Persistent radical cation solutions from the reaction between aromatics and bromine, chlorine or iodine chloride in 1,1,1,3,3,3-hexafluoropropan-2-ol at room temperature

Lennart Eberson,*[a]† Michael P. Hartshorn,[b] Finn Radner[a] and Ola Persson[a]

[a] *Chemical Center, Lund University, PO Box 124, S-221 00 Lund, Sweden*
[b] *Department of Chemistry, University of Canterbury, Christchurch, New Zealand*

The treatment of reactive aromatic compounds by bromine, chlorine or iodine chloride in 1,1,1,3,3,3-hexafluoropropan-2-ol gives persistent solutions of the corresponding radical cations, in spite of the fact that a nucleophile, a chloride or bromide ion, is simultaneously generated.

Persistent solutions of radical cations can be prepared by thallium(III) oxidation in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), $\tau_{1/2}$ being 10^2 times longer than in trifluoroacetic acid.[1] A contributing factor to this effect appears to be a drastic decrease in the radical cation–nucleophile rate constants.[2] Thus the bromide and chloride ions reacted with tris(4-bromophenyl)aminium ion in HFP at 20 °C with rate constants about 10^8 times slower than those obtained in acetonitrile. Carbocations are also kinetically stabilized in HFP.[3]

The fact that bromine and chlorine can act as 1e$^-$ oxidants towards easily oxidizable ArH and give radical cations of some persistence in solution or as solid salts is indicated by previous studies.[4] Recently the reactions of ICl with aromatic compounds were studied in acetonitrile[5] or dichloromethane[6] and it was suggested that the competing chlorination–iodination pathways depended on an electron transfer mechanism [eqns. (1)–(3)]. In a few cases, 1,4- **1** and 1,2-dimethoxybenzene **2** and

$$\mathrm{ArH} + \mathrm{ICl} \rightarrow \mathrm{ArH}^{\bullet+} + \mathrm{I}^{\bullet} + \mathrm{Cl}^- \tag{1}$$

$$\mathrm{ArH}^{\bullet+} + \mathrm{Cl}^- \rightarrow\rightarrow \mathrm{Ar{-}Cl} \tag{2}$$

$$\mathrm{ArH}^{\bullet+} + \mathrm{I}^{\bullet}\ (\text{or } \mathrm{I}_2) \rightarrow\rightarrow \mathrm{Ar{-}I} \tag{3}$$

1,4-dimethoxy-2,5-dimethylbenzene **3**, it was possible to demonstrate[6] the formation of ArH$^{\bullet+}$ by UV spectral observations in dichloromethane at −78 °C; by addition of a chloride ion source, the radical cation immediately disappeared. In view of the strong attenuation of nucleophile reactivity in HFP,[2] we

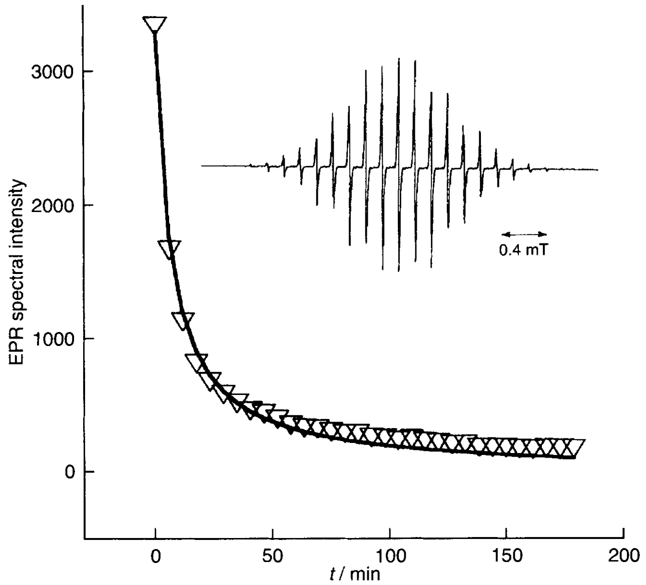

Fig. 1 Decay of the EPR spectrum (inset) of **4**$^{\bullet+}$, obtained by adding bromine to an excess of **4** in HFP. The solid curve is the best fit to the data, using the expression $1/Int - 1/Int_0 = kt$ with $k = 7.7 \times 10^{-7}$ Int^{-1} s^{-1}.

