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Kinetics of the Reaction of *N*-2,6-Trichlorobenzoquinonimine with Sodium Thiosulphate

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The reaction of *N*-2,6-trichlorobenzoquinonimine with sodium thiosulphate has been studied in aqueous solutions. The reaction follows second-order kinetics at pH 4.62. E_a, ΔG and ΔS being 6.2, 21.4 kcal/mol (26,90 kJ/mol) and —53.0 eu, respectively. The rate is acid catalyzed. The results are discussed in terms of nucleophilic addition of the thiosulphate ion.

(Keywords: Nucleophilic addition; N-2,6-Trichlorobenzoquinonimine)

Kinetik der Reaktion von N-2,6-Trichlorbenzochinonimin mit Natriumthiosulfat

Die Reaktion ist säurekatalysiert und folgt einer Kinetik zweiter Ordnung mit Werten von $E_a = 6{,}2$ kcal/mol (26 kJ/mol), $\Delta G = 21{,}4$ kcal/mol (90 kJ/mol) und $\Delta S = -53$ eu bei pH 4,62. Die Ergebnisse werden auf der Basis einer nucleophilen Addition des Thiosulfat-ions diskutiert.

Introduction

Quinones are known to undergo several types of reactions, including 1,4-additions[1–4], nucleophilic displacement of labile substituents[5–7] and oxidation—reduction reactions[2,8].

The reactions of quinones with thiol compounds have been the subjects of many investigators, who have shown the reaction products to be hydroquinones and/or their addition compounds with thiols[1,3,9,10]. The mechanism of the addition is still obscure.

No kinetic study of these reactions has been reported for the substrate under investigation (*N*-2,6-trichlorobenzoquinonimine). In connection with the dehydrogenation by quinones[11], it is of interest to study the nature of the reaction between this substrate, (as a derivative from *p*-benzoquinone) and sodium thiosulphate.

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N-2,6-trichlorobenzoquinonimine has wide applications. *Broich* et al.[12] used it as a reagent in the urine screening for drugs of abuse. *Szymanska*[13] used it in the colorimetric determination of coumarin in plant material. It also is an important reagent for determination[14] of free and total phenolic acids in human serum and urine.

Experimental

Pure reagent of *N*-2,6-trichlorobenzoquinonimine (substrate) a product of Schuchardt, München, was used without further purification. All chemicals employed were analar-grade.

Kinetics: Solutions of the substrate and of sodium thiosulphate containing acetate buffer in a separate flask were thermostated at a definite temperature. The reaction was started by mixing the two solutions, followed by a transfer into a thermostated 1 cm quarz cell for the ultraviolet spectrophotometer. The reaction was followed by measuring the change in the optical density of the reaction mixture at 305 nm, the maximum absorption in the substrate curve. All measurements were made on solutions in which the ionic strength was adjusted to 0.5.

Results

Kinetic Order of the Reaction

Experimental runs were carried out with substrate concentration of $7 \cdot 10^{-5}$ mol/l and sodium thiosulphate in large excess from $(50\text{-}300) \cdot 10^{-5}$ mol/l. Plots of $\log(A_t - A_\infty)$ versus time in minutes (Fig. 1) yielded straight lines up to 80% reaction completion. Fig. 1 shows that the reaction is first order in substrate at various sodium thiosulphate concentration. In Fig. 2 the first order constant is shown to be proportional to sodium thiosulphate concentration. Hence the reaction is also first order in sodium thiosulphate concentration.

It would appear therefore that the present reaction follows second order kinetics with respect to both reactants and the rate is given by

$$\mathrm{d}\,[\text{substrate}]/\mathrm{d}t = K\,[\text{substrate}]\,[Na_2S_2O_3]$$

Effect of Hydrogen Ion Concentration

Series of measurements were conducted at 32 °C where the range of *pH* was changed from 4.26-5.57. The medium consists of sodium acetate—acetic acid and the concentrations of the substrate and sodium thiosulphate were kept constant.

