



KINETICS OF REACTION BETWEEN THIOUREAS AND NAPHTHOQUINONES

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ABSTRACT

Kinetic studies have been carried out by conductivity and spectrophotometric methods for the electron transfer reaction of thiourea (TU), N-methylthiourea (MTU) and N,N'-dimethylthiourea (DMTU) with 2,3-dichloro-1,4-naphthoquinone (DCINQ) and 2,3-dibromo-1,4-naphthoquinone (DBNQ) in methanol at four different temperatures in the range 298-323 K and thermodynamic parameters have been evaluated. Energies of activation, E_a are relatively low and entropies of activation, ΔS^\ddagger are negative. The reaction between thioureas and naphthoquinones follows second order kinetics, first order in each reactant. The reactivity of donors and acceptors are found in the order MTU > TU > DMTU and DBNQ > DCINQ, respectively. Exner plot of $\log k_2$ at 323 K versus $\log k_2$ at 298 K is linear with an isokinetic temperature 530 K. The solid products have been isolated and characterized as 2-thioxo-2,3-dihydro-1H-naphtho[2,3-b]imidazole-4,9-diones by UV, IR, PMR and Mass spectral analyses. Though no direct evidence has been obtained, a mechanism consistent with the experimental results, involving outer and inner complexes as reaction intermediates has been proposed.

Keywords: Thioureas; Naphthoquinones; Nucleophilic substitution.

INTRODUCTION

Earlier kinetic studies¹⁻⁶ have focused attention on the nucleophilic substitution reaction of quinones by aromatic or aliphatic amines. However, systematic study involving the interactions of amides⁷ with quinones has received little attention and no kinetic study has been done for the reaction between thioureas and quinones. This prompted us to investigate the electron donor-acceptor interaction of thiourea (TU), N-methylthiourea (MTU) and N,N'-dimethylthiourea (DMTU) as donors with 2,3-dichloro-1,4-naphthoquinone (DCINQ) and 2,3-dibromo-1,4-naphthoquinone (DBNQ) as acceptors. Study on the reaction of thioureas has

special significance due to their antithyroid activity⁸. In addition, Slifkin⁹ has indicated the importance of quinones as models of many biological reactions in living systems.

EXPERIMENTAL

Materials: DCINQ¹⁰ and DBNQ¹¹ were prepared in the laboratory from 1,4-naphthoquinone and recrystallized from glacial acetic acid (mp 189 and 217°C, respectively). Thiourea (Fisher, AR) was purified by recrystallization from hot water (mp 177°C). Methyl thiourea (Fluka) was recrystallized from aqueous alcohol (mp 119°C) and N,N'-dimethyl thiourea (Fluka) from petroleum ether (mp 60°C). Methanol (Qualigens, AR) was fractionally distilled and the fraction distilling between 64 – 65°C was used. Stock solutions of donor and acceptor were prepared on the day of the experiment and kept in dark except during sampling.

Instruments: Conductivity measurements were done on a digital type direct reading conductivity meter (Control Dynamics Model APX-185) with a specially designed cell having bright platinum electrodes and temperature was kept constant to within $\pm 0.05^\circ\text{C}$ by circulating water from a thermostat (Toshniwal) through the cell holder. Perkin-Elmer Lambda 3B (UV-Visible), Jasco FT (IR) and Bruker-300 UltrashieldTM Avance 300 MHz (NMR) spectrometers were used for recording the spectra. Mass spectra were recorded in Sophisticated Instruments Facility Centre for Agrochemical Research, SPIC SCIENCE FOUNDATION, Chennai-32.

Isolation of solid products: About 100 mg of DCINQ in 150 mL methanol was mixed with about 1 g of DMTU. The mixture was boiled to reduce the volume of the solution to one-half and kept overnight. Shining violet crystals formed were filtered, washed repeatedly with cold alcohol and dried. The melting point was determined (189°C) and its purity was checked by TLC. For other systems also, solid products were prepared independently in a similar manner.

Kinetic measurements: All the reactions were followed under pseudo-first order conditions by keeping a minimum of ten-fold excess of donor over the acceptor. Immediately before the conductivity measurements, the donor and the acceptor solutions were mixed in a thermostated double walled glass container. A stopwatch was started when the addition of the second solution, either the donor or the acceptor, was exactly halfway through and the time of mixing was taken as zero time. The reaction was followed by measuring the conductivity (C_t) at definite time intervals. The readings were taken up to a completion of 60% or more of the reaction. The final value (C_∞) was measured after keeping the reaction mixture airtight in the dark for a period of 24 hrs, the usual time needed for the conductivity values to reach a constant value.

