The Effect of γ-Irradiation on the Mössbauer Line Widths in Tris(acetylacetonato)iron(III)

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Summary The very large (*ca.* 2 mm s^{-1}) line widths in the Mössbauer spectra of $Fe(acac)_3$ are reduced to *ca.* 0·6 mm s^{-1} by γ-irradiation.

IRON (III) high spin compounds often exhibit Mössbauer line widths which are broadened greatly from the natural line width of 0·19 mm s^{-1}. For example, several workers have reported full widths at half height of about 2 mm s^{-1} [1,2] for tris(acetylacetonato)iron(III) [$Fe(acac)_3$] species, making it difficult to resolve any quadrupole splitting. These large line widths have been attributed to the interaction of the nucleus with fluctuating electric and magnetic fields. However, recent papers[3] have reported substantially narrower line widths for $Fe(acac)_3$, and visual resolution of the quadrupole doublet was achieved after application of high pressures.[3] We now report the marked decrease in line width after γ-irradiation, and indicate how such large decreases in line width can be rationalized.

$Fe(acac)_3$ was prepared and recrystallized by standard methods.[4,5] The powdered compound was irradiated in a 2000 Ci Vikrad ^{60}Co unit giving a dose rate of $3·3 \times 10^5$ rads per hour. Total doses of $3·0 \times 10^8$ and $6·0 \times 10^8$ rads were given to two samples. There was no noticeable visible change in the colour of the crystals, and the i.r. and mass spectra[6] did not alter noticeably. In particular, the relative intensity of the molecular ion $Fe(acac)_3^+$ in the mass spectrum did not decrease noticeably. This evidence indicates that at least 90% of irradiated compound is still $Fe(acac)_3$.

The Mössbauer spectrum, however, changes appreciably, as shown in the Table and Figure. The line width before the irradiation (1·86 mm s) is similar to that reported previously,[2] and two peaks could not be fitted to the spectrum. After the dose of $3·0 \times 10^8$ rads, the line widths have narrowed markedly, and the small quadrupole splitting is just resolved visually (Figure). In addition, the peaks

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are beginning to broaden slightly in the wings. With the higher dose, the quadrupole doublet is well resolved, and the

Mössbauer parameters for γ-irradiated $Fe(acac)_3$ *at* 295K

Dose(rads)	C.S.[a] (mm s^{-1})	Q.S. (mm s^{-1})	Γ (mm s^{-1})
0	0·62	not resolved	1·86
$3·0 \times 10^8$	0·65	0·46	0·86
$6·0 \times 10^8$	0·69	0·67	0·59

[a] Relative to sodium nitroprusside.

line widths have decreased to 0·59 mm s^{-1}. The Fe^{III} line widths in potassium tris(oxalato)ferrate(III) $[K_3Fe(C_2O_4)_3]$ also decreased substantially on γ-irradiation, but decomposition often made it difficult to resolve the Fe^{III} peaks.[7]

It seems likely that the reduction in line width in $Fe(acac)_3$ is due to motional narrowing. One possibility is the conversion of a small proportion of $Fe(acac)_3$ into $Fe(acac)_3^-$. The extra electron could then jump easily from one complex to the next, providing an efficient relaxation mechanism. If the jumping rate for an electron is ν_e and the mole fraction of iron(II) is f, the jumping rate associated with a particular iron atom would be $f\nu_e$, and the line width Γ would be of the order of $\Delta^2(f\nu_e)$, where Δ is the quadrupole splitting from the d-electron in the absence of any relaxation. Taking Δ *ca.* 5 mm s^{-1} = 58 MHz and Γ *ca.* 0·5 mm s^{-1} = 5·8 MHz, we obtain $f\nu_e$ *ca.* $5·8 \times 10^8$ Hz which would probably be achieved with f well below 0·01.

It appears likely from this study that the line widths of other Fe^{3+} compounds which do not decompose on γ-irradiation will narrow markedly after exposure to γ-irradiation.

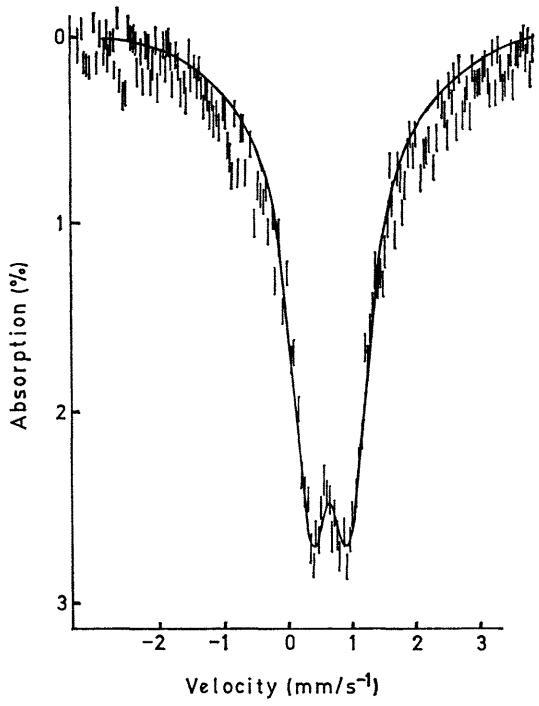

FIGURE. *Room temperature Mössbauer spectrum of* $Fe(acac)_3$ *after a dose of γ-irradiation of* $3·0 \times 10^8$ *rads.*

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[1] J. W. G. Wignall, *J. Chem. Phys.*, 1966, **44**, 2462.
[2] G. M. Bancroft, A. G. Maddock, W. K. Ong, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.
[3] A. R. Champion, R. W. Vaughan, and H. G. Drickamer, *J. Chem. Phys.*, 1967, **47**, 2583.
[4] F. C. Fernelius, *Inorg. Synth.*, 1946, **2**, 25.
[5] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, 1960, **62**, 440.
[6] G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, 1968, **7**, 870.
[7] G. M. Bancroft, K. G. Dharmawardena, and A. G. Maddock, *J. Chem. Soc.* (*A*), 1970, 2914.