon_{DA}$ determination were performed by using the Benesi–Hildbrand method with the aid of program based on a nonlinear least-squares fit. Van't Hoff plots were used for the determination of thermodynamic parameters of the CT complexes.

All UV–vis spectra were in each solvent recorded on a Perkin Elmer Lambda 45 spectrophotometer within the wavelength range 300–700 nm using the same solvent in the examined solution as a blank. Absorbance measurements as a function of time, at fixed

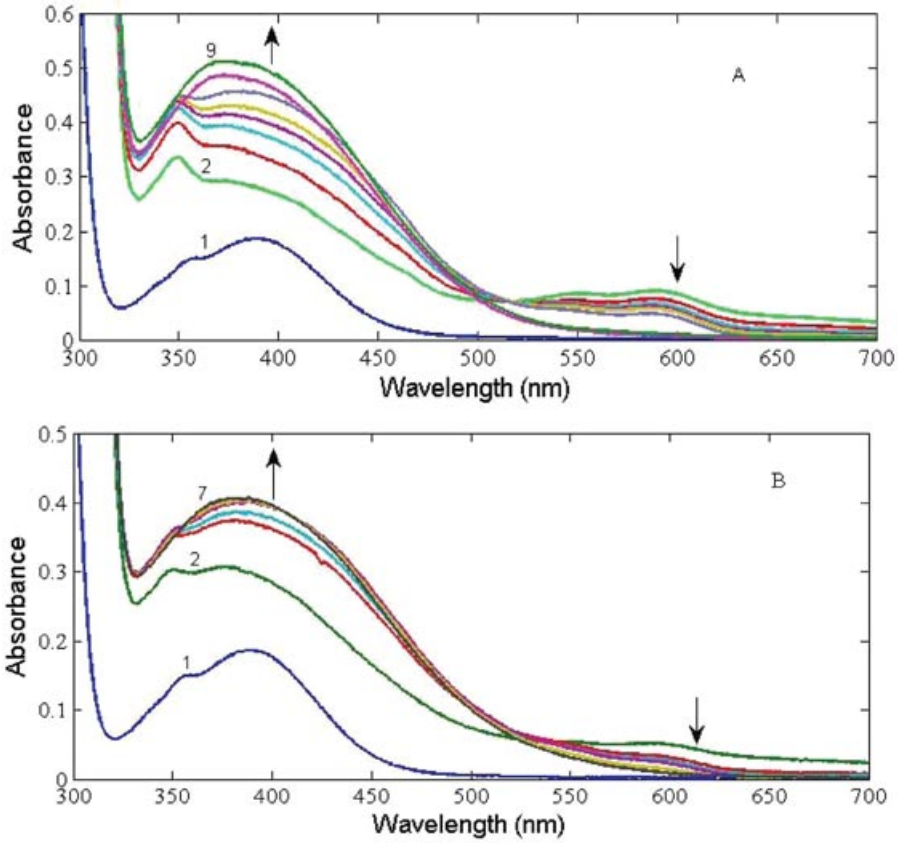


**Figure 2** (A) Electronic absorption spectra in the reaction of DDQ ($3.0 \times 10^{-4}$ M) and antipyrine ($2.0 \times 10^{-2}$ M) in DCM solution at 25°C: DDQ alone (1), 1 min after mixing (2), and at time intervals 2 min (3), 3 min (4), 4 min (5), 5 min (6), 9 min (7), 119 min (8), and 10 h (9). (B) Electronic absorption spectra in the reaction of DDQ ($3.0 \times 10^{-4}$ M) and antipyrine ($2.0 \times 10^{-2}$ M) in 1,2 DCE: DDQ alone (1), 1 min after mixing (2), and at time intervals 2 min (3), 3 min (4), 5 min (5), 10 min (6), and 16 min (7).

wavelengths, and thermodynamic studies were made with a Shimadzu UV-265 spectrometer. The apparatus was equipped with a temperature-controlled cell holder. Both sample and blank compartments were kept at constant temperature using a Shimadzu CPS-260 thermostat, which allowed the temperature to be maintained constant to ±0.1°C. Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. Donor solution was added by a Hamilton microsyringe.

