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Preliminary communication

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

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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.

$$(\text{n-Bu}_3\text{Sn})_2 \xrightarrow{h\nu} 2\ \text{n-Bu}_3\text{Sn}^\bullet$$

$$\text{n-Bu}_3\text{Sn}^\bullet + \text{RXR}' \xrightarrow{k_1} \text{n-Bu}_3\text{SnXR}' + \text{R}^\bullet \qquad (1)$$

(X = Se or Te)

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

$$\text{n-Bu}_3\text{Sn}^\bullet + \text{R}''\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{k_2} \text{n-Bu}_3\text{SnBr} + \text{R}''\text{CH}_2\text{CH}_2^\bullet$$

(R″ = 1-adamantyl)

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TABLE 1

KINETIC PARAMETERS FOR THE S_H2 REACTIONS OF n-$Bu_3Sn^•$ RADICALS WITH SOME DIALKYL 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_3SeCH_3	$CH_3^•$	165—228	-2.3 ± 0.1	-0.9 ± 0.1	3.7×10^5
$C_2H_5SeC_2H_5$	$CH_3CH_2^•$	158—253	-1.1 ± 0.1	0.3 ± 0.1	8.6×10^5
$(CH_3)_3CSe(CH_2)_3CH_5$	$(CH_3)C^•$	240—294	1.2 ± 0.2	2.8 ± 0.3	2.7×10^6
CH_3TeCH_3	$CH_3^•$	177—268	-1.1 ± 0.1	-1.4 ± 0.1	1.4×10^7
CH_3SCH_3	$CH_3^•$	173—298	—	—	$< 10^4$

[a] Errors are standard deviations.

Since the rate constants for the bimolecular self-reactions of $R^•$ and $R''CH_2CH_2^•$ will be approximately equal* [2] the rate constant ratio k_1/k_2 can be represented by:

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

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-$Bu_3Sn^•$ 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. Me_2S, Me_2Se, and Me_2Te), and increases as more stabilized alkyls are displaced (cf. Me_2Se, Et_2Se, and t-BuSe-n-Bu). However, the pre-exponential factors for Me_2Se, Et_2Se, 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.

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

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