Kinetics of Reaction of N-2, 6-Trichlorobenzoquinonimine with Sodium Thiosulphate in Water-Ethylene Glycol Mixtures

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The reaction of N-2, 6-trichlorobenzoquinonimine with sodium thiosulphate in water-ethylene glycol mixtures follows first order kinetics in the former over the temperature range 25-40°. The reaction rates increase with increasing dielectric constant of the medium and obey Arrhenius equation. The thermodynamic parameters of activation have been calculated and discussed. The results indicate high solvation of the transition state.

The reactions of quinones with thiol compounds have been the subject of many investigators who showed the reaction products to be hydroquinones and/or their addition compounds with thiols[1-4]. However, the mechanism of the addition of thiols remains still obscure although various thiols have been found to give the addition products of analogous type[1-4].

The substrate N-2, 6-trichlorobenzoquinonimine, a *p*-benzoquinone derivative, has been selected for the present investigation due to its wide importance. This compound has been introduced as a new reagent[5] for determining the drugs of abuse in urine and also for the colorimetric determination of a coumarin in plant materials[6]. Moreover, it is used in the determination of free and total phenolic acids in human serum and urine[7].

No study appears to have been carried out so far from the standpoint of solvent effect on the reaction between N-2,6-trichlorobenzoquinonimine and sodium thiosulphate. Hence, it was of interest to investigate this reaction in water-ethylene glycol mixture up to 72% alcohol by weight over the temperature range 25-40°.

Materials and Method

N-2, 6-Trichlorobenzoquinonimine was a product of Schuchardt-München, pure reagent grade (m.p. 65-67°) and was used without further purification. All chemicals employed were of analar grade.

Procedure

Solutions of the substrate and of sodium thiosulphate containing acetate buffer at *p*H 4.62 and appropriate amount of the organic solvent were thermostated at a particular temperature. The reaction was initiated by mixing the two solutions followed by a nimble transfer into a thermostated quartz cell for recording the UV absorption at different intervals of time. The unreacted substrate was calculated from the optical density measurements at 305 nm.

The kinetic reactions were conducted in the presence of excess thiosulphate. The pseudo first-order rate constant was calculated from Eq. (1).

$$K_t = 2.303 \log \frac{A_0 - A_\infty}{A_t - A_\infty} \qquad \ldots (1)$$

where A_0, A_t and A_∞ are the initial, at t time and final optical densities of the substrate. The obtained K value holds good constancy over 90% conversion.

Results and Discussion

The plots of $2 + \log(A_t - A_\infty)$ versus time were linear indicating the reaction between N-2, 6-trichlorobenzoquinonimine and sodium thiosulphate to be of first order. The pseudo first-order rate constants (K) for the reaction between the substrate $(7 \times 10^{-5} M)$ and sodium thiosulphate $(100 \times 10^{-5} M)$ in water-ethylene glycol mixtures at 25° are given in Table 1.

Table 1 shows that the value of K decreases with progressive increase in ethylene glycol concentrations. This trend can be attributed[8] to the decrease in dielectric constant of the medium and also to the decrease in acidity accompanying the addition of the organic solvent.

In the temperature range 25-40°, the rate of this reaction was found to follow the Arrhenius equation. The isocomposition energies of activation (E_c) were calculated from plots of $\log K$ versus $1/T$ as shown in Fig. 1. The values of E_c were found to be 25.15, 25.44,

Table 1 —Effect of Varying [Ethylene Glycol] on the Reaction Rate

wt% of ethylene glycol	$K \times 10^4$ s^{-1}	wt% of ethylene glycol	$K \times 10^4$ s^{-1}
0.00	13.05*	42.65	8.83
11.03	11.13	52.73	7.68
21.81	9.98	62.59	6.92
32.34	9.22	72.24	6.13

* From ref. 13
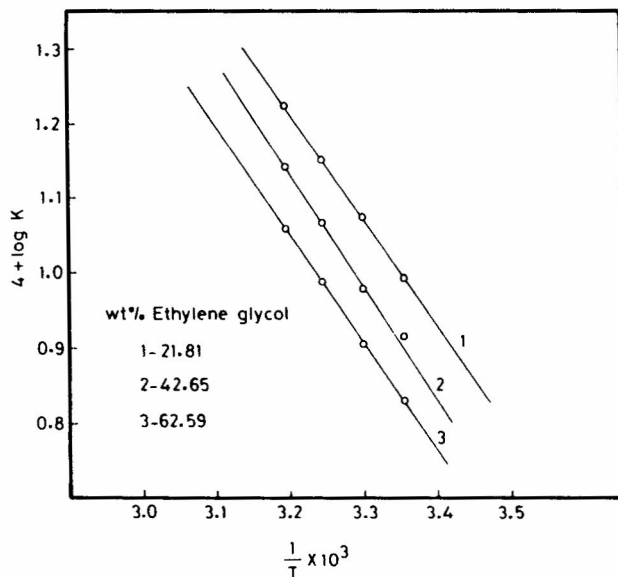
Fig. 1—Plots of log K versus $1/T$ for different ethylene glycol-water mixtures

