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SELENIUM DIOXIDE OXIDATION OF ETHYLENE

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The reaction of ethylene with selenium monochloride was reported by Boord and Cope (1) to produce bis (β-chloroethyl) selenide. Frick (2) reported that bis (β-chloroethyl) selenide dichloride was the product when selenium oxychloride was used. We have found that a similar reaction occurs when ethylene is reacted with selenium dioxide in acetic acid.

The reaction of ethylene at 50 p.s.i. with selenium dioxide in glacial acetic acid at 100-125°C. gave ethylene glycol diacetate, bis (β-acetoxy ethyl) selenide and bis (β-acetoxy ethyl) diselenide. Addition of sodium acetate to the reaction resulted in complete absence of I in the reaction products. In contrast, the addition of a strong mineral acid resulted in a shift of product distribution to favor I. The ability to control the product distribution in a selenium dioxide oxidation by changing the acidity is quite remarkable.

$$C_2H_4 + HOAc + SeO_2 \longrightarrow \underset{I}{AcOCH_2CH_2OAc} + \underset{II}{(AcOCH_2CH_2)_2Se} + \underset{III}{(AcOCH_2CH_2)_2Se_2}$$

The results in Table I show that not only the product distribution was affected by the change in acidity but also the utilization of selenium dioxide to form isolatable products. In addition to the products shown in the above equation, a large amount of ethylene glycol monoacetate was formed in the reaction which contained aqueous hydrochloric acid. The formation of large amounts of the glycol monoacetate is consistent with the mechanism which we propose for this reaction.

TABLE I

Oxidation of Ethylene with Selenium Dioxide (0.450 moles)

	Mole percent based on SeO_2			
	I	II	III	Total[1]
glacial HOAc	2.4	35.0	5.9	43.4
HOAc-NaOAc[2]	0	39.7	0.6	40.3
HOAc-$HClO_4$[3]	19.9	34.5	14.0	68.5
HOAc-HCl[4]	45.2[5]	3.2	0.7	99.1

1. Total yield of identified products based on moles of SeO_2.
2. 25 weight percent of NaOAc was added to the HOAc.
3. 2 weight percent of 70 percent $HClO_4$ was added to HOAc.
4. 20 weight percent of 36 percent HCl was added to HOAc.
5. In addition a 50.1 mole-percent yield of ethylene glycol monoacetate was produced.

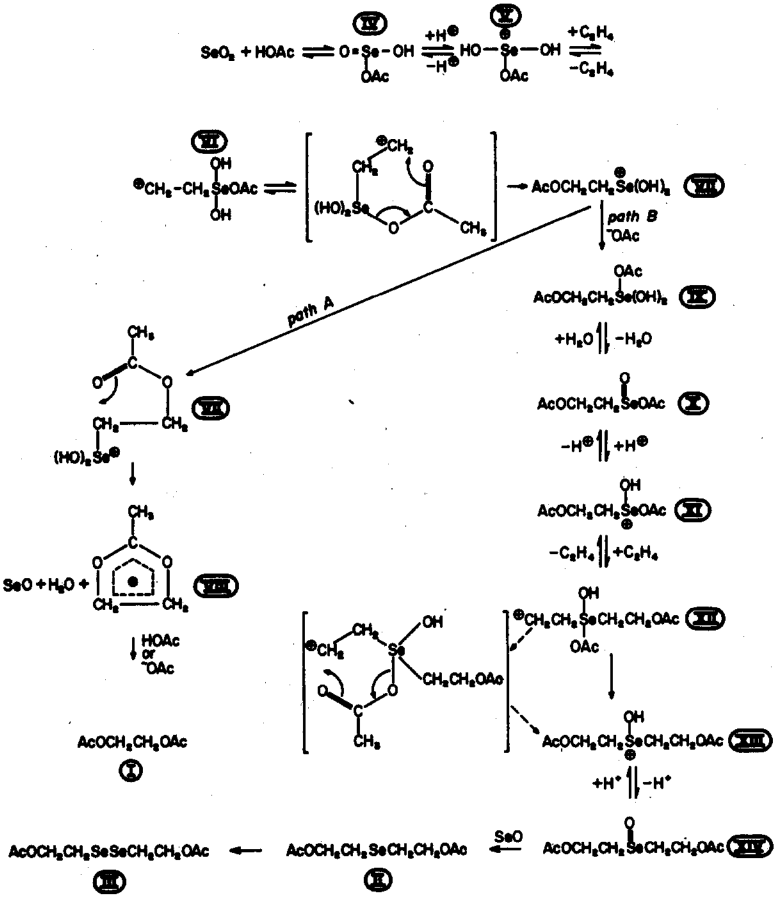
A further observation which is not evident from the data of Table I concerns the rate of reaction. Addition of mineral acid to the reaction mixture resulted in a greatly increased reaction rate. Whereas it took about 24 hours for ethylene absorption to cease for the reaction in glacial acetic acid, the reaction was complete within 2 hours when perchloric or hydrochloric acid was added to the reaction media. The increased rate caused by addition of the strong mineral acid is consistent with the mechanism postulated by Schaefer in which selenium dioxide is converted to its conjugate acid which is the reacting species (3).

