Radical Cations from Alkyl Iodides in Aqueous Solution

Hari Mohan and Klaus-Dieter Asmus *
Hahn-Meitner-Institut Berlin GmbH, Bereich Strahlenchemie, Glienicker Str. 100, 1000 Berlin 39, Federal Republic of Germany

Radical cations $RI^{+\cdot}$ and $(RI.{}^{\cdot}.IR)^+$ are generated upon $^{\cdot}OH$ radical-induced oxidation of alkyl iodides in acidic (pH < 4.5) aqueous solution. Their formation requires the reaction of protons with an intermediate $^{\cdot}OH$-adduct. Although alkyl iodide radical cations have been reported to exist in a solid, low-temperature matrix, they have so far not been detected in the liquid, particularly the aqueous phase. Both radical cations establish an equilibrium: $RI^{+\cdot} + RI \rightleftharpoons (RI.{}^{\cdot}.IR)^+$. For R = Me the stability constant of the 2σ–$1\sigma^*$ three-electron-bonded species has been estimated to $K \geqslant 5 \times 10^4$ mol^{-1} dm^3. $(RI.{}^{\cdot}.IR)^+$ exhibits a strong optical absorption band in the visible; $\lambda_{max.}$ is red-shifted with increasing electron-releasing power of R and ranges from 415 nm (R = Me) to 470 nm (R = s-C_4H_9). The molecular radical cation absorbs in a comparatively much narrower range from 310—320 nm. It is suggested that it exists as $(RI.{}^{\cdot}.OH_2)^+$, *i.e.* as an associate with one water molecule. The alkyl iodide radical cations are strong oxidants. $(MeI.{}^{\cdot}.IMe)^+$, for example, oxidizes I^- and Me_2S with rate constant values of 7.7×10^9 mol^{-1} dm^3 s^{-1} and 3.6×10^9 mol^{-1} dm^3 s^{-1}, respectively.

One-electron oxidation of organic molecules, M, leads not only to the respective molecular radical cations, $M^{+\cdot}$, but often a dimer radical cation complex, $M_2{}^{+\cdot}$, which can be stabilized. This is particularly true for aromatic systems and substrates which carry hetero functions such as sulphur, nitrogen, and other group V—VIII elements. The electronic structure of $M_2{}^{+\cdot}$ depends, however, on the actual nature of M and may vary significantly. $M_2{}^{+\cdot}$ Derived from aromatic compounds and observed in solid and liquid non-aqueous matrices generally constitutes a π-radical system.[1–5] The corresponding species from the heteroatom compounds, on the other hand, are most often characterized by a 2σ–$1\sigma^*$ three-electron bond, *i.e.* a bond which consists of two bonding and one antibonding electron between the two hetero atoms.

Experimental evidence for these radical species has been provided mainly by e.s.r., and by time-resolved techniques such as laser photolysis and pulse radiolysis. The latter are based on the fact that most of the $M_2{}^{+\cdot}$ species exhibit characteristic and strong optical absorptions, most often in the visible.[1–15]

Among the 2σ–$1\sigma^*$ radical species the $(R_2S.{}^{\cdot}.SR_2)^+$ are probably the most extensively investigated radical cations.[6–13] They are formed as intermediates during the oxidation of organic sulphides and have been found to be relatively long-lived not only in a low-temperature matrix but also in solution at room temperature (lifetimes of up to ms in aqueous solution, for example). Many other examples for such three-electron bonds in overall cationic, neutral, and anionic radical species, between two identical or different heteroatoms, and generated *via* inter- as well as intra-molecular association of two heterocentres, have in the meantime been described.[14–21] A particular group of dimer radical cations which is expected to exhibit a reasonable degree of stability are $(RI.{}^{\cdot}.IR)^+$. Such species have been claimed as transients in irradiated solid, low-temperature (77 K) matrices on the basis of e.s.r.,[22] and optical measurements[23] as well as in mass spectrometry.[24] In room-temperature solutions, however, no evidence could be produced so far for $(RI.{}^{\cdot}.IR)^+$ radical cations.[25–27] In fact, the results and conclusions drawn from the few studies on the $^{\cdot}OH$ radical-induced oxidation of alkyl iodides in aqueous and cyclohexane solutions are partially conflicting, and, furthermore, discussion has been limited to neutral radical species such as $RI(OH)^{\cdot}$ and $RI_2{}^{\cdot}$.

In the present study we are now able to identify the conditions under which $(RI.{}^{\cdot}.IR)^+$ and $RI^{+\cdot}$ radical cations can be generated and the main physical and chemical characteristics of these species.

Experimental

Investigations were carried out with aqueous solutions of alkyl iodides. The solvent was deionized, 'Millipore' filtered water. The alkyl iodides were generally obtained from Aldrich Chemical Co. Their purity was checked by gas chromatography. If necessary they were further purified by vacuum distillation or chromatographic methods to at least 99%. All other chemicals were of purest grade commercially available and used as received. Solutions were prepared by addition of appropriate amounts of alkyl iodides into deaerated water through a gas-tight septum and dissolution by aid of magnetic stirring.

To eliminate oxygen from the solutions nitrogen was bubbled through for *ca.* 1 h dm^{-3} solution. If the alkyl iodide oxidation or any other reaction was to be initiated by hydroxyl radicals the deoxygenated solutions were further saturated with N_2O (prior to the RI addition). This gas converts hydrated electrons—which are formed in about equal yield as $^{\cdot}OH$ in irradiated aqueous solutions as primary species—into hydroxyl radicals *via* $N_2O + e^-_{aq} \longrightarrow N_2 + OH^- + {}^{\cdot}OH$. As a result it becomes possible to study reactions of the $^{\cdot}OH$ radical selectively.

