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# Encounter geometry determines product characteristics of electron transfer from 4-hydroxythiophenol to *n*-butyl chloride radical cations

G.R. Dey <sup>a</sup>, R. Hermann <sup>b</sup>, S. Naumov <sup>c</sup>, O. Brede <sup>b,\*</sup>

<sup>a</sup> Applied Chemistry Division, Chemistry Group, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India <sup>b</sup> University of Leipzig, Interdisciplinary Group Time Resolved Spectroscopy, Permoser Strasse 15, D-04303 Leipzig, Germany <sup>c</sup> Institute of Surface Modification, Permoser Strasse 15, D-04303 Leipzig, Germany

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### Abstract

The electron transfer reaction between the *n*-butyl chloride parent ion and 4-thiophenol was studied using pulse radiolysis in solutions of 4-thiophenol in *n*-butyl chloride. It was found to have a diffusion-controlled rate constant of  $1.5 \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and to involve contributions from all functional groups, i.e. –SH, –OH and the aromatic ring. Consequently, thiyl and phenoxyl radicals and 4-hydroxythiophenol radical cations were observed as direct products of this ion–molecule reaction. This unexpected reaction behavior could be explained by the hypothesis that the encounter geometry of the reaction partners determines the product characteristics. © 1999 Elsevier Science B.V. All rights reserved.

# 1. Introduction

For pulse radiolytically initiated electron transfer from several one-ring phenols as well as naphthols and hydroxybiphenyls to *n*-butyl chloride radical cations ( $C_4H_9Cl^{+}$ , BuCl<sup>++</sup>), two reaction pathways have been identified, resulting in the formation of phenol radical cations (1) and competing with that in the direct formation of phenoxyl radicals (2) [1,2].

BuCl<sup>++</sup> + ArOH 
$$\rightarrow$$
 ArOH<sup>++</sup> + BuCl  
(Ar = aromatic ring), (1)

Recently we also studied the electron transfer and radical reactions taking place after the irradiation of solutions of aromatic thiols in *n*-butyl chloride [3]. In analogy to the phenols [1,2], the above-mentioned two channels for the ion-molecule reaction [cf. reactions (1) and (2)] were also observed – one forming thiophenol radical cations and the other generating thiyl radicals as the first observable products.

In this Letter, we report on pulse radiolysis studies of ionic and radical reactions in n-butyl chloride solutions of 4-hydroxythiophenol (HOArSH) where the two functional polar groups –SH and –OH could be involved in the reaction mechanism.

<sup>\*</sup> Corresponding author. Fax: +49-341-235-2317; e-mail: brede@mpgag.uni-leipzig.de

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# 2. Experimental

Pulse radiolysis experiments were performed with high-energy electron pulses (1 MeV, 15 ns duration) produced by a pulse transformer type electron accelerator ELIT (Institute of Nuclear Physics, Novosibirsk. Russia). The dose per pulse determined with an electron dosimeter was  $\sim 50$  Gy. Irradiation of the samples was carried out in an online flow system with an optical path length of 10 mm of a quartz cell. The optical detection system consists of a pulsed xenon lamp, a SpectraPro-500 monochromator (Acton Research), a R4220 photomultiplier tube (Hamamatsu) or a FND-1000 silicon photo diode (Laser Components), and a TDS 640 digitizing oscilloscope (Tektronix). More details about the pulse radiolysis apparatus are given elsewhere [4]. The solutions were purged with ultrapure  $N_2$  and  $O_2$ . 4-hydroxythiophenol from Aldrich was used as received. Spectrograde *n*-butyl chloride (Aldrich) was tested spectrometrically before use. All other chemicals used were analytical reagent grade.

### 3. Results and discussion

The main reactive species generated by the radiolysis of pure n-butyl chloride [5] are given by reaction (3)

$$BuCl - / / / \to BuCl^{+}, Bu^{;}Cl^{-}.$$
(3)

The radical cation BuCl<sup>++</sup> exhibits a broad absorption band with  $\lambda_{\text{max}} \approx 500$  nm and has a half-life of ~ 100 ns. In the presence of solute molecules with a lower ionization potential such as 4-hydroxy-thiophenol, the solvent radical cations (BuCl<sup>++</sup>) can undergo the rapid electron transfer reaction (4) [6]. Furthermore, it should be noted that because of its soft S–H bond, HOArSH can also undergo a relatively fast reaction (5) with the radiolytically formed butyl radical [cf. reaction (3)].

