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Preliminary communication

THE HOMOLYTIC REACTIVITY OF STANNACYCLOPENTANES

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Summary

t-Butoxyl radicals react with 1,1-dialkylstannacyclopentanes by an S_H2 ring-opening reaction at the tin centre, with a rate constant of 2.1×10^6 l mol^{-1} s^{-1} at 243 K for the dibutyl derivative.

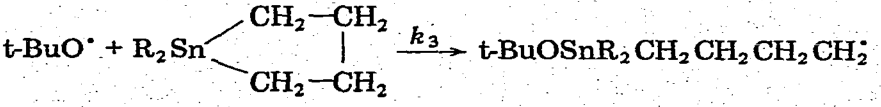
Acyclic tetraalkyl compounds of the metals of Group IVB are usually stable to air, but a number of small-ring metallocycloalkanes of the same elements do react, providing circumstantial evidence for a higher homolytic reactivity**. We have now established that this enhanced reactivity derives from a rapid ring-opening bimolecular homolytic substitution by an oxygen-centred radical at the metal centre***, and have determined the rate constant for one such process.

If di-t-butyl peroxide is photolysed in the presence of an acyclic tetraalkyltin, the ESR spectrum shows that the t-butoxyl radicals react at hydrogen centres in the α-methylene groups (eq. 2), and the rate constant has been determined to be about 10^5 l mol^{-1} s^{-1} at 233 K [3].

$$\text{t-BuOOBu-t} \xrightarrow{h\nu} 2\ \text{t-BuO}^{\bullet} \qquad (1)$$

$$\text{t-BuO}^{\bullet} + RCH_2Sn(CH_2R)_3 \rightarrow \text{t-BuOH} + R\dot{C}HSn(CH_2R)_3 \qquad (2)$$

Under the same conditions 1,1-dimethyl-, 1,1-diethyl- or 1,1-dibutyl-stannacyclopentane (I) show a strong spectrum of the ring-opened radical (II), with a pronounced alternating line-width effect. The spectrum of the radical (II; R = Bu) is illustrated in Fig. 1.



(3)

(I) (II)

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[**] Hexamethylsilacyclopropane is an excellent example [1].

[***] Reviewed by Ingold and Roberts [2].

Fig. 1. ESR spectrum of the radical t-BuOSnBu$_2$CH$_2$CH$_2$CH$_2$CH$_2^\cdot$ in cyclopropane at 153 K; $a(\alpha CH_2)$ 21.9 G (2H), $a(\beta CH_2)$ 28.0 G (2H), $a(\gamma CH_2)$ 0.9 G (2H). For the corresponding diethyl compound the values are $a(\alpha CH_2)$ 21.9 G (2H), $a(\beta CH_2)$ 27.6 G (2H), $a(\gamma CH_2)$ 0.9 G (2H) at 205 K.

Neither 1,1-diphenylstannacyclopentane nor 1,1-dibutylstannacyclohexane showed the formation of the ring-opened radical under the same conditions.

The rate constant for reaction 3 was determined by causing the organotin compound to compete with triisobutylborane for reaction with the t-butoxyl radicals [4].

$$\text{t-BuO}^\cdot + \text{B-i-Bu}_3 \xrightarrow{k_4} \text{t-BuOB-i-Bu}_2 + \text{i-Bu}^\cdot \tag{4}$$

From the relative intensities of the spectra of the radical II and of the isobutyl radical derived from reaction 4, the ratio k_3/k_4, and thence the absolute value of k_3 can be derived [4]. For 1,1-dibutylstannacyclopentane, $k_3 = 2.1 \times 10^6$ l mol^{-1} s^{-1} at 243 K, at least two orders of magnitude greater than the value for the same reaction with the acyclic compounds.

Molecular models show that the stannacyclopentane ring in the reactant I is strained but that the stannacyclohexane ring is strain free. The structure of the intermediate or transition state through which the reaction proceeds is probably approximately trigonal bipyramidal with the tetramethylene ring bridging apical and equatorial sites, and the high reactivity of the stannacyclopentanes probably results from the relief of ring strain as the attack of the alkoxyl radical induces the transition from tetrahedral to trigonal bipyramidal geometry.

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References

1 D. Seyferth and D.C. Annarelli, J. Amer. Chem. Soc., 97 (1975) 2273.
2 K.U. Ingold and B.P. Roberts, Homolytic Substitution Reactions, Wiley-Interscience, New York, 1971.
3 A.G. Davies and J.C. Scaiano, J. Chem. Soc. Perkin Trans II, (1973) 1777.
4 A.G. Davies, D. Griller and B.P. Roberts, J. Chem. Soc. (B), (1971) 1823.