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The mechanism of photochemical chain substitution of chlorine by sulpho group in 4-chloro-1-hydroxynaphthalene

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Abstract

On irradiation of 4-chloro-1-hydroxynaphthalene in aqueous solution of sodium sulphite the chain photosubstitution reaction of chlorine by sulphite is observed. There are two mechanisms of photoinitiation of a chain reaction: the interaction of the triplet molecule of substrate with its nonexcited molecule and an electron photoejection. Independently of the mechanism of photoinitiation two intermediates—a radical anion of 4-chloro-1-hydroxynaphthoxide anion and 4-chloro-1-naphthoxy radical are formed. Naphthoxy radicals react with reducing agents (sodium sulphite, potassium iodide) forming sulphite radical anions. The formation of two different radical anions leads to two competitive mechanisms of the chain substitution reaction: an $S_{RN}1$ mechanism and a mechanism with the participation of sulphite radical anions. © 1997 Elsevier Science S.A.

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1. Introduction

We have shown earlier [1] that on irradiation of 4-chloro-1-hydroxynaphthalene in an aqueous solution of sodium sulphite the substitution of chlorine by a sulpho group takes place. It has been suggested that the photoinitiation of chain substitution reaction is due to the interaction of a triplet substrate molecule with its ground state molecule giving a radical anion of 4-chloro-1-hydroxynaphthoxide anion. In this case a chain reaction proceeds by an $S_{RN}1$ mechanism [2,3] (Scheme 1)

$$^{-}OArCl^{-\cdot} \rightarrow {}^{-}OAr^{\cdot} + Cl^{-}$$

$$^{-}OAr^{\cdot} + SO_3^{2-} \rightarrow (^{-}OArSO_3^{-})^{-\cdot}$$

$$(^{-}OArSO_3^{-})^{-\cdot} + {}^{-}OArCl \rightarrow {}^{-}OArSO_3^{-} + {}^{-}OArCl^{-\cdot}$$

Scheme 1.

This mechanism of photoinitiation was subsequently confirmed experimentally for substitution of halogen by nucleophiles in 1-halogeno-2-hydroxynaphthalene [4]. The present paper deals with the study of other possible mechanisms of the initiation and propagation steps of chain substitution of chlorine by a sulpho group in 4-chloro-1-hydroxynaphthalene and discusses transients formed on photolysis.

2. Experimental details

4-Chloro-1-hydroxynaphthalene (Merck) was used by after sublimation in vacuum (0.001 mmHg). The molar absorption coefficients of 4-chloro-1-hydroxynaphthalene in aqueous solution of sodium sulphite ($pH = 9.1 \pm 0.1$) at various wavenumber are: 4770 mol^{-1} dm^3 cm^{-1} at 32000 cm^{-1} (313 nm) and 7030 mol^{-1} dm^3 cm^{-1} at 30400 cm^{-1} (the maximum of absorption of the reaction product, 4-sulpho-1-hydroxynaphthalene, having the molar absorption coefficient at this wavenumber 9900 mol^{-1} dm^3 cm^{-1}). 4-Chloro-1-hydroxynaphthalene and reaction product exist generally in ionic form in sodium sulphite solution. Sodium sulphite was "Reagent grade".

The quantum yields of chlorine photosubstitution by the sulpho group in 4-chloro-1-hydroxynaphthalene were determined from the ratio of the initial consumption of the substrate to the dose of absorbed light. Consumption of 4-chloro-1-hydroxynaphthalene was monitored by the absorption recorded on a Specord M40 spectrophotometer. A hydrogen lamp (500 W) was used for irradiation of the solutions. Light of the necessary wavelength was filtered out

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with glass filters for hydrogen lines (313 nm and 365 nm). The intensity of absorbed light was measured using a photocell calibrated with a ferrioxalate actinometer [5].

