Radiation Mechanisms. Part 9.[1] A Comparative Electron Spin Resonance study of Radiation Effects in Thallous and Thallic Salts

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Exposure of thallous salts to high-energy radiation usually yields Tl^{II} centres together with paramagnetic centres derived from the anions which show strong charge-transfer interaction with neighbouring thallous ions. Previous work on thallous acetate and nitrate is extended to the perchlorate, and to the corresponding Tl^{III} salts. The latter all gave Tl^{II} but centres derived from the anions generally failed to show any hyperfine interaction with neighbouring cations despite the high positive charge. The nature of the radicals detected and their mode of formation are discussed.

WE have recently found that radicals formed in irradiated salts of cations having a . . . .$d^{10}s^2$ configuration tend to exhibit strong electron-transfer effects with sets of neighbouring cations. Thus, for example, NO_3^{2-} in Pb^{II} nitrate weakly donates spin-density to neighbouring Pb^{2+} ions, whilst NO_3 in the same salt acts as an electron acceptor towards Pb^{2+}.[2] Thallous nitrate gave only NO_3, which interacts strongly with four neighbouring thallous ions,[3] and thallous acetate gave a Tl^{II} centre together with $H_2\dot{C}CO_2^-$ interacting with four neighbouring Tl^I ions.[4]

Our present aim was to study radiation products in Tl^{III} nitrate and acetate in order to contrast the behaviour of a d^{10} ion with its $d^{10}s^2$ counterpart We have extended this comparison to the two perchlorate salts since a great deal is known about the effects of high-energy radiation upon alkali-metal perchlorates,[5-7] and well defined products were expected.

Some work on Sn^{II} and Pb^{II} salts has been reported recently,[8] and a preliminary account of the formation of a Pb^{III} centre in Pb^{IV} acetate has appeared.[9] We have extended this work to a study of the radicals derived from the acetate ions in this salt to link in with our work on Tl^{III} acetate.

EXPERIMENTAL

Thallium(III) acetate sesquihydrate and thallium(III) nitrate trihydrate were obtained from Courtorch Chemicals Limited. Thallium(III) perchlorate hydrate was obtained from Ventron. These compounds were dried in a desiccator over P_2O_5 and pulverized to a fine powder under liquid nitrogen. Lead tetra-acetate and thallium(III) acetate (deuteriated) were prepared by standard methods. Thallium(I) perchlorate was prepared from thallium(I) carbonate and perchloric acid. All chemicals used were of highest purity available.

The samples were irradiated as fine powders in a ^{60}Co Vickrad source at a dose rate of 1.7 MCi h^{-1} for up to 2 h at 77 K. E.s.r. spectra were measured at 77 K on a Varian E3 X-band spectrometer using an insert Dewar filled with liquid nitrogen. Samples were annealed directly in this Dewar after decanting the nitrogen. Spectra were rapidly scanned and the samples were re-cooled to 77 K wherever significant spectral changes were observed.

Spectra at 4.2 K were run on a Varian V.4502-03 spectrometer at low power levels to avoid saturation effects.

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[2] M. C. R. Symons, D. X. West, and G. Wilkinson, *J.C.S. Dalton*, 1974, 2247.

[3] M. C. R. Symons, D. X. West, and G. Wilkinson, *J.C.S. Dalton*, 1975, 553.

[4] M. C. R. Symons, D. X. West, and G. Wilkinson, *Internat. J. Radiation Phys. and Chem.*, 1975, in the press.

[5] T. Cole, *J. Chem. Phys.*, 1961, **35**, 1169.

[6] J. R. Byberg, S. J. K. Jensen, and L. T. Muns, *J. Chem. Phys.*, 1967, **46**, 131.

[7] R. S. Eachus, P. R. Edwards, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 1704.

[8] H. C. Starkie and M. C. R. Symons, *J.C.S. Dalton*, 1974, 731.

[9] J. I. Isoya, H. Ishizuka, A. Yamasaki, and S. Fujiwara, *Chem. Letters*, 1972, 397.

