σ*-Electron Addition to 5-Halogenouracils in Neutral Glasses

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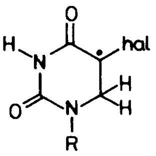
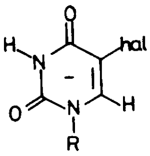
Summary Attachment of electrons to 5-halogenouracils in γ-irradiated or photolysed neutral organic and aqueous glasses produces σ*-radicals in bromo- and iodo-derivatives in addition to π*-anions, whereas in fluoro- and chloro-uracils, only π*-radicals are observed using e.s.r. spectroscopy.

ELECTRON capture by 5-halogenouracils is known to initiate a variety of reactions depending on the halogen substituent and the nature of the matrix surrounding the molecules. Exposure of single crystals to ionizing radiation has been shown, by e.s.r. spectroscopy, to give the radical (I), either *via* H-atom addition or *via* protonation subsequent to electron attachment. The formation of (I) appeared to be independent of the halogen substituent.[1] In contrast, electron addition to 5-halogenouracils in neutral or alkaline aqueous glasses at 77 K produced the π*-anion (II) and, upon warming, the 'uracil-yl' radical (III).[2] The rate of hal$^-$ detachment was found to increase in the order Cl, Br, and I as 5-substituents, the fluorouracil π*-anion being stable in the temperature range amenable to the glasses. Studies in aqueous solutions gave a similar tendency for halide ion elimination.[3]

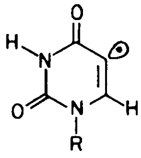
To probe this difference of reactions subsequent to electron capture in the aqueous and solid phase, we have exposed the range of 5-halogenouracil bases, ribo- and deoxy-ribosides, to ^{60}Co-γ-rays or to photoelectrons in



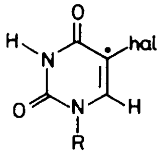
(I)



(II)



(III)



(IV)

neutral aqueous (12 M LiCl–D_2O) and organic (MTHF, CH_3OH, CD_3OD) (MTHF = methyltetrahydrofuran) glasses. For solutions of bromo- and iodo-derivatives, a new electron-addition species was detected in all matrices which we identify as the σ*-radical (IV). In these species, the excess electron is largely confined to the C–hal bond. In addition, π*-anions resulting from electron addition to the pyrimidine ring were observed. These latter anions were also produced in 5-fluoro- and 5-chloro-uracils which fail to stabilize σ*-species.

The linewidth of the σ*-features was found to vary with the matrix rigidity. Best resolution was obtained in MTHF-glasses. The corresponding *X*-band (9·5 GHz) e.s.r. spectrum for 5-bromouracil and 5-iodouracil is shown in the Figure. In all *X*-band spectra, evaluation of the perpendicular components of the hyperfine- and *g*-tensor proved difficult owing to extensive overlap with lines of solvent radicals. The assignment of structure (IV) was ascertained by theoretical spectra simulation using the MAGNSPEC[4] programme. Best fit to the observed lines

TABLE. E.s.r. parameters and spin densities of various bromo- and iodo-σ^*-radicals.

Radical	Hyperfine tensor components in G[a]			g- tensor		Orbital population[b]	
		$A_\parallel$	$A_\perp$	$g_\parallel$	$g_\perp$	a_s^2 (%)	a_p^2 (%)
F_3C–Br^-[c]	^{81}Br	263·6	114·2	2·0036	2·0212	1·9	20
BrU^-[d,e]	^{81}Br	373	143	1·997	2·030	2·7	32
$N{\equiv}C$-Br^-[f]	^{81}Br	587	180	2·00	2·07	3·7	54
F_3C-I^-[c]	^{127}I	373·1	178·8	2·0002	2·0483	3·3	28·5
IU^-[e,g]	^{127}I	505	220	1·991	2·044	4·3	42
$PhC{\equiv}C$-I[h]	^{127}I	639	263	1·98	2·09	5·3	55

[a] 1 G = 10^{-4}T. [b] Spin densities were calculated using the magnetic parameters listed by B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135. All hyperfine tensor elements were taken as positive. [c] A. Hasegawa, M. Shiotani, and F. Williams, *Faraday Discuss. Chem. Soc.*, 1977, **63**, 157. [d] BrU = 5-bromouracil. [e] This work. Data for other bromo and iodo σ^* radicals were closely similar to these. [f] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1974, **70**, 1280. [g] IU = 5-iodouracil. [h] D. J. Nelson and M. C. R. Symons, *Chem. Phys. Letters*, 1977, **47**, 436.

was obtained with the parameters given in the Table for g and A. Included in the Table are the parameters for a range of other σ^*-radicals which have been characterized recently by e.s.r. spectroscopy. The present data are seen to correlate well with these.