Two sets of experiments were performed, one at a fixed initial concentration of donor $[D]_0$ with six different concentrations of acceptor $[A]_0$ and the other vice versa. However, in both cases the condition $[D]_0 > [A]_0$ was maintained. The pseudo-first order rate constants (k_1) were calculated from the slopes of the linear plots ($r = 0.99 - 0.9999$) of $\log(C_\infty - C_t)$ versus time. The second order rate constants (k_2) were evaluated from the relation

$$k = \frac{k_1}{[\text{Donor}]}$$

Thermodynamic parameters were evaluated from the rate constants at four different temperatures in the range 298–323 K. The precision of the reported values is $\pm 5\%$.

With a view to provide further support for the kinetic study by conductivity measurement, the rates were determined spectrophotometrically also at 298 K for the systems TU–DCINQ and TU–DBNQ at 405 nm where the absorbance of reaction mixture continues to increase with time until the end of the reaction. The pseudo-first order rate constants (k_1) were calculated from the $\log (A_\infty - A_t)$ versus time plots

RESULTS AND DISCUSSION

Solutions of 1,4-naphthoquinones in methanol are yellow while those of the thioureas are colourless. When they were mixed, the yellow colour intensified slowly giving a reddish brown solution. The conductivity as well as absorbance of the solution increased gradually and reached a maximum within 3–6 hrs indicating a chemical reaction. The conductance/absorbance was

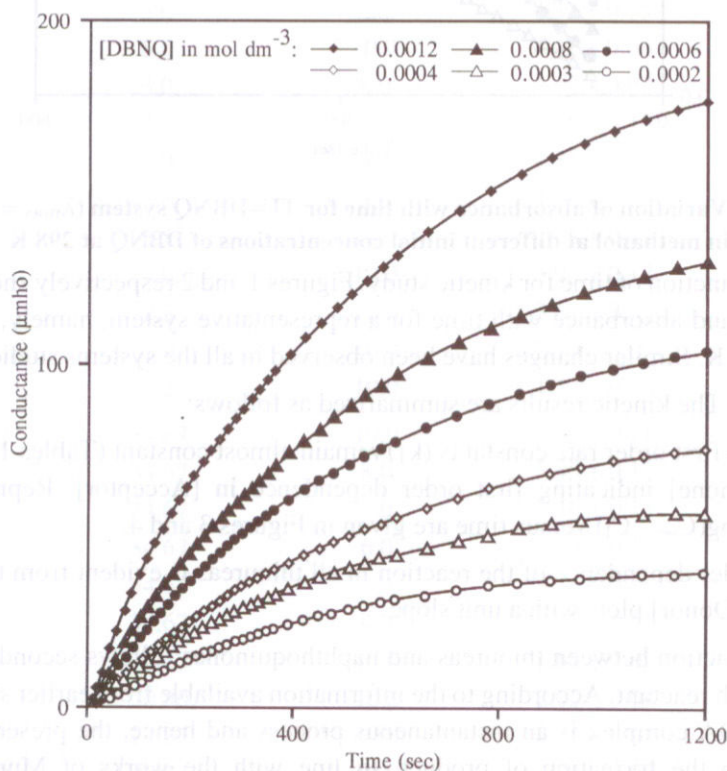


Figure 1. Variation of conductance with time for TU–DBNQ system in methanol at different initial concentrations of DBNQ at 298 K; [TU] = $0.0396 \text{ mol dm}^{-3}$; [DBNQ] in mol dm^{-3}