## RESULTS AND DISCUSSION

### Spectral Characteristics of the CT Bands

DDQ in halocarbon solvents reacts with antipyrine and gives characteristic long wavelength absorption bands, frequently with numerous vibrational maxima in an electronic spectrum. The electronic absorption spectra of DDQ ($3.0 \times 10^{-4}$ mol dm$^{-3}$) in the presence of a large excess of the antipyrine (i.e., [antipyrine]/[DDQ] = 67) were obtained as a function of time at 25°C in different solvents. Representative spectra in DCM and 1,2-DCE are shown in Fig. 2. Other systems studied show a similar spectral behavior with time. As seen, addition of the antipyrine to DDQ solution results in some absorption bands in the 500–700 nm spectral regions, presumably due to the formation of a CT complex, which causes the appearance of some new bands in this region. A careful examination of the absorption spectra of the antipyrine–DDQ systems studied reveals that the spectra are characterized by maximum absorption at wavelengths 350, 380, 543 (sh), and 585 nm. Such spectral features are close to those reported for a $DDQ^{\bullet-}$ radical ion [11–14] and indicate that the predominant chromogen with DDQ is the radical anion $DDQ^{\bullet-}$, which was probably formed by the dissociation of an original DA complex with a solvent. The

$$\text{D+A} \rightleftharpoons \underset{\pi\text{-}\pi \text{ complex}}{\text{D.A}} \qquad \text{very fast} \qquad (1)$$

$$\text{D.A} \xrightarrow{k_1} \underset{\text{Radical ions}}{\text{D}^{\bullet+}\,\text{A}^{\bullet-}} \qquad \text{slow} \qquad (2)$$

$$\text{D}^{\bullet+}\,\text{A}^{\bullet-} \xrightarrow{k_2} \underset{\text{Final product}}{\text{P}} \qquad \text{slow} \qquad (3)$$

**Scheme 1**

dissociation of the complex was promoted by ionizing power of the solvent.

The observed increase in the absorption band intensities of the antipyrine–DDQ complexes with lapse of time supports the supposition that the EDA complex formed is of the dative-type structure, which consequently converts to an ionic intermediate possessing the spectral characteristics of the $DDQ^{\bullet-}$ radical ion [15]. However, the observed gradual decrease in the intensity of the EDA bands in the 500–650 nm spectral regions could be due to the consumption of the ionic intermediate through an irreversible chemical reaction, whereas the continuous increase in the 350-nm band with lapse of time is indicative of the formation of the final reaction product. It is interesting to note that a shoulder appearing around 350 nm, in the spectrum of pure DDQ, is still present in the spectra of the DDQ–antipyrine system, revealing the fact that the quinine chromophore is probably not disturbed by the reaction of DDQ with a drug [16].

The above experimental observations seem to be in accord with the mechanism illustrated in Scheme 1, as proposed before [19,20].

## Kinetic Study of Antipyrine–DDQ Complexes

To investigate the kinetics of production and consumption of $DDQ^{\bullet-}$ radical ions (i.e., $k_1$ and $k_2$), the absorbance at 480 nm was monitored as a function of time in solutions containing reactants at an antipyrine to DDQ mole ratio of 67:1 at various temperatures. Absorbance–time plots for the antipyrine–DDQ system in DCM and 1,2-DCE solutions at different temperatures are shown in Fig. 3. For the pair of consecutive reactions given in Scheme 1, the concentrations of species involved as a function of time, under the pseudo–first-order condition, are given by Eqs. (4)–(6) [21]. where $[DA]_0$ is the initial concentration of the DA complex, and it is assumed that $[D^{\bullet+}A^{\bullet-}] = [P] = 0$ when $t = 0$.

$$[\text{D.A}] = [\text{D.A}]_0\, e^{-k_1 t} \qquad (4)$$

$$[D^{\bullet+}A^{\bullet-}] = \frac{[\text{D.A}]_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \qquad (5)$$

$$[\text{P}] = [\text{D.A}]_0 + \frac{[\text{D.A}]_0}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \qquad (6)$$

The absorbance of the reaction solution at time $t$ is given by Eq. (7):

$$A_t = \varepsilon_{\text{D.A}}[\text{D.A}] + \varepsilon_{D^{\bullet+}A^{\bullet-}}[D^{\bullet+}A^{\bullet-}] + \varepsilon_{\text{P}}[\text{P}] \qquad (7)$$

where $\varepsilon_{\text{D.A}}$, $\varepsilon_{D^{\bullet+}A^{\bullet-}}$, and $\varepsilon_{\text{P}}$ are the molar absorptivities of species D.A, $D^{\bullet+}A^{\bullet-}$, and product, respectively. Based on our observation, the monitored absorbance at 480 nm decreases with lapse of time and finally reaches near to zero. So, the product P was set as a nonabsorbing species ($\varepsilon_{\text{P}} = 0$).

