# Stepwise Construction of Sulfur and Selenium Chains ROBERT EARL DAVIS<sup>1</sup>, Purdue University

## Introduction

Sulfur and selenium have numerous allotropic forms, the most stable in the standard state having a high degree of catenation. Yet reactions of these elemental forms generally produce materials containing only a few VIb atoms. Likewise numerous compounds containing only one or two VIb atoms serve as sources for long catenated chains. Two such reactions will be discussed in great detail.

#### The Decomposition of Sodium Thiosulfate in Acid

The decomposition of acidified thiosulfate has received much study. The products<sup>2,9,13</sup> have been determined and various kinetic investigations have been made.<sup>2,8,9,11,12,13</sup> The products of the reaction are sulfur dioxide,  $S_c$ ,  $S_s$ , colloidal sulfur, various polythionic acids (H<sub>2</sub>S<sub>x</sub>O<sub>6</sub>), and hydrogen sulfides. The rate expressions of production of sulfur

 $d(sulfur)/dt = k_1 (S_2O_3^{-2})^{3/2} (H^+)^{1/2}$  (1)

and of sulfur dioxide

$$d(SO_2)/dt = k_{ii} (S_2O_3^{-2})^2 (H^+)^1$$
 (2)

have been observed.

These data have been interpreted by the author<sup>6</sup> as follows:

$$HS_{2}O_{3}^{-} + S_{2}O_{3}^{-2} \xrightarrow{K_{1}} HS_{3}O_{3}^{-} + SO_{3}^{-2}$$
(4)

$$HS_{3}O_{3}^{-} + S_{2}O_{3}^{-2} \xrightarrow{K_{2}} HS_{4}O_{3}^{-} + SO_{3}^{-2}$$
(5)

$$HS_{x}O_{3}^{-} + S_{2}O_{3}^{-2} \xrightarrow{R_{x}} HS_{x+1}O_{3}^{-} + SO_{3}^{-2}$$
(6)

$$HS_{3}O_{3}^{-} + S_{2}O_{3}^{-2} \xrightarrow{R_{7}} HS_{9}O_{3}^{-} + SO_{3}^{-2}$$
(7)

$$HS_{\mathfrak{d}}O_{\mathfrak{d}}^{-} \rightarrow S_{\mathfrak{s}} + HSO_{\mathfrak{d}}^{-}$$
(8)

The derivation of the rate equation from this reaction scheme can be easily done when

- (i) it is realized that in determining the rate of sulfur appearance the extent of reaction is only 0.01%, *i.e.*  $d(S_2O_3^{-2})/dt = d(HS_2O_3^{-})/dt = 0$
- (ii) the matrix of equations with these boundary conditions is now reduced to linear, first-order differential equations containing simplifying symmetry properties and
- (iii) several expansion series are used.

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The theory predicts a rate

 $d(sulfur)/dt \propto (S_2O_3^{-2})^n (H^*)^{1/2}$  2 > n > 1

compared to the experimental

 $d(sulfur)/dt \propto (S_2O_3^{-2})^{3/2} (H)^{1/2}$ 

When the extent of reaction is greater,  $d(S_2O_3^{-2})/dt \neq 0$ , and the system of competitive, bimolecular reactions cannot be solved in an analytical form. The steady state approximation can be used and the rate expression found is proportional to  $(S_2O_3^{-2})^2$  (H<sup>+</sup>)<sup>1</sup>, as found experimentally.

**Reactions (4)-(8) are visualized as nucleophilic displacement reactions at the sulfur atom. Equation (4) can be described as** 

$$\begin{array}{ccc} \mathbf{H} - \mathbf{S} - \mathbf{SO}_3 + \mathbf{S} - \mathbf{SO}_3^{-2} \rightarrow \mathbf{H} - \mathbf{S} - \mathbf{SO}_3^{-1} + \mathbf{SO}_3^{-2} & (9) \\ \text{for always for a intermediate } \mathbf{HS} \mathbf{O}_{-}^{-1} & \text{decomposes in an unimole} \end{array}$$

The sulfopolysulfane intermediate,  $HS_{9}O_{3}$ , decomposes in an unimolecular reaction forming an  $S_{8}$  ring.



