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CHLOROSULFINYLCHLORINATION AND CHLOROSULFONYLCHLORINATION OF ETHYLENE. CONVERSION OF β-CHLOROETHANESULFINIC ACID INTO A THIOETHER

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According to the general theory of electrophilic agents, their activity is determined by electron affinity and by the coordinative unsaturation of their central atoms (^{1,2}). As one example of the predominant influence of the latter factor, the greater susceptibility of thionyl chloride to hydrolysis in comparison with sulfuryl chloride was indicated (^{1}):

$$Cl_2S{=}O + :OH_2 \rightleftharpoons Cl_2S\cdots:OH_2 \longrightarrow Cl^- + Cl{-}S({=}O)OH + H^+ \text{ etc.} \tag{1}$$

From these considerations one could expect that $SOCl_2$ would prove more prone to addition at a π-bond than SO_2Cl_2. Indeed, the reaction of ethylene with thionyl chloride in the presence of $AlCl_3$ proceeded rapidly, with heating, and led to the formation of β-chloroethanesulfinyl chloride (chlorosulfinylchlorination):

$$CH_2{=}CH_2 + SOCl_2 \xrightarrow{AlCl_3} ClCH_2{-}CH_2{-}SOCl. \tag{2}$$

The interaction with sulfuryl chloride proceeded slowly and, together with β-chloroethanesulfonyl chloride $ClCH_2{-}CH_2{-}SO_2Cl$ (chlorosulfonylchlorination), gave still larger amounts of 1,2-dichloroethane.

By analogy with the behavior of $AlCl_3$ in NOCl (^{3}), $SnCl_4$ in $SeOCl_2$ (^{4}), and $FeCl_3$ in $SOCl_2$ (^{5}), we assume that dissolution of $AlCl_3$ in $SOCl_2$ leads to the formation of the chlorothionyl cation $Cl{-}\overset{+}{S}{=}O$:

$$SOCl_2 + AlCl_3 \rightarrow [ClSO]^+[AlCl_4]^- \rightleftharpoons Cl\overset{+}{S}O + AlCl_4^-. \tag{3}$$

This hypothesis is confirmed, according to our observations, by the heating that occurs on mixing the reagents and by other data (^{4,5}).

If the π-bond in ethylene is represented by an arc and the distribution of the π-electron density in the complex of $\overset{+}{S}OCl$ with ethylene by dotted lines, then the mechanism of chlorosulfinylchlorination may be represented as follows:

$$O{=}\overset{+}{S}{-}Cl + CH_2{=}CH_2 \rightleftharpoons \left[O{=}\overset{+}{S}{-}Cl \cdots CH_2{=}CH_2\right] \xrightarrow[-AlCl_3]{AlCl_4^-} ClOS{-}CH_2{-}CH_2Cl \tag{4}$$

It is possible that the more active donor of Cl^- is the complex (cf. (6))

$$Cl{-}S({=}\,O){-}Cl \cdots AlCl_4$$

The β-chloroethanesulfinyl chloride formed gives with $AlCl_3$ a stable complex $[ClCH_2{-}CH_2{-}\overset{+}{S}{=}O]AlCl_4^-$. Owing to the decrease in the electrophilicity of the sulfur atom, under the conditions of our experiments it did not enter into further reaction with ethylene.

When the reaction mixture was treated with a small amount of water, the sulfinic acid $CH_2Cl{-}CH_2SOCl$, rapidly formed as a result of hydrolysis, was isolated in the free state; with $SOCl_2$ the acid gave back the sulfi-

chloride, and under the action of Cl_2—a sulfochloride:

$$ClCH_2{-}CH_2{-}S({=}\,O)(OH) \;\cdots\; Cl{-}Cl \longrightarrow ClCH_2{-}CH_2{-}S({=}\,O)_2{-}Cl + Cl^- + H^+ \tag{5}$$

Conversely, the sulfochloride, when treated with sodium sulfite, was converted into the sulfinic acid:

$$ClCH_2{-}CH_2{-}SO_2{-}Cl + SO_3^{2-} \longrightarrow CH_2Cl{-}CH_2{-}\ddot{S}O_2 + ClSO_3^- \tag{6}$$