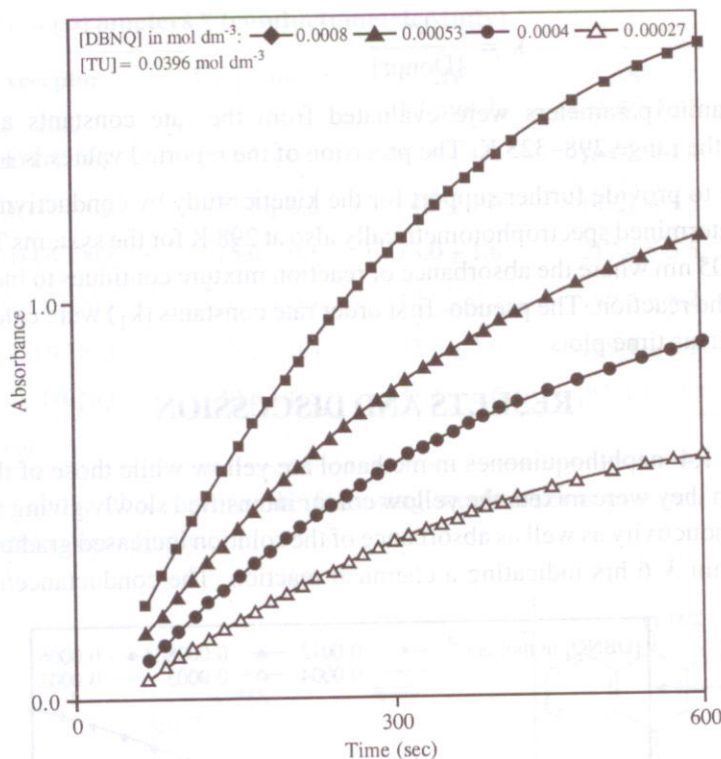


Figure 2. Variation of absorbance with time for TU-DBNQ system ($\lambda_{\text{max}} = 405 \text{ nm}$) in methanol at different initial concentrations of DBNQ at 298 K

monitored as a function of time for kinetic study. Figures 1 and 2 respectively show the increase in conductivity and absorbance with time for a representative system, namely, TU-DBNQ in methanol at 298 K. Similar changes have been observed in all the systems studied.

Kinetic results: The kinetic results are summarized as follows:

- (i) The pseudo-first order rate constants (k_1) remain almost constant (Tables 1–3) at different initial [Quinone] indicating first order dependence in [Acceptor]. Representative rate profiles of $\log(C_\infty - C_t)$ versus time are given in Figures 3 and 4.
- (ii) The first order dependence of the reaction in all thioureas is evident from the linear $\log k_1$ versus $\log [\text{Donor}]$ plots with a unit slope.

Thus, the reaction between thioureas and naphthoquinones follows second order kinetics, first order in each reactant. According to the information available from earlier studies^{12–15}, the formation of EDA complex is an instantaneous process and hence, the present kinetic study pertains only to the formation of product. In line with the works of Muralikrishna^{16,17}, Dwivedi^{3,18} and Murugesan¹⁵, in the presence of excess donor, the following general scheme may be formulated.

Table 1. Rate constants for the reactions of 2,3-dichloro-1,4-naphthoquinone with thioureas in methanol at 298 K (conductometric study)

System	10^2 [D] (mol dm ⁻³)	10^4 [DCINQ] (mol dm ⁻³)	10^3 k_1 (s ⁻¹)	10^2 k_2 (dm ³ mol ⁻¹ s ⁻¹)
TU-DCINQ	10.0	4.0	2.21 ± 0.02	2.21 ± 0.02
	10.0	5.0	2.22 ± 0.03	2.22 ± 0.03
	10.0	6.0	2.22 ± 0.03	2.22 ± 0.03
	10.0	7.0	2.22 ± 0.02	2.22 ± 0.02
	10.0	8.0	2.21 ± 0.02	2.20 ± 0.02
	10.0	10.0	2.24 ± 0.02	2.24 ± 0.02
	4.0	6.0	0.88 ± 0.02	2.21 ± 0.04
	6.0	6.0	1.33 ± 0.04	2.21 ± 0.06
	8.0	6.0	1.76 ± 0.03	2.20 ± 0.04
	12.0	6.0	2.65 ± 0.08	2.21 ± 0.06
	14.0	6.0	3.09 ± 0.16	2.21 ± 0.11
MTU-DCINQ	3.0	12.0	4.34 ± 0.05	14.47 ± 0.17
	3.0	10.0	4.42 ± 0.06	14.72 ± 0.20
	3.0	8.0	4.39 ± 0.07	14.64 ± 0.23
	3.0	6.0	4.35 ± 0.13	14.51 ± 0.43
	3.0	4.0	4.33 ± 0.12	14.43 ± 0.41
	3.0	3.0	4.38 ± 0.26	14.59 ± 0.86
	5.5	10.0	7.95 ± 0.42	14.45 ± 0.76
	4.0	10.0	5.92 ± 0.17	14.80 ± 0.44
	2.5	10.0	3.61 ± 0.05	14.44 ± 0.20
	2.0	10.0	2.90 ± 0.09	14.48 ± 0.43
	1.2	10.0	1.73 ± 0.05	14.42 ± 0.42
DMTU-DCINQ	34.67	10.0	3.36 ± 0.11	0.968 ± 0.031
	34.67	8.0	3.40 ± 0.12	0.981 ± 0.040
	34.67	7.0	3.46 ± 0.13	1.000 ± 0.037
	34.67	6.0	3.44 ± 0.13	0.991 ± 0.037
	34.67	5.0	3.35 ± 0.11	0.967 ± 0.033
	34.67	4.0	3.36 ± 0.11	0.971 ± 0.033
	17.33	10.0	1.68 ± 0.02	0.968 ± 0.012
	20.80	10.0	2.03 ± 0.04	0.976 ± 0.017
	24.27	10.0	2.35 ± 0.04	0.967 ± 0.018
	27.73	10.0	2.75 ± 0.07	0.992 ± 0.025
	31.20	10.0	3.09 ± 0.09	0.990 ± 0.030