Hexatomic sulfur would be obtained from  $HS_7O_3$ . Colloidal sulfur could be Sx macro rings and/or chains of H-Sx-SO\_3H or  $HSO_3$ -SxSO\_3H (x very large). The formation of the polythionates and hydrogen sulfide can be formulated as



The polysulfanes could be formed in analogous displacement reactions. All of the reactions steps are consistent with radiochemical data.

## The Oxidation of Iodide Ion with Selenous Acid

The rate of oxidation of iodide ion with selenium dioxide in aqueous acid medium<sup>10</sup>

$$H_{2}SeO_{3} + 4H^{*} + 6I^{-} \underset{K=6.8 \times 10^{13}}{\overset{K}{\rightleftharpoons}} 1/x Se_{x} + 2I_{3}^{-} + 3H_{2}0 \quad (12)$$

 $\mathbf{is}$ 

$$rate = \frac{(H_2 SeO_3) (H^+)^3 (I^-)^4}{k_{\alpha} (I_3^-) + k_{\beta} (H^+) (I^-)}$$
(13)

The interpretation of these data involves the following postulated scheme:

$$H_{2}SeO_{3} + H^{+} \underset{k_{-1}}{\rightleftharpoons} HSeO_{2}^{+} + H_{2}O$$
(14)

$$\operatorname{HSeO}_{2^{+}} + \operatorname{I}^{-} \underset{\mathbf{k}_{-2}}{\overset{\mathbf{k}_{2}}{\rightleftharpoons}} \operatorname{HSeO}_{2}\operatorname{I}$$
(15)

$$HSeO_{2}I + H^{*} \underset{k_{-3}}{\overset{k_{3}}{\rightleftharpoons}} H_{2}SeO_{2}I^{*}$$
(16)



Fig. 1.—Energy profile of reaction (12.). E in Kcal. R, reactants; AC, activated complex; P, products. Energy levels of the products  $(2I_{z} + 3H_{z}O + \frac{1}{2}Se_{x}$  are calculated with only the selenium promoted to higher states. Spin restricted transitions are labelled  $\Delta S \neq 0$ .

$$H_{2}SeO_{2}I^{*} + 2I^{-} \underset{k_{-4}}{\overset{k_{4}}{\rightleftharpoons}} I_{3}^{-} + HOSeOH$$
(17)

$$HOSeOH + H^* \underset{k_{-5}}{\cong} HOSe^* + H_2O$$
(18)

$$HOSe^{+} + I^{-} \underset{k_{-6}}{\stackrel{k_{6}}{\rightleftharpoons}} HOSeI$$
(19)

$$HOSeI + 2I \stackrel{k_7}{\rightleftharpoons} I_{s}^{-} + HSeO^{-}$$
(20)

$$HSeO^{-} + H^{+} \underset{k_{-s}}{\stackrel{k_{s}}{\rightleftharpoons}} HSeOH$$
(21)

$$HSeOH + H^{+} \underset{k_{-9}}{\stackrel{\otimes}{\Rightarrow}} HSeOH_{2}^{+}$$
(22)

$$HSeOH_{2^{*}} + HSeO_{3^{-}} \stackrel{k_{10}}{\rightleftharpoons} HSe-SeO_{3}H + H_{2}O$$
(23)  
$$k_{-10}$$

$$2HSeSeO_{3}H \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} HSe-Se-SeO_{3}H + H_{2}SeO_{3}$$
(24)

$$HSe_{x}SeO_{3}H + HSeSeO_{3}H \underset{k_{-x}}{\overset{k_{x}}{\rightleftharpoons}} HSe_{x_{+1}}SeO_{3}H + H_{2}SeO_{3} \quad (26)$$

$$HSe_{s}SeO_{3}H \rightleftharpoons_{k_{-17}}^{K_{17}} Se_{s} + H_{2}SeO_{3}$$
(27)

$$HSe_{y}SeO_{3}H \underset{k-y}{\overset{k_{y}}{\rightleftharpoons}} Se_{y} + H_{2}SeO_{3}$$
(28)

As the reaction order requires that  $k_{-1}$  (i  $\leq 5$ )  $\neq 0$ ,  $k_{-6}$  was set equal to zero. This reduces the rate expression to

$$rate = \left[\frac{(H_2SeO_3) (H^+)^{\circ}(I^-)^4 k_1 k_2 k_3 k_4 k_5 k_6}{k_{-1} k_{-2} k_{-3} k_{-4} k_{-5} (I_3^-) + k_{-3} k_{-2} k_{-3} k_{-6} (H^+) (I^-) + Q}\right]$$
  
where Q = f [k<sub>2</sub>, k<sub>3</sub>...k<sub>6</sub>, k<sub>-1</sub>,...k<sub>-5</sub>, (H<sup>+</sup>) (I<sup>-</sup>) (I<sub>3</sub><sup>-</sup>)] = small value experi-

mentally.

