Hyperfine Coupling to Iodine in α-Iodoalkyl Radicals: the Radical $H\dot{C}(I)CONH_2$ in γ-Irradiated α-Iodoacetamide

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Summary Reasons for supposing that a radical exhibiting well defined hyperfine coupling to ^{127}I, formed in γ-irradiated α-iodoacetamide, is $H\dot{C}(I)CONH_2$ are summarised.

Although the e.s.r. spectra of organic π-radicals containing α-chlorine and α-bromine are now well established,[1,2] we know of no spectra assignable to α-iodo-radicals, $R_2\dot{C}I$, either in fluid solution or in the solid state. Having observed a wide range of organic iodides both pure and in rigid solvents after exposure to ^{60}Co γ-rays, we have found that by far the best e.s.r. spectrum is obtained from α-iodoacetamide. Accordingly, we have studied powder and single crystal e.s.r. spectra, and conclude that the radical is the α-iodo-radical, $I\dot{C}HCONH_2$. (In fact, the best spectra were obtained for the *N*-deuteriated radical, $I\dot{C}HCOND_2$).

The radical exhibited hyperfine coupling to ^{127}I ($I = 5/2$) with $A_x = 250$, $A_y = 80 \pm 5$, and $A_z = 100 \pm 5$ G, and $g_x = 1{\cdot}991$, $g_y = 2{\cdot}053$, and $g_z = 2{\cdot}067$. No proton structure was resolved in the powder spectra, but single crystal spectra exhibited a double splitting varying between 10 and 22 G (see Figure). No coupling to ^{14}N was observed, but a marked increase in line-width for field close to the *x*-direction suggested a value in the region of 4 G for $A_x(^{14}N)$.

These results accord well with expectation for the suggested radical.[2] Thus the largest coupling occurs close

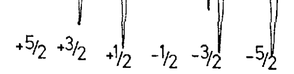

Figure. First derivative *X*-band e.s.r. spectrum for a single crystal of *N*-deuteriated iodoacetamide after exposure to ^{60}Co γ-rays at 77 K showing features assigned to $ICHCOND_2$ oriented between the *y* and *z* axes.

to the free-spin *g*-value, and we assign *x* to the direction normal to the radical plane. The *z* direction is then taken along the C–I bond, since this shows a very large positive *g-shift* of the same form, but far greater than, that for $R_2\dot{C}Br$ radicals. This is expected because of the larger spin–orbital coupling constant for iodine. Also, the six hyperfine features were evenly spaced along *z*, showing that no quadrupole effect operates in this direction.

If the signs of the coupling constants are taken to be positive for the *x*-direction and negative for the *y*- and *z*-directions, the estimated orbital population on iodine is far too high (*ca.* 56%), which does not accord with the values of the ^1H coupling. However, taking all signs to be positive, we estimate a π-spin density on iodine of *ca.* 26%. This can be compared with the similarly estimated values for delocalisation onto α-chlorine (*ca.* 16%) and α-bromine (*ca.* 19%). The steady increase agrees well with the decrease in electronegativity in this series.

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