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# Nucleophilic effects on the deprotonation of phenol radical cations

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## Abstract

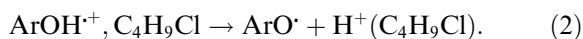
Considering dependence on their electronic structure, in non-polar surroundings phenol radical cations exhibit lifetimes between 100 and 500 ns and decay by deprotonation forming phenoxyl radicals. Adding various quenchers of different nucleophilicity, we determined a set of rate constants for the acceleration of deprotonation i.e. the reaction of phenol radical cations with the nucleophiles. The data are basically discussed in terms of Reichardt's polarity scale, also considering effects like competing electron transfer aided by comparing the differences of calculated adiabatic ionization potentials as well as spin densities and local charges on heteroatoms for phenols and the quenchers. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Organic radical cations appear as intermediates in a variety of chemical processes viz. one-electron-oxidations, photosensitized electron transfer and radiation-induced ion-molecule reactions [1,2]. They are metastable species having a deficit of one electron leading to generation of unpaired spin and charge, thereby causing reduction of strength in key bonds of the molecule. This property is enhanced by the polar nature of functional groups as e.g. in the case of phenols (ArOH) and thiophenols (ArSH) where phenol radical cations are generated [3–8].

In aqueous media however, phenol radical cations were not observed due to their low  $pK_a$  ( $\leq 0$ )

value [9]. In sharp contrast to this, we recently reported the generation of phenol radical cations ( $\text{ArOH}^{\cdot+}$ ) in non-polar solvents by electron transfer from phenol (ArOH) to the primary solvent radical cations ( $\text{C}_4\text{H}_9\text{Cl}^{\cdot+}$ , derived from 1-chlorobutane) using the technique of pulse radiolysis (1) [3,6]. Based upon these studies, it was observed that the phenol radical cations are metastable species which decay easily by monomolecular deprotonation into long-lived phenoxyl radicals ( $\text{ArO}^{\cdot}$ ) (2) [10].



In non-polar solvents such as *n*-alkanes, cycloalkanes, alkyl chlorides, etc., we characterized the phenol radical cations spectroscopically and kinetically. They were found to have lifetimes in the range of about 100 ns to 1  $\mu\text{s}$  (first-order decay

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rate constant of the order of  $10^6 \text{ s}^{-1}$ ) whereas the phenoxyl radicals as mono molecular deprotonation products (2) exhibit second-order decay rate constants of the order of  $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [6,10]. The stability and reactivity of phenol radical cations were found to be affected by the nature (electron-donating or electron-withdrawing) and the size (sterically hindering) of substituent on the aromatic ring [9,10]. Furthermore, in solvents of rather low polarity like cyclohexane ( $E_T^N = 0.006$ ) and *n*-dodecane ( $E_T^N = 0.012$ ) ( $E_T^N$  denotes the empirical Reichardt's scale) [11] the decay (2) was found to have a constant value [6].

Consequently it would be interesting to characterize the influence of nucleophilic quenchers on the deprotonation of the phenol radical cations. The present work therefore involves the pulse radiolytic generation of phenol radical cations in a representative non-polar solvent like 1-chlorobutane (1), followed by a study of their decay induced by quenchers (Q) of increasing polarity ( $E_T^N$  values ranging from 0.164 to 0.654) such as 1,4-dioxane, cyclohexanone, acetone, dimethylsulphoxide, acetonitrile, cyclohexanol and ethanol. In this context, to the best of our knowledge, it is the first time that such a set of data has been obtained, especially because of the difficulty of generating and detecting metastable radical cations.

## 2. Methods

### 2.1. Pulse radiolysis

The liquid samples were irradiated with high energy electron pulses (1 MeV, 15 ns duration)

generated by a pulse transformer electron accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The dose delivered per pulse was measured with an electron dosimeter and was usually around 100 Gy. Detection of the transient species was carried out using an optical absorption technique, consisting of a pulsed xenon lamp (XBO 900, Osram), a Spectra Pro-500 monochromator (Acton Research Corporation), a R955 photomultiplier (Hamamatsu Photonics) and a 1 GHz digitizing oscilloscope (TDS 640, Tektronix). Further details of this equipment are given elsewhere [8].

