Electron Spin Resonance Spectra and Structures of some σ* Radicals

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Summary E.s.r. data are presented for a variety of radicals derived from irradiated *N*-halogeno-amides and trialkyl phosphines and arsines, which have their unpaired electrons in anti-bonding σ orbitals.

APART from the halogen$_2^-$ V_K centres, few radicals having their unpaired electron in an anti-bonding σ-orbital are known.[1] We have studied various γ-irradiated *N*-chloro- and *N*-bromo-amides (see Table) and have obtained e.s.r. evidence for the presence of radical anions in which the unpaired electron appears to be almost entirely confined to a localised *N*-halogen σ* orbital. Approximate orbital populations, estimated from the nitrogen and halogen hyperfine tensor components in the usual manner,[1] given in the Table are in good accord with expectation for such radicals.

Hyperfine coupling constants and derived orbital populations for various σ radicals*

Radical[a]		Hyperfine tensor components (in G)[b]			Orbital populations	
		xx	yy	zz	$a_p^2(\%)$	$a_s^2(\%)$
$\overline{\mathrm{CO{\cdot}[CH_2]_2{\cdot}CO{\cdot}N}}\mathrm{Cl}^-$	(^{14}N)	45	45	68	45	9·6
	(^{35}Cl)	45	45	115	46·7[c]	4·0
$\overline{\mathrm{CO{\cdot}[CH_2]_2{\cdot}CO{\cdot}N}}\mathrm{Br}^-$	(^{14}N)	40	40	63	45	8·7
	(^{81}Br)	155	155	580	57[c]	3
MeCONHBr$^-$	(^{14}N)	45	45	69	47	9·6
	(^{81}Br)	150	150	560	53·2[c]	2·85
$(\mathrm{Et_3P})_2^+$	(^{31}P)	540	412	412	41·4	12·5
$(\mathrm{Bu_3P})_2^+$	(^{31}P)	550	418	418	42·7	12·7
$(\mathrm{Me_2PS})_2^-$	(^{31}P)	553	459	459	30·4	13·5
$(\mathrm{Et_3As})_2^+$	(^{75}As)	465	375	375	32·8	11·8

[a] Formed by exposure of the pure parent amides, phosphines and arsines to ^{60}Co γ-rays at 77 K. [b] Corrected where necessary using the full Breit–Rabi equation. [c] Using positive sign for $A_\perp$ (^{14}N and ^{35}Cl or ^{81}Br). When $\perp$ values for Cl or Br are taken as negative, the results indicate unacceptably high spin densities on the halogen atom.

Another type of σ* radical has been detected by e.s.r. spectroscopy in γ-irradiated phosphines and arsines at 77 K. These appear to be the dimers $\mathrm{R_3M{-}MR_3^+}$ (M = P or As) formed from the primary cation, $\mathrm{R_3M^+}$. A species with similar magnetic properties was prepared directly from $\mathrm{Me_2P(S){-}P(S)Me_2}$. The results and derived orbital populations are included in the Table.

In all cases, the form of the g-tensor also strongly supports these assignments with g_{zz} *ca.* 2·0023, and g_{xx} = *ca.* $g_{yy} \gg 2{\cdot}0023$. These results are of interest for the following reasons. (i) For the amides, the excess electron is accommodated in a σ* orbital in preference to a π* orbital† of the –C(:O)–N$^-$ group. This is an interesting contrast with the results for carboxylic acids and related compounds.[2] (ii) The spin density is almost equal on nitrogen and halogen

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† These orbitals are not strictly π* because the radicals were slightly pyramidal with respect to the carbonyl carbon.

despite the major difference in the nature of the atoms involved. We shall show elsewhere that this similarity is in accord with the relative electronegativities of the constituent atoms when compared with results for V_K centres. (iii) Although the halogen atom contribution to the σ^* orbital is primarily p_z, as is expected by analogy with Cl_2^- or Br_2^-, that from nitrogen is relatively rich in *s*-character. The *s*-contribution from M with R_3M–MR_3^+ radicals is even more significant, and the orbitals can most appropriately be described as being approximately sp^3 hybridised, and almost entirely localised on the two M atoms.

These results constitute a remarkably clear vindication of the semi-intuitive ideas regarding hybridisation and orbital localisation used so extensively by chemists. They also underline the fact that the concept of hybridisation is useful when describing the structure of species such as $R_3M\cdot$ or R_3M–MR_3^+, but possibly misleading if applied to bonding in species such as the halogen molecules.

Finally, mention should be made of the presence of a second radical with a large hyperfine coupling to ^{75}As (*ca.* 400 G) detected in γ-irradiated triethylarsine. These lines, which were almost isotropic, are very tentatively assigned to rotating Et_4As radicals or to related Et_3AsR radicals. Comparison with data for various alkyl–alkoxy radicals, $R_nP(OR)_{4-n}$,[3] suggests that an isotropic hyperfine coupling of this magnitude is reasonable for such radicals.

The only other radicals detected in the irradiated amides were normal carbon-radicals such as $H_2\dot{C}$–CONHBr. Other radicals detected in the phosphines and arsines have been reported previously.[4]

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[1] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, **1967**.

[2] See, *e.g.*, J. E. Bennett and L. H. Gale, *Trans. Faraday Soc.*, 1968, **64**, 1174.

[3] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, in the press; A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738.

[4] A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2290; 1971, 2388.