Irradiations were carried out by means of pulse radiolysis. The characteristic features of this radiation chemical technique have been described elsewhere.[28] The radical species are generated by short pulses of high-energy electrons from an accelerator. Pulse lengths were typically in the order of 1 µs, and absorbed doses per pulse amounted to 1—2 Gy (J kg^{-1}). In the N_2O-saturated solutions this corresponds to a yield of $^{\cdot}OH$ radicals in the order of 10^{-6} mol dm^{-3}, or $G = 6$ (species per 100 eV absorbed energy) in radiation chemical terminology.

Detection of the radicals was achieved by time-resolved optical and conductivity measurements. Dosimetry was based on the formation of $(SCN)_2{}^{-\cdot}$ radical anions in N_2O-saturated solutions of 10^{-3} mol dm^{-3} KSCN. The extinction coefficient of $(SCN)_2{}^{-\cdot}$ at 500 nm was taken to 7 200 mol^{-1} dm^3 cm^{-1}, and the equivalent conductance of an $(SCN)_2{}^{-\cdot}/H^+_{aq.}$ ion-pair to $\Delta\Delta$ =

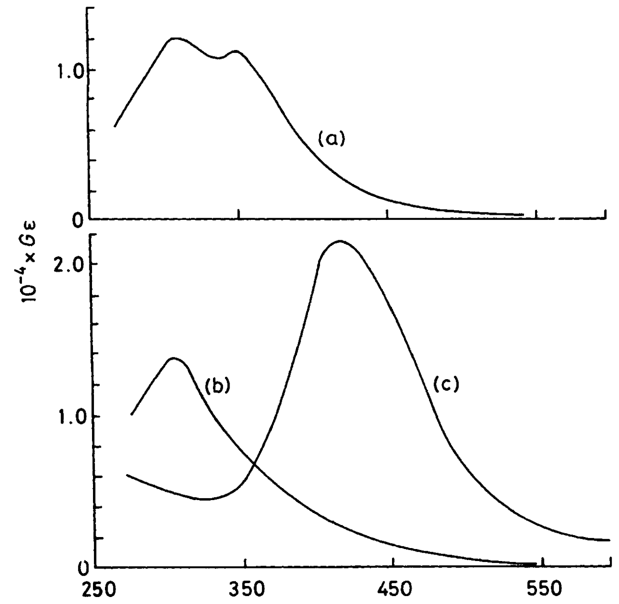

Figure 1. Transient absorption spectrum recorded immediately after a 1 µs pulse irradiation of an N_2O-saturated aqueous solution of: (a) MeI (10^{-3} mol dm^{-3}) at pH 5.7; (b) MeI (10^{-4} mol dm^{-3}) at pH 3.5; (c) MeI (8×10^{-3} mol dm^{-3}) at pH 3.5

$360\ \Omega^{-1}\ cm^2$. Error limits were minimized by signal averaging and generally did not exceed ±10%.

All experiments were carried out at room temperature.

Results

Oxidation of MeI *at pH* >5.—Pulse radiolysis of N_2O-saturated aqueous solutions of alkyl iodides leads to the formation of transient, optically absorbing species. Their identity varies with pH and the solute concentration. The species result from reaction of the alkyl iodide with $^{\bullet}OH$ radicals. The latter is concluded from the complete lack of these absorptions in the presence of an $^{\bullet}OH$ scavenger, *e.g.* t-butyl alcohol, at high enough concentrations.

Curve (a) in Figure 1 shows the transient absorption spectrum recorded immediately after a 1 µs pulse from an N_2O-saturated solution of 10^{-3} mol dm^{-3} MeI at pH 5.7. Two maxima are observed at 310 and 350 nm, respectively. The decay of both bands is of identical kinetics, namely exponential with a half-life of *ca.* 10 µs. This suggests the entire spectrum to be due to one single species. Since the conductivity of the solution does not change upon irradiation the transient must be of neutral character. Its rate of formation is essentially diffusion controlled ($k = 1.4 \times 10^9$ mol^{-1} dm^3 s^{-1} [29]). This would probably preclude any abstraction or substitution processes which are usually associated with some activation energies. Considering the electrophilic nature of the hydroxyl radical the transient absorption is consequently attributed to the adduct radical formed in the general reaction

$$RI + {}^{\bullet}OH \dashrightarrow RI(OH)^{\bullet} \qquad (1)$$

This is in agreement with work by Bühler *et al.*, who discuss the adduct in terms of a charge transfer complex.[27]

The spectral characteristics and the lifetime of the transient are found to be independent of the solute concentration, and also its yield attains a constant value above 5×10^{-4} mol dm^{-3} MeI. Changes of pH towards basic values (up to pH 10) have also practically no effect. At higher pH, the resolution of the two bands deteriorates; this is probably due to deprotonation of $RI(OH)^{\bullet}$ into $RI(O)^{-\bullet}$ radical anions.

