Study of a novel reaction between *N*,*N*′-diphenylthiourea and *p*-chloranil through a charge-transfer intermediate

Tridibranjan Roy, Kakali Datta, Mrinal K. Nayek, Asok K. Mukherjee, Manas Banerjee and Bejoy K. Seal *

Department of Chemistry, Burdwan University, Golapbag, Burdwan 713104, India

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The well-known electron acceptor, *p*-chloranil (A) and donor, *N*,*N*′-diphenylthiourea (B) have been observed to form a labile charge-transfer (CT) complex (AB), which decays slowly into two products *viz*. 2,3,5-trichloro-6-(*N*,*N*′-diphenylthioureido)benzo-1,4-quinone (P) and 5,6-dichloro-2,3-(*N*,*N*′-diphenylthioureylene)benzo-1,4-quinone (Q). The final products have been isolated in pure form and one of them, P, has been shown to exhibit sensitive solvatochromism. A detailed kinetic study of the decay process of the CT complex has been carried out and based on kinetic data, the following steps have been suggested for the decay process.

$$A + B \Longleftrightarrow AB\ (fast) \qquad AB \xrightarrow{k_1} (AB)'\ (slow)$$

$$(AB)' \xrightarrow{k_2} P + HCl \qquad P + B \xrightarrow{k_3} Q + HCl;\ k_3 \ll k_2$$

Electron donor–acceptor (EDA) or charge-transfer (CT) complexes are of current interest for their potential non-linear optical activity.[1] Formation equilibria of such complexes are currently being studied in micelles and micro-emulsions.[2–4] Although a vast literature exists on the spectroscopic and other physicochemical aspects[5–8] of these complexes, reports on detailed kinetic studies of chemical reactions proceeding through the ground states of such complexes are few in number.[9–12] Several such reactions have been carried out fairly recently.[13–20] In the present paper a detailed kinetic study (including isolation and characterisation of the products) on the reaction between *N*,*N*′-diphenylthiourea (a well-known electron donor) and *p*-chloranil† (an electron acceptor[2]) has been reported. Solvatochromism of one of the products has also been studied.

Experimental

Materials

p-Chloranil (Fluka AG) was purified by repeated sublimation to get bright yellow crystals (mp = 290 °C). *N*,*N*′-Diphenylthiourea (DPTU) was purified by recrystallisation from dried toluene. The solvents chloroform, carbon tetrachloride, dichloromethane and acetonitrile (for the kinetic study) and the other solvents (for the study of solvatochromism of P) were purified by standard methods[21,22] just before use.

Isolation of the final products

A mixture of DPTU and *p*-chloranil in a mole ratio slightly greater than 2:1 in chloroform was refluxed for 8 h in the dark. The blackish blue solution, after filtration, was extracted with aqueous 2% solution of $NaHCO_3$ to remove unreacted *p*-chloranil and then subjected to chromatographic separation on silica gel; eluents used are successively petroleum ether (PE), 50% mixture of benzene (Bz) and PE, Bz and 10% ethyl acetate (EtAc) in Bz. The blue compound (P) was collected in the benzene fraction and the brown compound (Q) in the 10% EtAc + Bz fraction. 2,3,5-Trichloro-6-(*N*,*N*′-diphenylthioureido)benzo-1,4-quinone (P) and 5,6-dichloro-2,3-(*N*,*N*′-diphenylthioureylene)benzo-1,4-quinone (Q) are isolated in pure form by repeated chromatography in the dark.

Characterisation of the final products

At first the stoichiometric ratio DPTU–*p*-chloranil required for the formation of P and Q was determined by Job's method of continuous variation. Mixtures containing the same total concentration of DPTU and *p*-chloranil but different molar ratios (in $CHCl_3$) were kept in the dark for 12 h and their absorbances were measured at 620 nm (the λ_{max} of isolated P). Absorbances of the same solutions were measured at 479 nm (the λ_{max} of isolated Q where P has no absorption) after keeping them for 24 h in the dark. Experimental data are shown in Table 1 and Job curves at these two wavelengths are shown in Fig. 1. Results indicate a 1:1 ratio for P and a 1:2 (*p*-chloranil–DPTU) ratio for Q. A Shimadzu UV-VIS 160A spectrophotometer fitted with a temperature-regulated cell holder was used.