RESULTS AND DISCUSSION

Thallium(II) centres can be identified by the appearance of a high-field feature in the 6 000 G region.[10] ^{205}Tl Has $I = \frac{1}{2}$ and is 70.48% abundant; ^{203}Tl has $I = \frac{1}{2}$ and is 29.52% abundant. Their magnetic moments are so close that only a single combined line is observed in most experiments. The 6 000 G component is the $(F = 1, M_F = -1) \rightleftharpoons (F = 1, M_F = 0)$ transition. The electron and nuclear spins are still strongly coupled at X-band frequencies, so that $F = (S + I)$ and M_F are good quantum numbers. The normal low-field transition $(F = 0, M_F = 0) \rightleftharpoons (F = 1, M_F = +1)$ is unobservable because of the very large hyperfine coupling. A second line at very high fields can also be observed, arising from the 'n.m.r.' transition: $(F = 1, M_F = 0) \rightleftharpoons (F = 1, M_F = +1)$, but these cannot be reached on the E3 spectrometer. We have checked their presence in selected cases using a standard Varian V5402 spectrometer, but this adds little to our knowledge of these systems.

Thallium(II) centres were clearly detected in the three Tl^{III} salts, and also in Tl^{I} perchlorate and acetate. They were not observed in irradiated thallous nitrate.[3] The spectrum for Tl^{II} in thallic acetate (Figure 1) is of particular interest since it shows x, y, and z components which are clearly split by extra hyperfine coupling either to protons or to other thallium nuclei. When $CH_3CO_2^-$ ions were replaced by $CD_3CO_2^-$ ions the same features appeared and, hence, we conclude that two other weakly coupled thallous nuclei are an integral part of this centre. A comparable situation was detected in our study[8] of irradiated tin(II) acetate, which contained an Sn^{I} centre exhibiting weak interaction to two inequivalent ^{119}Sn and ^{117}Sn nuclei.

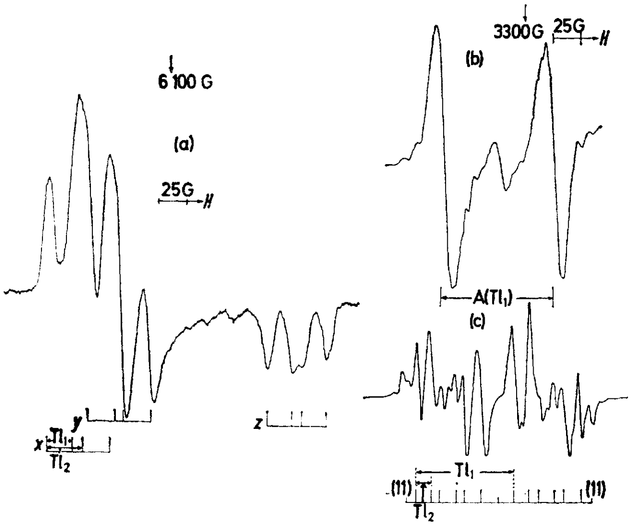

FIGURE 1 First derivative X-band e.s.r. spectra for thallium(III) acetate after exposure to ^{60}Co γ-rays at 77 K, showing (a) high-field features assigned to Tl^{II}, (b) features assigned to $D_2\dot{C}CO_2^-$ at *ca.* 77 K, and (c) features assigned to $H_2\dot{C}CO_2^-$ at *ca.* 130 K

These unusual centres require the presence of three normal cations and an excess electron so dispersed that the electron prefers to be almost completely localised on one cation, but still very weakly interacting with the other two. We envisage the occurrence of a major distortion amongst the ligands associated with the favoured cation, but in the absence of information from any ligand nuclei we are unable to deduce the nature of this distortion.