Fluorescence spectra were recorded with an LS 50 spectrofluorimeter (Perkin Elmer). The flash photolysis experiments were carried out with an excimer laser (ELIM 72, Special Design Bureau of the Estonian Academy of Science) at 308 nm with a laser pulse width about 15 ns and a maximum energy of about 60 mJ. The excitation light was focused to a beam 2 cm long and 2 mm wide, which crossed with the monitoring beam. Transient absorptions were monitored at with a 100 W home-made absorption spectrometer described earlier [6].

3. Results and discussion

On laser photolysis of 4-chloro-1-hydroxynaphthalene in aqueous solution of sodium sulphite the absorption spectrum of solvated electrons [7] in the region of 700 nm was observed (Fig. 1). The lifetime of solvated electrons was shown to decrease with increase of 4-chloro-1-hydroxynaphthalene concentration. The constant value of solvated electron absorbance under flash photolysis was maintained by variation of the laser beam intensity using the neutral glass filters. In this case the decay rate constant of solvated electrons depends linearly on the 4-chloro-1-hydroxynaphthalene concentration (Fig. 2). Hence it follows that the rate constant of interaction of solvated electrons with 4-chloro-1-hydroxynaphthalene is close to the diffusion rate constant and is equal to $(3.2 \pm 0.25) \times 10^9$ mol^{-1} dm^3 s^{-1}. Solvated electrons are known to react with aromatic molecules giving aromatic radical anions [3,7]. Then the radical anions formed

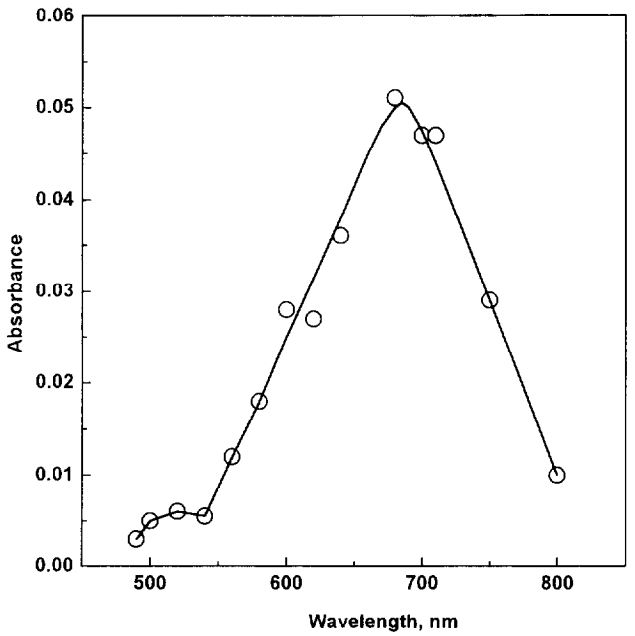


Fig. 1. The absorption spectrum of solvated electron at flash photolysis of 4-chloro-1-hydroxynaphthoxide anion in aqueous solution of sodium sulphite (0.2 mol dm^{-3}).

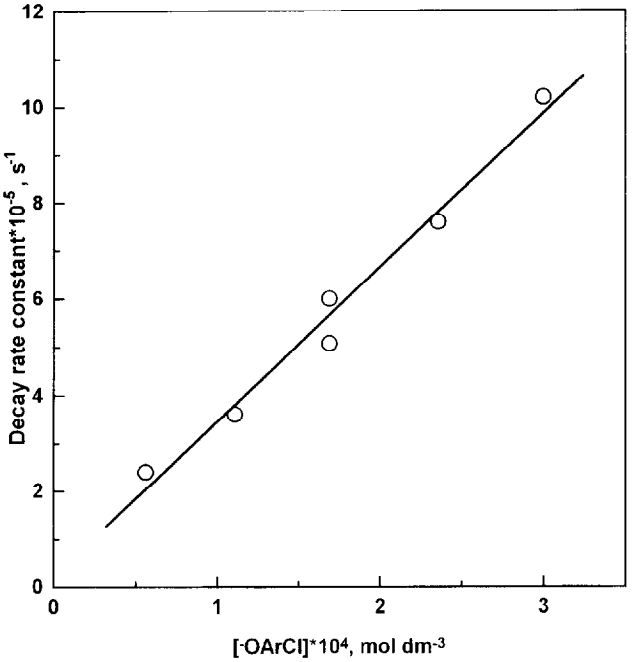


Fig. 2. The dependence of the decay rate constant of solvated electrons on 4-chloro-1-hydroxynaphthalene concentration.