Fig. 2—Variation of rate constant (K) with water concentration

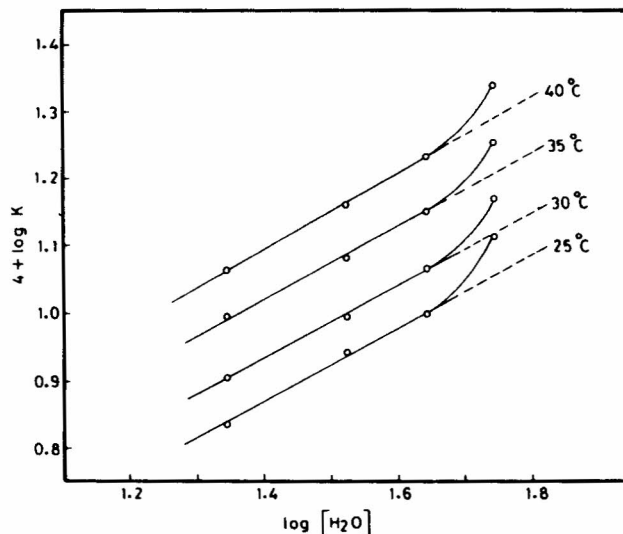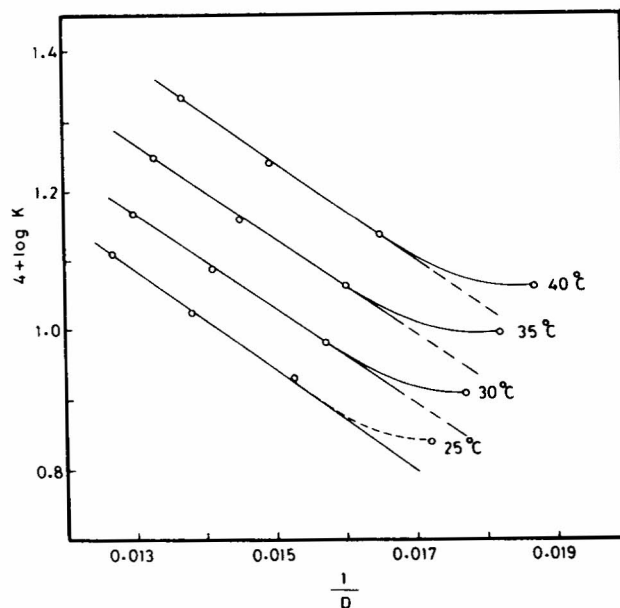Fig. 3—Variation of rate constant (K) with $1/D$ for ethylene glycol-water mixtures

and 26.82 KJ mol^{-1} at 21.81, 42.65 and 62.59% (w/w) of ethylene glycol respectively. These results indicate that the activation energy increases with the decrease in polarity of the medium. This trend is a clear indication of profound solvation changes in reactants and transition state, specially the latter, since it is the more polar entity[9].

Effect of varying water concentration

The dependence of rate constant on water concentration is shown in Fig. 2. The plot of log K versus log $[H_2O]$ gave a linear relationship at each temperature with the slope of nearly 0.5 indicating that every two molecules from the activated complex are solvated by one molecule of water. Moreover this value remained constant at different temperatures and solvent composition which implies that the structure of the transition state does not alter over the wide variation in reaction conditions.

The deviation from linearity (Fig. 2) at water concentration of 44.7 mol/dm^3, can be attributed to a considerable extent to the intercomponent association. The intercomponent hydrogen bonding results in a decrease in the extent of water-water hydrogen bonding so that ethylene glycol can be considered as a water-structure breaker.

Effect of dielectric constant

The dependence of reaction rate on the dielectric constant (D) of the medium was governed[10] by Eq. (2) which

$$\ln K = \ln K_\infty + \frac{Z\varepsilon\mu_0}{Kr^2} \cdot \frac{1}{DT} \qquad \dots (2)$$

predicts a linear plot between log K and $1/D$ with a negative slope for negatively charged ion-molecule reactions. In fact such linear plots with a negative slope have been obtained in the present study (of. Fig. 3). The curvature at low dielectric constant may be due to selective solvation[11] by water molecules.

The increase in reaction rate with an increase in dielectric constant indicates that the activated complexes are much more polar than the reactants.

Thermodynamic parameters

The activation parameters $\Delta H^{\neq}$ and $\Delta F^{\neq}$ showed a continuous trend with the variation in solvent composition with no evidence for extrema within the ethylene glycol composition range. The calculated results are given in Table 2.