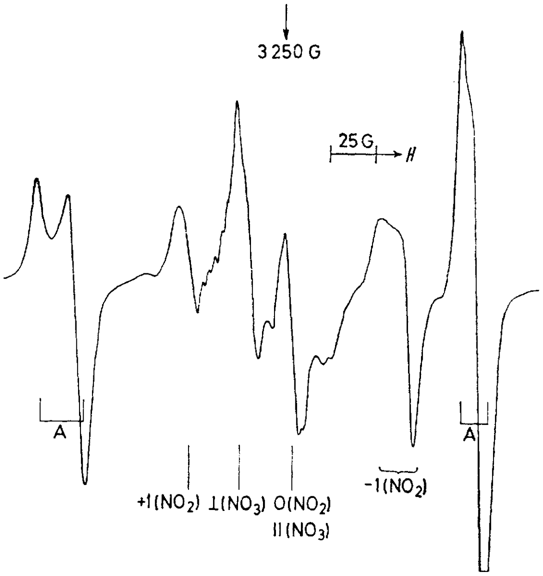

FIGURE 2 First derivative X-band e.s.r. spectra for thallium(III) nitrate after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to NO_3 and NO_2 radicals together with species A discussed in the text

Centres in Thallic Nitrate.—In addition to the Tl^{II} centre, features clearly assignable to NO_2 and NO_3 radicals were detected in the central ($g = 2$) spectral region. No feature for NO_3^{2-} could be observed (Figure 2). It is significant that no clear hyperfine coupling to neighbouring cations could be detected either for NO_2 or NO_3. In addition, a well defined, anisotropic, doublet (species A) was detected, together with a further relatively weak doublet with a coupling of *ca.* 650 G (species B).

Species A is clearly one of the significant radiation products. The doublet splitting of *ca.* 220 G (see Table) must stem from hyperfine coupling to a single type of $^{203/205}$Tl nucleus, and no splitting to ^{14}N could be resolved. Thus the species either does not contain nitrogen or the unpaired electron is confined to other nuclei. Although NO_3 is possible, the g-values are incorrect (Table) and, anyway, normal NO_3 is detected in good yield. Some product from one of the water ligands is possible, although OH radicals[11] can be ruled out because of the absence of any proton hyperfine coupling. An electron largely confined to an O^- ligand could give a weak coupling to thallium, but then a large positive g-value

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[10] M. C. R. Symons and J. K. Yandell, *J. Chem. Soc.* (*A*), 1971, 760.

[11] J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 2112.

would be expected. We suggest below that one of the centres in irradiated thallous perchlorate is O_3^-, which is a normal product from irradiated halogen oxy-ions.[12] A species $Tl^{III} \cdots O_3^-$ could certainly account for the spectrum of species A, but formation of O_3^- from NO_3^- is unprecedented, so far as we are aware, and does seem most improbable. One remote possibility is the formation of the radical NO_4^{2-}:

$$\cdot OH + NO_3^- \longrightarrow NO_4^{2-} (+H^+) \qquad (1)$$

with weak coupling to one Tl^{III}. The radical NO_4^{2-} has been tentatively postulated as a product in the radiolysis of aqueous nitrates.[13] The coupling to ^{14}N is in the region of 2 G and would not have been resolved, and the g-values are close to those now reported.