The substitution of Eqs. (4) and (5) in Eq. (7) and rearrangement results in

$$A_t = [\text{D.A}]_0\left(\varepsilon_{\text{D.A}} e^{-k_1 t} + \left(k_1 \varepsilon_{D^{\bullet+}A^{\bullet-}} \times \frac{e^{-k_2 t} - e^{-k_1 t}}{k_1 - k_2}\right)\right) \qquad (8)$$

The pseudo–first-order rate constants $k_1$ and $k_2$ at various temperatures were then evaluated by fitting the corresponding absorbance–time data to Eq. (8) using a nonlinear least-squares curve-fitting program KINFIT [22]. The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix [23] technique or the Powel procedure [24]. The adjustable parameters are $k_1$, $k_2$, $\varepsilon_{\text{DA}}$, and $\varepsilon_{D^{\bullet+}A^{\bullet-}}$. The output of the KINFIT program comprises the refined parameters, the sum of squares, and the standard deviation of the data. Measured and calculated absorbances as a function of time for $3.0 \times 10^{-4}$ M of DDQ and $2.0 \times 10^{-2}$ M antipyrine in DCM are shown in Fig. 4. A very good agreement between the observed and calculated absorbances further supports the occurrence of a reaction between antipyrine and DDQ via the proposed mechanism.

All the values obtained for $k_1$ and $k_2$ at various temperatures are summarized in Table I. The activation parameter, $E_a$, and transition state parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, were then calculated by using the corresponding Arrhenius plots and the Eyring transition-state theory [25], respectively; the results are given in Table II. The

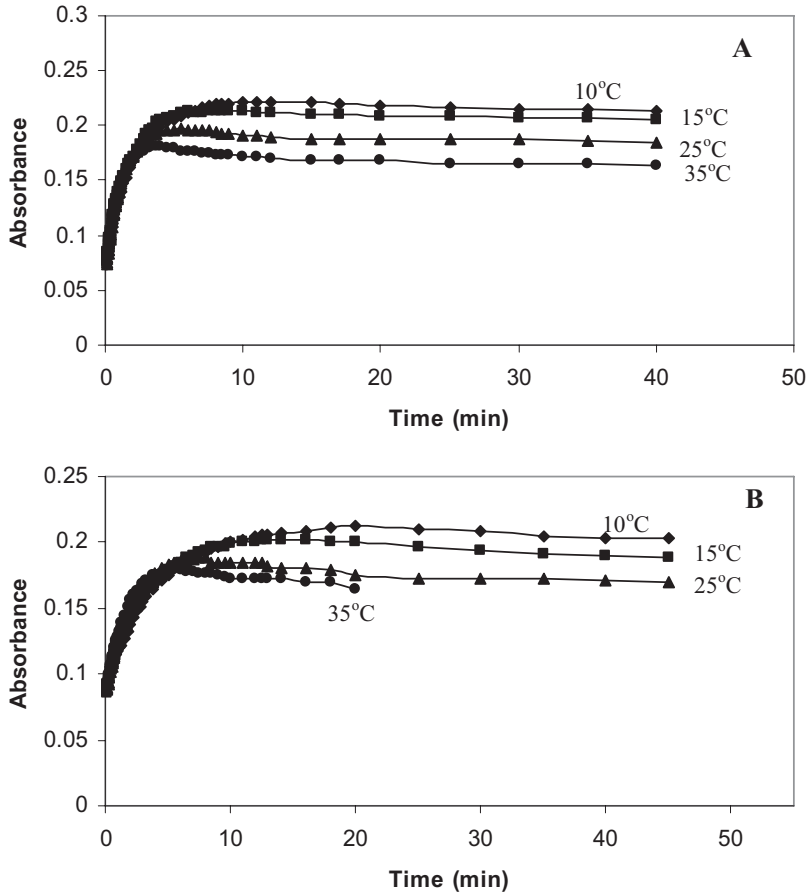


**Figure 3** Absorbance–time plots for a mixture of DDQ ($3.0 \times 10^{-4}$ M) and antipyrine ($2.0 \times 10^{-2}$ M) in (A) 1,2-DCE and (B) DCM solutions at different temperatures at 480 nm.

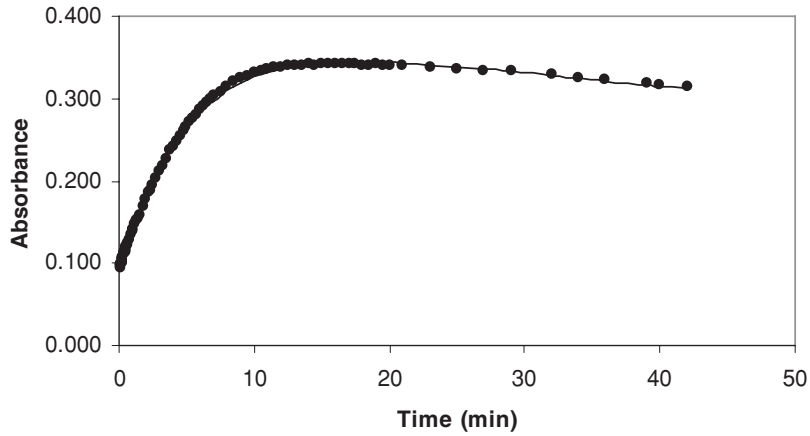


**Figure 4** Measured and calculated absorbance as a function of time for $3.0 \times 10^{-4}$ M of DDQ and $2.0 \times 10^{-2}$ M antipyrine in DCM solution. The nonlinear least-square fit according to Eq. (8) is shown as a solid line at 480 nm.