by this reaction may take part in the propagation step of the chain substitution reaction by an $S_{RN}1$ mechanism. Reduction of organic molecules by solvated electrons has received an application in $S_{RN}1$ nucleophilic aromatic substitution reactions [3,8,9]. In our case the quantum yield of the substitution reaction proceeding via a mechanism with participation of solvated electron is low since the quantum yield of formation of the solvated electrons is only 0.05 ± 0.025. The quantum yield of solvated electrons was calculated from the solvated electron absorption at 700 nm, the laser pulse energy and focusing of a laser beam onto the sample (see Section 2).

The main part of a chain substitution proceeds through the triplet state of 4-chloro-1-hydroxynaphthalene [1]. In this case the mechanism of photoinitiation of chain substitution reaction is most likely due to the electron transfer reaction between the triplet and nonexcited molecules of chloronaphthol [4]. It should be noted that neither fluorescence nor triplet molecules of 4-chloro-1-hydroxynaphthoxide anion are quenched by sodium sulphite up to concentration of 0.5 mol dm^{-3}. The interaction of the triplet molecules of 4-chloro-1-hydroxynaphthalene in ion form with their nonexcited molecules along with radical anions of 4-chloro-1-hydroxynaphthoxide anion produces 4-chloro-1-naphthoxy radicals. Similar to phenoxy radicals [10], naphthoxy radicals can react with sulphite ions to give sulphite radical anions. We have shown that the lifetime of naphthoxy radicals obtained by flash photolysis decreases in the presence of sodium sulphite. The sulphite radical anions take part in propagation step of a chain substitution reaction similarly to a chain substitution reaction photosensitized by dyes [11] (Scheme 2)

Initiation:

$$^3(^-OArCl) + {}^-OArCl \rightarrow {}^-OArCl^{-\cdot} + {}^{\cdot}OArCl$$

$$^{\cdot}OArCl + SO_3^{2-} \rightarrow {}^-OArCl + SO_3^{-\cdot}$$

Propagation:

$$^-OArCl + SO_3^{-\cdot} \xrightarrow{k_R} [{}^-OAr(SO_3^-)Cl]^{\cdot}$$

$$[{}^-OAr(SO_3^-)Cl]^{\cdot} \rightarrow {}^-OArSO_3^- + Cl^{\cdot}$$

$$Cl^{\cdot} + SO_3^{2-} \rightarrow Cl^- + SO_3^{-\cdot}$$

Termination:

$$SO_3^{-\cdot} + SO_3^{-\cdot} \xrightarrow{k_0} S_2O_6^{2-}$$

Scheme 2.

The contribution of the mechanism with participation of sulphite radical anions is small at high intensity of light because of the quadratic termination step (k_0). However it can compete with the $S_{RN}1$ mechanism at lower light intensities (Fig. 3). We could not notice this earlier [1] as we used a high intensity of light absorbed by substrate.

The contribution of the reaction with participation of solvated electrons may be determined by total quenching of the triplet molecules of 4-chloro-1-hydroxynaphthalene by heavy atoms. We carried out a substitution reaction in the presence of potassium bromide and potassium iodide. The quantum yield of the substitution of chlorine by sulpho group decreases on addition of KBr and KI (Fig. 4). The reaction quenching constants determined from Stern–Volmer dependence are equal to 20 ± 5 mol^{-1} dm^3 and 500 ± 100 mol^{-1} dm^3 for KBr and KI, respectively. These experiments also confirm participation of the triplet states in chain substitution reaction. It is noteworthy that the fluorescence of 4-chloro-1-hydroxynaphthoxide anion is only slightly quenched by bromide and iodide ions. The corresponding K_{SV} values are equal to 1 ± 0.2 mol^{-1} dm^3 for KBr and 3 ± 0.3 mol^{-1} dm^3 for KI. In addition, the quantum yield and lifetime of solvated electrons observed by laser photolysis are independent of KBr concentration up to 2 mol dm^{-3}. The photosubstitution quantum yield does not reduce to zero at high KBr concentration (Fig. 4). The quantum yield of the photosubstitution reaction observed at high KBr concentration corresponds to the substitution reaction proceeding with the participation of a radical anion of 4-chloro-1-hydroxynaphthoxide which is formed by reaction with solvated electron. A limiting value of the quantum yield of the substitution reaction in the presence of a high concentration of KBr is equal to 0.16 ± 0.02. This value is about 10% of the overall reaction quantum yield in the absence of triplet quenchers.

