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# Study of a Novel Reaction between *p*-Benzoquinone and Resorcinol in Aqueous Solution

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The kinetics of the simultaneous formation and decay of the charge-transfer (CT) complex between *p*-benzoquinone (A) as acceptor and resorcinol (B) as donor have been studied in aqueous solution. At 550 nm, the wavelength of absorption of the complex alone, the variation of the absorbance of the system with time suggests the following reaction path:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_2} \text{product(s)}$$

The rate constants $k_1$, $k_{-1}$ and $k_2$ have been found from an analysis of the absorbance data at different instants of time to be 0.25 $min^{-1}$, $0.05 \times 10^{-1}$ $min^{-1}$ and $2.48 \times 10^{-2}$ $min^{-1}$, respectively, and the molar absorption coefficient of AB was found to be $543 \pm 9.5$ at the experimental temperature, 25 °C. The stability constant of the intermediate CT complex, AB, was found to be $k_1/k_{-1} = 50$, a value somewhat greater than that found in methanol where AB does not decay into other product(s). It has been shown that, according to the above reaction scheme, $t_{max}$, the time required to reach the maximum absorbance, should be independent of the initial concentration $[A]_0$ of A with a fixed initial concentration $[B]_0$ of B and that $A_{max}$, the absorbance of the intermediate CT complex at $t = t_{max}$ should be directly proportional to $[A]_0$ with a fixed $[B]_0$. These theoretical predictions of the kinetics of the above reaction scheme have been verified experimentally with $[A]_0$ and $[B]_0$ of *ca.* $10^{-3}$ and $10^{-1}$ mol $dm^{-3}$, respectively.

Using aqueous solutions of A and B at concentrations of $10^{-2}$ and $10^{-1}$ mol $dm^{-3}$ respectively, the product(s) could be isolated in solid form. The solid, however, could not be precipitated from mixtures of non-aqueous solutions of A and B at similar concentrations, where the coloured CT complex is formed instantaneously, and is stable, not showing a gradual disappearance of colour. The solid (P) obtained from the aqueous mixture was found by NMR studies in $[^2H_6]$ dimethyl sulfoxide ($[^2H_6]$DMSO) to be a 1 : 1 resorcinol–*p*-benzoquinone molecular complex. This was further confirmed by some chemical tests in solutions of P in organic solvent and by conductometric titration of the solution of P in water–dioxan mixtures with $Na_2S_2O_3$. Elemental (C, H) analysis of P also confirmed the 1 : 1 stoichiometry. The IR spectrum of the solid in the form of a KBr pellet showed that it is either an H-bonded adduct of one molecule of A and one molecule of B or an H-bonded polymeric chain A···B···A···B···.



Studies of organic donor–acceptor complexes in aqueous solution are very few in the literature[1–4] in comparison with those carried out in non-aqueous media.[5,6] This is partly due to low solubilities of many organic acceptors and donors in water and to the high polarity of water which causes dissociation of the complex to a large extent. Interest in studies of donor–acceptor interactions in aqueous media has increased in the last two decades because the importance of water in cellular structure and function is rapidly being realised.[7] Slifkin[8] indicated the importance of quinones as models of many biochemical reactions in living systems.

The probable involvement of molecular (or CT) complexes in many chemical reactions has long been anticipated and studied.[9] Thus, *p*-benzoquinone (A) has been used as a cyclic dienophile in Diels–Alder reactions (where a CT complex is a probable intermediate) in benzene media.[10,11] The study of adducts of A is also biologically important. For example, Pryor *et al.*[12] have recently shown that among the four carcinogenic cigarette tars, the predominant one is a complex between A and hydrocarbon groups in a polymeric matrix. These facts have recently drawn the attention of theoretical chemists[13] to investigate the ground- and excited-state properties of *p*-benzoquinone. More information about the importance of quinones may be found in the monograph by Thomson.[14]

So far as kinetic studies with CT complexes are concerned, most of such studies are on the kinetics of their decay[15–18] (irreversible secondary reactions). The formation of such complexes in non-aqueous media occurs instantaneously on mixing the donor and acceptor solutions. There are very few reports in the literature[19] about the slow formation of such complexes in non-aqueous media. Michaelis[20] first studied the formation of the red molecular complex between A and resorcinol, B, in ethanol. The complex was later investigated by Yamashita *et al.*[21] in methanol. In both these media the CT complex is formed instantaneously and is stable, as evidenced by the persistence of its red colour.