IR spectra (KBr pellet) of the starting materials and of P and Q show that the 3150 cm^{-1} N–H stretching observed in DPTU is weak in P and shifted to a lower ν(2900 cm^{-1}). There is enough evidence, particularly with *p*-chloranil as the acceptor,[23] that N–H stretching is much weakened by complexation. This, together with the fact that P readily eliminates HCl in the presence of an excess of DPTU (or other alkalis) to form Q, leads to the proposition of structure **I** (Fig. 2) for P. In the IR spectrum of Q the N–H band is totally absent.

The proposed structures are consistent with the results of elemental analysis: P: $C_{19}H_{11}N_2O_2Cl_3S$ requires C, 52.11; H, 2.51; N, 6.4. Found C, 52.09; H, 2.49; N, 6.37%. Q: $C_{19}H_{10}N_2O_2Cl_2S$ requires C, 56.86; H, 2.49; N, 6.98. Found C, 56.90; H, 2.48; N, 6.95%. Further support for these structures is provided by ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra recorded with a Bruker AM-300L superconducting magnet NMR spectrometer using a 5 mm ^1H–^{13}C dual probe and operating with Bruker DISR 861 software (solvent $CDCl_3$,

† *p*-Chloranil is 2,3,5,6-tetrachlorobenzo-1,4-quinone.

Table 1 Results of Job type experiment in $CHCl_3$ at $\lambda = 620$ nm after 12 h and at $\lambda = 479$ nm after 24 h. A = *p*-chloranil, B = DPTU. Total conc. [A]+[B] = 1.0006×10^{-2} mol dm^{-3}. Temp = 297 K

			Absorbance[a]	
[B]/10^{-2} mol dm^{-3}	[A]/10^{-2} mol dm^{-3}	[B]/([A] + [B])	620 nm	479 nm
0.9339	0.0667	0.9333	0.116	0.173
0.8672	0.1334	0.8666	0.222	0.307
0.8005	0.2001	0.8000	0.303	0.492
0.7338	0.2668	0.7333	0.398	0.654
0.6671	0.3335	0.6666	0.483	0.732
0.6004	0.4002	0.6000	0.527	0.727
0.5003	0.5003	0.5000	0.532	0.660
0.4003	0.6003	0.4000	0.491	0.571
0.3335	0.6671	0.3333	0.466	0.516

[a] Against chloroform as reference.

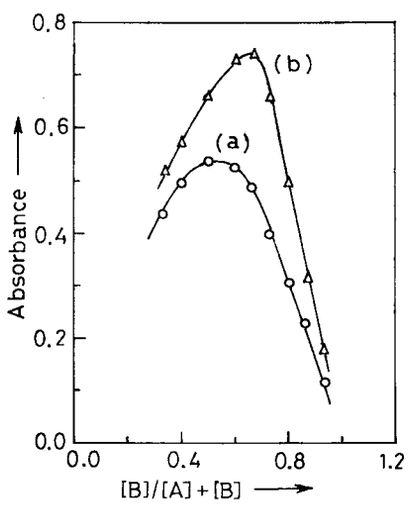

Fig. 1 Job curves: (a) at $\lambda = 620$ nm after 12 h and (b) at $\lambda = 479$ nm after 24 h.

internal standard TMS): ^{1}H NMR of P shows a broad peak at δ 4.35 corresponding to the N–H proton and an aromatic multiplet in the δ 6.5 to 8 region, the ratio of the signal intensities being nearly 1 : 10. DEPT in the aromatic region reveals four distinct branches, *viz*., δ 6.92 (dd, *J* 8.0, 0.3 Hz), 7.11 (dd, *J* 8.0, 8.0 Hz), 7.28–7.40 (m, *J* 9.2, 9.0, 2.7, 2.1 Hz) and 7.58 (dd, *J* 6.0, 0.17 Hz). The ^{1}H NMR spectrum of Q shows only an aromatic multiplet in the δ 6.8 to 8.0 region, with DEPT analysis, δ 6.84 (dd, *J* 7.3, 1.05 Hz), 6.99 (dd, *J* 7.5, 7.5 Hz), 7.19–7.3 (m, *J* 4.5, 7.8, 6.0, 5.4 and 2.1 Hz) and 7.46 (m, *J* 7.5, 4.0, 2.0, 1.8 Hz). ^{13}C chemical shift assignments of P and Q are shown in Fig. 2.