Table 1 Radical cations from ArH and ICl, Br_2 or Cl_2 in HFP at 22 °C

ArH	$E°(\mathrm{ArH}^{\bullet+}/\mathrm{ArH})$/V[c]	EPR spectrum[a] ($\tau_{1/2}$/min[b]) with ICl	Br$_2$	Cl$_2$
4,4′-Di-*tert*-butylbiphenyl	1.69	m	none	—
1,4-Dimethylnaphthalene	1.63	none	—	—
1,4-Dimethoxybenzene **1**	1.50	vs (36[d])	none	none
1-Methoxynaphthalene	1.47	s[e] (26)	none	—
2,2′-Dimethoxy-5,5′-dimethylbiphenyl	1.46	s (14)	none	—
Anthracene	1.41	w (< 1)	none	—
3,3′,4,4′-Tetramethyl-1,1′-binaphthalene	1.40	s (3)	m	—
1,4,5,8-Tetramethylnaphthalene	1.32	s (6.5)	vw	none
1,4-Dimethoxy-2,5-di-*tert*-butylbenzene	1.03	s (141[f])	m (> 2000)	—
1,4-Dimethoxy-2-methylbenzene	1.29[g]	s (49)	m	s (175)
1,4-Dimethoxy-2,3-dimethylbenzene **4**	1.22[g]	vs (1600)	vs (16[h])	s (29)
1,4-Dimethoxy-2,5-dimethylbenzene **3**	1.13[g]	vs	vs (> 5000)	—
9,10-Dimethylanthracene	1.11	vs (250)	s (50)	vs
Perylene	1.10	vs(> 5000)	—	vs (1340)

[a] vs = very strong, s = strong, m = medium, w = weak vw = very weak. [b] The quantity $\tau_{1/2}$ was calculated from the first-order kinetic expression, which is an approximation for the ArH$^{\bullet+}$-halide ion reaction. However, since the reactions were run under closely similar concentrations, $\tau_{1/2}$ provides a crude indication of the persistence of the solutions. [c] Versus the Ag/AgCl electrode. [d] In CH_2Cl_2, < 1 min. [e] The dehydrodimer radical cation, Ar–Ar$^{\bullet+}$, was formed. [f] In CH_2Cl_2 = *ca.* 10 min. [g] From ref. 6. [h] In the presence of 4.0 mmol dm^{-3} Bu_4NBr.