data given in Table I indicate that, in all cases studied, the pseudo–first-order rate constants increase with increasing temperature. It is also obvious that $k_1$ values in more polar solvents are larger than those in less polar ones. The order of $k_1$ is AN > 1,2-DCE > DCM. While an opposite solvent effect is observed on the rate of the second steps of the reactions, $k_2$. The $k_2$ values are in order AN < 1,2-DCE < DCM. A similar

**Table I** Rate Constants for CT Complex Formation between DDQ and Antipyrine at Different Temperatures[a]

| Solvent | Temperature (°C) | Rate Constant $k_1$ ($min^{-1}$) | Rate Constant $k_2$ ($min^{-1}$) |
|---|---|---|---|
| AN | 10 | $1.93 \pm 0.01$ | $(5.93 \pm 0.34) \times 10^{-4}$ |
| | 15 | $2.06 \pm 0.01$ | $(6.84 \pm 0.40) \times 10^{-4}$ |
| | 25 | $2.24 \pm 0.01$ | $(8.55 \pm 0.39) \times 10^{-4}$ |
| | 35 | $2.45 \pm 0.02$ | $(1.10 \pm 0.07) \times 10^{-3}$ |
| 1,2- DCE | 10 | $0.51 \pm 0.01$ | $(8.14 \pm 1.27) \times 10^{-4}$ |
| | 15 | $0.67 \pm 0.01$ | $(1.01 \pm 0.18) \times 10^{-3}$ |
| | 25 | $0.90 \pm 0.01$ | $(2.10 \pm 0.15) \times 10^{-3}$ |
| | | $1.10 \pm 0.03$[b] | $(3.00 \pm 0.32) \times 10^{-3}$[b] |
| | 35 | $1.22 \pm 0.03$ | $(3.45 \pm 0.20) \times 10^{-3}$ |
| DCM | 10 | $0.24 \pm 0.01$ | $(1.24 \pm 0.10) \times 10^{-3}$ |
| | 15 | $0.32 \pm 0.01$ | $(1.84 \pm 0.07) \times 10^{-3}$ |
| | 25 | $0.52 \pm 0.01$ | $(3.2\,4 \pm 0.10) \times 10^{-3}$ |
| | | $0.55 \pm 0.02$[b] | $(3.80 \pm 0.20) \times 10^{-3}$[b] |
| | 35 | $0.68 \pm 0.02$ | $(4.67 \pm 0.25) \times 10^{-3}$ |

[a]Listed uncertainties are one standard deviation.
[b]Values obtained by conductometric measurements.

**Table II** Activation Parameters for CT Complex Formation between DDQ and Antipyrine in Different Solvents[a,b]

| Solvent | $E_{a1}$ | $E_{a2}$ | $\Delta H_1^{o}\#$ (kJ/mol) | $\Delta H_2^{o}\#$ (kJ/mol) | $\Delta S_1^{o}\#$ (J/mol K) | $\Delta S_2^{o}\#$ (J/mol K) | $\Delta G_1^{o}\#$ (kJ/mol) | $\Delta G_2^{o}\#$ (kJ/mol) |
|---|---|---|---|---|---|---|---|---|
| AN | $6.6 \pm 0.2$ | $17.4 \pm 0.3$ | $4.2 \pm 0.2$ | $14.9 \pm 0.2$ | $-256.0 \pm 0.1$ | $-287.0 \pm 0.1$ | $81.1 \pm 0.2$ | $100.4 \pm 0.2$ |
| 1,2- DCE | $24.3 \pm 1.1$ | $39.6 \pm 7.5$ | $20.2 \pm 0.5$ | $42.4 \pm 1.6$ | $-211.4 \pm 0.1$ | $-187.9 \pm 0.1$ | $83.2 \pm 0.5$ | $98.5 \pm 1.6$ |
| DCM | $30.32 \pm 2.0$ | $38.2 \pm 2.4$ | $28.0 \pm 2.0$ | $35.8 \pm 2.4$ | $-191.1 \pm 0.1$ | $-207.2 \pm 0.1$ | $85.0 \pm 2.0$ | $97.6 \pm 2.4$ |

[a]Listed uncertainties are one standard deviation.
[b]$\Delta G$ values calculated at 25°C.