Owing to the very low solubility of *p*-chloranil (A) in the solvent used, determination of the pseudo order of the reaction with respect to DPTU (B) requires a very low concentration of the latter. Reaction mixtures with such low concentrations (~10^{-2} mol dm^{-3} in A and ~10^{-3} to 10^{-4} mol dm^{-3} in B) did not show appreciable spectral change within about two hours after mixing. For determination of the pseudo order with respect to A, the reverse was attempted, *i.e*., B was used in large excess, but it was found that the nature of variation of the spectrum of the A + B mixture was the same as that when they were taken in equimolar quantities (~10^{-2} mol dm^{-3} each); indeed it was observed that the rate depends on the product of the concentrations of A and B, which suggests the involvement of an AB adduct as intermediate. This was further supported by the appearance of a broad absorption band (different from those of *p*-chloranil and DPTU) centered at 475 nm, within a few minutes of mixing the reactant solutions. Owing to the non-availability of a stopped flow set up the time evolution of the system in this short period could not be studied. However, the change in the spectrum in the subsequent 1 h is slow and interesting and the kinetics of the reaction in this period have been followed and reported in this paper. A typical case showing the variation of absorbance, *D*, of the A + B mixture in chloroform at $\lambda = 392$ nm and 475 nm is shown in Table 2. The variation of the whole spectrum of the mixture at 294 K is shown in Fig. 3. Similar variation was observed in acetonitrile, dichloromethane and 2 : 1 mixture (by volume) of CH_2Cl_2 and CCl_4. A kinetic study was carried out at four temperatures in $CHCl_3$ medium. The effect of the solvent on the kinetics was studied at 297 K.

Table 2 Variation of absorbance of A + B mixture in chloroform medium with time at 297 K. $[A]_0 = 7.805 \times 10^{-3}$ mol dm^{-3}, $[B]_0 = 1.2324 \times 10^{-2}$mol dm^{-3}

	Absorbance[a]		
Time/min	475 nm	392 nm	620 nm
2	0.131	0.116	0.031
5	0.147	0.163	0.044
8	0.158	0.205	0.052
13	0.172	0.269	0.061
18	0.177	0.323	0.067
23	0.180	0.373	0.073
28	0.183	0.417	0.080
33	0.186	0.458	0.086
41	0.191	0.530	0.096
46	0.195	0.564	0.102
53	0.198	0.617	0.112

[a] Against chloroform as reference.

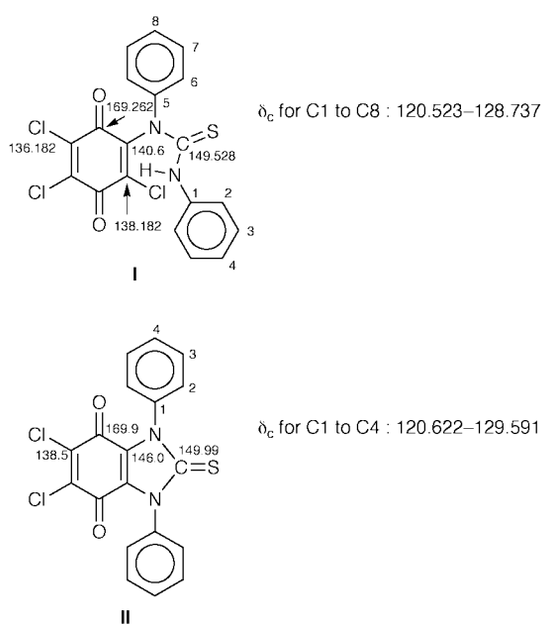

Fig. 2 Chemical shift assignment for ^{13}C of the compounds P (structure **I**) and Q (structure **II**).