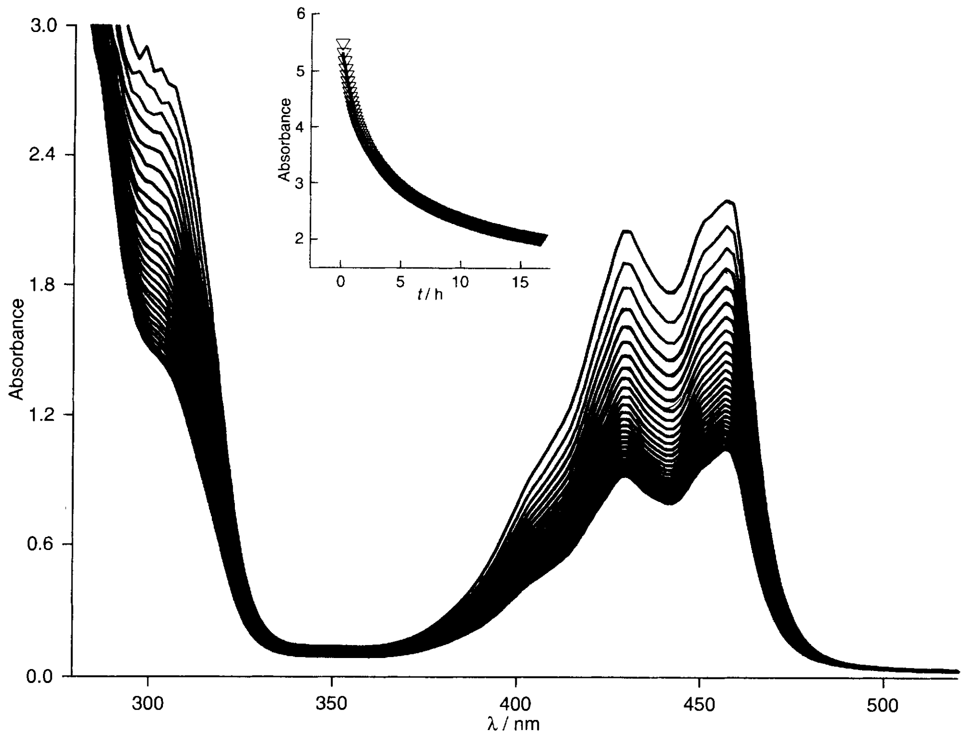

Fig. 2 UV spectra at 5 min intervals of a solution of $4^{\cdot +}$, obtained by the addition of bromine to an excess of **4** in HFP. The inset shows a kinetics trace (separate run) from the reaction; the curve represents the best fit to the expression $1/Abs - 1/Abs_0 = kt$ with $k = 2.8 \times 10^{-5}$ A^{-1} s^{-1}.

anticipated that this solvent would facilitate studies of the possible electron transfer nature of a wide variety of aromatic halogenations under conveniently accessible experimental conditions.

As shown in Table 1, the appearance of strong EPR spectra of radical cations from the reaction of ICl with suitable ArH in HFP could be monitored at room temperature. The upper limit of $E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH})$ lies around 1.6 V *vs.* Ag/AgCl, but can probably be extended upwards in case of sterically demanding substrates. In spite of the fact that chloride ion is co-generated with the radical cation, its persistence was sufficient for EPR and UV spectral monitoring; $\tau_{1/2}$ after ICl generation was decreased by about two orders of magnitude compared to the situation when 4-tolylthallium bis(trifluoroacetate) was used as the oxidant.[1]

Moreover, bromine or chlorine could also be used as $1e^-$ oxidants in HFP for ArH with $E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH}) \leq 1.4$ V giving radical cation solutions which could be monitored conveniently at room temperature (Table 1). Fig. 1 shows as an example the EPR spectral behaviour of 1,4-dimethoxy-2,3-dimethylbenzene **4** upon reaction with bromine in HFP at 22 °C. The preparative result of this reaction was the formation of 5-bromo-1,4-dimethoxy-2,3-dimethylbenzene in 92% yield (GLC). The EPR spectrum of $4^{\cdot +}$, with hfs constants in agreement with published values,[7] appeared very strongly immediately after mixing the reagents and decayed according to the second-order expression $1/x - 1/x_0 = kt$ with $k = 7.7 \times 10^{-7}$ Int^{-1} s^{-1} (Int = EPR spectral intensity). Similarly, the decay was monitored by UV spectroscopy (Fig. 2), resulting in $k = 2.8 \times 10^{-5}$ A^{-1} s^{-1} (A = absorbancy at 456 nm). The UV spectrum was very similar to that obtained for compounds **1** or **3** in dichloromethane at −78 °C.[6] Assuming that the extinction coefficient was the same in HFP as in dichloromethane, 8500 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ (ref. 6), k for the reaction between $\mathrm{ArH}^{\cdot +}$ and Br^- is 0.18(4) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$. With excess tetrabutylammonium bromide ion present, the reaction obeyed pseudo-first-order kinetics and a second-order rate constant of 0.17(1) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ was obtained.

The reaction between 1,4-dimethoxy-2,5-dimethylbenzene **3** and bromine behaved in the same way, the second-order rate constant being smaller, 0.0057(5) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ (UV spectroscopy). This might be as the ring positions in **3** are sterically more hindered than those in **4**.

Financial support (L. E.) from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation is gratefully acknowledged.

Footnote

† E-mail: Lennart.Eberson@maxkemi.lu.se

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Received, 2nd October 1995; Com. 5I06467H