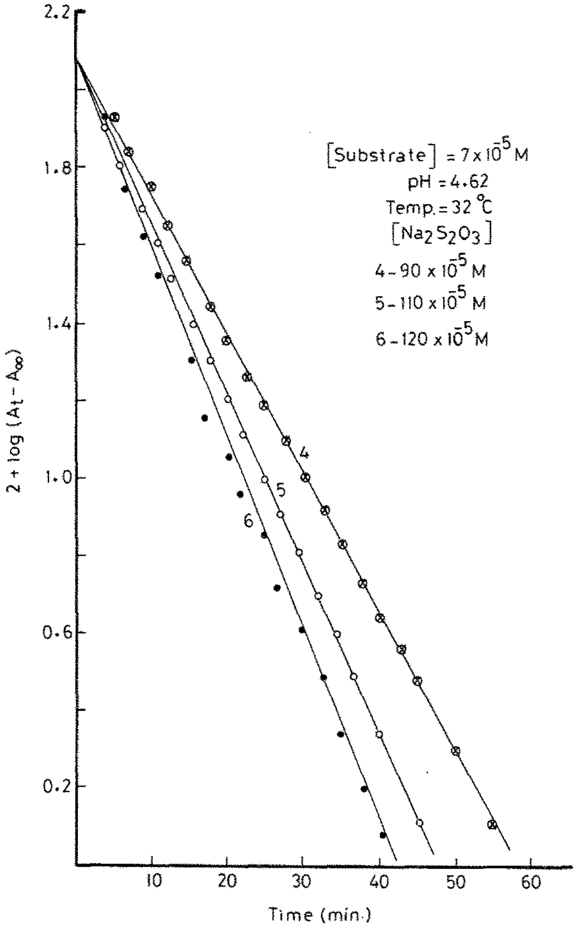


Fig. 1. Experimental runs at different concentrations of $Na_2S_2O_3$ followed by the absorbance at 305 nm

A plots of K versus $[H^+]$ yields a straight line as illustrated in Fig. 3. This indicates that the present reaction is shown to undergo general acid catalysis but not base catalysis. Hence, the rate may be expressed as follows:

$$\text{rate} = \{K_0\,[H_2O] + K_{H^+}[H^+] + K_{AH}\,[AH]\}\,[\text{substrate}]\,[S_2O_3^{-2}]$$

where K_{AH} is the catalytic constant for acetic acid and K_0 for noncatalyzed or solvent-catalyzed reaction.

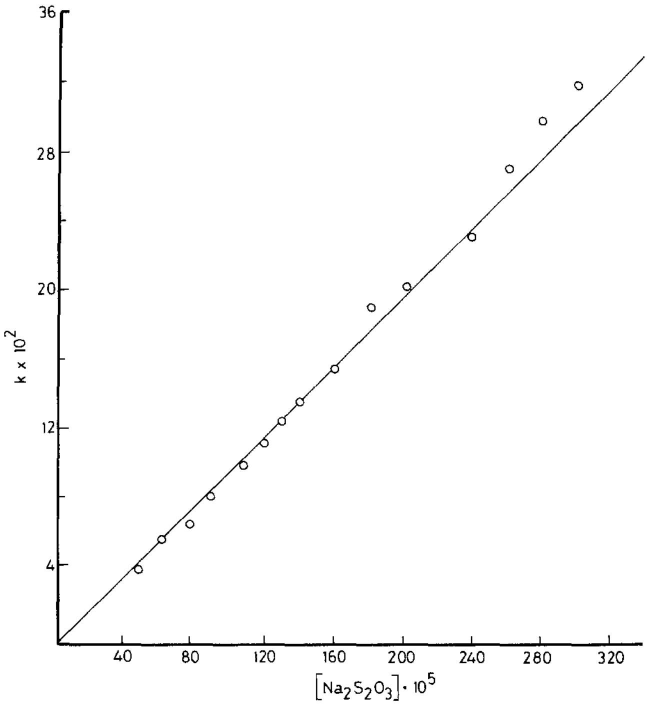


Fig. 2. Effect of sodium thiosulphate concentration on reaction rate; Substrate conc. = $7 \cdot 10^{-5}$ mol/l, *pH* = 4.62, $t = 32$ °C, $\mu = 0.5$

Effect of Temperature

The rates of the reaction were studied in the temperature range from 20-50 °C at *pH* 4.62. The concentrations of the substrate and sodium thiosulphate were kept constant.

From the dependence of the rate constant on temperature according to the *Arrhenius* equation (see Fig. 4) an activation energy of 6.2 kcal/mol was calculated.

Effect of Chloride Ion Concentrations

Kinetic measurements were carried out at *pH* 4.62 and 31 °C in the presence of different concentrations of Cl^- in the range of 0.01-0.4 mol/l. Complete independence of *K* upon the Cl^- concentration was proven. This indicates that the nucleophilic displacement of the chloride did not occur during the reaction. This was also confirmed by the titration of the substrate solution with silver nitrate using a silver—silver chloride electrode. The experiment showed no release of chloride ion.