**Table III** Conductivity ($\mu$S/cm) of $3.0 \times 10^{-4}$ M of DDQ before and after Addition of Antipyrine in Different Solvents (DDQ/Antipyrine = 67)

| | Solvent | | | |
|---|---|---|---|---|
| Solution | AN | 1,2-DCE | DCM | $CHCl_3$ |
| DDQ alone | 1.85 | 0.05 | 0.05 | 0.05 |
| Immediately after addition of antipyrine | 12.78 | 1.09 | 1.45 | 0.07 |
| 5 min after addition of antipyrine | 23.12 | 1.68 | 2.3 | 0.10 |
| 30 min after addition of antipyrine | 23.0 | 1.53 | 1.7 | 0.05 |

behavior was observed in the case of azacrown–DDQ systems [14,20]. It should be noted that the observed solvent effect on the $k_1$ and $k_2$ values is in support of the proposed two-step mechanism. The resulting $DDQ^{\bullet -}$ radical ions from the first step are expected to become more stabilized in AN as a solvent of higher solvating ability and dielectric constant than DCM [26]. Consequently, the rate of production of $D^+A^-$ is expected to increase in AN solution, while its consumption to the final product should be decreased in this solvent.

For supporting of the formation of ionic species in solution (i.e., $D^{\cdot +}$ and $DDQ^{\cdot -}$), the conductivity of solution was measured before and after addition of antipyrine to DDQ (Table III). The increase in the conductivity of solution indicates the formation of ionic species in the solution. The conductivity of a solution containing reactants at an antipyrine to DDQ mole ratio of 67 in 1,2-DCE, DCM, and chloroform solvents was also monitored as a function of time at 25°C. The conductivity–time plots show patterns similar to absorbance–time plots (Fig. 5) and further supports the occurrence of reactions between the antipyrine and DDQ via the two-step mechanism suggested. In the case of conductivity measurements, the observed

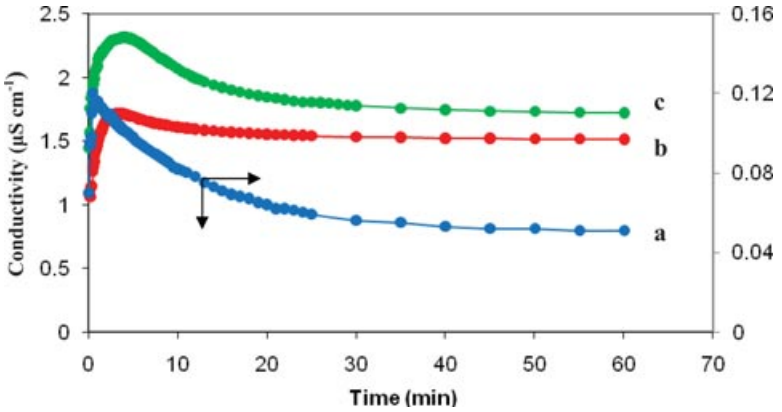


**Figure 5** Conductivity (μS/cm)–time plots for a mixture of DDQ ($3.0 \times 10^{-4}$ M) and antipyrine ($2.0 \times 10^{-2}$ M ) in (a) chloroform, (b) 1,2-DCE, and (c) DCM solutions at 25°C.

conductance–time data are also fitted to the proper equation using the KINFIT program. As seen from Table I, the $k_1$ values obtained by the conductometric method at 25°C for the DDQ–antipyrine system in 1,2-DCE and DCM solution are very similar to the those obtained with the spectrophotometric method. The $k_2$ values are also in fair agreement with each other. In chloroform with a low dielectric constant, the formation of ionic species was very negligible. Because of the little change in the conductivity of the solution in this case, the corresponding data were not fitted well.

From Table II, it is obvious that, in all solvents studied, the values of $E_{a1}$ and $\Delta H_1^{\#}$ are in agreement with the rate constants, i.e., $E_{a1}$ is less than $E_{a2}$. Moreover, $E_{a1}$ in more polar solvent AN is less than that in DCM as a solvent of lower polarity. As stated earlier, the rates of the first step, $k_1$ in more polar solvent, are higher than those in the solvents of lower polarity. But the value of $E_{a2}$ in AN is lower than DCM although the rate of the second step in AN solution is lower. The second step in AN is associated with a highly negative $\Delta S_2^{\#}$. The compensatory effect of $\Delta H^{\#}$ and $\Delta S^{\#}$ values would lead to $\Delta G^{\#}$ values that is consistent with the rate of the two processes. Thus the more negative $\Delta S_2^{\#}$ for the consumption of $DDQ^{\bullet -}$ radical ions in AN as compared with DCM may result in the lower rate constants.