The pulse radiolysis experiments of different phenols were performed in nitrogen-saturated solutions of 1-chlorobutane in the presence of small amounts of quenchers. The solutions were continuously passed through the sample cell with a path length of 1 cm.

### 2.2. Data analysis

The lifetimes  $\tau$  of the phenol radical cations (Tables 1 and 2) were obtained from simple pseudo-first-order exponential regression of the experimental time profiles.

The corresponding bimolecular rate constants  $k_{3a,b}$  for the deprotonation of phenol radical cations were obtained from the slope of a Stern-Volmer plot of lifetimes vs the concentration of the quencher.

### 2.3. Chemicals

All the phenols studied were commercially available. The solvents from Aldrich Sigma were

Table 1  
Lifetimes and quantum chemical data of the phenol radical cations in pure *n*-BuCl as solvent

Phenol radical cation	Lifetime [6] ( $\tau$ ) ns	S(O) <sup>a</sup> [10] DFT (BuCl)	$\Delta Q(\text{OH})^a$ [10] DFT (BuCl)	I.P. (adiabatic, vacuum) <sup>b</sup> eV (Lit. gas [12])
4-CN-ArOH <sup>+</sup>	110	0.204	0.204	8.50
ArOH <sup>+</sup>	270	0.201	0.213	8.01 (8.47)
4-Cl-ArOH <sup>+</sup>	330	0.189	0.203	7.97 (8.69)
4-MeO-ArOH <sup>+</sup>	340	0.153	0.176	7.13

<sup>a</sup> Atomic spin density at oxygen, S(O) and difference of Mulliken charges at the OH group between radical cation and singlet ground-state,  $\Delta Q(\text{OH})$  are calculated using Density Functional B3LYP/6-31G(d) Theory in BuCl [10].

<sup>b</sup> Adiabatic ionization potentials calculated in vacuum as the difference between electronic energies of the monomer radical cation and ground-state singlet.

Table 2

Bimolecular rate constants of 0.01 M phenol in *n*-BuCl in the presence of different quenchers

Quencher <sup>a,b</sup>	I.P. adiabatic vacuum <sup>c</sup> eV (Lit.) [13]	Polarity $E_T^N$ [11] <sup>d</sup> ( $\epsilon_T$ ) [13]	Rate constant ( $k_{3a,b}$ ) for deprotonation of phenol radical cation ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )			
			4-MeO-ArOH <sup>+</sup>	4-Cl-ArOH <sup>+</sup>	ArOH <sup>+</sup>	4-CN-ArOH <sup>+</sup>
1,4-Dioxane $q(\text{O}) = -0.47$ $\mu = 1.5$	8.53 (9.19)	0.164 (2.21)	$2.34 \times 10^6$	$2.19 \times 10^7$	$2.15 \times 10^7$	$9.50 \times 10^7$
<i>c</i> -Hexanone $q(\text{O}) = -0.46$ $\mu = 10.3$	8.45 (9.14)	0.281 (16.10)	$4.82 \times 10^6$	$4.92 \times 10^7$	$1.64 \times 10^9$	$9.63 \times 10^9$
Acetone $q(\text{O}) = -0.43$ $\mu = 9.0$	9.37 (9.71)	0.355 (20.56)	$2.76 \times 10^6$	$2.79 \times 10^7$	$1.52 \times 10^9$	$2.35 \times 10^{10}$
Dimethylsulphoxide $q(\text{O}) = -0.63$ $\mu = 13.5$	8.43 (9.01)	0.444 (46.45)	$7.01 \times 10^8$	$4.18 \times 10^{10}$	$1.25 \times 10^{10}$	$1.52 \times 10^{10}$
Acetonitrile $q(\text{N}) = -0.48$ $\mu = 11.8$	12.95 (12.19)	0.460 (35.94)	$5.32 \times 10^6$	$1.19 \times 10^8$	$3.67 \times 10^8$	$1.57 \times 10^{10}$
<i>c</i> -Hexanol $q(\text{O}) = -0.63$ , $q(\text{OH}) = -0.25$ $\mu = 6.2$	8.91	0.500 (15.0)	$1.23 \times 10^7$	$3.66 \times 10^9$	$2.98 \times 10^9$	$2.91 \times 10^{10}$
Ethanol $q(\text{O}) = -0.61$ $q(\text{OH}) = -0.22$ $\mu = 5.8$	10.05 (10.47)	0.654 (24.55)	$1.71 \times 10^7$	$2.37 \times 10^9$	$9.16 \times 10^{10}$	$1.94 \times 10^{10}$