E.s.r. parameters for radicals in irradiated thallous and thallic salts

Host	Radical	Hyperfine coupling to ^{203}Tl(G) [a] the number of Tl nuclei is given ( )	Hyperfine coupling to other nuclei (G) [a]	g-Values
$Tl(NO_3)_3 \cdot 3H_2O$	Tl^{II}	*ca.* 40 000 [b]		2.00
$Tl(NO_3)_3 \cdot 3H_2O$	NO_2		(^{14}N) 65(x), 47(y), 50(z)	2.002(x) 1.994(y) 2.005(z)
$Tl(NO_3)_3 \cdot 3H_2O$	NO_3		(^{14}N) *ca.* 3($\perp$)	2.024($\parallel$) $\sim$2.00($\perp$)
$Tl(NO_3)_3 \cdot 3H_2O$	Species A	232($\parallel$), 218($\perp$) (1)		2.013($\parallel$), 2.002($\perp$)
$Tl(NO_3)_3 \cdot 3H_2O$	Species B	680 (1)		$\approx$2.00
$Tl(OAc)_3$	Tl^{II}	*ca.* 40 000 [b] + 23(1), 30(1)		2.00
	$H_2\dot{C}CO_2^-$	85(1), 15(2)	(^1H) 21	2.00
$TlClO_4$	ClO_2(D)	163(6) [c]	(^{35}Cl) 13—25	*ca.* 2.008
	O_3^-(C)	290(1), 144(1), 22(1), 10(1)	12—15	2.017, 2.009, 2.002
	Tl^{II}	*ca.* 40 000		2.00
$Tl(ClO_4)_3$	Tl^{II}	*ca.* 38 000		2.00
	ClO_3		(^{35}Cl) 156($\parallel$), 109($\perp$)	2.006($\parallel$), 2.010($\perp$)
	ClO_4 ( )		(^{35}Cl) 7—10	*ca.* 2.00

[a] G = 10^{-4}T. [b] Either the g- or the A-values or both exhibit a slight non-axial symmetry. [c] Six equivalent Tl^+ ions assumed.

Species B is again too poorly defined for satisfactory identification. It is only present in low yield and we suggest that it is NO_3 formed fortuitously close to a Tl^I impurity in the nitrate. The magnitude of the $^{203/205}Tl$ coupling is about correct for such an interaction.[3]

Centres in Thallic Acetate.—In addition to the Tl^{II} centre (Figure 1a), a spectrum assignable to $H_2\dot{C}CO_2^-$ radicals was obtained. At 77 K the spectrum comprised two triplets separated by 98 G which became two singlets when $Tl(CD_3CO_2)_3$ was studied (Figure 1b). On annealing, the spectra became relatively well resolved and an extra small doublet splitting was apparent (Figure 1c). Methyl or $\dot{C}D_3$ radicals were not detected.

Centres in Thallous Perchlorate.—In addition to the single broad 6 000 G line assigned to Tl^{II}, a profusion of features covering *ca.* 1 000 G were detected in the $g = 2$ region (Figure 3). At least two different species are involved, species C comprising a set of four quartets, with species D being responsible for the weaker sets of lines flanking those for C. The small quartet splitting of *ca.* 12 G for C and *ca.* 15 G for D could both stem from hyperfine coupling to chlorine. [Both ^{35}Cl (75.53%) and ^{37}Cl (24.47%) have $I = 3/2$, and similar magnetic moments: the lines in Figure 3 are too broad for the isotope difference to be resolved.] On cooling to *ca.* 4.2 K the features for species D were greatly broadened, whilst those for C were unchanged. (The intermediate features α were also greatly broadened at 4.2 K.) This suggests that the quartet splitting for C is isotropic and stems from coupling to thallium nuclei, whilst that for species D is strongly anisotropic and stems from coupling to chlorine nuclei. Unfortunately, no well defined parallel or perpendicular features resulted for D at 4 K, but the great increase in bandwidth would accord with our assignment to ClO_2 radicals, provided these are rotating or librating in a well defined manner at 77 K. Single crystal spectra showed that the quartets for species D are somewhat anisotropic even at 77 K. In general, two sets of quartets were obtained which overlapped seriously. However, the coupling ranged from *ca.* 13 to *ca.* 25 G, which is reasonable for ClO_2 undergoing considerable libratory motion.

The intermediate features labelled (α) in Figure 3 were at first thought to be part of a septet of lines including the four assigned to C, there being an alternate broadening effect which left the four C features narrow. However, the α features were almost lost at *ca.* 4 K, whilst those for C were unaltered. We consider it unlikely that some motion, giving fast-exchange broadening at 77 K would not be sufficiently damped at *ca.* 4 K to give narrow components. Thus we suggest that the α lines belong to another, unidentified, radical. (Although some contribution from inner features of species D is probable.)