In the present paper we report a novel type of interaction between A and B in aqueous media. When aqueous solutions of the two components are mixed at concentrations of the order of $10^{-4}$ mol $dm^{-3}$ in A and $10^{-2}$ mol $dm^{-3}$ in B, a red colour gradually develops, reaches a maximum and then slowly vanishes leaving no solid residue. However, with slightly higher concentrations of the two components (for example, $10^{-2}$ mol $dm^{-3}$ of A and $10^{-1}$ mol $dm^{-3}$ of B) the disappearance of the red colour is accompanied by the formation of a brown–black precipitate. This means that the final product is sparingly soluble in water. The kinetics of the whole reaction, *e.g.* simultaneous reversible formation of a 1 : 1 CT complex and its slow but irreversible decay into a product of 1 : 1 stoichiometry, have been studied and the final product has been characterised in the present work by physical and chemical methods.

## Materials and Methods

Resorcinol and *p*-benzoquinone were commercial-grade reagents from Sigma. Both were purified by careful subli-

mation just before use. Their purity was checked by melting point, NMR and electronic spectral data.

To obtain the complex between A and B in water, aqueous solutions of both the components were mixed. A red colour, like that of the complex in ethanol, developed slowly. The colour intensity reached a maximum and then faded gradually. At a wavelength where the donor, acceptor and the final product(s) do not absorb and only the complex absorbs, the variation of the absorbance of the system with time is indicative of the formation and decay of a CT complex between A and B, which is an intermediate in a consecutive reaction of the type

$$\begin{array}{c} p\text{-benzoquinone (A)} + \text{resorcinol (B)} \rightleftharpoons \text{CT complex (AB)} \\ \downarrow \\ \text{product(s)} \end{array}$$

The reaction was followed spectrophotometrically at 550 nm in a quartz cell of 1 cm pathlength.

The final product was isolated using 0.1 mol $dm^{-3}$ solutions of each of the components. It was characterised by elemental (C, H) analysis, NMR studies in [$^2H_6$]DMSO solution and by conductometric titration of the A moiety in solution in a water–dioxon (5% water) mixture with $Na_2S_2O_3$. The IR spectrum of the solid in the form of a KBr pellet was also recorded.

To follow the kinetics of the reaction spectrophotometrically, two different sets of experiments were performed. In one set, absorbance measurements were carried out at a fixed $[B]_0$ with five different values of $[A]_0$. In another set, four different values of $[B]_0$ were used, keeping $[A]_0$ fixed. In both sets the condition $[B]_0 \gg [A]_0$ was maintained.

## Formulation of the Working Principle

Let us consider the reaction scheme:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_2} \text{product(s)} \qquad \text{(I)}$$

Such a scheme was suggested for deacylation of aspirin in the presence of poly(ethyleneimine) by Johnson and Klotz.[22] At any time, $t$, the rate of decrease of the concentration of A is given by

$$-d[A]/dt = k_1[A][B] - k_{-1}[AB] \qquad (1)$$

where square brackets denote concentrations at time, $t$. It is observed that the colour intensity at 550 nm (where A and B practically do not absorb) reaches a maximum within 1 h (with the initial concentrations mentioned in Tables 1 and 2), but the decay process (*i.e.* disappearance of colour) continues exponentially and practically reduces to zero in *ca.* 24 h. So we can assume that $k_2 \ll k_1$. Then, during the initial stages of the reaction,

$$[\text{product(s)}] \approx 0$$

$$[B] = [B]_0 - [AB] \approx [B]_0;$$

as B is taken in large excess

$$[AB] = [A]_0 - [A] - [\text{product(s)}] \approx [A]_0 - [A] \qquad (2)$$

Using eqn. (2) in (1) we have

$$d[A]/dt + k_1[A][B]_0 - k_{-1}[A]_0 + k_{-1}[A] = 0$$

which after the substitution

$$M = k_1[B]_0 + k_{-1} \qquad (3a)$$

reduces to

$$d[A]/dt + M[A] = k_{-1}[A]_0 \qquad (3b)$$

Multiplying both sides of eqn. (3*b*) by $\exp(Mt)$ and integrating we obtain

$$[A]\exp(Mt) = \{k_{-1}[A]_0 \exp(Mt)\}/M + I \qquad (4)$$

where $I$ is the integration constant. When $t = 0$, $[A] = [A]_0$ and one obtains from eqn. (4)

$$I = (1 - k_{-1}/M)[A]_0 \qquad (5)$$

Substitution of eqn. (5) in eqn. (4) gives, on rearrangement,

$$[A] = k_{-1}[A]_0/M + [A]_0 \exp(-Mt) - [k_{-1}[A]_0 \exp(-Mt)]/M \qquad (6)$$

The rate of formation of AB is,

$$d[AB]/dt = k_1[A][B] - (k_{-1} + k_2)[AB] = k_1[B]_0[A] - N[AB] \qquad (7a)$$

where

$$N = k_{-1} + k_2 \qquad (7b)$$

Substitution of eqn. (6) into eqn. (7*a*), multiplication by $\exp(Nt)$ and integration after rearrangement give

$$[AB]\exp(Nt) = [k_1k_{-1}[A]_0[B]_0 \exp(Nt)]/MN + \{k_1[A]_0[B]_0 \exp(N - M)t\}/(N - M) - \{k_1k_{-1}[A]_0[B]_0 \times \exp(N - M)t\}/M(N - M) + I' \qquad (8a)$$