 $BuCl^{+} + HOArSH \rightarrow BuCl + HOArSH^{+}$ , (4)

$$Bu' + HOArSH \rightarrow BuH + HOArS'$$
. (5)

Fig. 1 shows transient optical absorption spectra obtained at different times during the pulse radiolysis

of N<sub>2</sub>-purged solutions of  $5 \times 10^{-3}$  mol dm<sup>-3</sup> 4-hydroxythiophenol in *n*-butyl chloride. The spectrum after 100 ns, which is elicited here immediately after the electron pulse, exhibits two absorption bands with  $\lambda_{max}$  values at 340 and 510 nm and a shoulder at 560 nm. These main bands are to a considerable extent already formed during the electron pulse, and subsequently grow in amplitude within ~ 2 µs. By contrast, the shoulder disappears within ~ 200 ns. The main absorption is attributed to the thiyl radical HOArS<sup>-</sup>, which tallies with the literature [3,7].

Considering the time profiles at  $\lambda = 500$  nm (inset in Fig. 1), the majority of the thiyl radical absorption is evidently formed in a delayed manner, as expected for the radical H abstraction reaction (5). A bimolecular rate constant  $k_5 = 1 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> was determined from the dependence on scavenger concentration. Similar rate constants were found by Schöneich et al. [8] for the analogous reaction of aliphatic thiols. As can be seen, the growth of HOArS<sup>-</sup> is not purely exponential, which could be caused by superposition with the ionic processes discussed subsequently.

To remove the ionic contributions from the spectra of Fig. 1, we added 0.1 mol  $dm^{-3}$  ethanol as a scavenger for the parent ions of the solvent which acts under deprotonation.

$$BuCl^{+} + C_2H_5OH \rightarrow BuCl^{+} + C_2H_5OH_2^{+}.$$
 (6)

This produced divergent spectral behavior (Fig. 2), which differs from the initial situation (Fig. 1) by the disappearance of the fast transient absorption around 550 nm, a different relationship between the 520 and the 340 nm peak, and a slightly different spectral structure in the range between 400 and 460 nm. Furthermore, the time profiles given as insets exhibit more homogeneous time behavior without the marked fast initial step in Fig. 1. We therefore suppose that Fig. 2 gives the actual spectrum of the thiyl radical formed according to reaction (5).

To analyze the ionic processes ( $G_{\rm fi} \approx 0.2$ ), we decided to remove the dominating radical reaction ( $G \approx 3-4$ ) by rapid deactivation of the butyl radicals. This was performed by purging the sample with oxygen to transform the alkyl radicals in under 50 ns into alkylperoxyl radicals (7), which were found to



Fig. 1. Transient optical absorption spectra of pulse irradiated N<sub>2</sub>-purged  $5 \times 10^{-3}$  mol dm<sup>-3</sup> 4-hydroxythiophenol in *n*-butyl chloride after 100 ns ( $\bullet$ ) and 1.5 µs ( $\bigcirc$ ). The insets show the time profiles at 500 and 550 nm.

be non-reactive to HOArSH within our analysis time range.

$$Bu' + O_2 \to BuOO'. \tag{7}$$

Fig. 3 shows the spectral situation for a pulsed sample of  $5 \times 10^{-3}$  mol dm<sup>-3</sup> HOArSH in BuCl in the presence of oxygen. A minor part of the product transients is retained, which should only be of ionic origin. At a thiol concentration of  $5 \times 10^{-3}$  mol



Fig. 2. Transient optical absorption spectra of pulse irradiated N<sub>2</sub>-purged  $5 \times 10^{-3}$  mol dm<sup>-3</sup> 4-hydrxythiophenol in *n*-butyl chloride containing 0.1 mol dm<sup>-3</sup> ethanol after 100 ns ( $\bullet$ ) and 1.5 µs ( $\bigcirc$ ). The insets show the time profiles at 340 and 520 nm.

 $dm^{-3}$ , the signal of the butyl chloride parent ion practically disappeared, with the transients responsible for the absorption spectra given in Fig. 3 being generated instead. The short-lived absorption part absorbing between 500 and 600 nm is attributed to

the 4-hydroxythiophenol radical cation, in analogy to the thiophenols [3]. However, the longer-lasting radical spectrum consists of absorptions of two species which are insensitive to oxygen. One is the thiyl OHArS<sup> $\cdot$ </sup> (cf. Fig. 2), and the other with a marked



Fig. 3. Transient optical absorption spectra of pulse irradiated  $O_2$ -purged  $5 \times 10^{-3}$  mol dm<sup>-3</sup> 4-hydroxythiophenol in *n*-butyl chloride after 100 ns ( $\bullet$ ) and 1.5 µs ( $\bigcirc$ ). The insets show the time profiles at 340 and 520 nm.

absorption at 340 nm and smaller peak at ~ 440 nm is attributed to the phenoxyl  $\cdot$ OArSH. Phenoxyl radicals are known to exhibit absorption maxima at ~ 320 and ~ 410 nm, depending on further substituents in the aromatic ring [1,9,10]. In the case of

the thiyl substitution in the *p*-position, the absorptions are slightly shifted to longer wavelengths.