We have shown the ease of an analogous reaction of $SOCl_2$ with vinyl chloride; with acetylene it proceeded much more difficultly. It is possible that in addition reactions of $\dot{S}OCl_2$ to chloroethylenes an anomalous orientation will be observed (^{6}). When benzene was allowed to act on a strongly diluted solution of $AlCl_3$ in $SOCl_2$, benzenesulfinyl chloride was obtained, identified by conversion into the sulfochloride and then into benzenesulfamide:

$$ArH + \overset{+}{S}OCl \longrightarrow Ar \cdots H \cdots \overset{+}{S}OCl \longrightarrow Ar{-}SOCl + H^+ \tag{7}$$

When the product of the reaction of C_2H_4 with $SOCl_2$ was treated with water, separation of an oil was observed; investigation showed it to be dichlorodiethyl sulfide $(CH_2Cl{-}CH_2)_2S$ (1). Special experiments showed that solutions of sulfinic acid in HCl, on standing or on heating, likewise liberate (1) and SO_2 as a result of disproportionation according to the scheme ($R = ClCH_2{-}CH_2{-}$):

$$3RSO_2H \rightarrow R_2S + SO_2 + RSO_3H + H_2O. \tag{8}$$

The thioether was identified by its boiling and melting points and by its properties, in particular by oxidation with HNO_3 to the sulfoxide and by conversion with $C_6H_5SO_2NClNa$ into benzenesulfinimine. Oxidation with aqueous HNO_3 proceeded only in the presence of nitrogen oxides, probably by the mechanism

$$R_2\ddot{S} : + ONO \rightarrow R_2\ddot{S} \rightarrow O + : \dot{N}O; \quad NO + 2HNO_3 \rightleftarrows 3\dot{N}O_2 + H_2O.$$

On the basis of a number of data, in particular recent studies of the conversion of *p*-toluenesulfinic acid (7) into sulfinyl sulfone $CH_3C_6H_4S{-}SO_2{-}C_6H_4CH_3$, the following mechanism of reaction (8) is proposed:

$$RSO_2^- + H^+ \rightleftarrows RSO{-}OH \overset{+H^+}{\rightleftarrows} R{-}\overset{+}{S}O + H_2O \tag{9}$$

$$R{-}\overset{+}{S}{=}O + R{-}SO_2^- \rightleftarrows R{-}\ddot{S}{-}O{-}SO_2{-}R \rightleftarrows R{-}\overset{+}{\ddot{S}} + {}^- OSO_2{-}R \tag{10}$$

$$R{-}\overset{+}{\ddot{S}} + R{-}SO_2^- \longrightarrow R{-}\ddot{S}{-}SO_2{-}R^+ \tag{11}$$

$$ClCH_2{-}CH_2{-}\ddot{S} \cdots SO_2 \cdots CH_2{-}CH_2Cl \longrightarrow ClCH_2{-}CH_2{-}\ddot{S}{-}CH_2{-}CH_2Cl + SO_2 \tag{12}$$

In an acid medium, RSO_2H undergoes double ionization according to scheme (9). The cation

$$R{-}\overset{+}{\ddot{S}}{=}O$$

like

$$O{=}\overset{+}{N}{=}O \quad (^{8,2,9})$$

and

$$\mathrm{O} \leftarrow \overset{+}{\mathrm{S}}\mathrm{O{=}O} \quad (^{9}),$$

owing to dynamic conjugation, possesses ambident electrophilic reactivity; attacking $\mathrm{RSO_2^-}$ at the S atom, it gives, in a highly reversible reaction, sulfinyl sulfone $\mathrm{RSO{-}SO_2{-}R}$ (7), and at oxygen (see equation (10))—the mixed anhydride of sulfinic and sulfonic acids.