The integration constant $I'$ is obtained by putting $[AB] = 0$ at time $t = 0$:

$$I' = k_1k_{-1}[A]_0[B]_0/M(N - M) - k_1k_{-1}[A]_0[B]_0/MN - k_1[A]_0[B]_0/(N - M) \qquad (8b)$$

Thus from eqn. (8*a*) the concentration of AB at time $t$, is found to be,

$$[AB] = k_1k_{-1}[A]_0[B]_0/MN + k_1[A]_0[B]_0 \times [\exp(-Mt) - \exp(-Nt)]/(N - M) - \{k_1k_{-1}[A]_0[B]_0 \times [(1/M)\exp(-Mt) - (1/N)\exp(-Nt)]\}/(N - M) \qquad (9)$$

Eqn. (9) holds good up to a time for which the approximations in eqn. (2) are valid. For reasons mentioned earlier, these approximations may be supposed to hold up to a time, $t_m$, the time required by [AB] to reach its maximum value. Then the maximum absorbance, $A_m$, is given by

$$A_m = \varepsilon_{AB}[AB]_{max}; \quad l = 1 = \{k_1k_{-1}[B]_0/NM + k_1[B]_0 \times [\exp(-Mt_m) - \exp(-Nt_m)]/(N - M) + k_1k_{-1}[B]_0[\exp(-Mt_m)/M - \exp(-Nt_m)/N]/(N - M)\}\varepsilon_{AB}[A]_0 \qquad (10)$$

When $[AB] = [AB]_{max}$, $d[AB]/dt = 0$ which gives from eqn. (9),

$$\exp[(N - M)t_m] = (k_1/k_2)[B]_0 \qquad (11)$$

**Table 1** Variation of the absorbance of an A–B mixture at $\lambda = 550$ nm and 25 °C; $[A]_0 = 0.000\,916\,65$ mol dm$^{-3}$ and $[B]_0 = 0.100\,770\,8$ mol dm$^{-3}$

| time/min | absorbance |
|---|---|
| 1.580 | 0.0339 |
| 3.580 | 0.0443 |
| 5.000 | 0.0550 |
| 6.180 | 0.0642 |
| 7.660 | 0.0750 |
| 9.170 | 0.0860 |
| 14.380 | 0.1169 |
| 17.900 | 0.1371 |
| 21.150 | 0.1450 |
| 24.083 | 0.1539 |
| 27.580 | 0.1621 |
| 30.416 | 0.1668 |
| 33.083 | 0.1700 |
| 36.083 | 0.1720 |
| 38.880 | 0.1741 |
| 40.660 | 0.1742 |
| 43.500 | 0.1750 |
| 45.500 | 0.1742 |
| 47.000 | 0.1741 |
| 48.180 | 0.1741 |
| 50.260 | 0.1725 |
| 52.933 | 0.1719 |
| 55.750 | 0.1700 |
| 60.000 | 0.1650 |

**Table 2** Data showing independence of $t_m$ of the initial concentration of A at a fixed initial concentration of B ($[B]_0 = 0.100\,770\,8$ mol dm$^{-3}$) at 25 °C

| $[A]_0$/mol dm$^{-3}$ | $t_m$/min | $A_m$[a] |
|---|---|---|
| $9.1665 \times 10^{-4}$ | 43.50 | 0.1750 |
| $13.7480 \times 10^{-4}$ | 43.25 | 0.2585 |
| $18.3333 \times 10^{-4}$ | 43.25 | 0.3480 |
| $27.4990 \times 10^{-4}$ | 43.50 | 0.5500 |
| $36.6666 \times 10^{-4}$ | 43.50 | 0.7580 |

[a] At $\lambda = 550$ nm.