<sup>a</sup>  $q(\text{O})$  or  $q(\text{N})$  is the atomic charge on heteroatom calculated using RB3LYP/6-31G(d) DFT [12].<sup>b</sup>  $\mu$  is the dipole moment in  $10^{-30} \text{ C m}$  [11].<sup>c</sup> Same as mentioned for Table 1 above.<sup>d</sup>  $E_T^N$  is the Reichardt scale polarity [12] and  $\epsilon_T$  is the dielectric constant [13].

of HPLC spectroscopy grade. All solvents were checked spectroscopically before use.

#### 2.4. Quantum chemical approach

Using the Density Functional Theory hybrid B3LYP [12] with 6-31G(d) basis set methods, geometrical and quantum chemical parameters of phenols like spin density on oxygen ( $S(\text{O})$ ) and difference of Mulliken charge between radical cation and singlet ground state ( $\Delta Q(\text{OH})$ ) were calculated for 1-chlorobutane by means of the GAUSSIAN 98 program (Table 1). The adiabatic ionization potentials in vacuum (I.P.) were calculated as the difference between electronic energies

of the monomer radical cation and ground-state singlet. These values were then compared with values in the literature [13]. The solvent effect was taken into account by employing the Onsager Self-Consistent Reaction Field model (SCRF = Dipole) [14,15]. The Mulliken atomic charges on the heteroatom ( $q(\text{O})$  or  $q(\text{N})$ ) for the quenchers were calculated using RB3LYP/6-31G(d) by DFT (Table 2).

### 3. Results

Pulse radiolysis of nitrogen saturated 0.01 mol  $\text{dm}^3$  solutions of *para*-substituted ( $-\text{H}$ ,  $-\text{Cl}$ ,  $-\text{MeO}$ ,

–CN) phenols was done in the primary solvent 1-chlorobutane. The transient optical absorption spectra showed complete electron transfer (1) from phenols to the solvent radical cations within 30 ns (e.g. for 4-chlorophenol, inset (i) of Fig. 1). This yielded in a rapid manner phenol radical cations, identified as absorbing at 460 nm and characterized as mentioned in details elsewhere [6]. They were found to decay by monomolecular deprotonation (2) having lifetimes between 100 and 350 ns (Table 1) [6].

Upon addition of a quencher (Q), the lifetime ( $\tau$ ) of the phenol radical cation decreased with increasing concentration of the quencher ( $10^{-5}$ – $10^{-2}$  mol dm $^{-3}$ ). The observed rate constants ( $k_{\text{obs}} = 1/\tau$ ) when plotted against the concentration of the quencher ( $[Q]$ ) yielded a straight line having a slope equal to the bimolecular rate constant ( $k_{3a,b}$ ) of the decay reaction (3a) and (3b). This is obvious from the time profiles of the radical cations of 4-Cl-ArOH in the presence of ethanol (EtOH) (Fig. 1) and from the Stern-Volmer plot

