Preliminary communication
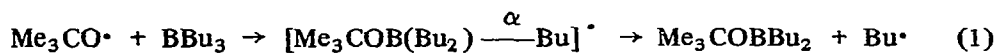
The reaction of tert-butoxyl radicals with stannic chloride

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Homolytic attack by radicals such as $RO\cdot$, $RS\cdot$, or $R_2N\cdot$ at a coordinatively unsaturated metal centre is often extremely rapid[1]. Examples are known where the products result from the scission of a bond in the position α (*e.g.* eqn. 1[3]) or β (*e.g.* eqn. 2[3]) to the metal in the transition state or intermediate.

$$Me_3CO\cdot + BBu_3 \rightarrow [Me_3COB(Bu_2)\overset{\alpha}{-\!-\!-}Bu]^{\cdot} \rightarrow Me_3COBBu_2 + Bu\cdot \quad (1)$$

$$Me_3CO\cdot + P(OEt)_3 \rightarrow [Me_3C\overset{\beta}{-\!-}OP(OEt)_3]^{\cdot} \rightarrow Me_3C\cdot + OP(OEt)_3 \quad (2)$$

In reaction 2 the intermediate phosphoranyl radical may be detected by ESR spectroscopy[3] but no intermediate has been observed in reaction 1.

We now report the observation of a third type of reaction, *viz.* γ-scission, which occurs when t-butoxyl radicals react with stannic chloride. Photolysis of di-t-butyl peroxide in the presence of a tetraalkyltin results in abstraction of hydrogen from the organometallic compound[4]. The introduction of chloro ligands at the tin to give alkyltin chlorides directs attack of the alkoxyl radical to the tin centre and results in displacement of an alkyl radical (α-scission): for tri-n-propyltin chloride the rate constant k_3 is 1.1×10^6 $l\cdot mol^{-1}\cdot sec^{-1}$ at $30°$ [4].

$$Me_3CO\cdot + Pr_3SnCl \rightarrow Me_3COSn(Pr_2)Cl + Pr\cdot \quad (3)$$
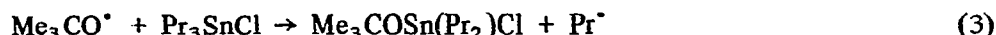
On the other hand if the peroxide is photolysed in the presence of stannic chloride (0.1–0.5 *M*) with or without a hydrocarbon diluent in an ESR spectrometer cavity, a strong spectrum of the methyl radical is immediately apparent (eqn. 4), although no intermediate 5-coordinate tin radical could be detected.

$$Me_3CO\cdot + SnCl_4 \rightarrow [Me\overset{\gamma}{-\!-}C(Me_2)OSnCl_4]^{\cdot} \rightarrow Me\cdot + Me_2C{=}O, SnCl_4 \quad (4)$$

When the reaction is carried out in the presence of tri-n-butylborane at $-50°$ the

superimposed spectra of methyl and n-butyl radicals were observed. The ratio k_4/k_1 determined[2] using eqn. 5 varied between 0.3 and 0.7 as the concentration ratio $[Bu_3B]/[SnCl_4]$ was decreased from 2.8 to 0.3.

$$\frac{k_4}{k_1} = \frac{[Me\cdot]}{[Bu\cdot]} \times \frac{[Bu_3B]}{[SnCl_4]} \tag{5}$$

If[2] $k_1 = 3 \times 10^7 \, l\cdot mol^{-1}\cdot s^{-1}$, then k_4 is about $10^7 \, l\cdot mol^{-1}\cdot sec^{-1}$ at $-50°$. This probably represents a lower limit because the methyl radicals undergo more rapid self-reaction than n-butyl radicals and are not removed entirely by radical—radical reactions. Consistent with the remarkably large value of k_4, the ratio $[Me\cdot]/[cyclo\text{-}C_5H_9\cdot]$ was $\geqslant 15$ (no cyclopentyl radicals were detected by ESR) at $-50°$ when di-t-butyl peroxide was photolysed in the presence of cyclopentane and stannic chloride in the molar ratio 30/1★.

The tetrachlorides of silicon or germanium do not react with t-butoxyl radicals to produce methyl radicals. Titanium tetrachloride reacts vigorously with di-t-butyl peroxide immediately the two are mixed in pentane solution. Stannic chloride reacted only very slowly with di-t-butyl peroxide at room temperature★★.

Such a reaction between a powerful Lewis acid and an alkoxyl radical should be fairly general provided that the Lewis acid does not entirely complex or otherwise react with the source of alkoxyl radicals.

REFERENCES

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★ In this experiment the sample was a mixture of t-BuOOBu-t (1.92 M), SnCl₄ (0.24 M), and C_5H_{10} (7.25 M). The rate constant for unimolecular β-scission of the t-butoxyl radical to give acetone and a methyl radical in an inert solvent at $-50°$ is about $8 \times 10^{-2} \, sec^{-1}$ [5]. This is to be compared with the quantity $k_4[SnCl_4]$ which is about $10^6 \, sec^{-1}$ at $-50°$.

★★ It is possible, though we believe unlikely, that part of the methyl radicals detected arise from direct photolysis of a 1/1 or 1/2 complex between di-t-butyl peroxide and stannic chloride.