## Spectrophotometric Study of Formation Equilibrium of the Complex of Antipyrine with DDQ

Job's method of continuous variation [27] was employed to determine the stoichiometry of the complex, in three different solvents. In this method, mixtures are prepared in which the sum of the molar concentrations of antipyrine and DDQ is kept fixed, while the ratio of concentrations is varied. The absorbance due to the formation of the DA complex in these mixtures was determined at 480 nm after applying a correction for absorption by DDQ at this wavelength. The maximum absorbance, as is well known, corresponds to the stoichiometric DA ratio in the complex. In the present case, the symmetrical curves with maximum at 0.5 mol fraction indicate the formation of 1:1 CT complex in all the solvents studied. The corresponding plots are shown in Fig. 6.

As seen in Fig. 7 during the first few seconds after the addition of antipyrine to the DDQ solution, a rather sharp step-functional increase in the absorbance at 480 nm was observed, as was previously reported [28–31]. This initial change in the absorbance ($\Delta A$) upon the mixing of antipyrine and DDQ was found to increase along with a rise in the mole ratio of antipyrine to DDQ. Such a dependence of $\Delta A$ on the antipyrine/DDQ mole ratio indicates the formation of the EDA complex between the DDQ and the donor used. The absorbance of the complex formed was measured using a constant acceptor concentration (in a given solvent) and varying concentrations of the donor depending on the solvent but always $[D]_0 > [A]_0$.

The equilibrium constant ($K_{DA}$) and molar absorbance ($\varepsilon_{DA}$) of the CT complex between DDQ and antipyrine are determined by using the Benesi–Hildebrand equation [32].

$$\frac{[A]_o}{Abs} = \frac{1}{K_{DA}\varepsilon_{DA}} \frac{1}{[D]_o} + \frac{1}{\varepsilon_{DA}} \tag{9}$$

where $[D]_0$ and $[A]_0$ are the concentrations of the antipyrine donor and iodine acceptor, respectively. $K_{DA}$ is the association equilibrium constant, and $\varepsilon_{DA}$ is the molar extinction coefficient of the complex. Figure 8 shows the Benesi–Hildebrand plots of

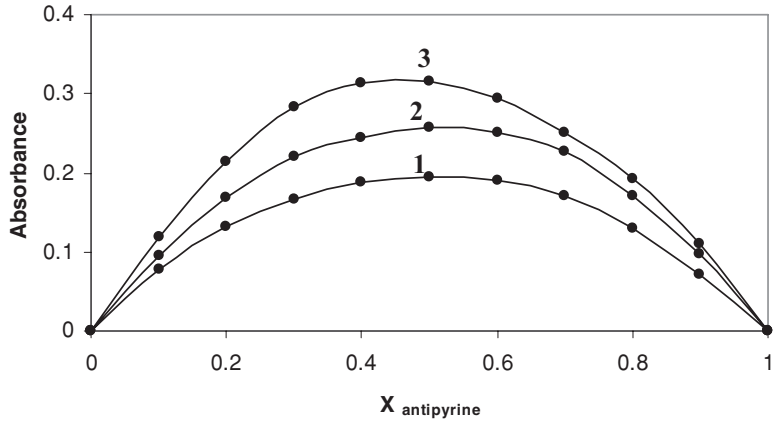


**Figure 6** Continuous variation plots for DDQ–antipyrine system in (1) chloroform, (2) DCM, and (3) 1,2-DCE at 25°C. Varying volumes of equimolar solutions of antipyrine and DDQ were mixed in a total volume of 2.5 mL; $\lambda = 480$ nm.

