The radical-anions of various alkyl-iodides[†]

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Exposure of a range of alkyl and substituted alkyl iodides in methanol glasses at 77 K to ionizing radiation gave EPR spectra assigned to the alkyl radicals. Irradiation of the pure compounds gave central features assigned to the alkyl radical-iodide ion adducts, together with outer features assigned to the primary σ*-radicals, R $\triangleq$ I.$^-$. These novel results are discussed in terms of the role of the media in governing the species formed. In the case of the I–CH$_2$CO$_2$– and I–CH$_2$OH derivates, species with very large hyperfine coupling to ^{127}I nuclei are thought to be the σ*-radicals I-CH$_2$CO$_2$ $\triangleq$ I$^-$ and I–CH$_2$O $\triangleq$ I$^-$, similar to the I $\triangleq$ OMe$^-$ radicals previously studied.

It is normally expected that when electrons add to alkyl halides, dissociative electron capture occurs to give alkyl radicals and halide ions.[1] However, when frozen compounds are used, novel species, showing normal EPR features for the radicals, but with extra hyperfine coupling to the halogen nuclei were detected.[2] Analysis of the halogen hyperfine data showed that the spin-densities on the halide ions were negligibly small. We then confirmed and extended this work, and suggested that a key factor was the change in orbital hybridisation for the alkyl radicals on flattening.[3] As the C–hal bond stretches, because of the antibonding effect of the added electron, so the alkyl radical tends to flatten, giving, finally, the free, planar, radical. Thus, the energy of the SOMO on carbon increases, and so the bond weakens. This is shown, diagramatically, in Fig. 1. We described the resulting adducts as weak charge-transfer complexes with the components remaining together because of the constraints of the rigid matrices.

Subsequently, we showed that on moving from R$_3$C–hal to R$_3$N–hal, dissociation did not occur, but novel σ*-radicals were detected. This was explained in terms of the far greater electron-affinity of the R$_3$N– groups.[4] Then we showed that when H $\triangleq$ hal- radicals were formed, the ^{1}H hyperfine coupling was reduced, and the halogen coupling was well defined, showing that these are genuine σ*-radicals.[5]

I now report that, under certain circumstances, various alkyl iodides, and also ethyl bromide, give genuine σ*-radicals. These σ*-radicals are of considerable importance in reaction mechanisms of radicals.[6,7]

Experimental

Reagents and solvents were of the highest grades available and were used without further purification. EPR spectra were measured at X-band frequencies using a Varian E109 spectrometer controlled by a home-made computer system. Modulation frequencies and scans were varied extensively, the results being invariant.

Samples were irradiated at 77 K under liquid nitrogen, in a ^{60}Co γ-ray source, and spectra were measured without warming. Later samples were allowed to warm by decanting the liquid nitrogen, and recooling whenever significant spectral changes were detected.

Results and discussion

Results are reported in Table 1 and typical EPR spectra are shown in Figs 2 and 3.

Using methanol (CD$_3$-OD) and aqueous methanol glasses, only the alkyl radicals were detected. However, when the pure derivatives, as finely powdered crystals, were used, quite distinct spectra were obtained. Generally two species, the normal adducts and a novel species thought to the the σ*-radicals
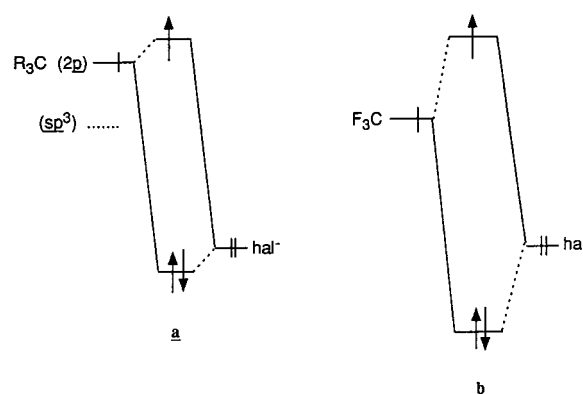

Fig. 1 Qualitative energy level diagram for the σ*-radicals and the corresponding adducts, showing how the change from ca sp^3- hybridisation on barbon to pure p-orbital character greatly weakens the bonding.
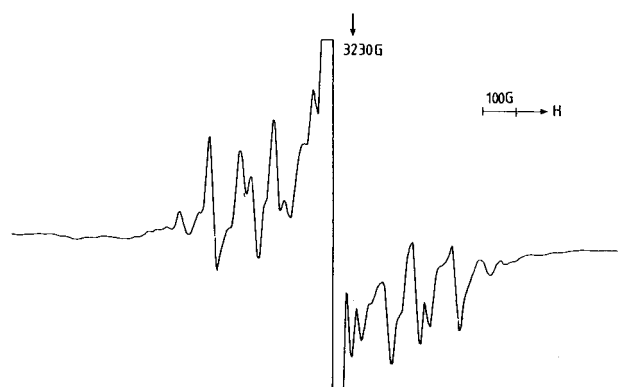