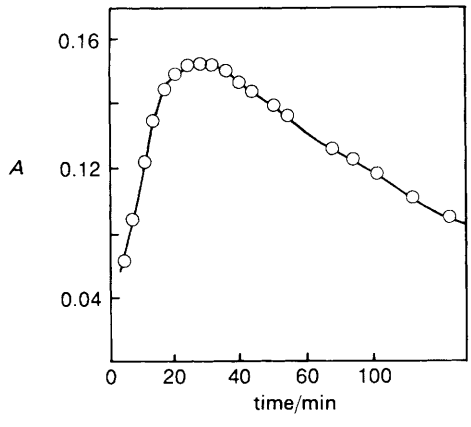


**Fig. 1** Plot of absorbance against time; $[A]_0 = 10.25 \times 10^{-4}$ mol dm$^{-3}$, $[B]_0 = 1765.8 \times 10^{-4}$ mol dm$^{-3}$

**Table 3** Kinetic data at fixed $[A]_0$ ($= 2.33 \times 10^{-3}$ mol dm$^{-3}$) and varying $[B]_0$ at 25 °C

| $[B]_0$/mol dm$^{-3}$ | $t_m$/min |
|---|---|
| 0.184 315 6 | 29 |
| 0.131 654 0 | 35 |
| 0.105 323 2 | 42 |
| 0.078 992 4 | 57 |

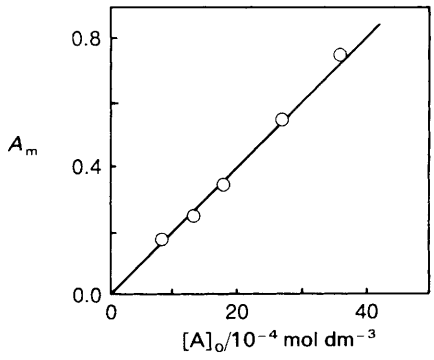


**Fig. 2** Plot of maximum absorbance ($A_m$) against $[A]_0$ with a fixed $[B]_0$ (see Table 2)

This shows that $t_m$ is independent of the initial concentration of $A$. So from eqn. (10), we should expect $t_m$ to be constant when $[B]_0$ is kept fixed, but $[A]_0$ is varied and, consequently, a plot of $A_m$ against $[A]_0$ with a fixed $[B]_0$ should be a straight line passing through the origin.

From eqn. (11) we find, after simplification,

$$\ln([B]_0/k_2) + k_2 t_m = k_1[B]_0 t_m - \ln k_1 \qquad (12)$$

Assuming a tentative value of $k_2$, the left-hand side of eqn. (12) can be calculated for each set of experimental data with a fixed $[A]_0$ and varying $[B]_0$ values. If the randomly chosen values of $k_2$ are far away from the real one, the left-hand side of eqn. (12) will deviate badly from linearity when plotted against $[B]_0 t_m$. However, if the chosen $k_2$s are close to the real $k_2$, such deviation would be small and we can calculate, for each $k_2$, a slope and intercept by the least-squares method applied to eqn. (12); the slope is expected to be *ca.* $k_1$ and intercept *ca.* $-\ln k_1$. To choose the correct $k_2$ from among these 'nearly reliable' values of $k_2$ we then define a 'test' function as

$$t_{test} = \ln(\text{slope}) + \text{intercept} \qquad (13)$$

which should be zero for the correct choice of $k_2$. By plotting the chosen 'nearly reliable' $k_2$s against $t_{test}$, we select that $k_2$ for which $t_{test} = 0$.

## Results of the Kinetic Study

The variation of absorbance, $A$, of the A–B mixture at $\lambda = 550$ nm with time is shown in Table 1. Fig. 1 shows that the plot of $A$ against time has a maximum as expected. Table 2 demonstrates the independence of $t_m$ on $[A]_0$ with a fixed $[B]_0$, verifying the validity of eqn. (11). Fig. 2 shows a plot of $A_m$ against $[A]_0$ at a fixed $[B]_0$. The plot is a straight line passing through the origin, thus showing the validity of eqn. (10).

In Table 3, a set of values of $t_m$ for a number of values of $[B]_0$ at a fixed $[A]_0$ are given. Some tentative values of $k_2$ were assumed and the slope and intercept of the linear plot of $\ln([B]_0/k_2) + k_2 t_m$ against $[B]_0 t_m$ were calculated for each $k_2$ by a least-squares method. $t_{test}$ was then evaluated for each $k_2$ using eqn. (13).

In Table 4, the values of the $t_{test}$ are shown against different assumed values of $k_2$. A plot of $k_2$ against $t_{test}$ is shown in

**Table 4** Assumed values of $k_2$ and corresponding calculated values of $t_{test}$

| $k_2$/min$^{-1}$ | $t_{test}$ |
|---|---|
| 0.025 | −0.0194 |
| 0.020 | −0.0672 |
| 0.022 | 0.0345 |
| 0.023 | 0.0224 |

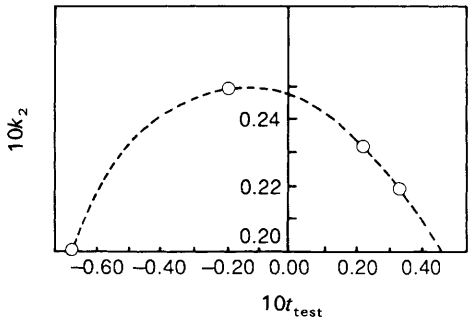


**Fig. 3** Plot of $t_{test}$ against assumed $k_2$ values

Fig. 3 and the value of $k_2$ which corresponds to $t_{test} = 0$ is found to be $2.48 \times 10^{-2}$ min$^{-1}$.