Data treatment

Since the conventional method of isolation for the determination of the reaction order could not be applied, we tried a number of schemes based on the following observations: (1) elimination of HCl was confirmed by classically testing the presence of HCl in the vapour over the reaction mixture while the reaction was on. (2) The intensity of the broad absorption band centered at 475 nm increases with time and simultaneously a new band at 390–400 nm (for the various solvents used) appears and intensifies with time (Fig. 3). (3) Two end

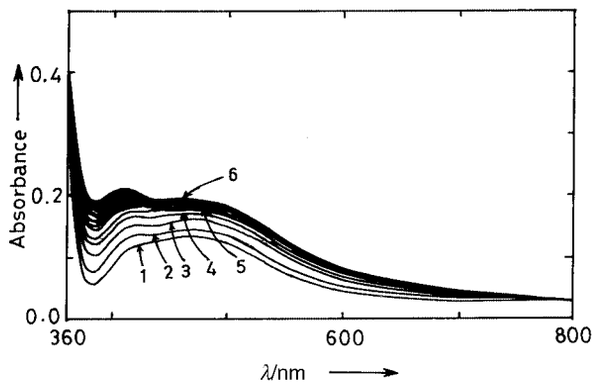

Fig. 3 Variation of the whole spectrum of the A + B mixture in chloroform at 294 K. $[A]_0 = 0.8317 \times 10^{-2}$ mol dm^{-3}, $[B]_0 = 1.0274 \times 10^{-2}$ mol dm^{-3}, (1) $t = 1$ min, (2) $t = 3$ min, (3) $t = 5$ min, (4) $t = 7$ min, (5) $t = 9$ min, (6) $t = 25$ min.

products P and Q were obtained and isolated. P could be converted into Q by adding DPTU or NaOH solution. (4) The intensities of the absorption bands were found to increase more rapidly when the product of the initial concentrations of the A and B increased. Out of various tentative schemes, experimental data were found to fit the following well:

$$A + B \rightleftharpoons AB\ (\textit{fast};\ \text{formation const.} = K) \quad AB \xrightarrow{k_1} (AB)'\ (\textit{slow})$$

$$(AB)' \xrightarrow{k_2} P + HCl \qquad P + B \xrightarrow{k_3} Q + HCl$$

The molecular complex, AB, has a broad absorption band with $\lambda_{max} = 475$ nm while its isomer, (AB)′ absorbs both at 390–400 nm and at 475 nm as revealed by Fig. 3. An initial 5 to 6 minutes are required for the establishment of the formation equilibrium of AB. After that the rate of formation of (AB)′ is given by eqn. (1), which yields eqn. (2) on integration, where

$$d[(AB)']/dt = k_1K[A]_0[B]_0 - k_2[(AB)'] \quad (1)$$

$$[(AB)'] = k_1K[A]_0[B]_0(1 - e^{-k_2t})/k_2 \quad (2)$$

square brackets denote molar concentrations of the species enclosed and the subscript 0 indicates values at $t = 0$. Absorbance (D') in the region 390–400 nm in $CHCl_3$, which is solely due to (AB)′, is then given by eqn. (3) and that at 475 nm by eqn. (4),

$$D' = k_1K[A]_0[B]_0\varepsilon_1(1 - \exp(-k_2t))/k_2 \quad (3)$$

$$D^{475} = k_1K[A]_0[B]_0\varepsilon_2(1 - \exp(-k_2t))/k_2 + K[A]_0[B]_0\varepsilon_3 \quad (4)$$

where ε_1 and ε_2 are the molar absorptivities of (AB)′ at some λ in the region 390–400 nm and at 475 nm respectively. A combination of eqns. (3) and (4) gives eqn. (5).

$$D^{475}/[A]_0[B]_0 = (\varepsilon_2/\varepsilon_1)D'/[A]_0[B]_0 + K\varepsilon_3 \quad (5)$$

A plot of $D^{475}/[A]_0[B]_0$ against $D'/[A]_0[B]_0$ is therefore expected to be linear with intercept $K\varepsilon_3$. During the first hour of study, absorbance at 390–400 nm increases appreciably with time but the development of the 620 nm absorption band (which corresponds to the formation of P) is too slow to be detected. Hence k_2 is very small and we can approximate eqns. (3) and (4) to the forms (6) and (7). With a suitable initial time t_1 these equations can be simplified to eqns. (8) and (9).