$R{-}\ddot{S}{-}O{-}SO_2{-}\dot{R}$. This anhydride undergoes ionization with formation of the cation $R{-}\ddot{S}^{+}$, and its reaction with $R\dot{S}O_2^-$ according to equation (11) gives the sulfenyl sulfone $R{-}\ddot{S}{-}SO_2{-}R$. Formation of the sulfenyl sulfone may also take place by a cryptionic reaction of the polarized anhydride molecule (in other words, the sulfenyl sulfonate) with the sulfinate anion. Alkylation according to a scheme of type (12) leads to the formation of a thioether and SO_2. Probably, some portion of the thioether is formed even before the reaction mixture is mixed with water, as a result of the action of $AlCl_3$ on $ClCH_2{-}CH_2SOCl$ by a mechanism similar to that expressed by equations (9)—(12) and according to a stoichiometric scheme analogous to (8).

$$3RSOCl \rightarrow R_2S + SOCl_2 + RSO_2Cl.$$

The slowness of the reaction of SO_2Cl_2 with ethylene should be explained by its low tendency to form the complex $[{}^{+}SO_2Cl]AlCl_4^-$ and by the lower coordinative unsaturation of the S atom in ${}^{+}SO_2Cl$ than in ${}^{+}SOCl$ (1,2,10). The formation of a nonionized complex

$$Cl_3Al \leftarrow O \leftarrow SOCl{-}Cl^{+\delta}$$

and the equilibrium

$$SO_2Cl_2 + AlCl_3 \rightleftarrows Cl_2 + O = \overset{+}{S} \rightarrow \ddot{O}: \;---\rightarrow AlCl_3^{-\delta}$$

favored the manifestation of a chlorinating effect; to diminish it the mixture was saturated with SO_2. It is possible that, to one degree or another, the formation of $ClCH_2{-}CH_2SO_2Cl$ in these cases occurred at the expense of the primary reaction of ethylene with $SO_2 \cdot AlCl_3$.

We give a description of several experiments.

1. 50.4 g of $SOCl_2$ and 15 g of $AlCl_3$ were saturated with ethylene with stirring; heating occurred. After absorption of C_2H_4 was complete, the mixture was poured onto 60 ml of ice water. After extraction with benzene, 6 g of 98% sulfinic acid $ClCH_2{-}CH_2SO_2H$ was isolated from $(CH_2Cl{-}CH_2)_2S$. The acid was identified by conversion into β-chloroethanesulfonyl chloride; for this purpose it was dissolved in 50

ml of water and saturated with chlorine. By ordinary treatment the sulfonyl chloride that separated was purified (6 g, b.p. 84° at 8 mm); upon treatment with chlorine of the aqueous layer without separation of the syrupy $ClCH_2{-}CH_2SO_2H$, the yield of sulfonyl chloride was more than 7 g, and with gradual introduction of 30 g of $AlCl_3$ and 8 liters of C_2H_4 into 33.6 g of $SOCl_2$ over 10 h and treatment with water at $-10°$, and then with chlorine, the yield of sulfonyl chloride reached 20 g.

Found, %: Cl 43.8; S 19.5

$C_2H_4O_2SCl_2$. Calculated, %: Cl 43.5; S 19.7

From the benzene extract in this experiment, 1.2 g of dichlorodiethyl sulfide $(ClCH_2{-}CH_2)_2S$ was isolated, b.p. 97° at 13 mm and m.p. 12°.

2. A mixture of 7.5 g of β-chloroethanesulfonyl chloride and 32 g of sodium sulfite in 60 ml of water was stirred and, by addition of 40% $NaOH$, a weakly alkaline reaction was maintained. After 2 h, 60% H_2SO_4 was added to give an acid reaction to Congo red, and the sulfinic acid was extracted with ether. After thorough removal of the ether in vacuo, colorless syrupy $ClCH_2{-}CH_2SO_2H$ remained. Upon treatment with bromine in water, 3 g of the acid gave β-chloroethanesulfonyl bromide in quantitative yield.
3. After carrying out the experiment for obtaining $ClCH_2{-}CH_2SO_2H$ according to the first variant of item 1, the aqueous solution mixed with syrup was treated with bromine. The oil that separated was extracted with benzene, dried, and distilled; in this way about 10 g of β-chloroethanesulfonyl bromide was obtained, b.p. 95° at 8 mm.