With this $k_2$ we calculated $\ln([B]_0/k_2) + k_2 t_m$ and linearly correlated it with $[B]_0 t_m$ and found the most probable $k_1$ from the least-squares slope and intercept. The value was found to be $k_1 = 0.25$ min$^{-1}$.

**Table 5** Conductometric titration data of a freshly prepared solution of A in 95% dioxan–5% water with $Na_2S_2O_3$[a]

| no. of drops of $Na_2S_2O_3$ solution | conductance/μS |
|---|---|
| 0 | 0.73 |
| 1 | 3.49 |
| 2 | 6.50 |
| 3 | 9.70 |
| 4 | 12.5 |
| 5 | 19.1 |
| 6 | 27.0 |
| 7 | 38.5 |
| 8 | 53.6 |
| 9 | 70.5 |
| 10 | 90.6 |
| 11 | 107 |
| 12 | 134 |

[a] [A] = 0.001 g cm$^{-3}$, $[Na_2S_2O_3]$ = 0.9615/20 mol dm$^{-3}$. 50 drops of $Na_2S_2O_3$ = 2.35 cm$^3$. [A] found by conductometric titration, $1.023 \times 10^{-3}$ g cm$^{-3}$. Composition of titrant: 1 cm$^3$ of A solution, 8.5 cm$^3$ dioxan and 0.5 cm$^3$ water.

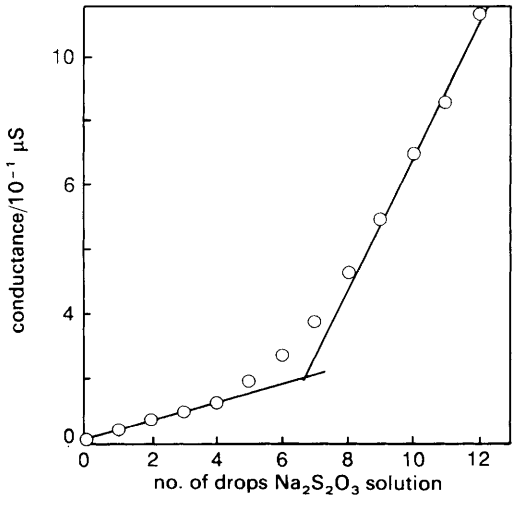


**Fig. 4** Conductometric titration of A with $Na_2S_2O_3$ solution

**Table 6** Conductometric titration data of a freshly prepared solution of the product P in 95% dioxan–5% water with aqueous $Na_2S_2O_3$ solution[a]

| no. of drops of $Na_2S_2O_3$ solution | conductance/$10^{-3}$ μS |
|---|---|
| 0 | 0 |
| 1 | 0 |
| 2 | 0.40 |
| 3 | 0.40 |
| 4 | 0.44 |
| 5 | 0.53 |
| 6 | 0.65 |
| 7 | 0.94 |
| 8 | 1.20 |
| 9 | 1.96 |
| 10 | 3.00 |
| 11 | 4.10 |
| 12 | 5.90 |

[a] [P] = 0.002 g cm$^{-3}$ (in 95% dioxan). $[Na_2S_2O_3]$ = 0.051 02 mol dm$^{-3}$. 50 drops of $Na_2S_2O_3$ solution = 2.05 cm$^3$. Volume of titrant taken = 10 cm$^3$.

For determination of $\varepsilon_{AB}$ and $k_{-1}$ we can rearrange eqn. (9) as

$$\varepsilon_{AB} = \{k_1 k_{-1}[A]_0[B]_0/MN + k_1[A]_0[B]_0 \times [\exp(-Mt) - \exp(-Nt)]/(N - M) - k_1 k_{-1}[A]_0[B]_0 \times [(1/M)\exp(-Mt) - (1/N)\exp(-Mt)]/(N - M)\}^{-1} A \quad (14)$$

Using trial values of $k_{-1}$ we calculated $\varepsilon_{AB}$ from some chosen sets of experimental data in Table 1 in the time interval between $t = 3$ and 47 min. That value of $k_{-1}$ was accepted for which $\varepsilon_{AB}$ was fairly constant. It was found that $k_{-1} = 0.05 \times 10^{-1}$ min$^{-1}$ gave a constant value of $\varepsilon_{AB} = 543 \pm 9.5$ with a very small coefficient of variation (*i.e.* standard deviation/mean) *e.g.* 0.017.