Table 2. Rate constants for the reactions of 2,3-dibromo-1,4-naphthoquinone with thioureas in methanol at 298 K (conductometric study)

System	$10^2 [D]$ (mol dm ⁻³)	$10^4 [DBNQ]$ (mol dm ⁻³)	$10^3 k_1$ (s ⁻¹)	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
TU-DBNQ	3.0	2.0	2.24 ± 0.01	7.47 ± 0.05
	3.0	3.0	2.23 ± 0.01	7.45 ± 0.03
	3.0	4.0	2.24 ± 0.02	7.47 ± 0.08
	3.0	6.0	2.24 ± 0.01	7.48 ± 0.04
	3.0	8.0	2.23 ± 0.02	7.44 ± 0.06
	3.0	12.0	2.24 ± 0.01	7.47 ± 0.05
	6.0	8.0	4.45 ± 0.03	7.41 ± 0.05
	5.0	8.0	3.66 ± 0.03	7.32 ± 0.05
	4.0	8.0	2.91 ± 0.02	7.28 ± 0.06
	2.0	8.0	1.47 ± 0.01	7.32 ± 0.03
	1.0	8.0	0.746 ± 0.002	7.46 ± 0.02
MTU-DBNQ	1.0	10.0	6.24 ± 0.16	62.39 ± 1.64
	1.0	8.0	6.12 ± 0.24	61.23 ± 2.42
	1.0	6.0	6.44 ± 0.15	64.39 ± 1.53
	1.0	4.0	6.27 ± 0.25	62.66 ± 2.49
	1.0	3.0	6.14 ± 0.19	61.40 ± 1.90
	1.0	2.0	6.18 ± 0.31	61.84 ± 3.09
	2.0	8.0	12.01 ± 0.31	60.06 ± 1.54
	1.6	8.0	10.05 ± 0.52	62.84 ± 3.23
	1.4	8.0	8.48 ± 0.40	60.55 ± 2.82
	1.2	8.0	7.55 ± 0.22	62.95 ± 1.81
DMTU-DBNQ	9.0	10.0	4.35 ± 0.06	4.83 ± 0.07
	9.0	8.0	4.33 ± 0.06	4.81 ± 0.06
	9.0	6.0	4.39 ± 0.09	4.88 ± 0.10
	9.0	5.0	4.34 ± 0.11	4.82 ± 0.12
	9.0	4.0	4.36 ± 0.12	4.85 ± 0.14
	9.0	3.0	4.37 ± 0.13	4.86 ± 0.15
	14.0	10.0	6.74 ± 0.32	4.81 ± 0.23
	12.0	10.0	5.83 ± 0.15	4.86 ± 0.13
	7.0	10.0	3.36 ± 0.05	4.80 ± 0.07
	5.5	10.0	2.66 ± 0.02	4.83 ± 0.05
	4.5	10.0	2.16 ± 0.03	4.81 ± 0.07

Table 3. Rate constants for the reactions of thiourea with 2,3-dichloro-1,4-naphthoquinone and 2,3-dibromo-1,4-naphthoquinone in methanol at 298 K (spectrophotometric study at 405 nm)

System	$10^2 [D]$ (mol dm ⁻³)	$10^4 [A]$ (mol dm ⁻³)	$10^3 k_1$ (s ⁻¹)	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
TU-DCINQ	10.0	2.0	2.21 ± 0.14	2.21 ± 0.14
	10.0	3.0	2.24 ± 0.12	2.24 ± 0.12
	10.0	4.0	2.28 ± 0.06	2.28 ± 0.06
	10.0	5.0	2.24 ± 0.07	2.24 ± 0.07
	6.5	4.0	1.48 ± 0.00	2.27 ± 0.01
	8.0	4.0	1.79 ± 0.03	2.27 ± 0.02
	12.0	4.0	2.67 ± 0.21	2.22 ± 0.02
TU-DBNQ	3.96	2.67	3.10 ± 0.06	7.82 ± 0.15
	3.96	4.00	3.16 ± 0.05	7.98 ± 0.13
	3.96	5.30	3.13 ± 0.04	7.89 ± 0.10
	3.96	8.00	3.09 ± 0.03	7.79 ± 0.07
	3.30	4.00	2.57 ± 0.03	7.78 ± 0.08
	4.40	4.00	3.44 ± 0.02	7.82 ± 0.05
	4.84	4.00	3.80 ± 0.04	7.84 ± 0.07
	5.28	4.00	4.03 ± 0.08	7.63 ± 0.14