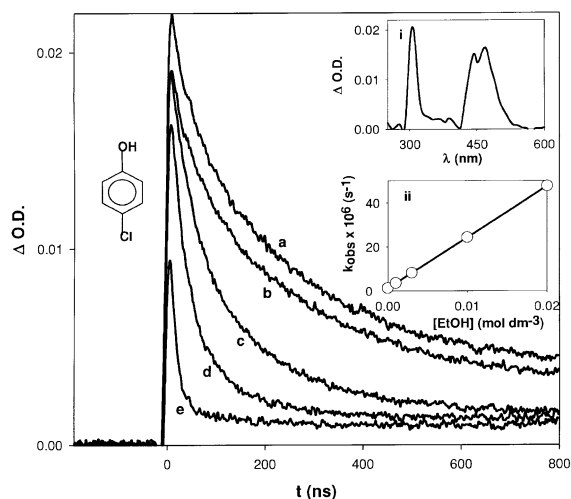


Fig. 1. Time profiles of 4-chlorophenol radical cations (4-ClArOH $^{\cdot+}$  at 460 nm) generated by pulse radiolysis in nitrogen saturated *n*-chlorobutane (a) and in samples containing in addition  $1 \times 10^{-3}$  mol dm $^{-3}$  (b);  $3 \times 10^{-3}$  mol dm $^{-3}$  (c);  $1 \times 10^{-2}$  mol dm $^{-3}$  (d) and  $2 \times 10^{-2}$  mol dm $^{-3}$  (e) ethanol. The inset (i) is the absorption spectrum of 4-ClArOH radical cations obtained by pulse radiolysis of 4-chlorophenol in *n*-chlorobutane. The inset (ii) is the Stern–Volmer plot of observed rate constant ( $k_{\text{obs}}$ ) against concentration of ethanol [EtOH].

(inset (ii)). The observation was found to be a general behavior for all the studied phenols in the presence of all quenchers mentioned here, with the difference being in the quenching efficiency (Table 2). It is evident that as the polarity of Q increases (from 1,4-dioxane to ethanol) there is a marked general trend of increasing rate constants (Table 2 and log  $k_{3a,b}$  values as shown in Fig. 2).

#### 4. Discussion

The polarity of the quenchers (Q) can be gauged by a number of parameters like empirical Reichardt scale ( $E_T^N$ ) [11], dielectric constant ( $\epsilon_T$ ) [13], Mulliken atomic charge ( $q(O)$  or  $q(N)$ ) [12], dipole moment ( $\mu$ ), etc. (Table 2). The Mulliken atomic charge gave information about the electron density around the heteroatom considered, and hence reflected the nucleophilicity of the quencher. The plots of log  $k_{3a,b}$  vs dielectric constant and vs dipole moments were similar to each other as

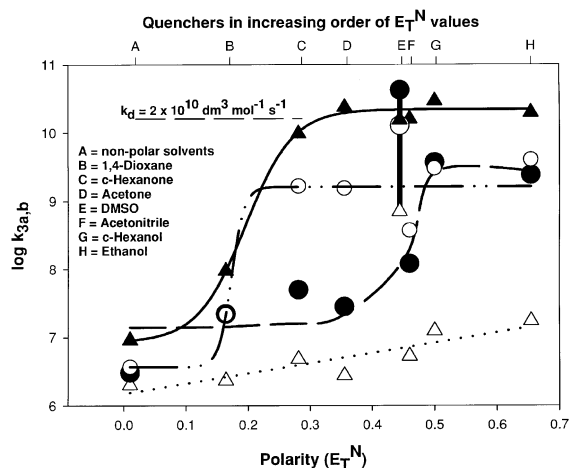
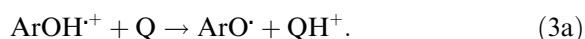


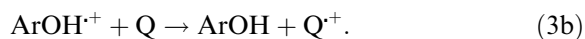
Fig. 2. Variation of bimolecular rate constant ( $k_{3a,b}$ ) for deprotonation of radical cations of ( $\cdots \Delta \cdots$ ) 4-MeO-ArOH, ( $-\cdots \bullet -\cdots$ ) 4-Cl-ArOH, ( $-\cdots \circ -\cdots$ ) 4-ArOH and ( $-\blacktriangle -$ ) 4-CN-ArOH, with polarity ( $E_T^N$ ) of quenchers. The horizontal dashed line on the top represents the value of the diffusion-controlled rate constant for the deprotonation of the phenol radical cations in non-polar solvents. The vertical thick solid line connects the points for the bimolecular rate constants for the deprotonation of phenol radical cations in the presence of DMSO as quencher.

expected. The analyses were done using all these parameters and compared. While there was no simple correlation between these different factors, the  $E_T^N$  however gave the best results.