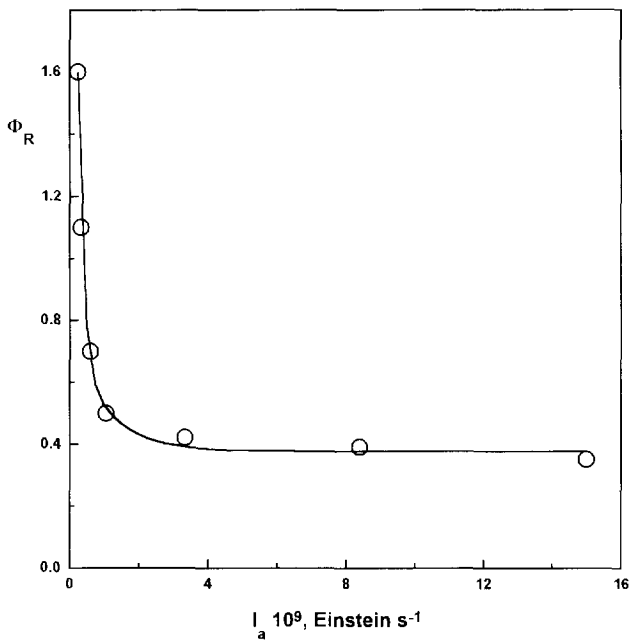


Fig. 3. The dependence of the quantum yield of the photosubstitution of chlorine by sulpho group in 4-chloro-1-hydroxynaphthalene on light intensity at irradiation 365 nm. The concentration of 4-chloro-1-hydroxynaphthalene is 1.4×10^{-4} mol dm^{-3}, and that of sodium sulphite is 0.2 mol dm^{-3}.

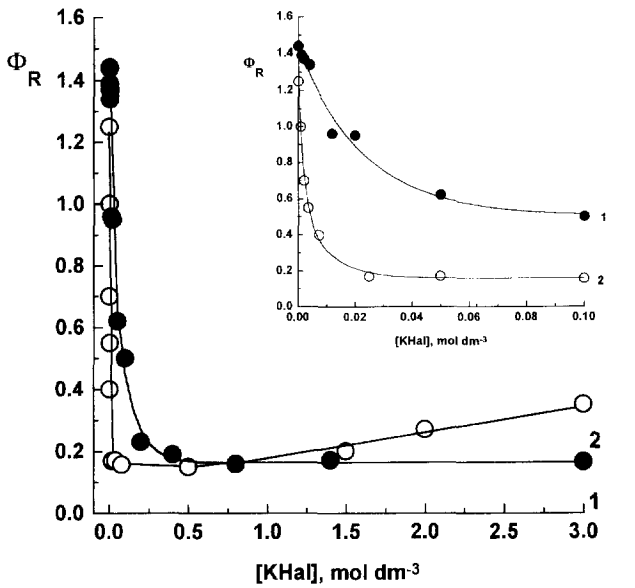
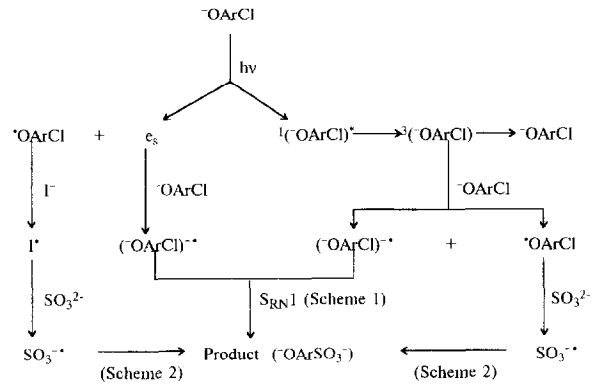