Hence, the rate law may be written as,

$$\frac{d[\text{Product}]}{dt} = k_2 [\text{EDTA complex}] [\text{Donor}]$$

As the donor was in excess, the acceptor could be assumed to be totally consumed in the complex formation.

$$\therefore [\text{EDA complex}] = [\text{Acceptor}]$$

$$\frac{d[\text{Product}]}{dt} = k_2 [\text{Acceptor}] [\text{Donor}]$$

This equation represents the observed results.

The rate constants evaluated from conductivity and spectrophotometric methods agree reasonably (Tables 1-3). From the k_2 values, it is evident that the order of reactivity among thioureas is DMTU < TU < MTU. However, if polar effect alone were the predominant factor

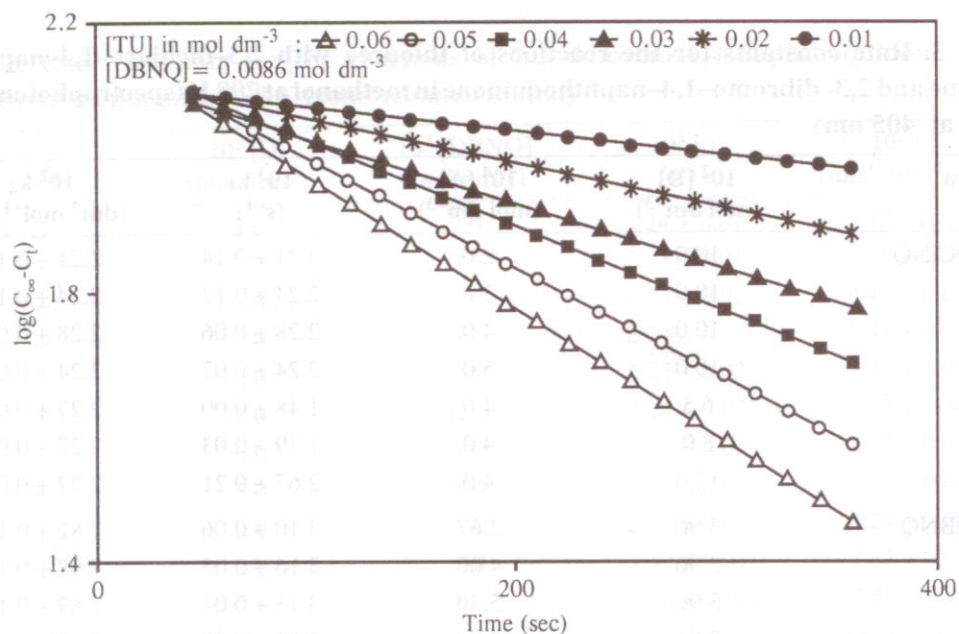


Figure 3. Pseudo-first order rate plots for TU-DBNQ system at different initial concentrations of thiourea in methanol at 298 K

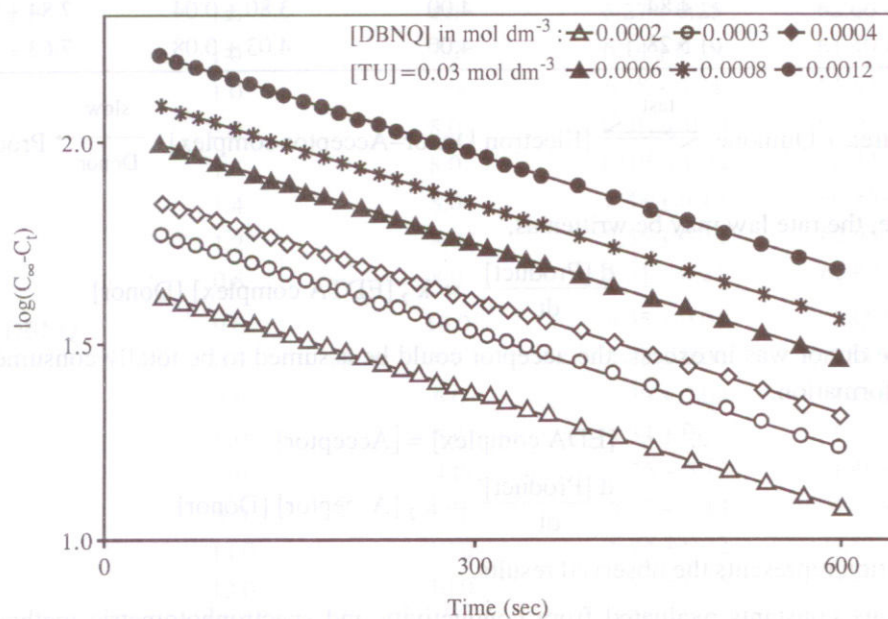


Figure 4. Pseudo-first order rate plots for TU-DBNQ system at different initial concentrations of DBNQ in methanol at 298 K