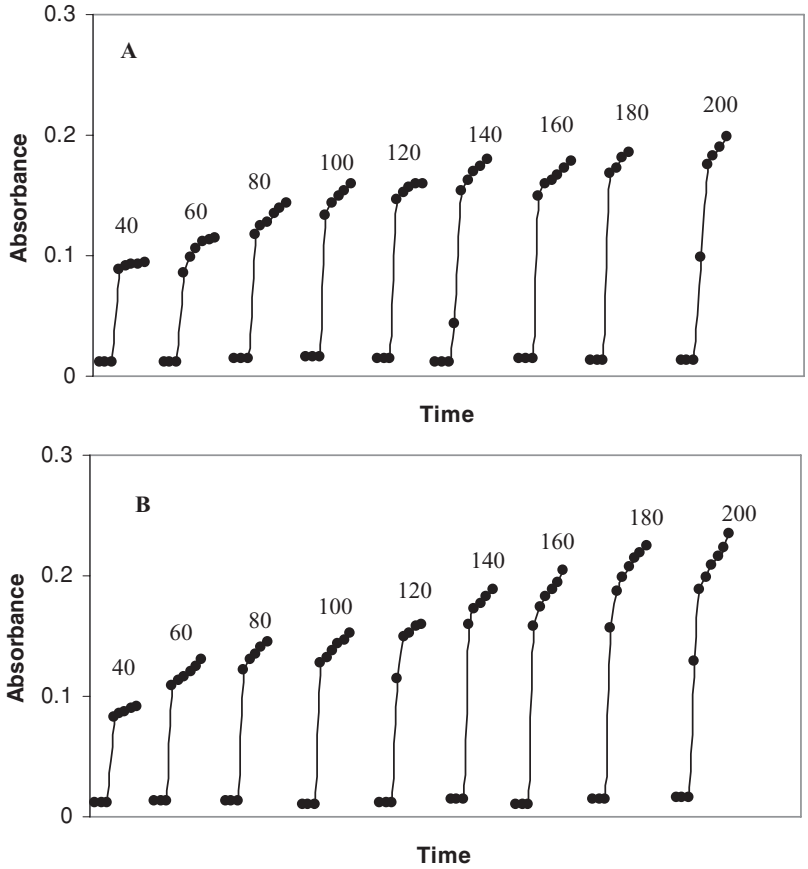


**Figure 7** Absorbance–time plots for a $3.0 \times 10^{-4}$ M solution of DDQ in 1,2-DCE in the presence of different [antipyrine]/[DDQ] mole ratios at (A) 25°C and (B) 35°C. The corresponding molar ratio value is given on each plot.

$[A_0]$/Abs against $1/[D]_0$ from the data obtained from Fig. 7. A quite satisfactory straight relationship was obtained, showing a 1:1 CT complex. The $\varepsilon_{DA}$ and $K_{DA}$ values were evaluated from the intercept and slope of the linear plot between $[A_0]$/Abs and $1/[D]_0$. Linear regression analysis was carried out in the final stages of computation of $K$ in each case. The values evaluated for $K$ at all solvents are given in Table IV. The data given in Table IV revealed that the stability of the resulting complexes increases with increasing polarity of the solvent from chloroform to AN. A similar solvent effect on the stability and charge transition energies of

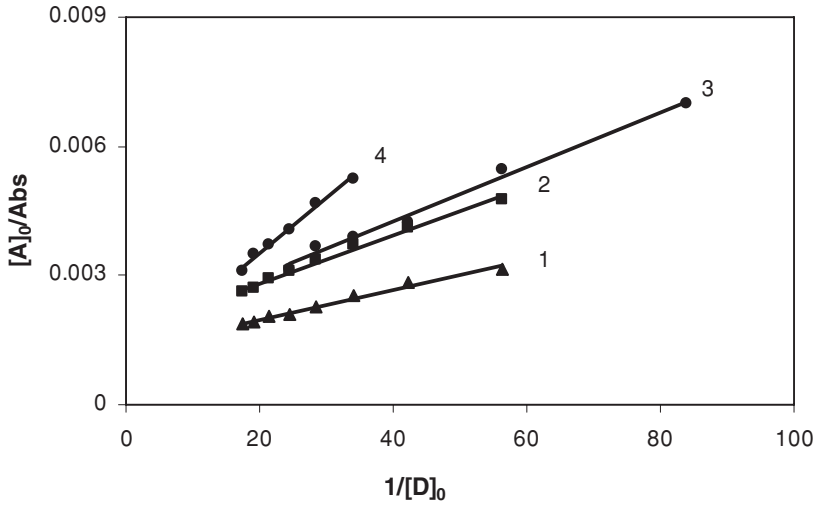


**Figure 8** Benesi–Hildebrand plots of DDQ with antipyrine in 1,2-DCE (1), DCM (2), AN (3), and chloroform (4) solutions.

**Table IV** Calculated Formation Constants, Molar Absorptivities at Different Temperatures and Thermodynamic Parameters for the Antipyrine–DDQ System in Different Solutions[a]