$$D' = k_1K[A]_0[B]_0\varepsilon_1 t \quad (6)$$

$$D^{475} = k_1K[A]_0[B]_0\varepsilon_2 t + K[A]_0[B]_0\varepsilon_3 \quad (7)$$

Table 3 Enthalpy of formation (ΔH_f) of AB and enthalpy (ΔH^*) of activation for the isomerisation step

Temp/K	$k_1r/10^{-3}$ min^{-1}	$K\varepsilon_3$	Thermodynamic parameters obtained
294	7.500	1676	$\Delta H_f = (-7.07 \pm 0.15)$ kcal mol^{-1}
297	5.834	1495	
304	10.200	1147	$\Delta H^* = (-17.19 \pm 5.9)$ kcal mol^{-1}
309.3	31.150	912	

Table 4 Effect of relative permittivity of the medium on the rate of the isomerisation step (at 297 K)

Solvent	Relative permittivity (d)	$k_1r/10^{-3}$ min^{-1}
$CHCl_3$	4.6	5.8
$CH_2Cl_2 + CCl_4$(2 : 1 by vol)	5.1	6.8
CH_2Cl_2	8.1	15.1
CH_3CN	36.0	37.0

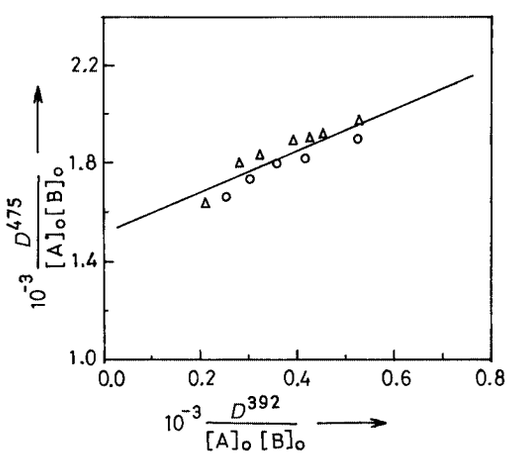

Fig. 4 Plots showing the validity of eqn. (5). ○ for $[A]_0[B]_0 = 1.0993 \times 10^{-4}$ (mol dm^{-3})^2, and Δ for $[A]_0[B]_0 = 0.9619 \times 10^{-4}$ (mol dm^{-3})^2.

$$D' - D'_1{}' = k_1K[A]_0[B]_0\varepsilon_1(t - t_1) \quad (8)$$

$$D^{475} - D_1^{475} = k_1K[A]_0[B]_0\varepsilon_2(t - t_1) \quad (9)$$

Results of kinetic study

In all the cases studied, eqns. (5), (8) and (9) were found to be valid. One typical plot for each of these eqns. is shown in Figs. (4) and (5). From the intercept of the plot of $D^{475}/[A]_0[B]_0$ against $D'/[A]_0[B]_0$, $K\varepsilon_3$ was determined. The slope of the plot gave $k_1K[A]_0[B]_0\varepsilon_2$ according to eqn. (9). Thus an effective rate constant k_1r, where $r = \varepsilon_2/\varepsilon_3$, was determined. Assuming molar absorptivities in a particular solvent do not vary with temperature, the enthalpy of formation of the complex AB was estimated from a plot of $\ln(K\varepsilon_3)$ against $1/T$ (Fig. 6a) and the enthalpy of activation for the isomerisation step was obtained from a plot of $\ln(k_1r)$ against $1/T$ (Fig. 6b). Results are summarised in Table 3. The effect of solvent on k_1r is given in Table 4. It was found that k_1r increases with increase in relative permittivity (d) of the solvent and the plot of $\ln(k_1r)$ against $(d - 1)/(2d + 1)$ is fairly linear, as shown in Fig. 7, the correlation being given by eqn. (10) with a correlation coefficient of 0.84. This

$$\ln(k_1r) = 22.93(d - 1)/(2d + 1) - 14.2 \quad (10)$$

suggests that the isomerisation step AB→(AB)′ involves a charge separated species $A^- \cdots B^+$ as an intermediate (activated state) so that an increase in solvent polarity decreases the activation energy for this step, as proposed by Laidler and