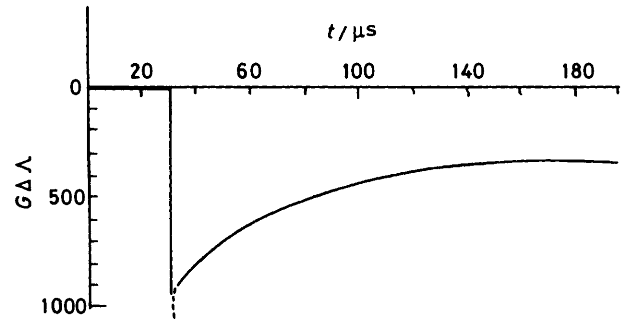

Figure 2. Conductivity-time signal from pulse-irradiated (*ca.* 1 µs pulse), N_2O-saturated solution of MeI (10^{-4} mol dm^{-3}) at pH 3.5

Oxidation of MeI *at pH* <5.—A significantly different picture is observed in more acidic solutions, *i.e.* at pH <5. Curve (b) in Figure 1 exhibits the transient absorption spectrum obtained immediately after the pulse in a low concentration, namely 10^{-4} mol dm^{-3} solution of MeI at pH 3.5. It is noted that only one strong absorption band is present which peaks at 310 nm and exhibits an appreciable tailing on the low-energy side. Comparison with a 10^{-4} mol dm^{-3} solution at pH 5.7 (not shown in Figure 1) shows that the total absorption at 310 nm has considerably increased at pH 3.5 while at 350 nm it remains essentially the same.

Time-resolved conductivity measurements reveal that the formation of the absorbing species is accompanied by a loss in conductance (Figure 2). This is indicative of replacement of the highly conducting H^+_{aq} by a normal cationic species. The conductivity signal is of transient nature like the optical signal. All these observations suggest the absorption to be due to the molecular radical cation formed in the general reaction

$$RI(OH)^{\bullet} + H^+_{aq} \dashrightarrow RI^{+\bullet} + H_2O \qquad (2)$$

The decay of $MeI^{+\bullet}$ occurs exponentially, with $t_{\frac{1}{2}} \approx 17$ µs at 10^{-4} mol dm^{-3} methyl iodide.

The radical cation yield can be evaluated from the conductivity changes. Assuming a specific conductivity of $\Lambda = 50\ \Omega^{-1}\ cm^2$ for $RI^{+\bullet}$, *i.e.* an average value for a normal monovalent cation, replacement of the free proton ($\Lambda = 315\ \Omega^{-1}\ cm^2$ at 18 °C) by $RI^{+\bullet}$ would result in $\Delta\Lambda = -265\ \Omega^{-1}\ cm^2$. At pH 3.5, for example, $G\Delta\Lambda = -880\ \Omega^{-1}\ cm^2$. Thus, the radiation chemical yield calculated amounts to $G = 3.3$. The maximum possible yield corresponds to $G \approx 6$, *i.e.* to the yield of $^{\bullet}OH$ radicals. Extrapolation from the pH dependence of the measurable $G(RI^{+\bullet})$ in Figure 3 indicates that this value may be expected at *ca.* pH 2. Experimentally this could not be verified, however, owing to the technical limitations of the conductivity technique.[30] The results, nevertheless, suggest that reaction (2) is reversible.

In the acid range the nature of the absorbing species varies also with the concentration of the alkyl iodide. This is illustrated by curve (c) in Figure 1 which represents the transient absorption spectrum obtained from a pulse-irradiated, N_2O-saturated solution of MeI (8×10^{-3} mol dm^{-3}) at pH 3.5. The species exhibits a maximum at 415 nm. The concentration dependence of the total absorption at this wavelength, measured in terms of $G\varepsilon$ immediately after a 1 µs pulse, is displayed in Figure 4. In order to attain a maximum yield, relatively high solute concentrations (*ca.* 10^{-2} mol dm^{-3}) are

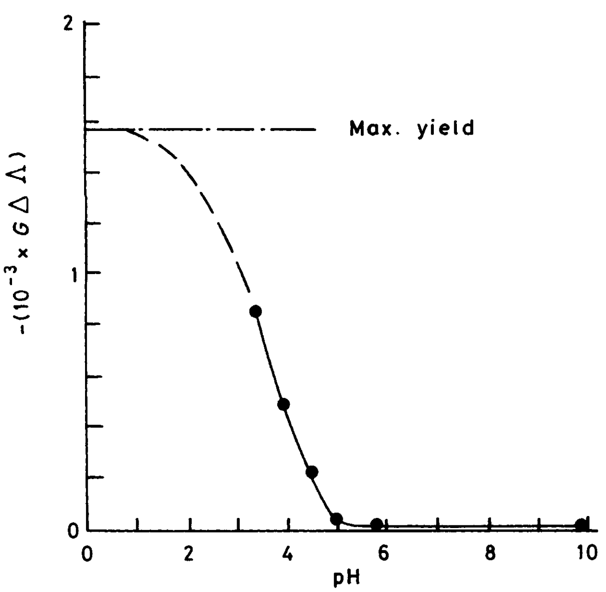

Figure 3. Yield of radical cations calculated from conductivity measurements as a function of pH. Solution: N_2O-saturated MeI (10^{-4} mol dm^{-3}) [maximum yield corresponds to G ($^{\bullet}OH$)]

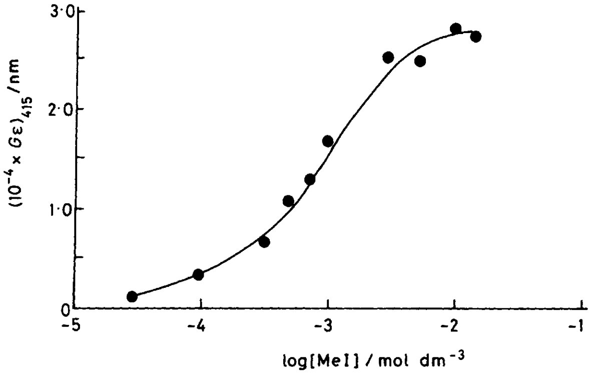

Figure 4. Yield of $(\mathrm{MeI.^{\bullet}.IMe})^{+}$, given in terms of $G\,\varepsilon$ at 415 nm, as a function of MeI concentration. Solutions: N_2O-saturated, pH 3.5

required. The curve corresponds to the depletion of the $\mathrm{MeI}^{+\bullet}$ band at 310 nm (at $\geqslant 5 \times 10^{-4}$ mol dm^{-3} methyl iodide).