in deciding the reactivity, the expected sequence should be $TU < MTU < DMTU$. The higher reactivity of MTU than that of TU may be attributed to the + I effect of the methyl group in the MTU molecule. However, in the case of DMTU, the rate is slightly less even than that for TU. This may be because the increase in donor strength by the + I effect of methyl groups in DMTU is outweighed by steric factors. Seal *et al.*¹⁹ observed a similar trend in the electron donor-acceptor interaction between naphthalene-1,4,5,8-tetracarboxylic dianhydride and a series of methylated anilines. The higher rates observed for the reactions of DBNQ than DCINQ may be due to the fact that Cl^- is a poor-leaving group than Br^- ^{16,20,21}. The dependence of rate on the nature of leaving group suggests that C-X bond ($X = Cl$ or Br) in the acceptor is broken in the rate-determining step.

The second order rate constant measured conductometrically at 298, 308, 315 and 323 K and the activation parameters calculated are presented in Tables 4 and 5, respectively. The energies of activation, E_a are relatively low and entropies of activation, ΔS^\ddagger are negative. Many electron transfer interactions show such a behaviour^{2,6,22}. The negative ΔS^\ddagger values indicate the formation of a crowded transition state with a definite orientation of reactants. With a given quinone, as expected based on rate constants, the energy (E_a), enthalpy (ΔH^\ddagger) and free energy (ΔG^\ddagger) of activation are in the order $MTU < TU < DMTU$. However, the reactions of DBNQ have higher E_a values in spite of their greater reaction rates than the reactions of DCINQ. This may be due to the increase in energy of the transition state by the steric interactions of bulky bromine atoms. The formation of the product is accompanied by decrease of steric strain and hence, the higher rate. Significantly large changes in ΔH^\ddagger and ΔS^\ddagger with negligible change in ΔG^\ddagger in the reaction series can normally be attributed to the enthalpy-entropy compensation effect. Exner plot²³ of $\log k_2$ at 323 K versus $\log k_2$ at 298 K (Fig 5) is linear ($r = 0.9846$) with an isokinetic temperature of 530 K. The existence of good correlation implies that all the reactions so correlated follow a similar mechanism²³.

Table 4. Variation of second order rate constant (k_2) with temperature in methanol (conductometric study)

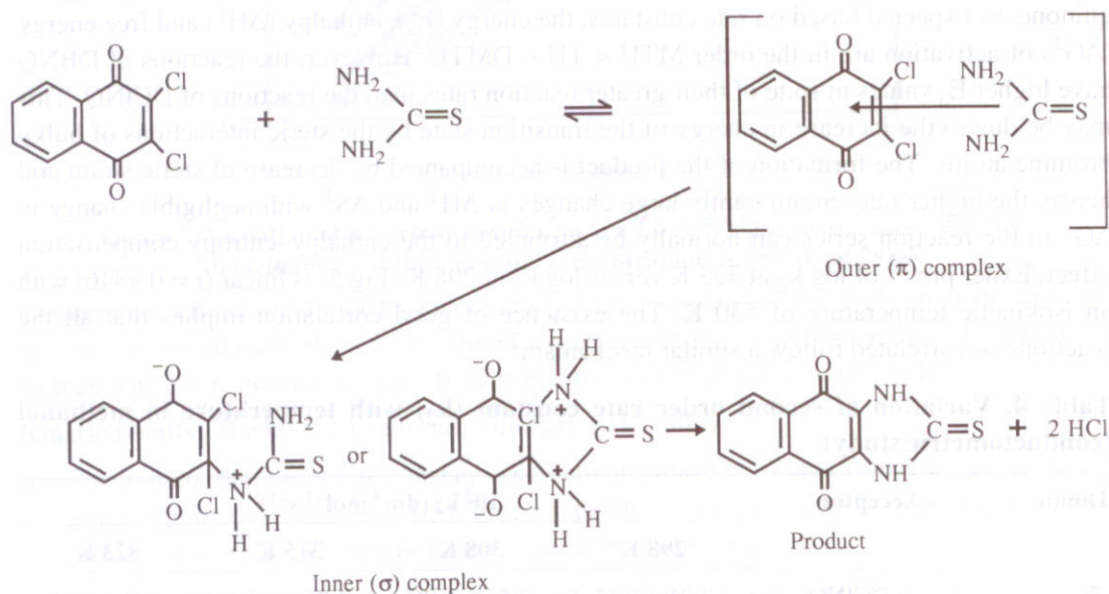
Donor	Acceptor	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)			
		298 K	308 K	315 K	323 K
TU	(i) DCINQ	2.21 ± 0.11	3.56 ± 0.06	4.86 ± 0.04	6.81 ± 0.15
	(ii) DBNQ	7.46 ± 0.04	12.07 ± 0.12	16.48 ± 0.55	23.46 ± 0.32
MTU	(i) DCINQ	14.54 ± 0.41	18.10 ± 0.30	20.64 ± 0.32	23.62 ± 0.58
	(ii) DBNQ	62.09 ± 2.29	81.76 ± 0.90	96.69 ± 0.97	117.0 ± 1.35
DMTU	(i) DCINQ	0.978 ± 0.028	1.66 ± 0.04	2.33 ± 0.05	3.35 ± 0.06
	(ii) DBNQ	4.83 ± 0.11	8.32 ± 0.23	11.73 ± 0.54	17.12 ± 1.75

