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AN NMR AND ESR STUDY OF THE HYDROGEN EXCHANGE REACTION BETWEEN TRIMETHYLTIN HYDRIDE AND TRIMETHYLSTANNYL RADICALS

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A rapid hydrogen exchange reaction was found to take place between tin hydrides[1]. A radical exchange mechanism was formulated[2] and qualitatively shown by the observation of exchange broadening in the NMR spectrum of trimethyltin hydride in the presence of trimethylstannyl radicals[3]. A quantitative investigation is presented, now. Furthermore, the influence of hydrogen exchange reactions on the ESR spectra of short living tin-centred radicals in solution is discussed. Whereas silicon- and germanium-centred free radicals can easily be observed during photolysis of di-t-butyl peroxide with the corresponding hydrides[4], only the trimethylstannyl and, more recently, the tris-(2-phenyl-2-methylpropyl)stannyl radical have been described[5,6].

The following reaction scheme is given for the photochemical reaction of di-t-butyl peroxide with trimethyltin hydride

$$(\text{t-BuO-})_2 \xrightarrow{2r} 2\ \text{t-BuO}\cdot \qquad [1]$$

$$\text{t-BuO}\cdot + \text{Me}_3\text{SnH} \longrightarrow \text{t-BuOH} + \text{Me}_3\text{Sn}\cdot \qquad [2]$$

$$\text{Me}_3\text{Sn}^{(a)}\cdot + \text{Me}_3\text{Sn}^{(b)}\text{H} \xleftrightarrow{k} \text{Me}_3\text{Sn}^{(a)}\text{H} + \text{Me}_3\text{Sn}^{(b)}\cdot \qquad [3]$$

$$2\ \text{Me}_3\text{Sn}\cdot \xrightarrow{k_1} \text{Me}_6\text{Sn}_2 \qquad [4]$$

In the case of slow exchange, the line broadenings are given by[7,8)]

$$\Delta H_{ms}\ (\text{NMR}) = \frac{1}{\pi}\, k \sqrt{\frac{r}{2k_1}} \quad [\text{Hz}] \qquad [5]$$

$$\Delta H_{ms}\ (\text{ESR}) = \frac{1}{\pi}\, k \left[\text{Me}_3\text{SnH}\right] \quad [\text{Hz}] \qquad [6]$$

Fig. 1 shows NMR spectra a) without and b) during irradiation of $(t\text{-BuO-})_2$ (0.2 m) with Me_3SnH (0.25 m) and tetramethyl silane (0.1 m) in cyclohexane-d_{12} with the filtered light of a 1000 W Hg-Xe compact arc lamp ($\lambda >$ 305 nm; further experimental details see [9]). The doublet at δ = 0.05 ppm is due to Me_3SnH and broadened during irradiation. Fig. 2 shows values of ΔH_{ms} plotted against $\sqrt{r}$.

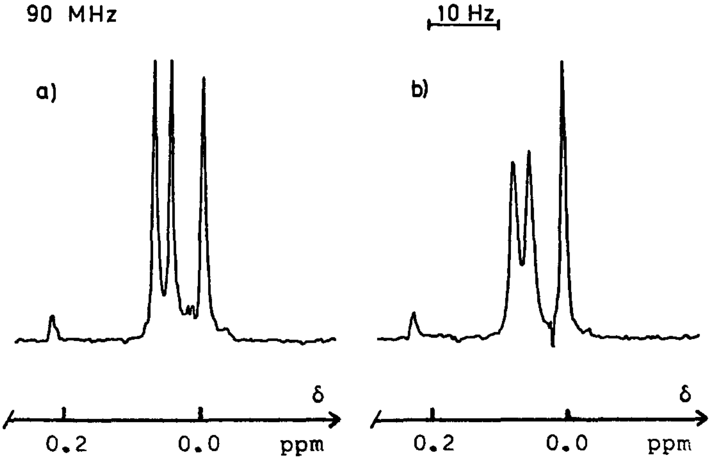

Fig. 1: NMR spectra a) without and b) during irradiation of $(t\text{-BuO-})_2$ with Me_3SnH in cyclohexane-d_{12} at 25°C

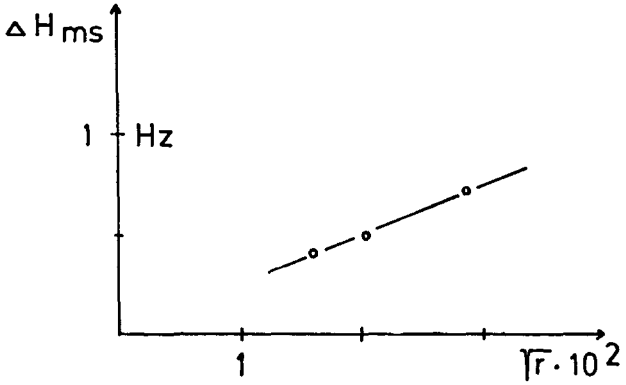

Fig. 2: NMR line broadening of the Me_3Sn doublet during irradiation of $(t\text{-BuO-})_2$ with Me_3SnH in cyclohexane-d_{12} at 25°C