Optical absorbance at 415 nm is caused by a positively charged species. This is evident from complementary conductivity measurements which show no difference in the signals between the low and the high solute concentration experiments.

On the basis of all these observations we suggest the 415 nm absorption to be due to a dimer radical cation formed in the general equilibrium

$$\mathrm{RI}^{+\bullet} + \mathrm{RI} \rightleftharpoons (\mathrm{RI.^{\bullet}.IR})^{+} \qquad (3)$$

The main element of its electronic structure is suggested to be a 2σ–$1\sigma^{*}$ three-electron bond between the two iodine atoms in analogy to several similar species with other hetero atoms.[6–21] The antibonding σ^{*} electron renders the iodine–iodine bond relatively labile and thus serves as a rationale for the establishment of the equilibrium.

Oxidation of Other Alkyl Iodides.—Principally the same observations have been made for other alkyl iodides. The results obtained in neutral solution all confirm the transient $\mathrm{RI(OH)}^{\bullet}$ adduct as described by Bühler *et al.*[27] At lower pH, radical cations can now be identified, namely $\mathrm{RI}^{+\bullet}$ at low solute concentrations and with $\lambda_{max.}$ of 310—320 nm, and $(\mathrm{RI.^{\bullet}.IR})^{+}$ at higher solute concentrations with absorptions peaking in the 415—470 nm range. The relationship between the two radical cations according to equation (3) is demonstrated for the $^{\bullet}OH$ induced oxidation of EtI at pH 3.5 as an additional example in Figure 5. The transient spectra recorded at different ethyl iodide concentrations show the formation of the $[\mathrm{EtI.^{\bullet}.IEt}]^{+}$ ($\lambda_{max.}$ = 425 nm) at the expense of $\mathrm{EtI}^{+\bullet}$ ($\lambda_{max.}$ = 315 nm) with increasing EtI concentration.

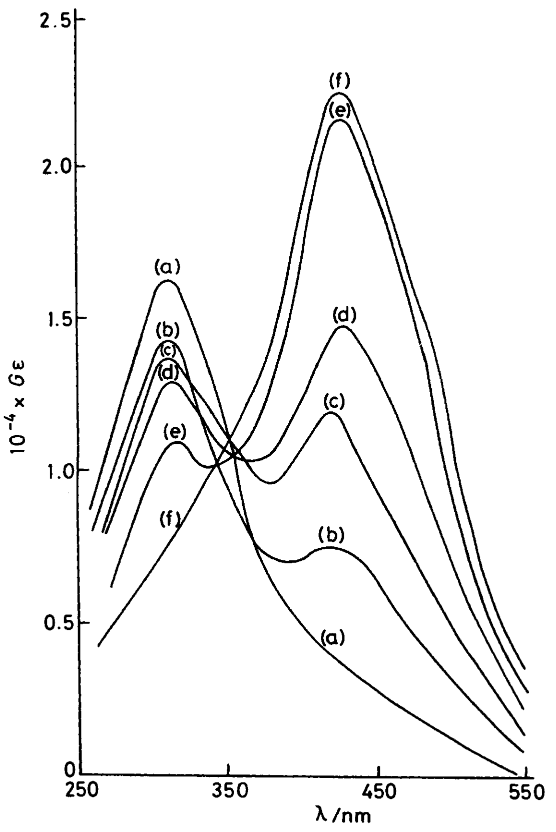

Figure 5. Transient absorption spectra recorded immediately after a *ca.* 1 μs pulse in N_2O-saturated, pH 3.5 solutions of various EtI concentrations (in mol dm^{-3}) (a) 1×10^{-4}; (b) 3×10^{-4}; (c) 5×10^{-4}; (d) 1×10^{-3}; (e) 2×10^{-3}; (f) 4×10^{-3}

The individual $\lambda_{max.}$ for the $(\mathrm{RI.^{\bullet}.IR})^{+}$ exhibit a significant dependence on the nature of the substituent R. The actual values are listed in the Table together with the extinction coefficients. The latter are based on the radical cation yields as evaluated from the conductivity measurements. The ε-values for $(\mathrm{RI.^{\bullet}.IR})^{+}$ were derived from high solute concentration experiments and are all found to be in the order of 6 000 mol^{-1} dm^{3} cm^{-1}. No extinction coefficients are given for the corresponding species from s-C_4H_9I, n-$C_5H_{11}I$, n-$C_6H_{13}I$, and c-$C_6H_{11}I$. Owing to the low solubility of these compounds the $\mathrm{RI}^{+\bullet}$ cannot quantitatively be converted into $(\mathrm{RI.^{\bullet}.IR})^{+}$, and it is impossible to distinguish between these two radical cations by means of conductivity to determine their relative yields. The extinction coefficients for the $\mathrm{RI}^{+\bullet}$ species were obtained from low concentration experiments and are seen to be in the magnitude of 4 000 mol^{-1} dm^{3} cm^{-1}.