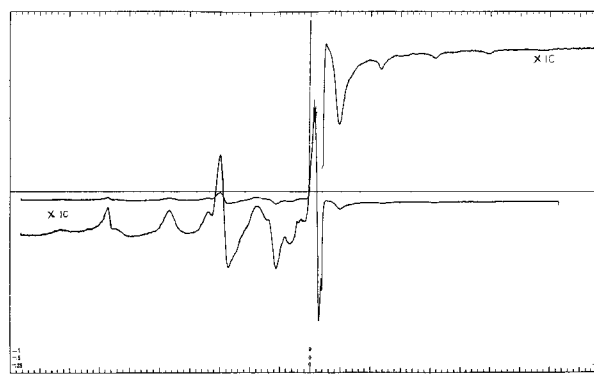**Fig. 2** First derivative X-band EPR spectrum for C$_2$D$_5$I after exposure to ^{60}Co γ-rays at 77 K.

Fig. 3 As for Fig. 1, for I–CH$_2$CO$_2$-NA$^+$ at 77 K, showing features assigned to I–CH$_2$C(O)CO $\triangleq$ I$^-$-σ* centres.

Table 1 EPR parameters assigned for a range of R• ---hal⁻ adducts and corresponding σ*-radicals

Compound	radical (nucleus)	Hyperfine parameters[a]				$g_{//}$	$g_|$	Ref.
		$A_{//}$	$A_|$	A_{iso}	$2B$			
CH$_3$-I	Adduct ^{1}H	–	–	21	–	2.003	2.003	This work and [b]
	^{127}I	78	56	63.3	14.7			
CH$_3$CH$_2$-I	Adduct ^{1}H		–	ca. 25	–	2.003	2.003	This work and [b]
	^{127}I	95	80	85	10			
(CD$_3$CD$_2$-I)	α* ^{127}I	195	130	151.7	43.3			This work
I-CH$_2$CO$_2$⁻	^{127}I[d]	540	420	460	80	2.004	2.003	This work
I-CH$_2$OH	^{127}I[d]	520	435	463	57	2.004	2.003	This work

[a]G = 10$_{–4}$T.
[b]A.R. Lyons, M.C.R. Symons and S.P. Mishra, *Nature*, 1974, **249**, 341.
[c]Not resolved.
[d]See text.

Table 2 Estimated spin-densities on iodine for σ*-radicals using data for I2•⁻ radicals for comparison (2B = 193 G)

Radicals	Me• ---I⁻	Et• --- I⁻	Et º I⁻	ICH$_2$CO$_2$ º I
spin-density	3.8%	2.7%	11.2%	21.%

were detected. (Table 1). On annealing, the latter spectra were lost irreversibly, with concomitant growth of the adduct spectra (Figs 2 and 3).

The individual proton hyperfine features for the alkyl radicals were well defined, but for their bromide or iodide adducts features were broader and, for example, α- and β-proton splittings were not resolved. However, for the σ*-radicals, only broad envelope parallel and perpendicular features were obtained, with well defined ^{127}I features only. Those for the C$_2$H$_5$-derivative were wider than those for the C$_2$D$_5$-derivative, showing that there is considerable delocalisation onto the alkyl groups.

The ^{127}I and ^{81}Br hyperfine data were divided into isotropic and antisotropic contributions in the usual way. After correction for orbital magnetism, these were used to obtain accurate p-orbital populations, by comparison with the data for the V$_k$ centre I$_2$•⁻ (Table 2),[9] since this must have half the spin-density on each atom. For the bromide, the ^{81}Br components were used, but the ^{79}Br components were well defined in the out features.

In all cases, for the pure compounds, central features assigned to the electron-loss centres were present. These were too broad and ill-defined to warrant interpretation. They are thought to be of the type R–CHI, with broad anisotropic hyperfine coupling to ^{127}I.[8] For solutions in CD$_3$OD, the central features were due to D$_2$ COD radicals. It is noteworthy that no EPR signals, and no violet colours characteristic of trapped electrons were detected. This confirms that electron-addition was efficient.

The results show that on electron-addition, several of these derivatives give all three species at 77 K, starting with the initial s*-species R º I⁻, going on to the adducts, R• --- I⁻, and then giving the simple radicals R•. The σ*-derivatives are

formed in the crystalline iodides, together with some adducts. These grow in on annealing as the σ*-radical spectra decay. Finally, the simple radicals are formed in methanol glasses.

It seems that conversion to the adducts is a very subtle event. I suggest that it is a function of the extent of packing around each anion. When this is sufficiently loose, the bonds break. Then, in a good anion-solvating medium, the iodide ions are pulled off completely.

The derivatives I-CH$_2$CO$_2$⁻ and I-CH$_2$OH give a different σ*-adduct with iodine hyperfine splittings close to that found for species identified as I º OMe⁻ and I º O(H)Me.[9] This is presumably I–CH$_2$C(O) – OI⁻ for the former, and I OCH$_2$I⁻ for the latter.

References

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