We conclude that species C only exhibits hyperfine coupling to thallium nuclei, there being one strongly coupled cation, two very weakly coupled cations, and one giving an intermediate coupling (see Table). The nature of this centre is not clear, except that it probably does not contain chlorine, since all known chlorine species derivable from perchlorate ions exhibit hyperfine coupling to chlorine nuclei that would have been detected if it occurred for species C.

The single crystal results confirm that the hyperfine coupling constants are all isotropic, but that the g-value is not. In general, two sets of lines were obtained which moved between the limits set by the outer

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

[13] D. Zimmerman and M. C. R. Symons, *J.C.S. Faraday II*, in the press.

shoulders flanking each quartet in the powder spectrum (Figure 3). From these, the principle components of the g-tensor were calculated (see Table). These are quite close to those characteristic of O_3^- radicals,[12,14] which are often formed by radiolysis of perchlorate salts.[7] We conclude that species C is O_3^- interacting with several neighbouring thallous ions. Another possibility is the radical ClO_4. This is expected to have a fairly isotropic coupling to chlorine in the region of 10 G, and a spread of g-values that would be markedly dependent upon the environment.[15] We think this possibility is extremely improbable since thallous ions are powerful electron donors and ClO_4 must be an extremely strong acceptor, so that the reaction

$$ClO_4 + Tl^+ \longrightarrow ClO_4^- + Tl^{2+} \qquad (2)$$

could hardly be prevented even at 77 K.

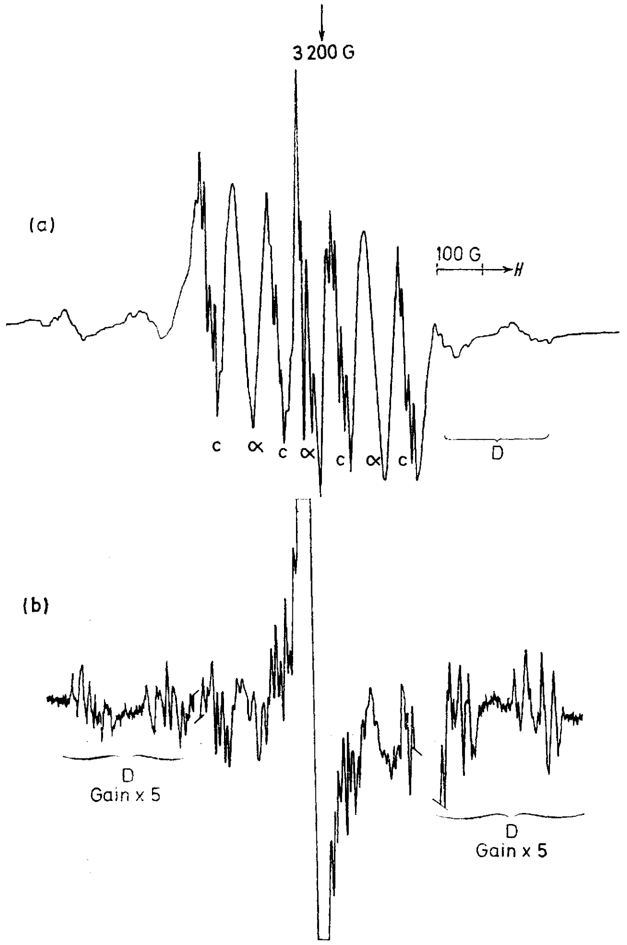

FIGURE 3 First derivative X-band e.s.r. spectra for thallium(I) perchlorate after exposure to ^{60}Co γ-rays at 77 K, showing (a) features (C) assigned to O_3^- and (D) assigned to ClO_2. Features α are discussed in the text, and (b) showing a typical single-crystal spectrum

Centres in Thallic Perchlorate.—Again, a well defined Tl^{II} centre was detected. The major species in the $g = 2$ region has a well defined set of four parallel and four perpendicular features for both ^{37}Cl and ^{35}Cl nuclei (Figure 4). The resulting magnetic data (Table) are close to those normally found for ClO_3,[5-7] and we conclude that, unless some extreme coincidence is occurring, such as that for BrO_3 and BrO_3^{2-} radicals,[16] this species is ClO_3, exhibiting no detectable coupling to neighbouring thallic ions.