The formation of $(\mathrm{RI.^{\bullet}.IR})^{+}$ *via* the forward reaction of equilibrium (3) occurred at practically the same rate (within experimental limits of error) as the initiating $^{\bullet}OH$ addition to

Table. Values of $\lambda_{max.}$ and ε for $\mathrm{RI}^{+\cdot}$ and $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ radical cations. Error limits: $\lambda_{max.}$ ± 10 nm; ε ± 10%

	$\mathrm{RI}^{+\cdot}$		$(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$	
R	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	ε/mol^{-1} dm^3 cm^{-1}
Me	310	3 900	415	6 000
Et	315	4 450	425	6 850
n-C_3H_7	315	4 050	435	5 650
i-C_3H_7	320	4 400	450	5 700
n-C_4H_9	320	4 650	450	6 050
s-C_4H_9	315	3 700	470	*a*
n-C_5H_{11}	320	4 250	445	*a*
c-C_6H_{11}	315	3 650	470	*a*
n-C_6H_{13}	315	4 150	450	*a*

[a] Not evaluated since $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ concentration cannot be determined (see text).

the alkyl iodide. Since both reactions (3) and (1) depend on the RI concentration it is therefore impossible to determine the absolute value of k_3. The rate constant k_1 represents however a lower limit, *i.e.* $k_3 \geqslant k_1$.

The decay kinetics of the $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ absorptions follow essentially an exponential rate law but some second-order contributions are also indicated. Measured half-lives under our pulse radiolysis conditions range from about 25 μs for $(\mathrm{MeI}^{\cdot}.\mathrm{IMe})^+$ to just a few μs for the species derived from the higher iodides.

The $\mathrm{RI}^{+\cdot}$ and $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ radical cations do not react with molecular oxygen. This complies with a general chemical characteristic of positively charged radicals and in particular three-electron-bonded species.[19]

Hydrolysis of Alkyl Iodides.—One aspect which seriously hampers the investigations of some of the higher alkyl iodides is hydrolysis. For example, it was not possible to detect any radical cation from the oxidation of t-C_4H_9I. Instead transient absorption bands with $\lambda_{max.}$ = 390 and >700 nm were observed which are characteristic for $\mathrm{I}_2^{-\cdot}$ radical anions.[31] The latter are formed upon oxidation of I^- and these have been identified as hydrolysis products by ion chromatography. Corresponding hydrolysis processes with the other iodides were fortunately much slower, particularly under slightly acid conditions. This ensured unambiguous observation of $\mathrm{RI}^{+\cdot}$ and $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ radical cations with freshly prepared solutions within a 1—1.5 h period.

Oxidation Reactions by $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$.—The observation that the lifetime of the $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ seemingly depended on the degree of hydrolysis of the alkyl iodide, *i.e.* on the I^- concentration, suggested that the radical cations can act as oxidants. The reaction sequence

$$(\mathrm{RI}^{\cdot}.\mathrm{IR})^+ + \mathrm{I}^- \dashrightarrow \mathrm{I}^{\cdot} + 2\mathrm{RI} \qquad (4)$$

$$\mathrm{I}^{\cdot} + \mathrm{I}^- \rightleftharpoons \mathrm{I}_2^{-\cdot} \qquad (5)$$

was proven by deliberate addition of I^- ions, but keeping $[\mathrm{I}^-] < [\mathrm{RI}]$ to ensure quantitative primary oxidation of the alkyl iodide. The formation of $\mathrm{I}_2^{-\cdot}$ was evident from its optical absorption. The rate constant for reaction (4) was evaluated from the effect of an increasing I^- concentration on the decay of the $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ absorption. For the reaction of $(\mathrm{MeI}^{\cdot}.\mathrm{IMe})^+$ with I^-, for example, a bimolecular rate constant of k_4 = 7.7 × 10^9 mol^{-1} dm^3 s^{-1} was evaluated (solutions: 5 × 10^{-3} mol dm^{-3} MeI and 5 × 10^{-5}—2 × 10^{-4} mol dm^{-3} I^-; pH 3.5).

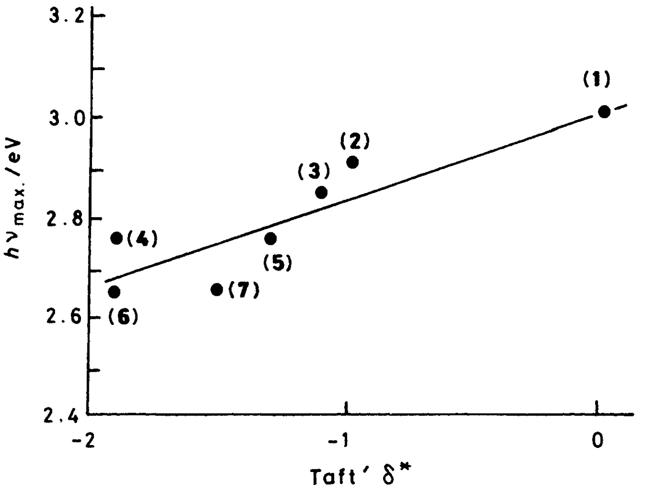

Figure 6. Plot of $h\nu_{max.}$ in eV (converted from $\lambda_{max.}$ for $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$) as a function of Taft's inductive σ* parameter. Compounds (**1**) MeI; (**2**) EtI; (**3**) n-C_3H_7I; (**4**) i-C_3H_7I; (**5**) n-C_4H_9I; (**6**) s-C_4H_9I; (**7**) c-$C_6H_{11}I$

