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Preliminary communication

Anchimerically assisted cleavage of a one-electron bond in the $[Me_2N(CH_2)_3Sn^nBu_3]^{+\cdot}$ radical cation

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Abstract

Following γ-radiolysis of $Me_2N(CH_2)_3Sn^nBu_3$ in a $CFCl_3$ matrix at 77 K, only features from n-butyl radicals were observed, whereas $^nBu_4Sn^{+\cdot}$ is a relatively stable species with the positive-hole localised in *one* of the C–Sn bonds: thus there is a facile anchimerically assisted cleavage of the $C^{+\cdot}$–Sn one electron bond in the $[Me_2N(CH_2)_3Sn^nBu_3]^{+\cdot}$ radical cation.

Despite the extensive use of the Freon radiolysis technique in the study by ESR spectroscopy of organic radical cations [1,2], there have been comparatively few such studies of organometallic radical cations [3–9]. These are important intermediates in the chemistry of organometals which are efficient single electron donors under various conditions [10,11]. The fate of the resulting radical cation appears to depend strongly on the structural characteristics of the metal centre and on the substituents present, but fragmentations of the type shown in eq. 1 have been observed directly by ESR in certain cases, even under cryogenic conditions [3–9].

$$R_4M^{+\cdot} \longrightarrow R_3M^+ + R^\cdot \qquad (1)$$

The present communication highlights an example in which a substituent that is formally remote from the metal centre exerts a pronounced influence on the fragmentation of an organotin radical cation. We first consider results for $[^nBu_4Sn]^{+\cdot}$ radical cations formed in a solid $CFCl_3$ matrix at 77 K. The spectrum (Fig. 1) reveals a small yield (*ca.* 20% by double integration) of n-butyl radicals which almost certainly arise from the excitation of the $[^nBu_4Sn]^{+\cdot}$ radical cation by

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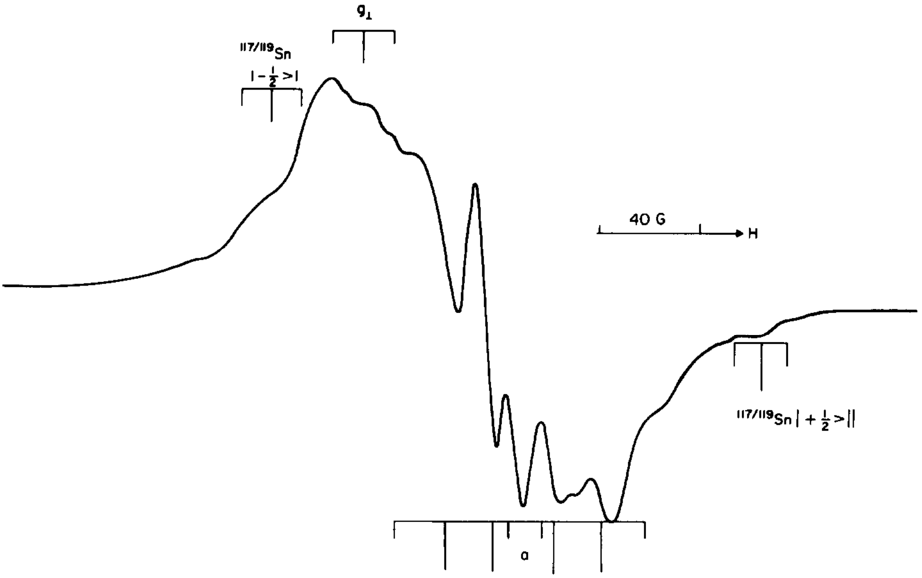


Fig. 1. ESR spectrum assigned to $[^n\text{Bu}_4\text{Sn}]^{+\cdot}$ radical cations and to (a) n-butyl radicals, following γ-radiolysis of $^n\text{Bu}_4\text{Sn}$ in solid $CFCl_3$ at 77 K.

the exoergicity of the electron transfer step (eq. 2), *ca.* 3.5 eV, given the difference in ionisation potentials [12] between R_4Sn and $CFCl_3$.

$$[\text{CFCl}_3]^{+\cdot} + {}^n\text{Bu}_4\text{Sn} \longrightarrow \text{CFCl}_3 + [{}^n\text{Bu}_4\text{Sn}]^{+\cdot} \qquad (2)$$

In support of this, we observed no further growth of these signals on annealing up to the melting point of the matrix, *ca.* 160 K, and so the $[^n\text{Bu}_4\text{Sn}]^{+\cdot}$ radical