Found, %: Cl + Br 55.6

$C_2H_4O_2SClBr$. Calculated, %: Cl + Br 55.8

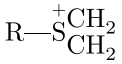
4. A mixture of 32 g of $SOCl_2$ and 32 g of $AlCl_3$ was saturated with 6 liters of ethylene; after dilution with 50 ml of water, extraction of the thioether with benzene, they extracted with ether and dried the extract with $MgSO_4$. After removal of the ether, slightly yellowish $ClCH_2{-}CH_2SO_2H$ remained. When 5 g of sulfinic acid was treated with 15 g of thionyl chloride, heating occurred and HCl and SO_2 were evolved.

The mixture was then heated for 30 min at 100°, the excess $SOCl_2$ was distilled off, and β-chloroethanesulfinyl chloride was distilled at 81° and 9 mm. About 5 g of colorless sulfinyl chloride was obtained; in contrast to the sulfonyl chloride, it fumes in air and is rapidly hydrolyzed by water with formation of sulfinic acid. In titration of 0.735 g of the product after mixing with water, 20.15 ml of 0.5 N caustic soda was consumed, 100.7% of theory.

5. One hundred grams of sulfuryl chloride was saturated with 8 g of SO_2, 10 g of $AlCl_3$ was added, and the mixture was again saturated with SO_2

(7 g). Thereafter 10 liters of C_2H_4 was passed through for 25 h (with interruption). Absorption of ethylene occurred without noticeable heating. The mixture was poured into 100 ml of water, the oil was separated, dried with K_2CO_3, and distilled. From the fraction up to 100°, after removal of SO_2Cl_2 with aqueous ammonia, 9.5 g of 1,2-dichloroethane, b.p. 84°, was obtained; and from the higher-boiling fraction, on distillation in vacuo, about 8 g of β-chloroethanesulfonyl chloride, b.p. 85° at 8 mm, was obtained. Without the use of SO_2, absorption of ethylene proceeded more rapidly and with heating to 30–35°, but led to the formation of almost exclusively dichloroethane. For identification of this sulfonyl chloride with that obtained according to item 1 from the sulfinic acid, they were converted into β-diethylaminoethanediethylsulfamide, $(C_2H_5)_2N—CH_2—CH_2SO_2N(C_2H_5)_2$, its hydrochloride, m.p. 127° (% N 10.18), and picrate, m.p. 118° (% N 14.66).

6. After carrying out the reaction according to item 1 with 30 g of $SOCl_2$, 10 g of $AlCl_3$, and 4 liters of ethylene, mixing with 60 ml of water, and extracting the thioether with benzene, the aqueous layer and syrup were heated for 4 h at 90°. The dichlorodiethyl sulfide that separated was isolated, dried with $CaCl_2$, and distilled. About 2 g of thioether was obtained, b.p. 90° at 7 mm and m.p. 12-14°. Similar results were observed on heating syrupy $CH_2Cl—CH_2SO_2H$ with conc. HCl. The anomalous formation of $(ClCH_2—CH_2)_2S$ was also observed by us under the action of $C_6H_5SO_2Cl$ on an alkaline solution of $(HOCH_2—CH_2)_2S$, apparently through the formation of benzenesulfonates, their ionization into $C_6H_5SO_3^-$ and cations of the type



$$R—\overset{+}{S}\genfrac{}{}{0pt}{}{CH_2}{CH_2}$$

and addition to the latter of Cl^- at carbon. This reaction is analogous to the conversion of ethylene chlorohydrin into dichloroethane, investigated by us earlier (^{11}), but in the present case it proceeded rapidly at 20° in aqueous solution.

In the experimental part of the investigation in 1946–1948, P. P. Fomin participated, and in the preparation for publication—V. G. Kuz' min, to whom we express our deep gratitude. Other authors (^{12}) were not able, in the same period, to effect the addition of SO_2Cl_2 to C_2H_4 in the presence of $AlCl_3$.

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* See the footnote in ([6]).

Note: Figure translations are in progress. See original paper for figures.

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