Fig. 4. The dependence of the quantum yield of the photosubstitution of chlorine by sulpho group in 4-chloro-1-hydroxynaphthalene on concentration of (1) KBr and (2) KI for irradiation at 313 nm.

In a contrast to KBr, the quantum yield of the photosubstitution reaction in the presence of KI decreases at low but then increases at high concentrations of KI (Fig. 4). It should be noted that a minimum value of the quantum yield on this curve is the same as the limiting one for KBr. The minimum value of quantum yield in the presence of KI in the same manner as for KBr is due to the substitution reaction with participation of solvated electrons. The increase of the reaction quantum yield at high concentrations of KI is caused by another mechanism (e.g. by participation of naphthoxy radicals which are formed simultaneously with formation of solvated electrons). Iodide anions are good electron donors and may react with naphthoxy radicals giving iodine atoms. Then iodine atoms are reduced by sulphite ions with the



Scheme 3.

formation of sulphite radical anions [12], which take part in the chain reaction (Scheme 2). A similar effect is observed at high concentrations of sodium sulphite in the present KBr. At high concentrations of KBr (3 mol dm^{-3}) and sodium sulphite (1.2 mol dm^{-3}) the quantum yield of the substitution reaction increases 1.5 times in comparison with the reaction carried out in the presence of a high concentration of KBr and a low concentration of sodium sulphite (0.2 mol dm^{-3}). The increase of sodium sulphite concentration in the absence of KBr does not lead to an increase of the reaction quantum yield as the reaction proceeding through the sulphite radical anion makes a small contribution to the quantum yield in comparison with the $S_{RN}1$ mechanism (through the radical anion of the substrate).

It was shown that in the presence of a high concentration of KI the quantum yield of substitution reaction depends linearly on concentration of 4-chloro-1-hydroxynaphthalene and increases with decrease of light intensity. The results obtained refer equally to irradiation of solutions both by 313 nm and 365 nm and are in agreement with equation for the reaction quantum yield (Scheme 2) [11]:

$$\Phi_R = \Phi_i^{1/2} k_R [\,^-OArCl] (2k_0)^{-1/2} I_a^{-1/2}$$

where Φ_i is the quantum yield of photoinitiation and I_a is the intensity of the light absorbed by 4-chloro-1-hydroxynaphthoxide anion.

Furthermore, it was shown that similarly to substitution reactions photosensitized by dyes [13] the reaction quantum yield at a high concentration of KI increases on addition of inorganic salts. These facts indicate that the photosubstitution reaction in the presence of a high concentration of KI proceeds with the participation of sulphite radical anions.

Thus, the possible mechanisms of photoinitiation and propagation of chain substitution reaction of chlorine by sulpho group in 4-chloro-1-hydroxynaphthalene in aqueous solution of sodium sulphite can be presented by Scheme 3.

4. Conclusions

The results of this paper show that for chain photosubstitution of chlorine by sulpho group in 4-chloro-1-hydroxynaphthalene in aqueous solution of sodium sulphite two mechanisms of photoinitiation are observed: the interaction of the triplet molecule of the substrate with its nonexcited molecule and an electron photoejection. Independently of the mechanism of photoinitiation two intermediates – a radical anion of 4-chloro-1-hydroxynaphthoxide anion and a 4-chloro-1-naphthoxy radical – are formed in each case. Naphthoxy radicals interact with reducing agents (sodium sulphite, or potassium iodide) giving sulphite radical anions. Hence there are two competition mechanisms for the propagation step: the $S_{RN}1$ mechanism with the participation of substrate radical anions and the mechanism with participation sulphite radical anions.

Acknowledgements

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