The postulated chemical steps are based on analogies of the behavior of the oxy acids of sulfur and selenium.<sup>7</sup> The stepwise buildup of selenium chains is an extension of the mechanism of the decomposition of thiosulfate. The intermediate of reaction (21), HSeOH, is not decomposed in this scheme to water and atomic Se. The ground state of atomic selenium with a valency configuration of  $[4s]^2[4p]^4$  is  ${}^{2}P_{2}$ . The singlet  ${}^{1}D_{2}$  state of the same designation lies 27.37 kcal. about the ground state<sup>1</sup> while the  ${}^{1}S_{0}$ state is 64.17 kcal. above Se( ${}^{8}P_{2}$ ). Then atomic Se has a  $\Delta H^{\circ}f$  of the rekcal./mole from the gray hexagonal form. Thus the  $\Delta H^{\circ}f$  of the re-

action  $\xrightarrow{1}$  Sex  $\rightarrow$  Se (<sup>3</sup>P<sub>2</sub>) can be calculated to +47.32 kcal./mole x (amorp)  $\xrightarrow{2}$  (g) (<sup>3</sup>P<sub>2</sub>) can be calculated to +47.32 kcal./mole at 25°.

It is, therefore, quite unlikely that atomic selenium is a reaction intermediate. The transition from a singlet to a triplet state would be a relatively slow process due to spin restrictions even though the selenium atom has moderately strong spin-orbit coupling. Besides  $Se({}^{\circ}P_2)$  is a INDIANA ACADEMY OF SCIENCE

high energy species and a higher activation energy should be observed if it is an intermediate. The stepwise buildup of a selenium chain by nucleophilic displacement reactions is then a more attractive theory. These criteria apply to other oxidations by SeO<sub>2</sub> and to reactions involving elemental selenium. Kinetic data on several of these reactions will be published in the near future.

In particular, evidence has been obtained for the importance of esters of HOSeOH during the selenium dioxide oxidation of ketones.<sup>3,4,5</sup> A postulated reaction sequence would be ( $\overline{\lambda}$  a general base)



The ultimate fate of the HSeOH would be given by equations (21) through (28) and the final emergence of an  $Se_s$  ring

# Energetics of Sulfur and Selenium

Foundational to the foregoing discussion has been the energetics of the various allotropic forms of these VIa elements. The following tables summarize the data available.

State	$\Delta H^{\circ}_{208}$ kcal./g. atom
S <sub>8</sub> ∝	0.00
$S_s \beta$	0.07
Se	25.3 gas phase
$S_2  ^{3}\Sigma_{g}$	- 29.86
<sup>1</sup> Δ <sub>8</sub>	
<sup>1</sup> Σ <sub>g</sub>	+
<sup>3</sup> Σ <sub>u</sub>	- 120.8
$(^{3}\pi_{u})$	) 198
S <sup>3</sup> P	53.25
$^{1}D_{2}$	79.5
<sup>1</sup> S。	119.5

Heats of Formation of Various Allotrops of Sulfur

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ş	State	H° <sub>208</sub> kcal/g. atom	
Se	hexagonal	0.00	
	precipitated	1.05	
$\mathrm{Se}_2$		33.14	gas
Se	${}^{3}\mathbf{P}_{2}$	48.23	
	${}^{3}\mathbf{P}_{1}$	53.8	
	${}^{3}\mathbf{P}_{o}$	55.4	
	$^{1}\mathrm{D}_{2}$	75.5	
	<sup>1</sup> S <sub>0</sub>	112.3	

### Heats of Formation of Various Allotrops of Selenium

These data can be used to exclude monoatomic and diatomic sulfur or selenium as intermediates in numerous reactions.

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