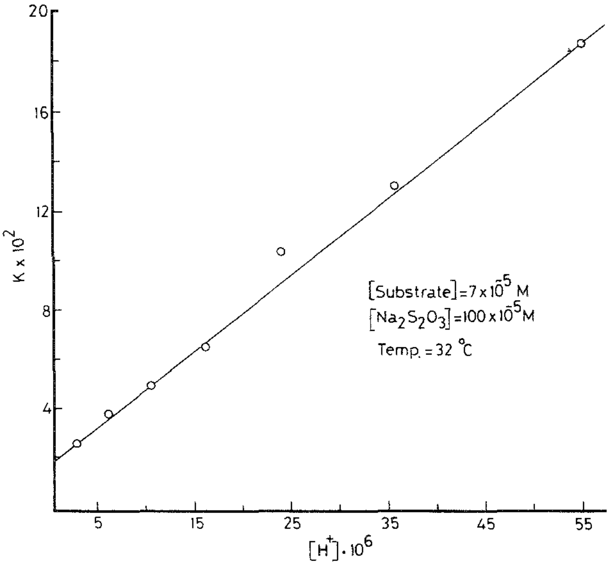


Fig. 3. Effect of hydrogen ion concentration on the rate constant; [substrate] = $7 \cdot 10^{-5}$ mol/l [$Na_2S_2O_3$] = $100 \cdot 10^{-5}$ mol/l, t = 32 °C, $\mu = 0.5$

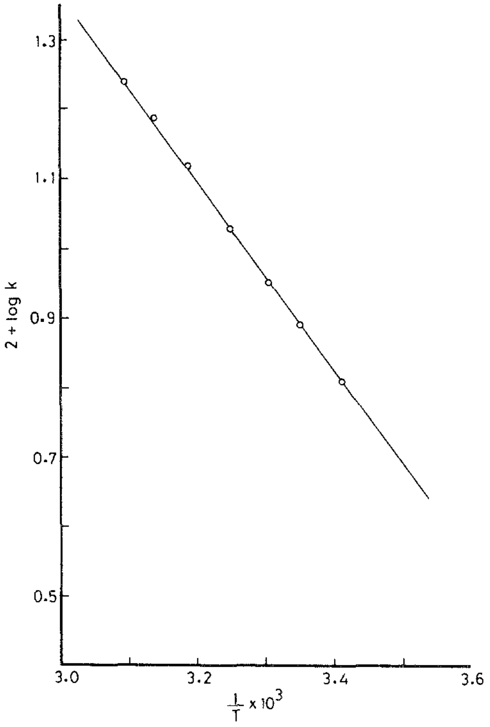


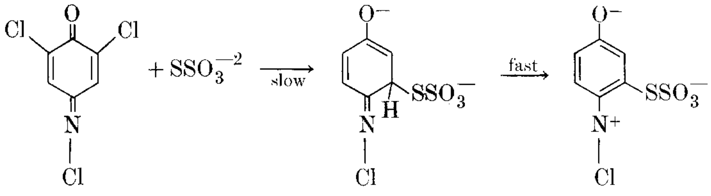
Fig. 4. *Arrhenius* plot

Discussion and Mechanism

The structure of the substrate—thiosulphate adduct has not been established unambiguously, since this adduct could not be isolated. This was also observed by *Bishop* et al.[15] in the reaction between substituted benzoquinone and sodium sulphite.

The dependence of the reaction rate on acid in the system as well as on substrate and thiosulphate demonstrates that the reaction is general acid catalyzed. In a similar situation involving the acid-catalyzed hydration of acetaldehyde, *Bell* and *Darwent*[16] suggested a mechanism involving a loose association between substrate and acid by hydrogen bonding, followed by attack of the nucleophile. Furthermore, this is the mechanism generally accepted for most carbonyl addition reactions[17,18].

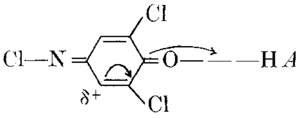
The present addition satisfies second-order kinetics: rate $= K$ [substrate] $[S_2O_3^{-2}]$, and is subject to general acid catalysis. The reaction at pH 4.6 probably has a mechanism involving a nucleophilic addition of thiosulphate ion.



1 **2**

The adduct **1** should rapidly be stabilized by prototropy to form derivative **2**. A similar scheme has been proposed for the reaction of *p*-benzoquinone with sodium thiosulphate[10].

The observed general acid catalysis is ascribed to an increased reactivity toward the nucleophilic attack at the β carbon atom by hydrogen bonding to carbonyl oxygen (**3**).



3

Energy and entropy of activation at *pH* 4.62 are 6.2 kcal/mol and — 53 eu, respectively. These values resemble those of other reactions of α, β unsaturated compounds, e.g. the reaction of methyl vinyl ketone with aniline[10] ($E_a = 5\text{-}6$ kcal/mol; $\Delta S^* = -50$ eu). These reaction seem to possess a highly negative entropy of activation, reflecting a crowded transition state with hindered motion of the reactants.

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