## Kinetic Studies on the Ligand Coupling Reactions of Tetraphenyl Sulfurane, Selenurane, and Tellurane. Thermal Stability for Hypervalent Chalcogen Compounds with Four Carbon-Chalcogen Bonds

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**Abstract:** Ligand coupling kinetics of tetraphenyl sulfurane, selenurane, and tellurane have been studied by the variable temperature NMR experiments. The first examples of the activation parameters for the ligand coupling (self decomposition and C-C bond formation) have been obtained for the reactions at three pentacoordinated chalcogenium centers; S, Se, Te.

There is considerable interest on the preparation, structure, and reactivity of hypervalent organochalcogen compounds.<sup>2,3</sup> Recently, we reported the detection and isolation of  $\sigma$ -sulfuranes and  $\sigma$ -selenuranes bearing four aryl ligands and the characterization of their structures in solution and solid-state.<sup>4</sup> However, no kinetic studies on the thermal reactions of hypervalent chalcogen compounds with four carbon-chalcogen bonds have been reported.<sup>5</sup> We present here the first example of the activation parameters for the ligand coupling reactions of pentacoordinated tetraphenyl sulfurane, selenurane, and tellurane by the variable temperature NMR techniques.



Scheme 1

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Figure 1. <sup>1</sup>H NMR Spectra of 1-3; initial (upper) and final (lower) spectra at present temperature. #: benzene.

Tetraphenyl sulfurane (1) and selenurane (2) were generated in situ by the reactions of the corresponding triphenylsulfonium or selenonium salt in THF- $d_8$  with an equivalent of PhLi under an argon atmosphere at -105 and -78 °C, respectively.<sup>4</sup> Tetraphenyl tellurane (3)<sup>6</sup> which was prepared from tellurium tetrachloride by the known method<sup>7</sup> was dissolved in toluene- $d_8$  at room temperature under an argon atmosphere. The <sup>1</sup>H NMR spectra of 1-3 in solution reveal the presence of three kinds of protons (*ortho, meta*, and *para*-protons) as shown in Figure 1 and clearly indicate the formation of pentacoordinated tetraphenyl sulfurane, selenurane, and tellurane. Thermolysis of tetraphenyl chalcogen compounds 1-3 in THF or toluene gives diphenyl chalcogenides and biphenyl quantitatively (Scheme 1).<sup>8</sup>

The ligand coupling reactions were monitored by <sup>1</sup>H NMR spectroscopy<sup>9</sup> (Figure 1) at the following temperatures (1: -82, -77, -72, -67 °C; 2: -15, -11, -5, 0 °C; 3: 52, 63, 74, 84 °C) as a function of time. The decay of the protons of 1 (*meta* and *para*), 2 (*meta* and *para*), and 3 (*ortho*) was monitored by the peak areas of the protons in the parentheses and followed simple first-order kinetics under the present temperatures employed. Plots of  $\ln([a]/[a-x])$  versus time, where [a] was initial concentration and [a-x] was concentration as a function of time, gave good straight lines. Representative kinetic data are shown in Figure 2 (typical examples), and the measured rate constants,  $k_1$ , are listed in Table 1.

Activation parameters for the ligand coupling reactions of tetraphenyl chalcogen compounds 1-3 were determined from the temperature dependence of the rate constants  $k_1$ . Arrhenius plots were linear and gave the values for activation energy,  $E_{act}$  (Table 1). Eyring plots were also linear and allowed for a determination of the activation parameters,  $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$ , and  $\Delta G^{\neq}$  (Figure 3, Table 1).

A comparison with the activation parameters for the ligand coupling reactions of selenurane 2 and tellurane 3 reveals, besides a small entropic contribution in both cases, a higher energy barrier to carbon-chalcogen bond



Figure 2. Representative kinetic data for the ligand coupling reactions of 1-3. [a]: initial concentration; [a-x]: concentration as a function of time.



Figure 3. Eyring plots with standard deviation for the ligand coupling reactions of 1-3.

compd	solvent		Eact	∆G≠298	ΔH≠	∆S≠
		(s <sup>-1</sup> )	(kcalmol-	<sup>1</sup> )(kcalmol <sup>-1</sup> )	(kcalmol <sup>-1</sup> )	(eu)
1	THF-d8	2.48x10 <sup>-4</sup> (-67 °C) 1.22x10 <sup>-4</sup> (-72 °C)	10.9	17.5	10.5	-23.5
		5.00x10 <sup>-5</sup> (-77 °C) 3.25x10 <sup>-5</sup> (-82 °C)				
2	THF-d8	2.20x10 <sup>-4</sup> (0 °C) 1.30x10 <sup>-4</sup> (-5 °C)	21.3	20.4	21.3	3.1
		5.31x10 <sup>-5</sup> (-11 °C) 2.21x10 <sup>-5</sup> (-15 °C)				
3	toluene-d8	3.91x10 <sup>-4</sup> (84 °C) 1.77x10 <sup>-4</sup> (74 °C)	29.0	26.9	28.4	5.2
		3.00x10 <sup>-5</sup> (63 °C) 8.26x10 <sup>-6</sup> (52 °C)				

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a) Values shown are least-square treatments of Arrhenius and Eyring plots.

scission in tellurane 3, which we ascribe to a reduced stabilization of the hypervalent molecules (S<Se<Te). Thus both  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  support the unimolecularity of the rate determing step. While  $E_{act}$  of sulfurane 1 is in the expected value for decreasing the stability of hypervalent compound of sulfur compared with those of the selenium and tellurium,  $\Delta S^{\neq}$  for the reaction of 1 is relatively large and negative as compared to those of 2 and 3, suggesting highly ordered to transition state in which a carbon-carbon bond should be formed simultaneously with scission of two carbon-sulfur bonds in 1, but the basis of this ordering is unclear at this time. Further detailed studies of these hypervalent chalcogen compounds bound to four carbon ligands are in progress.

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- 8. In THF solution, ligand coupling reaction of tetraphenyl tellurane 3 could not occur under reflux condition.
- 9. The <sup>1</sup>H NMR spectra were recorded on a JEOL EX-270.