$$SeO_2 + H^+ \rightleftharpoons HSeO_2^+$$

However, when we attempted to cause reaction of ethylene with selenium dioxide in aqueous hydrochloric acid (in the absence of acetic acid) no reaction occurred. Addition of a small amount of acetic acid to the reaction mixture resulted in an immediate but slow absorption of ethylene. Therefore, it seems that acid catalysis of the reaction of ethylene with selenium dioxide is ineffective—except in the presence of acetic acid. The catalysis of selenium dioxide oxidations by acetic acid explains why acetic acid is reported to be a good solvent for these reactions (4). A mechanism to explain this interesting relationship is given below.

The important feature of this mechanism is formation of a selenium acetate (IV) which is subsequently converted to its conjugate acid (V). As in Schaefer's mechanism the conjugate acid acts as an electrophile and attacks a double bond forming a carbonium ion. The formation of the carbonium ion is considered to be reversible on the basis of the results in hydrochloric acid. In hydrochloric acid, a carbonium ion analagous to VI must be formed between selenious acid and ethylene. In the presence of acetic acid, the carbonium ion rearranges and proceeds to products, but in the absence of acetic acid, it reverts to starting materials. The hydrochloric acid solution absorbed only a very small amount of ethylene which not only indicates a reversible addition, but also that the equilibrium favors predominantly free ethylene.

The effect of acetate on the reaction is in assisting the primary carbonium ion product (VI) to undergo internal rearrangement via a six-membered cyclic intermediate. The role of acetate as a specific catalyst for selenium dioxide reactions is readily understood by this mechanism. This mechanism also predicts that in acetic acid, acetate esters are not formed by esterification of alcohols but are primary reaction products.


SeO₂ + HOAc
IV
V
+H⊕
−H⊕
+C₂H₄
−C₂H₄
VI
⊕CH₂-CH₂SeOAc
(HO)₂Se
AcOCH₂CH₂Se(OH)₂
VII
path B
⁻OAc
path A
AcOCH₂CH₂Se(OH)₂
IX
+H₂O
−H₂O
AcOCH₂CH₂SeOAc
X
−H⊕
+H⊕
AcOCH₂CH₂SeOAc
XI
−C₂H₄
+C₂H₄
VIII
(HO)₂Se⊕
SeO + H₂O +
XVIII
HOAc
or
⁻OAc
AcOCH₂CH₂OAc
I
⊕CH₂CH₂SeCH₂CH₂OAc
XII
CH₂CH₂OAc
AcOCH₂CH₂SeCH₂CH₂OAc
XIII
+H⁺
−H⁺
AcOCH₂CH₂SeCH₂CH₂OAc
XIV
SeO
AcOCH₂CH₂SeCH₂CH₂OAc
II
AcOCH₂CH₂SeSeCH₂CH₂OAc
III

Intermediate VII can react by two different pathways. Path A leads to formation of ethylene glycol diacetate and Path B to organoselenium compounds.

Reaction by Path A involves a neighboring group displacement of $Se(OH)_2$ by acetate to give a non-classical carbonium ion (VIII) which reacts either with acetate ion or acetic acid to give ethylene glycol diacetate. In aqueous media, water competes with acetate ion or acetic acid to give ethylene glycol monoacetate.

Addition of acetate ion to the reaction resulted in essentially complete conversion of VII to IX by attack on the positively charged selenium atom. The formation of less than 0.02 percent (estimated limit of detectability) of I suggests that direct displacement of $Se(OH)_2$ from VII by SN_2 attack of acetate ion is a very minor reaction. These facts lend support to the neighboring group participation in the pathway leading to glycol esters.

According to Path B, the intermediate VII reacts with acetate ion to give the seleno ester X. Compound X is in equilibrium with its conjugate acid XI which reacts with ethylene. The addition product undergoes internal acetate shift to give the conjugate acid XIII. Loss of a proton from XIII gives bis(β-acetoxy ethyl)selenoxide (XIV).

The pathway by which the selenoxide (XIV) is reduced to selenide is unknown at the present time; as is the path by which the diselenide forms.

One possible mechanism for conversion of the selenoxide to the selenide is disproportionation of the selenoxide with SeO or Se which are present in the reaction medium. Disproportionation of sulfoxides with lower valence states of sulfur has been demonstrated in sulfur chemistry (5).

The diselenide could be formed by reaction of the selenide with metallic selenium. The analogous formation of disulfides by reaction of sulfides with sulfur is unknown in sulfur chemistry. However, sulfur is known to react with sulfides. Wessely and Siegel reported the formation of trithiones by reaction of sulfur with alkyl sulfides (6). Disulfides are known to be produced when hydrocarbons react with elemental sulfur (7). Therefore, it is conceivable that diselenides could be formed by reaction of the selenide with finely dispersed selenium metal which is produced in the reaction.

This investigation is being continued to obtain additional information on the oxidation of ethylene and propylene by selenium dioxide in acetic acid.

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