The stability constant of the intermediate AB is found to be $k_1/k_{-1} = 50$. This value is higher than the stability constant ($K$) of the CT complex between A and B in methanol, *viz.* $K \approx 1$ as found by Yamashita *et al.*[21]

## Composition of the Final Product

When A and B were taken at concentrations of $10^{-2}$ and $10^{-1}$ mol dm$^{-3}$, respectively, the same kind of colour change occurred but a brownish black precipitate was obtained. It was separated, washed repeatedly with water and was taken as the final product, P. It was found to be sparingly soluble in water, but soluble in alcohol, dimethyl sulfoxide (DMSO), dioxan and water–dioxan mixtures containing the latter in excess; all these solutions are red to brown in colour depending on the amount of solute present.

P responded to the following chemical tests: (*a*) Its solutions in NaOH produced a red dye with benzene diazonium chloride indicating the presence of a phenolic OH group.

(*b*) When KI solution mixed with starch was added to ethanolic solutions of P in dilute acetic acid, a blue colour developed and disappeared within *ca.* 2 min. In a separate experiment we observed that an aqueous solution of resorcinol (B) consumes $I_2$ dissolved in KI(aq) and HI is produced in the reaction. Although we did not study this reaction in detail, we could infer that in the ethanolic solution of P, both A (which liberates $I_2$ from KI) and B (which consumes the liberated $I_2$) were present.

(*c*) $SO_2$ and aqueous $Na_2S_2O_3$ solution decolorised the ethanolic solution of P by reducing the A present in P.

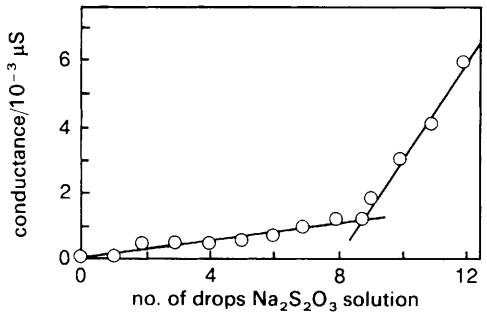


**Fig. 5** Conductometric titration of the compound P with $Na_2S_2O_3$

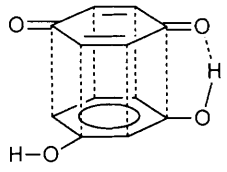


**Fig. 6** Probable structure of the CT complex in solution with one hydrogen bond

(*d*) Ethanolic solution of P acted as a good indicator in acid–base titrations; in alkaline solution it is blue–violet and in acid solution faintly wine red. Unlike phenolphthalein, P gave alkaline colour with $NaHCO_3$. Note that when an aqueous solution of B is made alkaline with NaOH and then an aqueous solution of *p*-benzoquinone is added, no blue–violet colour develops immediately.

(*e*) An attempt to determine the melting point of P failed because white B sublimed off and collected in the upper part of the capillary before melting.

It was observed that A could be conductometrically titrated in a mixture of 5% water–95% dioxan (by volume) with standard aqueous $Na_2S_2O_3$ solution. A representative set of data and a curve for such a titration are given in Table 5 and Fig. 4. With the assumption that the $S_2O_3^{2-}$ ion reduces A according to the equation

$$2S_2O_3^{2-} + A = p\text{-quinol} + S_4O_6^{2-} + 2OH^-$$

the calculated amount of A from titration was found to be within *ca.* ±1% of the amount of A actually taken. In a water–dioxan mixture of the same composition as above, P was soluble and could be conductometrically titrated, for which a representative set of data and a curve are given in Table 6 and Fig. 5. The result of this titration conforms to the fact that P contains A and B in a 1 : 1 molar ratio.

