Two Fragmentation Pathways of Radical Reduced Transients of Aryltrimethylammonium Cations in Water. Photoelectron Injection Study

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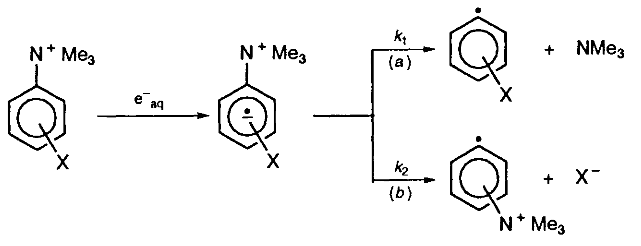
The decay rates of radical reduced transients (RRTs) of aryltrimethylammonium cations (5×10^3–2.5×10^8 s^{-1}) and the reduction potentials of RRT decay products $E_{\frac{1}{2}} = -(1.06–1.47)$ V (*vs.* SCE) have been determined in water using photoelectron injection.

The study of elementary transformations of the radical reduced transients (RRTs) of substituted aromatic molecules is interesting because of their key role as intermediates in different reactions.[1–6] Of particular importance are the aryltrimethylammonium (ATMA) cations, the one-electron reductions of which produce neutral radicals. The intermediate can decompose either to form the aryl radical and trimethylamine, or to eliminate the halide ion (Scheme 1).[3]



Scheme 1

Since an unpaired electron is assumed to locate mainly on the benzene ring, these radicals can be considered to be of the zwitterionic type.[7] The possibility of fragmentation through the pathway [Scheme 1(*a*)] allows ATMA cations to be used as model reagents in the reactions with radical anions of arenes to determine the factors that rule the competition between the S$_N$ and ET pathways.[7] However, the fragmentation pathway [Scheme 1(*b*)] must be taken into account, at least for bromine and iodine substituted cations in aprotic solutions.[3]

In this communication, we report on the decay rates of short-lived electron adducts for the aryltrimethylammonium $XC_6H_4N^+Me_3$ (**1a–m**) and 1-naphthyltrimethylammonium (**2**) salts, taken as perchlorates in aqueous solutions. Furthermore, the reduction potentials have been measured for the decay products which presumably could be either the corresponding aryl radicals or their mercury adducts.[8] For this purpose the technique of pulsed laser photoelectron injection from metal into electrolyte solution (PIMES),[1,9–11] has been employed. In PIMES experiments, the reduced transient arises from the scavenging of solvated electrons generated in the solution bulk by a relevant solute. Recently, PIMES has been used to determine the decay rates ($k_c = k_1 + k_2$) of the short-lived radical anions (10^4–10^9 s^{-1}) as well as to record the time-resolved photopolarograms of the decay products of radical anions of halobenzoic acids.[1,2]

The measurements were carried out in 0.5 mol dm^{-3} aq KCl, pH = 6–7 (+KOH), 22 °C, using a replaceable fixed mercury electrode in a pulsed laser photoelectrochemical set-up (described in detail earlier[1,10,11]). Pulsed nitrogen (337 nm) and XeF (351 nm) lasers were used. At laser wavelengths, the light absorbance was negligibly small for all of the solution phase species. (The light path in solution was 0.1–0.2 mm; the compound concentrations were varied up to 1–10 mmol dm^{-3} depending on solubility; the extinction coefficients of compounds at the wavelength used were no more than 10.) The intensity of incident light was reduced to 30–50 kW cm^{-2} and the magnitude of the transient electrode photopotential U(t) was less than 1–2 mV. Under pulse illumination, U(t) arises due to the intensity of incident light and was reduced to 30–50 kW cm^{-2} and the magnitude of the transient electrode photopotential U(t) was less than 1–2 mV. Under pulse illumination, U(t) arises due to the charging of the double layer capacity C with the photocharge Q(t) and then decays upon discharging through external resistor R.[1,10] For rather long delay times ($t > 10$ μs) the residual photocharge $Q_\infty = Q(t \to \infty)$ was recorded as the area under the exponential U(t) decay: $U(t) = Q_\infty/C \exp(-t/RC)$. The decay rate k_c was determined from the dependence of the residual charge Q_∞ on the scavenger concentration N_a which can be obtained from eqn. (1) (for the

$$\frac{Q_{\text{lim}}}{2Q_0} = 1 - \exp(-x_1/l_a); \quad Q_{\text{lim}} = Q_\infty(N_a)_{N_a \to \infty} \qquad (1)$$

oxidation of RRT on the photoelectrode).[1] Here Q_0 is the full photoinjected charge; x_1 is the mean distance between e^-_{aq} and the photoelectrode plane; $l_a = (D_a/k_c)^{\frac{1}{2}}$; D_a is the RRT diffusion coefficient taken for all transients as equal to its value for toluene, $D_a = 8 \times 10^{-6}$ cm^2 s^{-1}.[12] The dependences of $Q_0(E)$ and $x_1(E)$ on electrode potential E have been determined earlier, using N$_2$O as the scavenger whose radical anion has a very short lifetime ($k_c \geqslant 5 \times 10^9$ s^{-1}).[10] The procedure used to obtain photopolarograms $v(E) = Q_\infty(E)/Q_0(E)$ and to determine k_c is similar to that described in ref. 1.† A check measurement when the delay times were varied from 0.01 to 1 ms and the laser was used at 427 nm found no differences in K_c and $v(E)$.

