Migration of Radicals in Crystal Sites: Thallous and Plumbous Ions as Electron Donors and Electron Acceptors: an Electron Spin Resonance Study

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Summary The radicals NO_2, NO_3, NO_3^{2-}, CO_2^-, and $\dot{C}H_2CO_2^-$, prepared by high energy radiation in $Pb(NO_3)_2$, $TlNO_3$, $TlHCO_2$ and TlOAc have e.s.r. spectra which exhibit large, temperature-dependent, hyperfine interaction with various types of Tl^+ and Pb^{2+} ions which arise from slight electron-transfer either to or from the radicals depending on their structures.

EXPOSURE of lead nitrate to ^{60}Co γ-rays at 77 K gave NO_3 and NO_3^{2-} radicals, whereas irradiation at room temperature gave, after long exposure, mainly NO_2 radicals.[1] Thallous nitrate gave only NO_3 radicals at 77 K, but again, NO_2 was formed at room temperature. Thallous formate gave mainly CO_2^- radicals at 77 K whilst thallous acetate gave mainly $\dot{C}H_2CO_2^-$ radicals.

These results are unexceptional for such anions, but are of interest in that the e.s.r. spectra reveal the presence of strong interactions with the cations which describe the cavities containing these radicals. A typical spectrum, for NO_3 in thallous nitrate, illustrates this (Figure).

The e.s.r. spectral data are summarised in the Table. In contrast with cations having s^2,p^6 configuration, such as Na^+, which interact only by an electron-accepting mechanism,[2] the d^{10},s^2 cations under consideration can act both as electron donors and acceptors. Thus, with electron excess radicals, such as NO_3^{2-}, we would expect the cations to act as acceptors, which would result in a weak, but highly

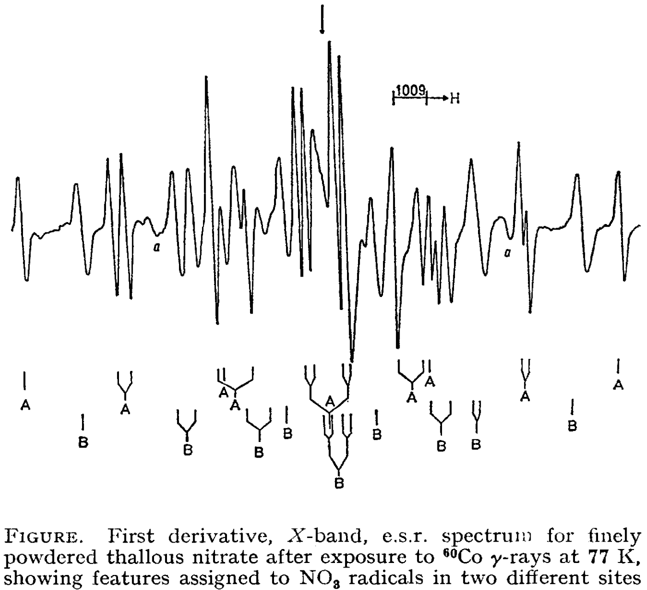

FIGURE. First derivative, *X*-band, e.s.r. spectrum for finely powdered thallous nitrate after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to NO_3 radicals in two different sites (A and B). These radicals each exhibit hyperfine coupling to two strongly and two more weakly coupled thallous ions. there is a marked Breit–Rabi effect which splits out certain components of the degenerate lines, and the field-dependence of this second order effect is well illustrated in this spectrum.

[a] Extra features from an unidentified species.

TABLE. Some values for the hyperfine coupling to ^{205}Tl and ^{207}Pb for various radicals in irradiated thallous and plumbous salts

Host	Radical	Temp. (K)	Hyperfine coupling to ^{205}Tl or ^{207}Pb (G)[a,b]
$TlNO_3$[d]	NO_3	4·2	(A) 320(2) *ca.* 650(2) (B) 330(2) *ca.* 490(2)
		77	(A) 285(2) *ca.* 610(2) (B) 315(2) *ca.* 410(2)
$TlHCO_2$	CO_2^-	77	420(2); 310(2); 47(2).
$TlMeCO_2$	$\dot{C}H_2CO_2^-$	77	158(2); 40(1); 20(1)
$Pb(NO_3)_2$	NO_3^{2-}	77	$_{\parallel}$*ca.* 34, $_{\perp}$*ca.* 0(3), $_{\parallel}$*ca.* 8, $_{\perp}$*ca.* 0(1)[e]
	NO_3[c]	77	43
		ca. 200	32
	NO_2	77	311(1) 12·5(2)
		R.T.	85(3)