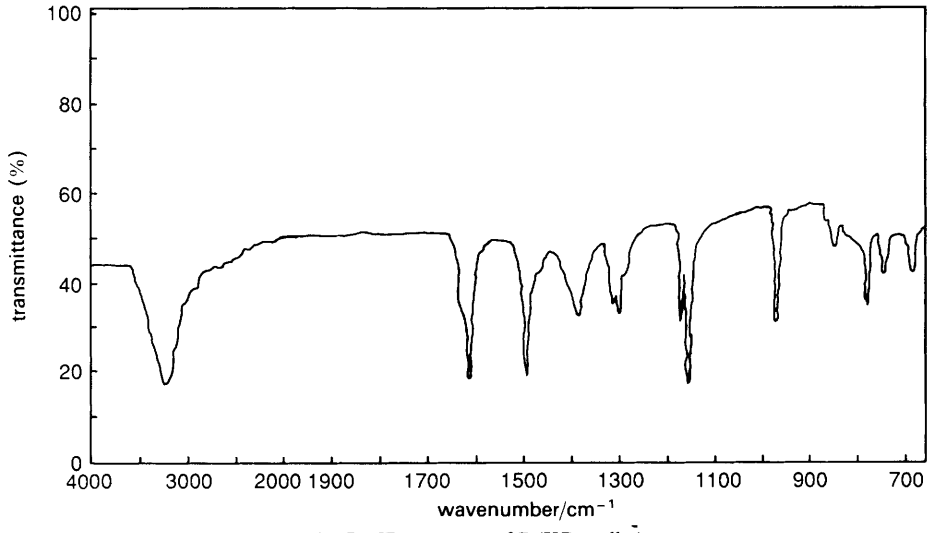


**Fig. 7** IR spectrum of B (KBr pellet)

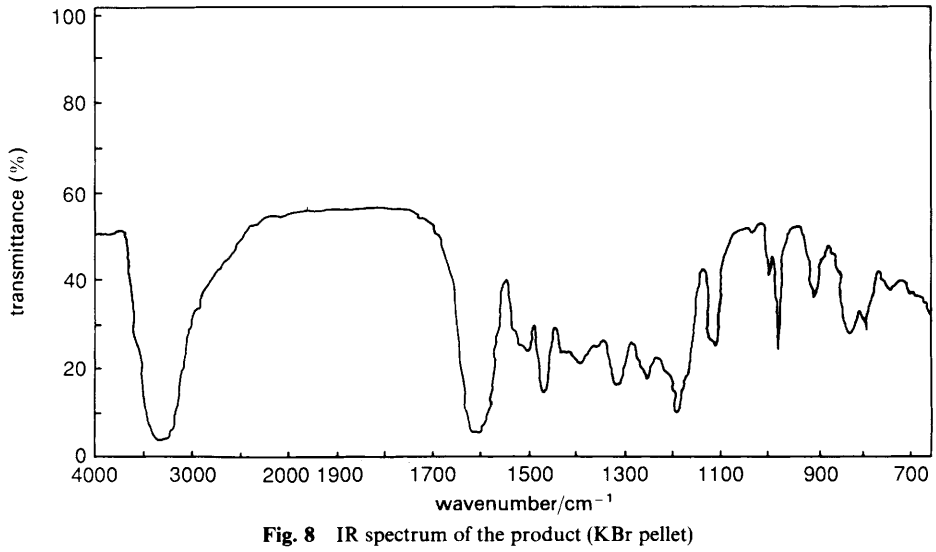


**Fig. 8** IR spectrum of the product (KBr pellet)

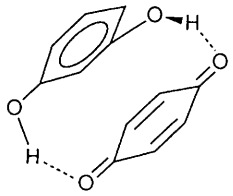

**Fig. 9** Probable structure of the product in the solid state with two hydrogen bonds

## NMR Analysis of the Product(P) in [$^2H_6$]DMSO

In [$^2H_6$]DMSO, A shows a sharp singlet at $\delta = 6.9$ ppm; B shows two signals: one sharp singlet at $\delta = 9.3$ due to the protons of the phenolic —OH group[23] and an aromatic multiplet in the range $\delta = 6.2$–7.2. The product P in the same solvent shows a broad doublet at $\delta = 9.3$ and 9.8 and an aromatic multiplet which, when compared with that of B, shows an additional peak at $\delta = 6.85$, characteristic of A. This reveals that in [$^2H_6$]DMSO solution, P exists as a loose molecular association of A and B. In a sandwich type of configuration, one —OH group of B is close to the carbonyl oxygen of A, thus enabling the formation of a hydrogen bond, but the other —OH group is away from the second carbonyl oxygen of A as shown in Fig. 6. This splits the singlet at $\delta = 9.3$ of pure B into a doublet in the complex. The integrated areas under the components of this doublet are not equal. In the solution of P, there is a rapid reversible exchange between the complexed and uncomplexed form, *viz.*

$$B + A \rightleftharpoons \text{complex}$$

Hence one component of the —OH doublet shows the time-averaged[23] $\delta$ of the complexed and uncomplexed B and the other component is due to the hydrogen-bonded —OH of the complexed B.

In all the NMR spectra a singlet of low intensity was observed at $\delta = 2.5$, which may be ascribed to the residual protons of [$^2H_6$]DMSO.