The decay rates k_c are listed in Table 1. The k_c value substantially depends on the nature of the substituent and its position in the ring and varies in the range of more than four orders of magnitude. A fair agreement between the k_c values as well as the rate constant of the reaction with hydrated electron obtained for **1h** by PIMES and pulse radiolysis techniques,‡ confirms the reliability of the former method and that this one really studies adducts of hydrated electron attachment.

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† We also recorded the modulated stationary photocurrents (pulsed nitrogen laser) using a high-quality filter tuned to the repetition frequency (370 Hz) of a laser. This variant of measurements yielded the same results as the pulsed measurements.

‡ V. V. Konovalov and O. Brede, pulse radiolysis set-up of the Central Institute of Radiation Research, Leipzig.

Table 1 Decay rates (k_c) of the product of $XC_6H_4N^+Me_3$ salts reduced by e^-_{aq}

	X	k_c/s^{-1}	$-E^{CV\,a}_{\frac{1}{2}}$/V (*vs.* SCE)
1a	H	$(4 \pm 1) \times 10^6$	2.56
1b	3-F	$(1.4 \pm 0.5) \times 10^7$	—
1c	3-Cl	$(1.5 \pm 0.5) \times 10^8$	2.16
1d	3-Br	$(2.5 \pm 1) \times 10^8$	2.02 (2.61)
1e	3-Me	$(7 \pm 2) \times 10^6$	2.65
1f	3-OMe	$(1 \pm 0.4) \times 10^7$	2.59
1g	3-CO_2Me	$\leqslant 5 \times 10^3$	1.94
1h	4-Ph	$(1.3 \pm 0.4) \times 10^{5\,b}$	2.34
1i	4-Cl	$(1 \pm 0.3) \times 10^7$	—
1j	4-Br	$(1.5 \pm 0.7) \times 10^8$	2.06 (2.58)
1k	4-Me	$(1.5 \pm 0.5) \times 10^7$	2.66
1l	4-OMe	$(2.3 \pm 1) \times 10^7$	2.72
1m	4-CO_2Me	$(2.5 \pm 1) \times 10^5$	—
2	$C_{10}H_7N^+Me_3$	$(3.3 \pm 0.7) \times 10^5$	2.00

[a] Half-wave reduction potential in DMF[13] (half-wave reduction potentials, $E_{\frac{1}{2}}$, of RRT decay products). [b] $1.5 \pm 0.2 \times 10^5$; V. V. Konovalov and O. Brede, pulse radiolysis set-up of the Central Institute of Radiation Research, Leipzig.

We have also obtained the photopolarograms of the RRT decay products, $\nu(E)$.* Some of the $\nu(E)$ curves are depicted in Fig. 1. It appeared that $\nu(E)$ values recorded at fairly long delay times after the laser pulse ($t \geqslant 1$ ms) coincide for the same isomers of bromo- and chloro-derivatives (**1c**, **d**, **i**, **j**). At the same time, the values observed for the unsubstituted salt **1a** and compounds with X = 3,4-Me, 3,4-OMe or 4-CO_2Me (**1e–g**, **k**, **l**) are quite different from those for the halogen derivatives, but close to each other. Such a difference in the photopolarograms of the decay products is believed to be important evidence for the two different fragmentation reactions of the primary reduced form. Then, it is assumed that for the bromo- and chloro-derivatives, Scheme 1(*b*) is realized with the expulsion of a halide anion, whereas Scheme 1(*a*) is realized for other salts. The intermediate character of $\nu(E)$ for a fluorine substituted salt (**1b**) is likely to point out that the rates of decay *via* the two reaction pathways are comparable to each other. The reduction potentials of decay products are: $E_{\frac{1}{2}} = -1.06$ (**1c**, **d**, **i**, **j**); -1.35 ± 0.05 (**1e–g**, **k**, **l**); -1.4 ± 0.05 (**1h**); and -1.47 ± 0.05 V (*vs.* SCE) (**1n**). The shift of $E_{\frac{1}{2}}$ corresponds well to the anticipated change in the radical electron affinity due to a substituent or lateral ring.