Table 5. Activation parameters * (conductometric study)

Donor	Acceptor	E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
TU	(i) DCINQ	35.9 ± 0.2	33.6 ± 1.4	-164.2 ± 4.8	84.6 ± 0.1
	(ii) DBNQ	37.3 ± 0.5	34.9 ± 1.0	-149.7 ± 3.5	81.4 ± 0.1
MTU	(i) DCINQ	15.6 ± 0.5	13.0 ± 1.6	-217.4 ± 5.5	80.6 ± 0.1
	(ii) DBNQ	20.1 ± 0.4	17.7 ± 2.3	-189.4 ± 8.2	76.6 ± 0.1
DMTU	(i) DCINQ	39.2 ± 0.4	37.1 ± 2.0	-159.1 ± 6.9	86.5 ± 0.1
	(ii) DBNQ	40.3 ± 0.5	38.1 ± 6.5	-142.4 ± 22.8	82.4 ± 0.2

*Solvent : Methanol

Based on the above observations, the following mechanism is proposed for TU–DCINQ system as representative example.



Characterization of products

IR and UV spectra were recorded for the products of all the six systems while PMR and mass spectra only for DMTU–DCINQ and DMTU–DBNQ systems. The spectra of the products formed by DCINQ and DBNQ with a given donor are almost identical indicating the formation of same product in both the reactions, thus supporting the proposed mechanism. The UV–vis spectra of the isolated product in methanol showed resemblance with the spectra of the reaction

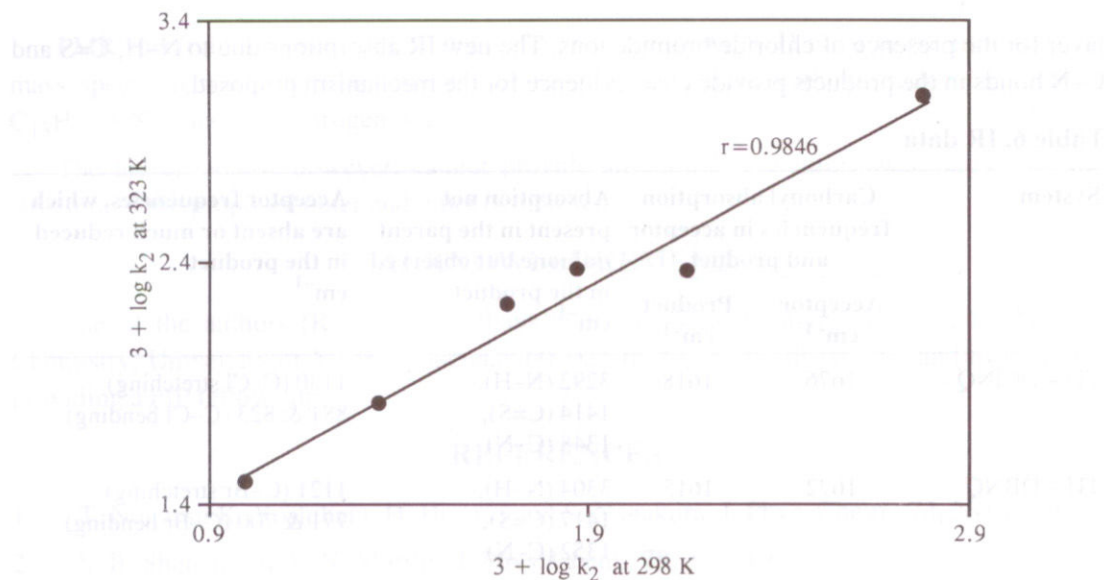
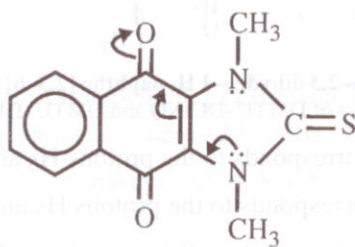