By taking $2k_1 = 3.1 \cdot 10^9$ l/mol·sec, a value of $k = 4 \cdot 10^6$ l/mol·sec is derived[10]. It follows from [6] that appreciable line broadenings have to be expected in the ESR spectrum of $Me_3Sn\cdot$ while using high concentrations of the hydride. Fig.3 shows ESR spectra of $Me_3Sn\cdot$ taken during irradiation of $(t\text{-}BuO\text{-})_2$ (2 m) with Me_3SnH at different concentrations in n-pentane at -80°C. Whereas a well resolved spectrum of $Me_3Sn\cdot$ is observed with $[Me_3SnH] = 0.4$ m, only broad signals are found with $[Me_3SnH] = 2$ m. At -40°C, only a poorly resolved spectrum is observed, even with $[Me_3SnH] = 0.4$ m. At -110°C, a well resolved ESR spectrum of $Me_3Sn\cdot$ can be observed with $[Me_3SnH] = 2$ m, too.

With $n\text{-}Pr_3SnH$ and $n\text{-}Bu_3SnH$, well resolved ESR spectra of $n\text{-}Pr_3Sn\cdot$ and $n\text{-}Bu_3Sn\cdot$ are observed at -80°C using low concentrations of the hydrides. Et_3SnH, however, only gives a broad signal, even at -110°C. ESR data of the radicals are given in Table I. It was reported that $[C_6H_5\text{-}C(CH_3)_2\text{-}CH_2]_3SnH$ gives well resolved spectra even at +120°C. Because of the bulky groups at the tin atom, the k value seems to be reduced in this case.

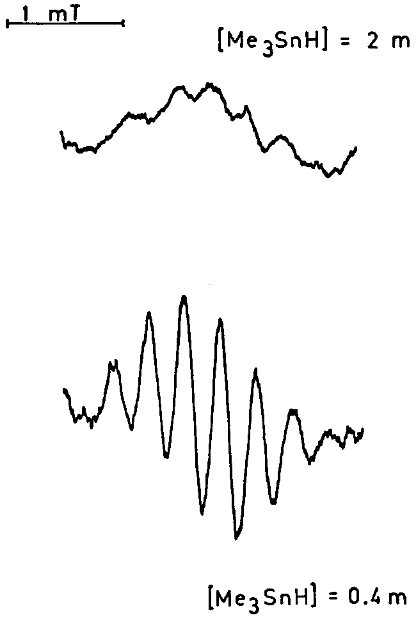

Fig.3: ESR spectra of $Me_3Sn\cdot$ during irradiation of $(t\text{-}BuO\text{-})_2$ with Me_3SnH in n-pentane at -80°C

Table I: ESR data of trialkyltin radicals in n-pentane at -80°C

	g value	$a_H(\beta)(mT)$
$Me_3Sn\cdot$	2.0163	0.31
$Et_3Sn\cdot$	2.015	not resolved
$n-Pr_3Sn\cdot$	2.0160	0.30
$n-Bu_3Sn\cdot$	2.0160(11)	0.31

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REFERENCES

1) W.P.Neumann and R.Sommer, Angew.Chem. 75 (1963) 788

2) W.P.Neumann, "The Organic Chemistry of Tin", Wiley, London, 1970

3) M.Lehnig, Chem.Phys. 8 (1975) 419

4) J.K.Kochi, in "Advances in Free-Radical Chemistry", Vol.V, ed.G.H.Williams, Elec Science, London, 1975, p.189

5) G.B.Watts and K.U.Ingold, J.Amer.Chem.Soc. 94 (1972) 491

6) H.U.Buschhaus, M.Lehnig, and W.P.Neumann, J.C.S.Chem.Comm.,1977, 129

7) C.S.Johnson, J.Chem.Phys. 39 (1963) 2111

8) K.Scheffler and H.P.Stegmann, "Elektronenspinresonanz", Springer, Berlin-Heidelberg-New York, 1970

9) M.Lehnig, F.Werner, and W.P.Neumann, J.Organometal.Chem. 97 (1975) 375

10) D.J.Carlsson and K.U.Ingold, J.Amer.Chem.Soc. 90 (1968) 7047

11) P.Blum and A.G.Davies observed $n-Bu_3Sn\cdot$ in cyclopropane at -110°C and reported a g value of 2.0158 (personal communication)