A relatively weak, poorly defined, central triplet or quartet was also obtained (Figure 4) which may well be due to ClO_4 radicals. These lines were lost irreversibly on slight annealing. As mentioned above, the radical ClO_4 is expected to exhibit a small fairly isotropic coupling to chlorine, probably in the region of 11 G, and a fairly large spread of g-values.[15] Hence, we suggest that the central features stem from non-interacting ClO_4 radicals.

Centres in Lead(IV) *Acetate.*—In addition to the Pb^{III} centre detected previously,[9] we obtained well-defined spectra for methyl and $H_2\dot{C}CO_2^-$ radicals. However, we were unable to detect ^{207}Pb hyperfine satellite features for either of these radicals. This is particularly surprising for $H_2\dot{C}CO_2^-$ radicals in view of the well-defined interaction with thallium observed for this radical in thallium(III) acetate.

Radiation Mechanisms.—All the salts containing d^{10} ions gave good yields of the $d^{10}s^1$ species. It might therefore be supposed that the other products would either be the primary electron-loss species or some

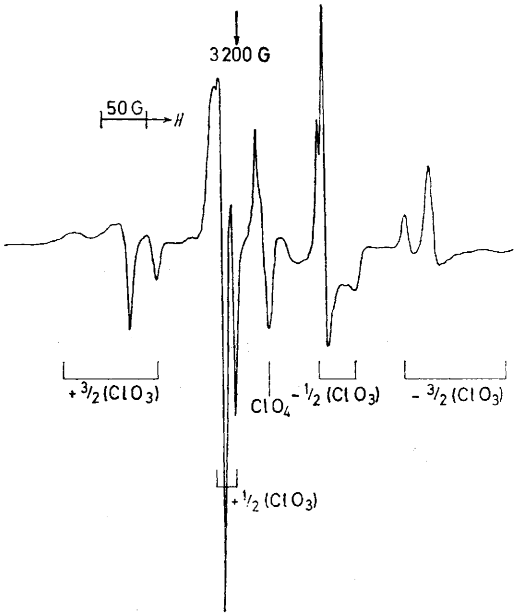

FIGURE 4 First derivative X-band e.s.r. spectrum for thallium(III) perchlorate after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to ClO_3 and ClO_4

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[14] A. D. McLachlan, M. C. R. Symons, and M. G. Townsend, *J. Chem. Soc.*, 1959, 952.

[15] I. N. Marov and M. C. R. Symons, *Russian J. Inorg. Chem.*, 1971, **16**, 633.

[16] J. R. Byberg, S. J. K. Jensen, and B. S. Kirkegard, *J. Chem. Phys.*, 1974, **61**, 138.

product thereof. For thallium(III) perchlorate this would be ClO_4 and that is probably formed. However, another major product was ClO_3. This could be derived from ClO_4 by oxygen-atom transfer to Tl^{III} or to another ClO_4^-, but neither the ion TlO^{3+} nor the peroxide ClO_5^- are very likely products. It seemed possible that sufficient chlorate impurity was present to allow electron transfer from this to ClO_4:

$$ClO_4 + ClO_3^- \longrightarrow ClO_4^- + ClO_3 \qquad (3)$$

However, the relative yields of Tl^{II}, ClO_4, and ClO_3 radicals were independent of dose, which eliminates this mechanism. We conclude that the ClO_3 was formed by an alternative electron-capture process:

$$ClO_4^- + e^- \longrightarrow (ClO_4^{2-})$$

$$(ClO_4^{2-}) + Tl^{3+} \longrightarrow Tl^{2+} + ClO_4^- \qquad (4)$$

$$\text{or} \qquad \longrightarrow ClO_3 + TlO^+ \qquad (5)$$

Steps (4) and (5) are in direct competition and seem to occur with comparable probabilities.