## IR Spectrum of the Solid P

The IR absorption spectra of B and the solid product P in the form of KBr pellets were recorded and are depicted in Fig. 7 and 8. From the identifiable bands the following observations could be made. (*a*) The very intense and broad O—H stretching frequency was raised from 3200 $cm^{-1}$ in B to 3300 $cm^{-1}$ in P. (*b*) Two sharp and intense peaks at 1610 and 1490 $cm^{-1}$ in B, assignable to aromatic C—C multiplet bond stretching,[21] disappeared in the product P and in their place, a very intense and slightly broadened peak centred around 1620 $cm^{-1}$ appeared. This may be due to the overlap of the C=O stretching frequency (1660–1690 $cm^{-1}$)[24] of A with the ones cited above for B. (*c*) The C—O stretching frequency at 1380 $cm^{-1}$ in B is markedly shifted to 1460 $cm^{-1}$ in P. (*d*) The O—H bending frequency at 1150 $cm^{-1}$ in B is shifted to 1190 $cm^{-1}$ in P. (*e*) The medium absorption near 1250 $cm^{-1}$ which is found in the IR spectrum of P (Fig. 8) but not in that of B (Fig. 7) may be attributed to the alkenic C—H bending[24] of A; it is known that A is a cross-conjugated system[25] (*i.e.* one H—C=C—H is cross-linked to an $\alpha,\beta$-unsaturated dicarbonyl moiety). The absorptions in the range 700–850 $cm^{-1}$ are observed in both Fig. 7 and 8. In Fig. 7, the absorption peaks at 700–800 $cm^{-1}$ are characteristic of the aromatic C—H stretching of the B ring which has three adjacent hydrogen atoms.[24] The C—H stretch of the $\alpha,\beta$-dicarbonyl moiety of A also falls in this range and overlaps with the peaks of B, showing a broad, branched absorption near 800–850 $cm^{-1}$.

These observations suggest that both the —OH groups in B are hydrogen bonded to the carbonyl oxygen atoms of A such that the O—H and C—O stretching and O—H bending in B are hindered in P. This, together with the low solubility of P in water and the 1 : 1 stoichiometry obtained from the titration result, suggests two possibilities: (i) In the solid state, P has a structure as shown in Fig. 9. (ii) P is a hydrogen-bonded polymeric chain B–A–B–A.... Both are in conformity with 1 : 1 stoichiometry and the elemental analysis results, *i.e.* 65.8% C (expected 66%) and 4.6% H (expected 4.58%).

## Conclusion

The following arguments are in favour of both the possibilities mentioned above: The first point to note is the slow reversible formation of the CT complex in aqueous media in contrast to the almost instantaneous formation of the same when the components are mixed in non-aqueous media. This may be due to strong hydration effects including hydrogen bonding. Both A and B are strongly hydrated in aqueous solution and desolvation is necessary before complex formation. The free —OH group in the structure in Fig. 6 is also a suitable site for hydrogen bonding with water; this stabilises the intermediate CT complex and makes the stability constant appreciably higher than that observed in non-aqueous media.

According to Mulliken's theory,[26] the charge-transfer or dative form, $B^+$–$A^-$, has a very low contribution to the ground state of a CT complex. Hence, if there is scope for further stabilisation through hydrogen bonding the complex will try to achieve it even if it has to forego the weak charge-transfer forces of stabilisation. The CT complex in aqueous solution, therefore, chooses either of the two processes: (i) Isomerisation to the structure in Fig. 9 where both the —OH groups of B are hydrogen-bonded to the C=O groups of A. This process also requires dehydration around the free —OH group of the CT complex (Fig. 6) and tilting of one hexagonal plane relative to the other, which, in turn, causes the slow disappearance of the $\pi$–CT absorption band. The final isomeric form is much less polar and therefore has a low solubility in aqueous media. (ii) Rotation of one ring plane relative to the other making an H bond at one C=O group of A and permitting another molecule of B to form a second H bond at the other C=O group. The polymeric chain thus formed is much less polar than the structure in Fig. 9 and is very sparingly soluble in water.

The weak point in the proposed structure (Fig. 9) is that it cannot account for the observed 1 : 1 stoichiometry even when there is a large excess of B, and one end of A appears to struggle to make a second H bond with the same molecule of B by tilting the ring plane; it would be much easier for A to attach itself to a second B by a rotation, as described in (ii) above. However, this leads to a polymeric chain structure which accounts not only for the 1 : 1 stoichiometry and the observed C, H percentage, but also for the very low solubility in water and the observed change of colour. However, the kinetic data and their mathematical analyses are in favour of an isomerisation process rather than polymerisation kinetics. The true structure of P, therefore, still remains uncertain and further investigation is required.

We therefore conclude that in aqueous media A and B slowly form a CT complex which, simultaneously with its reversible formation, either isomerises or polymerises irreversibly into a form sparingly soluble in water. When this form is dissolved in ethanol, dioxan or DMSO, it reverts back to the coloured CT complex (Fig. 6) where one —OH of B is H bonded to A and the other is free as evidenced by NMR data. This sandwich-type CT complex turns blue in alkaline media because the phenolic —OH groups ionise and

make B a stronger $\pi$-donor, causing a red shift in the absorption band.

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