

Preliminary communication

BIMOLECULAR HOMOLYTIC SUBSTITUTION OF DIALKYL SELENIDES AND TELLURIDES WITH TRI-*n*-BUTYLTIN RADICALS

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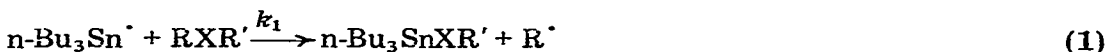
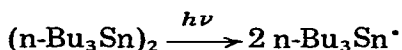
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Summary

The rate constants for the S_H2 reactions of tri-*n*-butyltin radicals with several dialkyl selenides and tellurides have been measured by EPR spectroscopy.

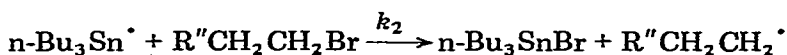
Bimolecular homolytic substitution (S_H2) reactions at oxygen and sulfur have been recognized for many years [1]. Studies of such processes have been confined mainly to those which lead to scission of the O—O bond of peroxides and the S—S bonds of di- and polysulfides. There are few examples of C—O or C—S cleavage and there have been no specific studies of S_H2 reactions at selenium or tellurium [1]. We wish to report that tri-*n*-butyltin radicals undergo extremely rapid S_H2 reactions with dialkyl selenides and tellurides.

Photolysis using quartz optics and a high pressure mercury lamp of a hydrocarbon solution of hexa-*n*-butylditin and a dialkyl selenide or telluride directly in the cavity of a Varian E-4 EPR spectrometer gave a strong EPR signal due to the appropriate alkyl radical. There was no EPR signal in the absence of the ditin.



(X = Se or Te)

Bromine abstraction from primary alkyl bromides was found to be competitive with reaction 1, i.e.,



(R'' = 1-adamantyl)

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TABLE 1

KINETIC PARAMETERS FOR THE S_H2 REACTIONS OF $n\text{-Bu}_3\text{Sn}^\cdot$ RADICALS WITH SOME DI-ALKYL SELENIDES, TELLURIDES AND SULFIDES^a

RXR'	R [•]	Temperature range (K)	log (A_1/A_2)	$E_1 - E_2$ (kcal/mol)	k_1 at 25°C (mol ⁻¹ sec ⁻¹)
CH ₃ SeCH ₃	CH ₃ [•]	165–228	-2.3 ± 0.1	-0.9 ± 0.1	3.7 × 10 ⁵
C ₂ H ₅ SeC ₂ H ₅	CH ₃ CH ₂ [•]	158–253	-1.1 ± 0.1	0.3 ± 0.1	8.6 × 10 ⁵
(CH ₃) ₃ CSe(CH ₂) ₂ CH ₃	(CH ₃) ₃ C [•]	240–294	1.2 ± 0.2	2.8 ± 0.3	2.7 × 10 ⁶
CH ₃ TeCH ₃	CH ₃ [•]	177–268	-1.1 ± 0.1	-1.4 ± 0.1	1.4 × 10 ⁷
CH ₃ SCH ₃	CH ₃ [•]	173–298	—	—	< 10 ⁴

^a Errors are standard deviations.

Since the rate constants for the bimolecular self-reactions of R[•] and R''CH₂CH₂[•] will be approximately equal* [2] the rate constant ratio k_1/k_2 can be represented by:

$$\frac{k_1}{k_2} = \frac{[R^\cdot][R''CH_2CH_2Br]}{[R''CH_2CH_2^\cdot][RXR']}$$

Values of A_1/A_2 and $E_1 - E_2$ were determined for various RXR' by measurements of relative radical concentrations over a range of temperature. These values are listed in Table 1 together with absolute values for k_1 at 25°C. The latter was calculated from the known value for k_2 at this temperature (viz., 1.9×10^7 mol⁻¹ s⁻¹ [3]). An estimated upper limit for the rate constant of the reaction of $n\text{-Bu}_3\text{Sn}^\cdot$ with dimethyl sulfide is included for comparison.

The kinetic data in Table 1 are "normal" for S_H2 processes. That is, the S_H2 reactions at Se and Te are very fast and k_1 increases on going down the Periodic Table (cf. Me₂S, Me₂Se, and Me₂Te), and increases as more stabilized alkyls are displaced (cf. Me₂Se, Et₂Se, and *t*-BuSe-*n*-Bu). However, the pre-exponential factors for Me₂Se, Et₂Se, and *t*-BuSe-*n*-Bu show an unexpected variation and the activation energies increase rather than decrease as the leaving alkyl radical becomes more stabilized. Similar, though less pronounced behavior has been observed in *t*-alkoxydealkylation at boron and has been attributed to steric factors [4].

Finally, we note that dialkyl selenides and tellurides also undergo rapid S_H2 reactions when attacked by trimethylsilyl, phenyl, or perfluorophenyl radicals.

Acknowledgement

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* That is, the reactions, $2R^\cdot \rightarrow$ products and $2R''CH_2CH_2^\cdot \rightarrow$ products will both occur at, or close to the diffusion-controlled limit [2].

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