For thallic nitrate, electron-loss would give NO_3, and this was, indeed, obtained in good yield. We again have a difficulty in explaining the formation of NO_2. We have given evidence elsewhere that NO_2 is usually a breakdown product of NO_3^{2-} rather than NO_3.[13] We therefore postulate a competition similar to that in reactions (4) and (5).

$$NO_3^- + e^- \longrightarrow (NO_3^{2-}) \qquad (6)$$

$$Tl^{III} + NO_3^{2-} \longrightarrow Tl^{II} + NO_3^- \qquad (7)$$

$$\text{or} \qquad \longrightarrow NO_2 + TlO^+ \qquad (8)$$

For thallic acetate, electron-loss gives CH_3CO_2 which should rapidly lose CO_2 to give methyl radicals. These were not detected, but $\dot{C}D_3$ radicals were clearly formed in $Tl(CD_3CO_2)_3$. We suggest that $\dot{C}H_3$ radicals extract hydrogen atoms efficiently at 77 K:

$$CH_3 + CH_3CO_2^- \longrightarrow CH_4 + H_2\dot{C}CO_2^- \qquad (9)$$

but that this process is relatively slow for the perdeuteriated species. This is supported by the observation that $\dot{C}D_3$ radicals were lost on annealing slightly above 77 K.

The reactions of thallous perchlorate are less understandable. Electron loss to give ClO_4 would be followed by rapid electron transfer:

$$ClO_4 + Tl^+ \longrightarrow ClO_4^- + Tl^{2+} \qquad (10)$$

but could also result in loss of oxygen:

$$ClO_4 \longrightarrow ClO_2 + O_2 \qquad (11)$$

before transfer could occur.

Electron addition to give ClO_4^{2-} is expected, but ClO_4^{2-} (ref. 17) radicals were not detected. This must be the source of O_3^-:

$$ClO_4^{2-} \longrightarrow O_3^- + ClO^- \qquad (12)$$

but why this reaction should be so ready is not clear to us.

Taken together with our previous work on salts containing . . . $d^{10}s^2$ ions, we conclude that electron loss by the cations is an inefficient direct process, and that the $d^{10}s^1$ ions are probably largely formed by secondary electron-transfer processes, such as in reaction (10). This competes with other possible reactions of the primary electron-loss centre, as in equation (11), or possibly this centre may be so stabilised by its environment that it does not react to give Tl^{II} at all, as in the case of NO_3 in thallous nitrate.[3]

Interaction with Thallium Cations.—Our results, in contrast with those for Pb^{2+}, show that Tl^+ acts overwhelmingly as an electron donor towards neighbouring radicals giving large isotropic hyperfine coupling constants as expected for an incipient . . . .$d^{10}s^1$ configuration. Even with such weak acceptors and potential donors as CO_2^- or O_3^- it seems to prefer the role of donor. Thallic ions, on the other hand, show no interaction with strong acceptors such as ClO_3, NO_3, or NO_2. The weak interaction between Tl^{III} and $H_2\dot{C}CO_2^-$ ions probably results because of co-ordination *via* the negative carboxyl group on which some spin-density resides. In no instance have we detected strong interaction indicative of covalency to thallium such as was detected for radicals such as $Me_3Sn\cdot$ obtained from organic tin and lead derivatives.[18,19]

The tendency for acceptor radicals to spread their interaction amongst several neighbouring ions seems to be characteristic of $d^{10}s^2$ ions, and we conclude that, for weak charge-transfer interaction, coupling to several ions is energetically favoured over a stronger interaction with just one cation. No doubt, however, the crystal structure dictates the actual form that this particular interaction takes.[2,3]

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[17] M. B. D. Bloom, R. S. Eachus, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1235.

[18] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[19] S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1966.