[a] 1 G = 10^{-4} T. [b] The number in parentheses gives the number of equivalent cations. [c] On standing at room temperature these signals slowly decayed in favour of features for "normal" NO_3, having no detectable coupling to ^{207}Pb, but a resolved ^{14}N coupling (*cf.* ref. 1). [d] In the normal γ-form, two types of interaction (Type A and Type B) were detected in about equal amounts. In the high-temperature α- and β-forms type B predominated. [e] The tensor axes for these interactions make angles of about 45° with those for the ^{14}N coupling. The g values for NO_3^{2-} ($g_{\parallel} = 1{\cdot}985$, $g_{\perp} = 1{\cdot}991$ are less than those usually observed).

anisotropic, hyperfine coupling and negative g-shift from the configuration d^{10},s^2,p^1. In contrast, with electron deficient radicals such as NO_3, electron donation to give the d^{10},s^1 configuration should dominate, with a resulting isotropic hyperfine coupling to the metal and no extra g-shift. (Both effects could, in principle, occur in the same system, depending upon the relative orientation of the ions and consequent overlap possibilities.) Our results show that NO_3 and NO_2 act as electron acceptors, so that the hyperfine coupling from ^{207}Pb or $^{203/205}Tl$ is large and isotropic, and there are no appreciable g-shifts. In contrast, NO_3^{2-} acts as an electron donor, and the ^{207}Pb hyperfine coupling is relatively small, but strongly anisotropic (Table). In this case, both $g_{\parallel}$ and $g_{\perp}$ have been shifted to low values relative to the normal results for NO_3^{2-}. (ref. 3)

There is also a tendency for more than one of the cavity cations to be involved in these charge-transfer interactions, and for the trapped radicals to migrate within their cavities at temperatures above 77 K. Although molecular motions in solids have been extensively studied by n.m.r. and e.s.r., these studies have been confined to changes in the magnetic properties of the moving species. Thus librations or rotations are probed, but not translatory motion within the cavities. Our results reveal rotatory motion from changes in the radical parameters, but also translatory motion from changes in the cation hyperfine coupling.

For example, at 77 K, NO_2 in lead nitrate is stationary, and exhibits a large coupling to one ^{207}Pb cation and a weak coupling to two equivalent cations, the remaining Pb^{2+} ions in the cavity being without interaction.

On warming, the NO_2 starts to rotate about its long axis (y), and simultaneously, the three interacting lead ions become equivalent, with a reduced total hyperfine interaction. Examination of a model suggests that the NO_2 radicals, as they rotate, jump between three equivalent lead ions, but the reduced total coupling suggests that they move towards a more central position with increasing temperature.

Similarly, with NO_3 in thallous nitrate, at low temperature there is a strong coupling to two equivalent Tl^+ ions and a weaker coupling to two others. As the temperature increases so both types of Tl^+ ions exhibit smaller coupling constants, the changes being completely reversible. Thus the NO_3 radicals are moving on average to a more remote (central) site in their cavities. (The situation is involved because there are two alternative sites in normal thallous nitrate, but they both behave in a similar manner.)

The CO_2^- anion in thallous formate acts as a weak electron acceptor rather than as a donor. This result reflects the high ionisation potential of Tl^+ and also illustrates the ability of CO_2^- to act as an electron acceptor. The CO_2^- ion at 77 K interacts strongly with two equivalent Tl^+ ions, strongly with two more, and very weakly with a further two Tl^+ ions. On annealing, there was no change in these coupling constants, showing that the CO_2^- ions enjoy no freedom of movement in their formate sites.

The total hyperfine interaction with Tl^+ ions was greatly reduced for $H_2\dot{C}CO_2^-$ radicals in thallous acetate. This arises because the radicals are co-ordinated *via* oxygen which bears only a small fraction of the total spin-density.

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[1] R. M. Golding and M. Henchman (*J. Chem. Phys.*, **1961**, **40**, **1554**) detected NO_2 and NO_3 radicals at room temperature, but failed to detect ^{207}Pb hyperfine interaction.

[2] J. H. Sharp and M. C. R. Symons, in 'Ions and Ion Pairs in Organic Reactions,' vol. I, ed. M. Szwarc, Wiley, New York, **1972**.

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