Figure 5. Exner plot of $\log k_2$ at 323 K versus $\log k_2$ at 298 K for thioureas-naphthoquinones series; Solvent : Methanol

mixture at the end of the reaction, indicating that the isolated solid product and the product in the reaction mixture are the same.

The infrared spectra of the parent compounds and products (in the form of KBr pellet) were recorded and the frequencies are given in Table 6. The presence of carbonyl frequency in all the products clearly indicates that the product is not of the Schiff type reaction and can be a substitution one. A slight decrease in the carbonyl absorption for the products may be due to extended conjugation involving the lone pair of electrons from the hetero atoms. The absence of N-H stretching frequency at $\sim 3300 \text{ cm}^{-1}$ in the products of DMTU further indicates the loss of proton on nitrogen of the donor moiety. However, the peak observed at $\sim 3300 \text{ cm}^{-1}$ for the products of TU and MTU is due to the presence of the N-H remaining after the loss of one hydrogen atom during substitution. That the substitution has taken place is further corroborated by the absence of C-Cl or C-Br absorptions in the IR spectra of the products. The formation of HCl/HBr was ascertained by shaking the reaction mixture with water and testing the aqueous

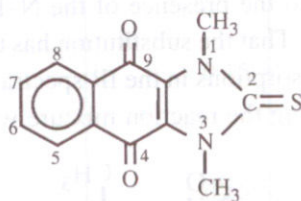


layer for the presence of chloride/bromide ions. The new IR absorptions due to N–H, C=S and C–N bonds in the products provide clear evidence for the mechanism proposed.

Table 6. IR data

System	Carbonyl absorption frequencies in acceptor and product		Absorption not present in the parent quinone but observed in the product cm^{-1}	Acceptor frequencies, which are absent or much reduced in the product cm^{-1}
	Acceptor cm^{-1}	Product cm^{-1}		
TU – DCINQ	1676	1618	3292 (N–H), 1414 (C=S), 1348 (C–N)	1130 (C–Cl stretching) 881 & 823 (C–Cl bending)
TU – DBNQ	1672	1615	3304 (N–H), 1417 (C=S), 1352 (C–N)	1121 (C–Br stretching) 771 & 700 (C–Br bending)
MTU – DCINQ	1676	1633	3286 (N–H), 1435 (C=S), 1365 (C–N)	1130 (C–Cl stretching) 881 & 823 (C–Cl bending)
MTU – DBNQ	1672	1635	3301 (N–H), 1439 (C=S), 1368 (C–N)	1121 (C–Br stretching) 771 & 700 (C–Br bending)
DMTU – DCINQ	1676	1655	1459 (C=S), 1376 (C–N)	1130 (C–Cl stretching) 881 & 823 (C–Cl bending)
DMTU – DBNQ	1672	1651	1453 (C=S), 1371 (C–N)	1121 (C–Br stretching) 771 & 700 (C–Br bending)

As expected, the products of DMTU–DCINQ and DMTU–DBNQ systems have identical PMR and mass spectra. PMR spectrum recorded in DMSO has three signals in the intensity ratio 1 : 1 : 3.



1,3-Dimethyl-2-thioxo-2,3 dihydro-1 H-naphtho [2,3-b] imidazole-4,9-dione
(Proposed product of DMTU–DCINQ and DMTU–DBNQ systems)

- (i) singlet at $\delta = 8.1$ ppm corresponds to the protons H_5 and H_8 .
- (ii) singlet at $\delta = 7.7$ ppm corresponds to the protons H_6 and H_7 .
- (iii) singlet at $\delta = 3.2$ ppm corresponds to the six protons of the two N–methyl groups.

PMR spectrum also provides evidence for the absence of N–H bond in the product. The mass spectrum has molecular ion peak at m/e 258 in accord with its molecular formula $C_{13}H_{10}O_2N_2S$ and with nitrogen rule.

The present study; however, cannot provide any conclusive information regarding the structure of the proposed outer and inner complexes.

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