The results in Table 2 show that $\Delta F^{\neq}$ slightly increases linearly with increasing ethylene glycol concentration. According to the theory of absolute reaction rates, this is indicative of solvation of the reactants. The above trend is in agreement with the increase in isocomposition activation energy in the same direction. The enthalpy of activation $(\Delta H^{\neq})$ varies with organic solvent concentration but remains almost independent of temperature. The change in entropy $(\Delta S^{\neq})$ is not linear. According to Hudson and Saville[12], this is due to specific solvation and the random distribution of the two components is not valid.

Mechanism

The reaction of N-2, 6-trichlorobenzoquinonimine with thiosulphate can be expressed by the following equation,

$$\frac{d[\text{Substrate}]}{dt} = K[\text{Substrate}][\text{Thiosulphate}] \qquad \dots (3)$$

It was shown that only the rates and not the mechanism of this reaction in all ranges of solvent composition were influenced by the solvent. Further, the kinetics of the reaction in aq. buffered[13] and in water-ethylene glycol mixtures were similar. In an earlier paper[13] we have proposed a suitable mechanism for this reaction involving a nucleophilic addition of the thiosulphate ion. The reaction showed a general acid catalysis and the rate was expressed by Eq. (4)[13,14],

$$\text{Rate} = K_0[\text{H}_2\text{O}] + K_\text{H} \cdot [\text{H}^+]$$
$$+ K_\text{AH}[\text{AH}][\text{Substrate}][\text{Thiosulphate}] \qquad \dots (4)$$

where K_AH is the catalytic constant for acetic acid and K_0 the solvent catalyzed rate constant.

According to the proposed mechanism, hydrogen ions are required for the protonation of the carbonyl oxygen and the imino nitrogen in the substrate molecule to form the activated complex. Since hydrogen ions would be less freely available in the more basic solvent mixtures, the rate constant decreases with successive addition of ethylene glycol. Furthermore, the higher negative value $(-221.75\,JK^{-1}mol^{-1})$ of the entropy of activation can be ascribed to the high solvation of transition state by the solvent molecules.

Table 2—Thermodynamic Parameter, $\Delta F^{\neq}$ and $\Delta H^{\neq}$ in KJ mol^{-1} and $\Delta S^{\neq}$ in J K^{-1}mol^{-1}

Thermo-dynamic parameter	Wt % of ethylene glycol			
	0.00	21.81	42.65	62.69
At 20°C				
$\Delta F^{\neq}$	89.450	90.111	90.416	91.023
$\Delta H^{\neq}$	23.372	22.656	22.966	21.678
$-\Delta S^{\neq}$	221.527	226.363	226.333	223.806
At 30°C				
$\Delta F^{\neq}$	90.646	91.224	91.763	92.203
$\Delta H^{\neq}$	23.330	22.614	22.928	24.284
$-\Delta S^{\neq}$	222.170	226.430	227.191	224.149
At 35°C				
$\Delta F^{\neq}$	91.918	92.320	92.855	93.219
$\Delta H^{\neq}$	23.288	22.573	24.242	24.246
$-\Delta S^{\neq}$	222.141	226.446	222.760	224.149
At 40°C				
$\Delta F^{\neq}$	92.713	93.437	93.814	94.349
$\Delta H^{\neq}$	23.259	22.531	24.204	24.183
$-\Delta S^{\neq}$	221.919	226.534	222.400	224.137

The fact that the energy of activation is low and $(-\Delta S^{\neq})$ is fairly large deduces the condition that $E < -T\Delta S$ at room temperature. Th—is indicates that both the reaction rate and the orientation of reacting species are controlled by entropy of activation.

References

1 Proyer W A, *Mechanism of sulfur reaction* (McGraw-Hill, New York) 1962, 71.
2 Thomson R H, *J org Chem*, **16** (1951) 1082.
3 Blackhall A & Thomson R H, *J chem Soc*, (1953) 1138.
4 Fieser L F & Turner R B, *J Am chem Soc*, **69** (1947) 2335.
5 Broich J R, Hoffman D B, Andryauskas S, Calente L & Umberger C J, *J Chromatogr*, **60** (1971) 95.
6 Szymanska M, *Acta Pol Pharm*, **29** (1972) 511.
7 Svobodova D, Krenek P, Fraenkl M & Gasparic J, *Microchim Acta*, **2** (1978) 197.
8 Elsemongy M, Abu Elamayem M S & Moussa M N, *Z physik Chem*, **94** (1975) 69.
9 Clasttone S, Laidler K J & Eyring H, *The theory of rate processes*, (McGraw-Hill, New York) 1941.
10 Edward S, Amis & James F Hinton, *Solvent effects on chemical phenomena*, Vol I (Academic Press, New York) 1973, 254.
11 Keith J & Peter A, *Trans Faraday Soc*, **52** (1956) 2000.
12 Hudson R F & Saville B J, *J chem Soc*, (1955) 4114.
13 Harfoush A, Zaghloul A & Abdel-Halim F, *Mh Chem*, **113** (1982) 837.
14 Yoshiro O, Yasuhiko S & Sumio G, *J Am chem Soc*, **90** (1968) 3469.