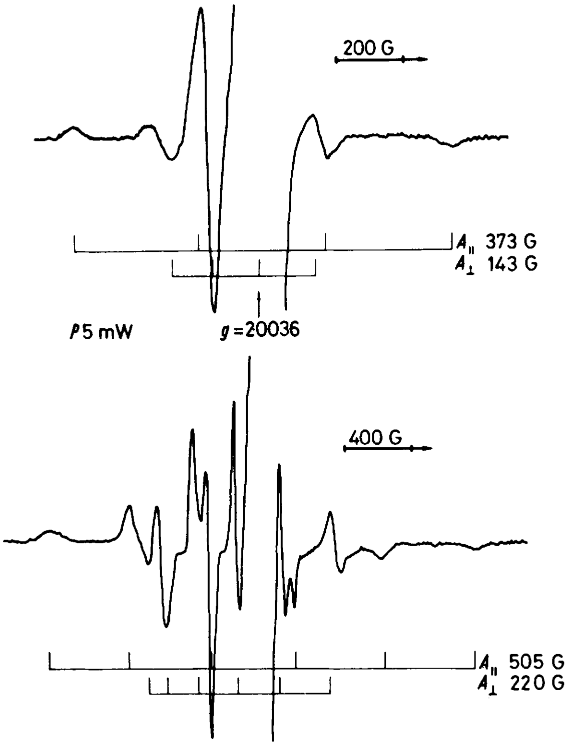


FIGURE. First derivative X-band (9273 MHz) e.s.r. spectrum of the σ^*-radical of 5-bromouracil (5 mM) (top) and 5-iodouracil (5 mM) (bottom) in an MTHF-matrix at 77 K. The stick spectrum was calculated using the parameters given in the Table.

The inability of 5-fluoro- and 5-chloro-derivatives to stabilize the σ^*-radicals accords with their greater C–hal bond strength. In these compounds, π^*-anions were observed in the methanol glasses on annealing. When the solvent radicals decayed, the doublet signal characteristic of the π^*-radical[2] remained. Similar results were obtained for the 5-bromo- and 5-iodo-uracils in methanol glasses. The ether glass proved unsuitable for the detection of π^*-anions in all components since the central region of the spectra was masked by solvent radicals which were lost only when the matrix became mobile.

It would be of interest to follow the fate of both the σ^*- and π^*-anions in order to assess their possible connection with halide elimination. Previous studies with aqueous neutral and alkaline glasses seemed to show that π^* addition was directly followed by halide ion loss to give the uracil-yl radicals (III)[2] The detection of σ^*-anions strongly suggests that these species are significant intermediates in the dissociation process. Thus we suggest that when π^* addition is favoured, subsequent dissociation is preceded by electron migration from the π^* to the σ^* orbital. Unfortunately, we have not yet been able to detect this sequence of events with certainty. A broad, structureless singlet of the type attributed to the uracil-yl radicals (III) was observed on annealing glasses containing the bromo and iodo σ^* anions, but intense absorption in the central region from solvent radicals have made it impossible to monitor all three species systematically. To reach a more definitive conclusion about this question we are exploring the possibility of detecting these radicals by u.v. spectroscopy in the expectation that their absorption bands will be distinguishable from each other.

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[1] For a recent survey: J. Hüttermann, in 'Excited States in Organic Chemistry and Biochemistry,' eds. B. Pullman and N. Goldblum, Reidel, Dordrecht, Holland, 1977, p. 85.

[2] L. D. Simpson and J. D. Zimbrick, *Internat. J. Radiat. Biol.*, 1975, **28**, 461; M. D. Sevilla, B. Failor, and G. Zorman, *J. Phys. Chem.*, 1974, **78**, 696.

[3] See *e.g.* K. Bhatia and R. H. Shuler, *J. Phys. Chem.*, 1973, **77**, 1888.

[4] J. H. Mackey, M. Kopp, E. C. Tynan, and T. F. Yen in 'Electron Spin Resonance of Metal Complexes,' ed. T. F. Yen, Plenum, New York, 1960, p. 33.