A group of organic compounds which can readily be oxidized are alkyl sulphides. The rate constant for the overall reaction

$$(\mathrm{MeI}^{\cdot}.\mathrm{IMe})^+ + 2\mathrm{Me_2S} \dashrightarrow (\mathrm{Me_2S}^{\cdot}.\mathrm{SMe_2})^+ + 2\mathrm{MeI} \qquad (6)$$

for example, was determined as k_6 = 3.6 × 10^9 mol^{-1} dm^3 s^{-1} (solutions: 5 × 10^{-3} mol dm^{-3} MeI and 5 × 10^{-5}—5 × 10^{-4} mol dm^{-3} $\mathrm{Me_2S}$; pH 3.5). This reaction could conveniently be monitored *via* the decay and the formation of the absorptions of the two respective three-electron-bonded radical cations (415 and 465 nm, respectively). The diffusion-controlled rate for reaction (6) and the fact that the sulphur-centred radical cations themselves readily undergo oxidation reactions[8,19] renders the $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ an excellent oxidant. This in turn is consistent with the observation that oxidation of the alkyl iodides to their radical cations is relatively difficult. Potent one-electron oxidants like $\mathrm{CCl_3OO}^{\cdot}$, Tl^{2+}, Ag^{2+} and others which all oxidize alkyl sulphides[19,32,33] to $\mathrm{R_2S}^{+\cdot}$ and $(\mathrm{R_2S}^{\cdot}.\mathrm{SR_2})^+$ fail to oxidize RI.

Discussion

Our pulse radiolysis study has unambiguously shown that $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ and $\mathrm{RI}^{+\cdot}$ radical cations can exist in solution and establish an equilibrium between each other according to equation (3). Their formation requires low pH (<4.5), and for the three-electron-bonded species high alkyl iodide concentrations (>10^{-3} mol dm^{-3}). Both conditions have not been employed in earlier investigations.[26,27]

The $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$ radical cations exhibit properties similar to other 2σ–1σ* three-electron-bonded species. One characteristic feature is a pronounced optical absorption in the visible.[10] Experimental data[10,12] and theoretical considerations[34] of analogous species attributes this absorption to a transition from the uppermost bonding to the singly occupied antibonding σ* level. The former is essentially σ but will be affected by the two non-bonding electron pairs residing on each of the two iodine atoms in $(\mathrm{RI}^{\cdot}.\mathrm{IR})^+$. The optical transition energies represent consequently a measure of the strength of the three-electron bond, as has been demonstrated in particular for $(\mathrm{R_2S}^{\cdot}.\mathrm{SR_2})^+$ radical cations.[10,12,13,35]

Any substituent R may electronically interact with neighbouring functions. Electron release by R into the three-electron bond, for example, can be expected to increase the electron density in the half-empty antibonding orbital. As a consequence the three-electron bond will be further weakened, the difference between σ and σ^* energy levels will become smaller, and the corresponding absorption will be red-shifted.[10,12] Quantification of this effect is possible by a linear free energy relationship between the measured optical transition energy and the electron-releasing power of R, *i.e.* Taft's inductive σ^* parameter.[36] A corresponding plot ($\lambda_{max.}$ converted into $h\nu$, in eV, *vs.* σ^*) of our present data on $(RI.^{\bullet}.IR)^+$ radical cations is shown in Figure 6. Despite some scatter a reasonably linear relationship can be established. The underlying mathematical equation is:

$$h\nu\ [\text{eV}] = 3.0 + 1.8\ \sigma^*$$

The uncertainty of the slope is relatively high and is estimated to ± 0.5. It may be noted though that the deviations from the straight line seem purely statistical and can be accounted for by an error limit of ± 10 nm for $\lambda_{max.}$

Since the magnitude of the slope indicates how effective electron release is by R into the three-electron bond, it seems appropriate to compare our value with two others which have been evaluated for two sulphur-centred systems.[12] In case of the iso-structural $(RS.^{\bullet}.SR)^-$ radical anion a slope of 0.49 had been found. This comparatively low value is, however, understandable since electron release into a negatively charged centre should be less effective than into a positively charged as in $(RI.^{\bullet}.IR)^+$. For $(R_2S.^{\bullet}.SR_2)^+$ radical cations (with unbranched alkyl groups) the corresponding slope amounted to 1.4. This means that the relative effect of electron release into the three-electron bond is still smaller than in the iodine-centred radical cation, particularly in view of the fact that the sulphur-centred species carry twice as many electron-releasing groups. Perhaps this finding is related to the position of iodine in the periodic table which renders this element electronically 'softer' than sulphur.