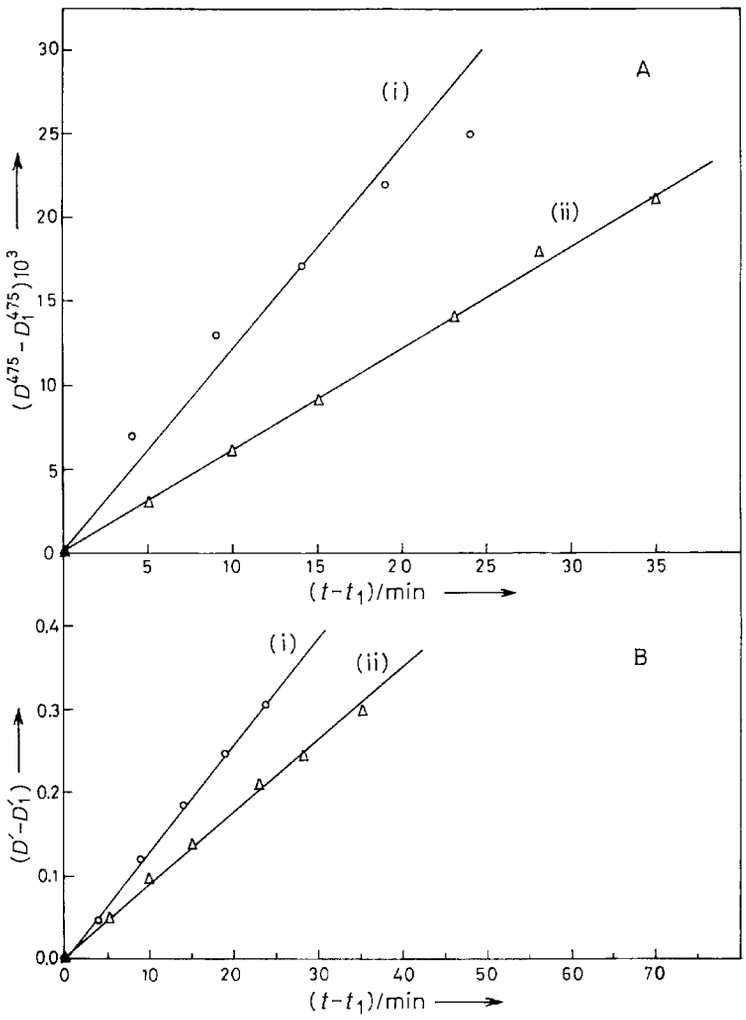

Fig. 5 Plots showing the validity of eqns. (8) and (9) in chloroform at 297 K. (A) at $\lambda = 475$ nm with (i) $[A]_0[B]_0 = 1.0993 \times 10^{-4}$ (mol dm^{-3})^2, and (ii) $[A]_0[B]_0 = 0.9619 \times 10^{-4}$ (mol dm^{-3})^2. (B) at $\lambda = 392$ nm with the same set of concentrations as in (A).

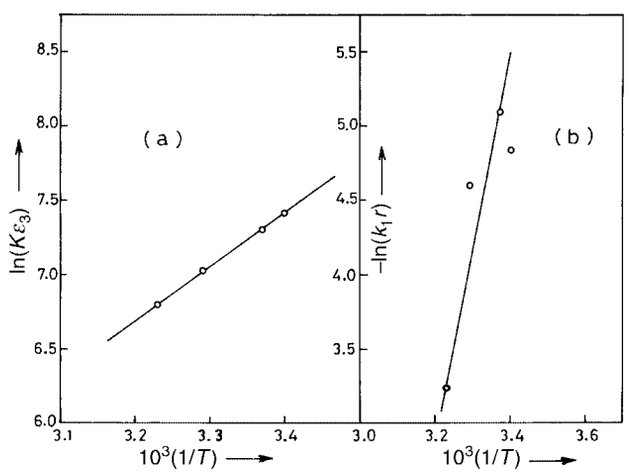

Fig. 6 (a) Plot of $\ln(K\varepsilon_3)$ against $1/T$ for evaluation of ΔH_f of AB. (b) Plot of $\ln(k_1 r)$ against $1/T$ for evaluation of activational parameters.

Eyring.[24] This is similar to the observation by Karmakar and Basu[16] in the reaction of halanils with procaine, benzocaine and lignocaine.