Hence we can state that as result of an ion-molecule encounter (8), not only should electron transfer in the narrow sense occur as given in reaction (4), but also the direct formation of thiyl and phenoxyl radicals proceeding with the same time law as the electron transfer should occur, i.e. in this case more or less within the electron pulse.

$$\rightarrow \text{HOAr}^{+}\text{SH} + \text{BuCl}, \quad (8a)$$
  
BuCl^+ + HOArSH  $\rightarrow$  HOArS' + H<sup>+</sup> (BuCl),  
(8b)  
$$\rightarrow \cdot \text{OArSH} + \text{H}^{+} (\text{BuCl})$$

(8c)

At lower concentrations of HOArSH, we determined the bimolecular rate constant for the overall reaction (8) from the concentration-dependent change of the time profiles of BuCl<sup>++</sup> absorption at 500 nm, obtaining  $k_8 = 1.5 \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. This value is slightly higher than the diffusion-controlled limit expected for *n*-butyl chloride. This may be explained by a small contribution from non-relaxed positive holes [6,11], which are a particular initial radiation chemical phenomenon.

The fate of the hydroxythiophenol radical cation is determined by a decay independent of the scavenger concentration (and therefore first-order) of  $k_9 \approx 6.7 \times 10^6 \text{ s}^{-1}$ , which generates further thiyl radicals in a delayed manner. This fact is responsible for the complex time law of the time profile at 500 nm shown as an inset in Fig. 1.

$$HOAr^{+}SH \to HOArS^{+}H^{+}(BuCl).$$
(9)

This behavior is analogous to that of phenol and thiophenol radical cations [1-3].

To find out more about the influence of the electronic structure of the transient species on the reaction dynamics, we employed semi-empirical open-shell quantum-chemical calculations. Using the PM3 method [12,13] with unrestricted Hartree–Fock wavefunction geometries, energies for the radical ground states and the radical cations of HOArSH as well as of energy-minimized conceivable intermediate complexes and charge distributions were calculated using HyperChem 5.01. HyperChem uses atomic charges, which are commonly employed in molecular orbital theory.

The binding energies of the phenoxyl and thiyl radicals were calculated to be -5865.4 and -5850.3 kJ mol<sup>-1</sup>, respectively. It can be seen that the energy difference between the two species is only 15.1 kJ

 $mol^{-1}$  and, therefore, both forms ought to be relatively stable. The charge distributions obtained of the radical and ionic transients of 4-hydroxythiophenol are shown in Fig. 4. Only for the radical cation is there a marked charge at the sulfur atom of about the same as all four protons at the aromatic ring, which could explain the relative stability of this species.

As experimentally established, thivl, phenoxyl radicals and radical cations of 4-HOArSH are the rapidly formed observable transient products generated in the ion-molecule reaction (IMR) (8) of nbutyl chloride radical cations with HOArSH. The simultaneous appearance of these three products of reaction (8) indicates that the IMR does not only proceed via the sterically unspecific electron transfer reaction over distances longer than molecular bonds (8a), but can also occur via the much more specific reaction channels (8b, 8c) attributed to defined intermediate state geometries. This could happen via energetically favorable encounter structures prebonded between the phenolic hydrogen or the thiol hydrogen (or sulfur), which decay immediately after encountering to form the radicals and solvent-stabilized protons observed.

Such structures as are shown in reaction (10) were also quantum-chemically investigated and found to



Fig. 4. Charge distribution of the radical cation and the radicals of 4-HOArSH.



Fig. 5. Reaction diagram depicting charge transfer and H-abstraction processes under pulse radiolytic conditions of 4-hydroxythiophenol in *n*-butyl chloride solutions.

be energetically favorable with distances of  $\sim 2.2$  Å between the partner atoms, i.e. comparable with a chemical bond (cf. Fig. 5). Within these encounter complexes, immediate deprotonation also occurs driven by the high proton affinity of the chlorine atom.

# 4. Conclusions

We thus reached the surprising conclusion that in such a simple IMR involving relatively small molecules (but in the case of HOArSH with three different functionalities), product control depends on the encounter geometry of the reaction partners. This situation is illustrated by the diagram in Fig. 5. The solvent parent ion can meet the aromatic ring in different orientations. Electron transfer occurs more or less specifically from this ring to the solvent cation, whereas the positive charge is stabilized within the aromatic system with the involvement of the functional groups SH and to a lesser extent OH. The other attack possibilities are the approach of the two polar groups –SH and –OH with the subsequent formation of an intermediate complex charged structure as outlined in the diagram on the basis of quantum-chemical results. Within these complexes, deprotonation of the polar groups of the 4-hydroxythiophenol should be favored by the high proton affinity of the chlorine atom. Hence butyl chloride distinctly stabilizes the proton, contributing to the reduction of reaction enthalpy.

As far as we are aware, such a reactivity dependent on encounter geometry among small parent ions and more functional molecules has hitherto not been observed. One reason for such an exotic mechanism could be the involvement of two similar polar groups forming energetically favorable encounter complexes, which decay faster as the positive charge can be distributed over the whole molecule.

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