Additional bond weakening due to steric hindrance by the alkyl groups is not expected in $(RI.^{\bullet}.IR)^+$. It would have shown up as a negative deviation (too low transition energies) from the straight line in the linear free energy plot in Figure 6. Such an effect had been observed for $(R_2S.^{\bullet}.SR_2)^+$ where two substituents are located at each sulphur atom; but only for branched, bulky alkyl groups which would lead to a distortion of bond angles and orbital orientation.[12]

The accuracy of the linear free energy correlation would have been higher if measurements could have been extended to radical cations which carry substituents of higher or lower electron-releasing power than those investigated, *e.g.* t-butyl or hydrogen. $(t\text{-}C_4H_9I.^{\bullet}.ItC_4H_9)^+$ and $(HI.^{\bullet}.IH)^+$, by extrapolation from Figure 6, would absorb at *ca.* 515 nm and 320 nm, respectively. Generation of the former failed because of solute hydrolysis as mentioned already. Our search for $(HI.^{\bullet}.IH)^+$ *via* oxidation of HI also, was unsuccessful. The only transient species observable was the completely deprotonated form, namely $I_2^{-\bullet}$ ($\lambda_{max.} = 385$ nm) which was stabilized under very acidic conditions in $HClO_4$ (3 mol dm^{-3}). This result is, however, understandable. Three-electron-bonded hydrogen-substituted radical cations generally seem to be much better acids than their parent compounds. For example, the first pK of H_2S is 7, while $(H_2S.^{\bullet}.SH_2)^+$ can be stabilized only at pH < 2 and its corresponding anion $(HS.^{\bullet}.SH)^-$ exists at pH > 3.[37] Since pK(HI) < -9 it therefore seems practically impossible to stabilize $(HI.^{\bullet}.IH)^+$ under any conditions.

The thermodynamic stability of the three-electron bond in $(RI.^{\bullet}.IR)^+$ can only be estimated. Its involvement in equilibrium (3) is reflected in the plot of Figure 4. This is, however, not the real pK curve. The main reason is that at low solute concentrations the decay of the $(RI.^{\bullet}.IR)^+$ takes place at the same time scale as its formation. The real thermodynamic pK curve will consequently be shifted to the left and, by extrapolation, K_3 is expected in the order of 10^4—10^5 mol^{-1} dm^3. An estimate *via* the kinetic relationship $K_3 = k_3/k_{-3}$ is also associated with uncertainties. This pertains not only to k_3 but also to k_{-3} which describes the dissociation of the three-electron bond. Assuming that the first-order decay of the $(RI.^{\bullet}.IR)^+$ absorption is due to this process—and not to other possible pathways such as deprotonation—a reasonable value of $K_3 \geqslant 1.4 \times 10^9/2.8 \times 10^4 \geqslant 5 \times 10^4$ mol^{-1} dm^3 is evaluated for the methylated species. Stability constants of this order of magnitude have been measured for $(R_2S.^{\bullet}.SR_2)^+$ radical cations.[35]

The molecular radical cations denoted so far as $RI^{+\bullet}$ should probably be written as an associate with a water molecule, namely $(RI.^{\bullet}.OH_2)^+$. Such a structure has also been considered for the analogous sulphide radical cation, $(R_2S.^{\bullet}.OH_2)^+$,[38] and would be consistent with general theoretical treatments.[34] (The difference in electronegativity of the two heteroatoms prevents, of course, a symmetrical spin and charge distribution). An interaction of the oxidized iodine atom with an individual water molecule would, in fact, also be consistent with the interpretation of the optical spectra. The absorption band at 350 nm of the neutral $^{\bullet}OH$-adduct (which may be viewed as $RI.^{\bullet}.OH$) has been assigned to a transition in the (IOH)-component of the radical.[27] Our measurements have shown that the total absorption at 350 nm does not change with pH, *i.e.* the same value is determined in acid solutions where $(RI.^{\bullet}.OH_2)^+$ is suggested to exist.

While our investigations substantiate earlier findings by Bühler *et al.*,[27] on the neutral $^{\bullet}OH$-adduct they produced no evidence for a $RI_2^{\bullet}$ species. The latter had been suggested to exist as charge-transfer species $(RI^+I)^-)^{\bullet}$ or iodine atom adduct $RI{\cdot}I$,[22,23,26,27] and in our terminology may be addressed as three-electron-bonded species $RI.^{\bullet}.I$. It seems that sufficient stabilization of such a species is restricted to systems in which iodine atoms are produced and RI is present at very high concentration. Examples include irradiated RI matrices. We tried to add $^{\bullet}Me$ radicals (from $^{\bullet}OH + Me_2SO \dashrightarrow Me^{\bullet} + MeSO_2H$) to I_2 in aqueous solution but failed to detect any transient ascribable to $MeI_2^{\bullet}$. Nevertheless we cannot completely eliminate the possibility of such a species being formed in the oxidation reaction of some alkyl iodide solutions. The radical $RI_2^{\bullet}$ has been claimed to absorb at *ca.* 390 nm[23,25] and thus may be hidden in the 385 nm band of $I_2^{-\bullet}$ which was generated (and its negative charge identified by conductivity measurements) whenever I^- ions were present.

The optical absorption bands found for the molecular and dimer radical cation in aqueous systems do not match those claimed for these species in pure alkyl iodide or hydrocarbon matrix at 77 K.[23] The lack of the associated water molecule (at least in the case of the molecular radical cation) and the rigidity of the matrix are probably the major reasons. Some misinterpretation due to the failure to note $I_2^{-\bullet}$ generation[23] and non-consideration of ionic processes in the aqueous phase[25] may have contributed to the until now inconsistent picture.

Formation of radical cations, and in particular of $(RI.^{\bullet}.IR)^+$, has now unambiguously been demonstrated to occur in aqueous solution. These species show the interesting physical features of a 2σ–$1\sigma^*$ three-electron bond. They also act as strong oxidants, and this property is discussed in further detail in a separate publication.[39]

Acknowledgements

This work has been supported by the International Bureau of the KFA Jülich within the terms of an agreement on scientific co-operation between the Federal Republic of Germany and the Republic of India. H. M. has been on deputation from Bhabha Atomic Research Centre, Bombay, India. We also thank Mr. Ylan, Dr. Veltwisch, and Dr. Göbl for some experimental contributions during the early stages of this project.