Solvatochromism of the blue compound P

The broad, long wavelength absorption band of the compound P (having molar absorptivity 710 at $\lambda = 620$ nm in $CHCl_3$) was found to be appreciably sensitive to solvent polarity. The transition energy (Z', eV) calculated from the λ_{max} of this band,

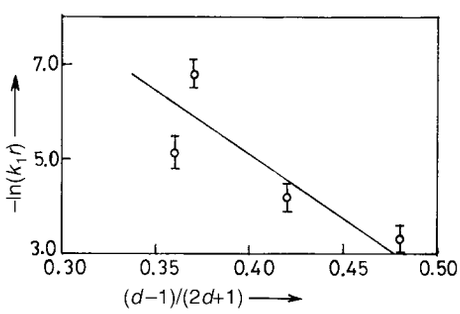

Fig. 7 Effect of solvent polarity on the rate of the isomerisation step.

varies linearly with the $E_T(30)$ and Z-polarity indices[25–31] of solvents. Nine different solvents were studied and the results are shown in Table 5 and Fig. 8. Except for benzene and toluene the plot of Z' *vs.* Z and $E_T(30)$ are fairly linear, the correlation being given by eqn. (11).

$$Z' = 0.154\ Z + 35.28, \text{ corrln. coeff.} = 0.99$$

$$Z' = 0.174\ E_T(30) + 38.43, \text{ corrln. coeff.} = 0.89 \quad (11)$$

The deviation of benzene and toluene may be attributed to the π-donor ability of the solvent molecules to form an intermolecular CT complex with the solute P whose molecule has a π-acceptor moiety. These results indicate that P may well be used as a probe material for measuring polarity of non-aromatic solvents. The electronic absorption spectra of Q, however, did not show such sensitive solvatochromism.

Table 5 Solvatochromism of the blue compound P. The $E_T(30)$ and Z values were collected from refs. 25–31

Solvent	λ_{max}/nm of P	Transition energy $(Z)'$/ev	$E_T(30)$	Z
CCl_4	650	42.72	32.5	
C_6H_6	611.5	45.37	34.5	
$C_6H_5CH_3$	611	45.40	33.9	
$CHCl_3$	620	44.78	39.1	63.2
CH_2Cl_2	613	45.29	41.1	64.2
CH_3CN	598	46.43	46.0	71.3
C_2H_5OH	582	47.71	51.9	79.6
CH_3OH	578	48.04	55.4	83.6
Propan-2-ol	594	46.74	48.6	76.3

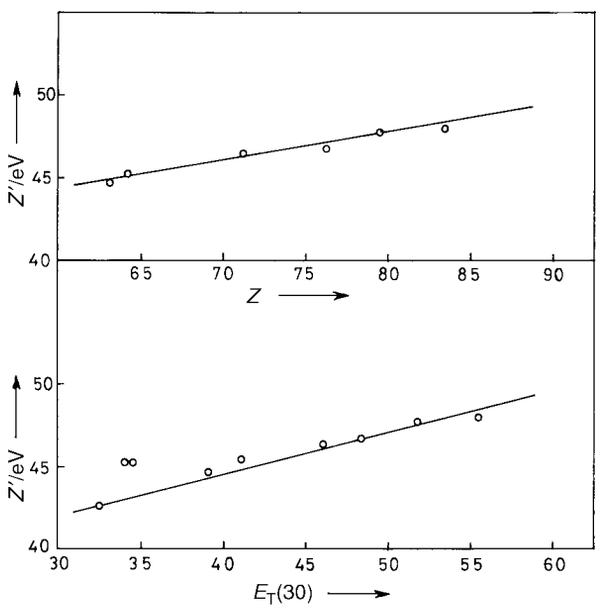

Fig. 8 Plot of transition energy, Z', of P against $E_T(30)$ and Z-values of a number of solvents.

Conclusion

p-Chloranil and *N*,*N*′-diphenylthiourea have been shown to react *via* a 1 : 1 molecular complex as an intermediate giving two products, P and Q. In the 1 : 2 stoichiometry as obtained by Job's method, the second molecule of DPTU is required for abstraction of HCl from P. The reaction path has been established by kinetic study. One product, P, shows solvatochromism sensitive enough to be used as a probe material for measuring the polarity of nonaromatic solvents.

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