The increase in the bimolecular rate constants for the deprotonation of the phenol radical cations with increasing quencher polarity can be explained by an increase in nucleophilicity of Q (3a). Thus the nucleophile approaches the phenol radical cation in the direction of the highest charge density localized on the phenolic oxygen atom. As a consequence, the phenol radical cation then undergoes deprotonation to form a phenoxyl radical (3a).



It is evident that while for 4-MeO-ArOH the rate constant increases in a linear proportion with polarity, in the case of 4-CN-ArOH it becomes sigmoidal and saturates at near diffusion-controlled reaction rates (curve fits shown in Fig. 2). The linear relation between reaction rate and polarity signifies the nucleophilic reaction of the quencher (3a). Therefore the deviation from linearity suggests competition by electron transfer from the quencher (3b).



In the case of 4-chlorophenol, there is a linear relation up to acetonitrile ( $E_T^N = 0.460$ ), while in the case of phenol and 4-cyanophenol the deviation from linearity begins from 1,4-dioxane ( $E_T^N = 0.164$ ) itself, indicating that in the latter two phenols the deprotonation of the phenol radical cations is by a combination of two reaction pathways, (3a) and (3b). Furthermore, it is obvious that for any particular quencher (Q), the rate constant  $k_{3a,b}$  varies with the kind of phenol. Thus  $k_{3a,b}$  is the highest for 4-CN-ArOH and least for 4-MeO-ArOH implying that it depends on the kind of *para*-substituent, which can be explained by the electronic stabilization factors of the substituents. Hence, the methoxy (electron-donating character) group is stabilizing the radical cation on the phenol to the maximum extent while the cyano (electron-withdrawing character) group causes the opposite. This could be well understood in terms of charge difference

( $\Delta Q$ ) and can also be correlated with the spin density on oxygen ( $S(O)$ ) values of the phenol radical cations [6,10]. Thus the high positive charge character on the oxygen atom in the case of 4-CN-ArOH<sup>+</sup> as compared to the ground state makes it easier for the deprotonation reaction to occur. Besides, 4-cyanophenol has a higher IP value than the other phenols (Table 1) so in the presence of some quenchers like 1,4-dioxane, *c*-Hexanone and DMSO (having comparative I.P. values), electron transfer reaction (3b) is highly possible. This is reflected in the high values of  $k_{3a,b}$ .

The exceptional behaviour of DMSO can be explained in two ways, firstly by considering the difference in the adiabatic ionization potentials (I.P.) between the quencher and the phenol radical cations (Tables 2 and 1 respectively). Here it should be mentioned that our calculated I.P. values (estimated as the difference between the electronic energies of the monomer radical cation in the relaxed state and the ground singlet state) for phenol radical cations were found to correspond reasonably well with those reported in the literature, in particular looking at the general trend [12]. Besides, it should also be noted that for the solvents the I.P. values are determined in the ground state. Hence these values are taken not in the absolute sense but more as relative values for comparison.

Here it is obvious that DMSO has the lowest I.P. value. This implies that besides the nucleophilic reaction (3a), there is also the further possibility of a competing electron transfer from DMSO (3b). This could explain the nearly diffusion-controlled rate constants  $k_{3a,b}$  in the presence of DMSO for all phenols. While it is known that in chlorinated hydrocarbons, there is a possible interaction between DMSO and chloride anions, this can be ruled out in the present work, in the face of competition from the higher concentration of phenols [16,17]. On the other hand, cyclohexanone with a similar I.P. value behaves differently. This difference might be explained by noting the high electron density ( $q(O)$ ) for DMSO (Table 2) localized on oxygen which causes a pronounced localization of negative charge in the molecule, making it a better nucleophile than cyclohexanone.

## 5. Conclusions

In this Letter, as a new case we present reactivity data of metastable phenol radical cations which describe well their deprotonation and its dependence on the polarity and therefore also nucleophilicity of the surroundings. These data demonstrate well the validity of electronic effects and furthermore, enable extrapolation also to aqueous systems. Hence from our measurements the lifetime of the phenol radical cations in neutral water might be estimated to be in between a few picoseconds and some microseconds, which seem to be in agreement with the EPR measurements in extremely acidic media [18–21]. The present work could therefore be generalized as a method for characterizing metastable radical cations even under polar conditions.

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