The indications that for bromo-derivatives **1d**, **j** the fragmentation of reduced forms involves the expulsion of bromide anion have been obtained by cyclic voltammetry in dimethylformamide (DMF) solutions.[13] Two reduction waves [$E^{cv}_{\frac{1}{2}} = -2.06/-2.58$ V (**1j**) and $-2.02/2.58$ V (**1d**)] have been observed for each of them. Since the potential of the second wave is the same for both of the substances, and coincides with that of the nonsubstituted salt **1a**, this wave is assumed to correspond to the reduction of the dehalogenated salt. At the same time, for chlorine the substituted salt **1c** most probably no dehalogenation occurs in aprotic solvents because only one reduction wave (-2.16 V) is observed. The reduction of **1c** by the benzophenone radical anion in tetrahydrofuran solution leads to chlorobenzene formation,[13] *i.e.* the C–N bond scission rather than C–Cl is evidently favourable in aprotic solution. A possible reason for the change in the decay direction of chlorine substituted RRT on going from DMF to aqueous solution is that an increase in the solvent polarity favours the formation of two ions *via* Scheme 1(*b*) instead of the formation of two neutral species *via* Scheme 1(*a*).

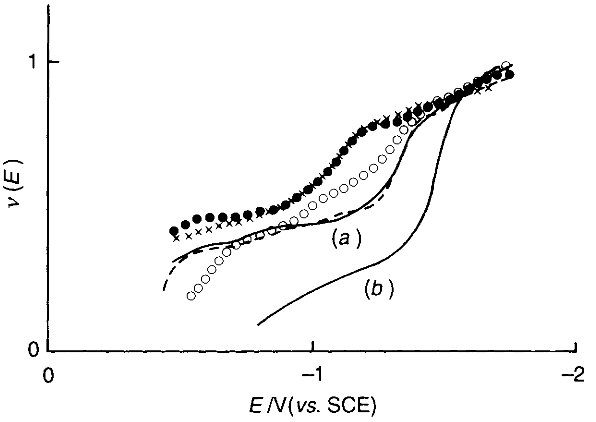

Fig. 1 Transient photopolarograms $\nu(E)$ of the decay products of the reduced transients in 0.5 mol dm^{-3} KCl + H_2O. Laser wavelength, 337 nm; delay time, 1 ms. (●), **1i**; (×), **1d**; (○), **1b**; (– – –), **1e**; (*a*), **1a**; (*b*), **1h**.

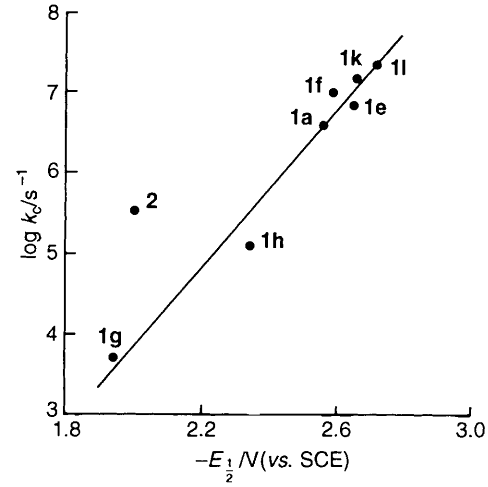

Fig. 2 Dependence of the decay rates (k_c) in water on the reduction half-wave potentials of salts in DMF, $E^{cv}_{\frac{1}{2}}$[13]

For the radical anions of substituted aromatic compounds, log k_c is known to be linearly proportional to the standard reduction potential E_0 of the parent molecule which is related to the energy of the lower non-occupied π^*-orbital.[13,14] The data in Fig. 2 indicate a fair agreement between $E^{cv}_{\frac{1}{2}}$,† and log k_c for salts **1a**, **e–g**, **k**, **l** except for halide derivatives for which k_c is substantially higher than is expected from the $E^{cv}_{\frac{1}{2}}$ values. This divergence testifies once again in favour of the above conclusion that quite another fragmentation pathway occurs for Cl and Br-compounds.

In conclusion the data obtained demonstrate that the trimethylammonium group can be expelled in much the same manner as a chlorine atom. This promises that a wide range of such compounds will be involved both as substrates in the reactions of nucleophilic substitution of the $S_{RN}1$ type and as the model reagents in the study of the competition between S_N and ET mechanisms.[7,13]

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* $\nu(E)$ is proportional to the electron transfer number of photoelectrochemical processes, depending on the competition of reduction and oxidation electrode reactions.[1,9]

† In the first approximation E_0 is close to the half-wave potential $E^{cv}_{\frac{1}{2}}$.[9]

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Paper 3/02136J
Received 14*th April* 1993
Accepted 20*th August* 1993