References

1 O. W. Howarth and G. K. Fraenkel, *J. Am. Chem. Soc.*, 1966, **88**, 4514.

2 B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, 1969, **65**, 2576, 2582, 2588.

3 M. A. J. Rodgers, *Chem. Phys. Lett.*, 1971, **9**, 107.

4 S. Egusa, S. Arai, A. Kira, M. Imamura, Y. Tabata, *Radiat. Phys. Chem.*, 1977, **9**, 419.

5 K. Hayashi, M. Irie, D. Lindenau, and W. Schnabel, (*a*) *Eur. Polym. J.*, 1977, **13**, 925; (*b*) *Radiat. Phys. Chem.*, 1978, **11**, 139.

6 B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc.*, *Perkin Trans. 2*, 1973, 1748.

7 M. C. R. Symons, *J. Chem. Soc.*, *Perkin Trans. 2*, 1974, 1618.

8 M. Bonifačić, H. Möckel, D. Bahnemann, and K.-D. Asmus, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 675.

9 W. B. Gara, J. R. M. Giles, and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1979, 1444.

10 K.-D. Asmus, *Acc. Chem. Res.*, 1979, **12**, 436.

11 J. T. Wang and Ff. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 1184.

12 M. Göbl, M. Bonifačić, and K.-D. Asmus *J. Am. Chem. Soc.*, 1984, **106**, 5984.

13 K.-D. Asmus, Preprints Div. Petr. Chem.; Am. Chem. Soc. Anaheim Meeting, 1986, 870.

14 A. R. Lyons and M. C. R. Symons, *J. Chem. Soc.*, *Faraday Trans. 2*, 1972, **68**, 1589.

15 R. W. Alder, R. Gill, and N. C. Goode, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 973.

16 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1980, 1497.

17 M. Bonifačić and K.-D. Asmus, *J. Chem. Soc.*, *Perkin Trans. 2*, 1980, 758.

18 R. S. Glass, M. Hojjatie, G. S. Wilson, S. Mahling, M. Göbl, and K.-D. Asmus, *J. Am. Chem. Soc.*, 1984, **106**, 5382.

19 K.-D. Asmus, in 'Radioprotectors and Anticarcinogens,' eds. O. F. Nygaard, M. G. Simic; Academic Press, New York, 1983, 23.

20 J. E. Packer, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 1015.

21 E. Anklam, H. Mohan, and K.-D. Asmus, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 629.

22 S. P. Mishra and M. C. R. Symons, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 1492.

23 J. P. Mittal and W. H. Hamill, *J. Am. Chem. Soc.*, 1967, **89**, 5749.

24 (*a*) R. F. Pottie and W. H. Hamill, *J. Phys. Chem.*, 1959, **63**, 877; (*b*) A. J. Lorquet and W. H. Hamill, *ibid.*, 1963, **67**, 1709.

25 M. Ebert, J. P. Keene, E. J. Land, and A. J. Swallow, *Proc. R. Soc. London*, *Ser. A*, 1965, **287**, 1.

26 J. K. Thomas, *J. Phys. Chem.*, 1967, **71**. 1919.

27 U. Brühlmann, H. Büchler, F. Marchetti, and R. E. Bühler, *Chem. Phys. Lett.*, 1973, **21**, 412.

28 K.-D. Asmus, in 'Methods in Enzymology,' vol. 105, ed. L. Packer, Academic Press, New York, 1984, 167.

29 J. Shankar, K. V. S. Rama Rao, and L. V. Shastri, *J. Phys. Chem.*, 1969, **73**, 52.

30 K.-D. Asmus and E. Janata, in 'The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis,' J. H. Baxendale, F. Busi, eds., Reidel, Dordrecht, 1982, 91.

31 (*a*) J. K. Thomas, *Trans. Faraday Soc.*, 1965, **61**, 702; (*b*) J. H. Baxendale, P. L. T. Bevan, and D.A. Scott, *ibid.*, 1968, **64**, 2389.

32 K.-O. Hiller and K.-D. Asmus, *Int. J. Radiat. Biol.*, 1981, **40**, 597.

33 J. Mönig, M. Göbl, and K.-D. Asmus, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 647.

34 T. Clark, *J. Comput. Chem.*, 1981, **2**, 261; 1982, **3**, 113; 1984, **4**, 404.

35 J. Mönig, R. Goslich, and K.-D. Asmus, *Ber. Bunsenges. Phys. Chem.*, 1986, **90**, 115.

36 R. W. Taft, *J. Am. Chem. Soc.*, 1953, **75**, 4231; *ibid.*, 1958, **80**, 2436; *J. Chem. Phys.*, 1957, **26**, 93.

37 S. A. Chaudhri and K.-D.Asmus, *Angew. Chem.*, 1981, **93**, 690; *Angew. Chem.*, *Int. Ed. Engl.*, 1981, **20**, 672.

38 S. A. Chaudhri, M. Göbl, T. Freyholdt, and K.-D. Asmus, *J. Am. Chem. Soc.*, 1984, **106**, 5988.

39 H. Mohan and K.-D. Asmus, *J. Phys. Chem.*, in the press.

Received 2nd *January* 1987; *Paper* 7/002