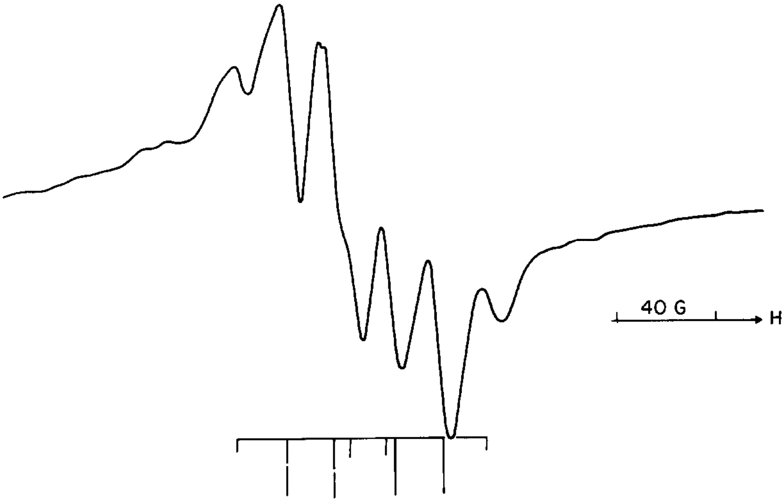
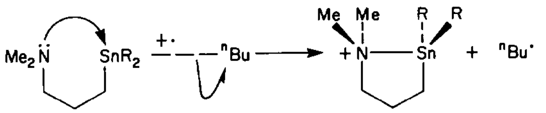


Fig. 2. ESR spectrum recorded as described for Fig. 1 from $Me_2N(CH_2)_3Sn^nBu_3$, showing exclusively features from n-butyl radicals.

cations that are responsible for the majority of the spectrum are relatively stable once thermalised. The ESR parameters [$g_\perp = 2.047$; $g_\parallel = 1.999$; $A_\perp(^{117/119}\mathrm{Sn}) = 78$ G; $A_\parallel(^{117/119}\mathrm{Sn})$ *ca.* 200 G; $a(2\mathrm{H}) = 14$ G] are very similar to those measured previously [5–7] for the $[\mathrm{Me_4Sn}]^{+\cdot}$ radical cation, and show that the positive hole is strongly confined to a unique C–Sn bond: when these data are used along with the atomic hyperfine parameters calculated by Morton and Preston [13] for ^{119}Sn from the Herman–Skillman wavefunction [14], which allows for relativistic effects, a negligible 5*s* contribution of 0.8% and a 5*p* involvement of 16% is obtained for the tin unit, which must therefore be planar. If the organic unit is also planar, the 14 G coupling implies a C(2*p*) occupancy of *ca.* 60%, but this is probably a lower limit, since some bending, as was deduced for the $[\mathrm{Me_4Sn}]^{+\cdot}$ analogue, will render these (negative) α-couplings more positive, so that they fall in absolute magnitude.

A contrast is provided by the closely related compound, $\mathrm{Me_2N(CH_2)_3Sn^nBu_3}$, which shows only features from n-butyl radicals (Fig. 2) under identical conditions and so its radical cation is highly unstable towards fragmentation even at 77 K, and is probably not an energy minimum. Consideration of ionisation potential data for $\mathrm{R_3N}$ and $\mathrm{R_4Sn}$ compounds favours the electron loss as being from the $-\mathrm{CH_2Sn^nBu_3}$ unit, and so the structure of the initial radical cation should be similar to that of $[\mathrm{^nBu_4Sn}]^{+\cdot}$. We therefore suggest reaction 3 to account for the observed $\mathrm{C^{+\cdot}}$–Sn bond cleavage.



(3)

From bond energy data, we estimate that the strength of a one electron $\mathrm{Sn^{+\cdot}}$–C σ-bond should be *ca.* 25–30 kcal/mol and that of a two electron Sn–N σ-bond *ca.* 80–90 kcal/mol so that reaction 3 will be a strongly enthalpy-driven process.

The silicon analogue, $[\mathrm{Me_2N(CH_2)_3SiMe_3}]^{+\cdot}$, is observed as a normal nitrogen centred π-radical [15,16] [$A_\parallel(^{14}\mathrm{N}) = 45$ G; $a(8\mathrm{H}) = 27$ G], in accord with previous mechanistic conjecture from photochemical studies of compounds of this type [17], and is entirely stable under our conditions.

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