| Solvent | Temperature (°C) | Formation Constant ($K_{DA}$) | $\varepsilon_{DA}$ | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/ mol K) | $\Delta G^o$ (kJ/mol) |
|---|---|---|---|---|---|---|
| AN | 10 | 123.2 ± 8.7 | 350 ± 12 | −28.5 ± 2.5 | −61.3 ± 8.5 | −11.1 |
| | 15 | 83.9 ± 8.2 | 452 ± 25 | | | −10.8 |
| | 25 | 59.6 ± 5.7 | 568 ± 35 | | | −10.2 |
| | 35 | 44.2 ± 6.6 | 582 ± 61 | | | −9.6 |
| 1,2- DCE | 10 | 61.5 ± 2.0 | 563 ± 8 | −24.6 ± 1.5 | −52.6 ± 5.2 | −9.7 |
| | 15 | 51.7 ± 3.4 | 664 ± 20 | | | −9.5 |
| | 25 | 39.6 ± 1.6 | 781 ± 17 | | | −8.9 |
| | 35 | 25.7 ± 2.2 | 980 ± 48 | | | −8.4 |
| DCM | 10 | 45.5 ± 3.1 | 565 ±19 | −21.3 ± 1.5 | −43.0 ± 5.1 | −9.1 |
| | 15 | 35.6 ±1.9 | 528 ±14 | | | −8.9 |
| | 25 | 29.3 ± 2.0 | 582 ± 22 | | | −8.4 |
| | 35 | 20.9 ± 3.2 | 730 ± 58 | | | −8.0 |
| Chloroform | 10 | 14.1± 1.2 | 789 ± 48 | −50.2 ± 4.5 | −154.4 ± 15.3 | −6.5 |
| | 15 | 12.1± 1.1 | 883 ± 62 | | | −5.8 |
| | 25 | 6.3 ± 0.6 | 1185 ± 22 | | | −4.2 |
| | 35 | 2.5 ± 0.9 | 2541 ± 893 | | | −2.7 |

[a]Listed uncertainties are one standard deviation.

different CT complexes has been reported in the literature [33–35]. It has been suggested that the observed trend in the stability of the CT complexes could be due to the high stabilization of the excited states in which the charge is probably more separated than in the ground states.

## Thermodynamic Parameters of the CT Complex

The Van't Hoff equation, which shows that the equilibrium constant of one reaction increases with the temperature if the process is endothermic but decreases if it is exothermic, may be expressed as follows:

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$$

where $\Delta H^o$ and $\Delta S^o$ are changes in enthalpy and entropy of the reaction, respectively. The experimental stability constants in the three solvents determined at 283–308 K were plotted according to this equation. For the studied systems, there is no evidence for the deviation from the linearity of the plot of ln $K_{DA}$ versus $1000/T$ over the investigated temperature range

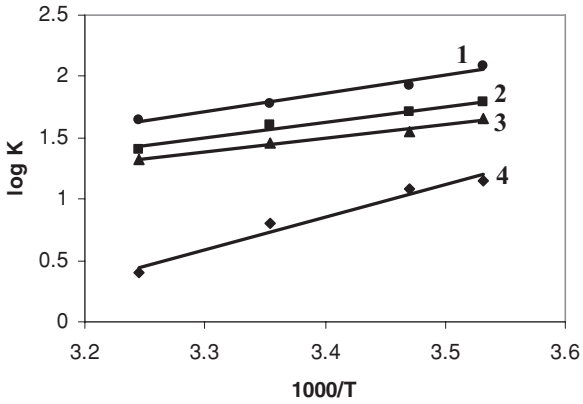


**Figure 9** Van't Hoff plots of ln $K$ vs. $1/T$ for the antipyrine–DDQ system in AN (1), 1,2-DCE (2), DCM (3), and chloroform (4) solutions.

(Fig. 9). The values of $\Delta H^{\circ}$ and $\Delta S^{\circ}$ were calculated from the slope and intercept of the linear Van't Hoff plots, respectively, and are given in Table IV. These values show that complexation is exothermic and enthalpy driven with a negative entropic contribution. The negative enthalpies show that the complex formation is spontaneous, whereas negative entropy indicates a decrease in the degree of freedom of the components upon complexation. The values of $\Delta H^{o}$ and $\Delta S^{o}$ were used to compute $\Delta G^{o}$ from the Gibbs free energy change relation: $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$. The negative values of $\Delta G^{o}$ at all temperatures confirm the feasibility of the process and also indicate the spontaneous nature of complexation. The change of the standard free energy decreases with increasing temperature regardless of the nature of the solvent. The decrease in the value of $-\Delta G^{o}$ with increasing temperature indicates that the complexation is less favorable at higher temperatures. Table IV summarizes the values of these thermodynamic properties. There is not a correlation between the value of $\Delta H^{o}$ and stability constants for molecular complexes. It seems that the weight of $\Delta S^{o}$ on the $K_{DA}$ values is higher than those of $\Delta H^{o}$. The free energy of the complex increases in absolute value in the order AN > 1,2-DCE > DCM > chloroform. This fact indicates that the thermodynamic stability of the species increases with the solvent polarity.

## CONCLUSION

In this work, the EDA complex formation of DDQ as a model for biologically important quinones with antipyrine, a drug, has been studied in different solvents. From the foregoing discussion, it may be concluded that the DDQ forms the CT complex of 1:1 stoichiometry with antipyrine in all solvents studied. The spectroscopic and thermodynamic parameters of the complex were found to be highly solvent dependent.

The authors would like to thank Dr. Saeid Azizian for helpful discussions.

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