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Abstract

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MECHANISM OF HYDROLYSIS OF VINYL ETHERS

HYDROLYSIS OF VINYL ETHYL, VINYL ISOPROPYL, AND VINYL-*n*-BUTYL ETHERS

(Presented by Academician M. I. Kabachnik, 12 VII 1961)

The presence of an oxygen atom located next to an ethylenic bond makes simple and complex vinyl ethers highly reactive compounds. They are characterized by addition and polymerization reactions proceeding under mild conditions [1,2]. With water, simple and complex vinyl ethers react according to the scheme

$$CH_2{=}CH{-}O{-}X + H_2O \rightarrow CH_3CHO + XOH, \qquad (I)$$

giving acetaldehyde and an alcohol if X is alkyl, or a carboxylic acid if X is acyl. However, whereas vinyl acetate and other complex vinyl ethers are hydrolyzed very rapidly in alkaline medium and are considerably more stable in neutral and acidic media [3], vinyl alkyl ethers are stable in alkaline medium and are readily hydrolyzed under acid catalysis [1,4]. The mechanism of hydrolysis in the two cases is apparently different. The mechanisms of polymerization of simple and complex vinyl ethers also differ, since the former polymerize under the action of acidic reagents [1], and the latter under the action of peroxides, irradiation, and other initiators of radical processes [2]. The different course of the same reactions depending on whether simple or complex vinyl ethers are involved makes these compounds interesting and convenient objects for studying changes in reaction mechanism with changes in the structure of the reacting substances.

Below are presented the results of a study of the mechanism of hydrolysis of vinyl ethyl, vinyl-*n*-butyl, and vinyl isopropyl ethers, as well as of α-chloroethyl ether, using O^{18}. Direct experimental data on the direction of bond cleavage in the hydrolysis of vinyl and α-haloalkyl ethers are absent from the literature. Experiments with vinyl ethyl, vinyl isopropyl, and vinyl-*n*-butyl ethers were carried out by us under conditions of catalysis by sulfuric acid and by mercuric sulfate. Hydrolysis of vinyl isopropyl ether was also carried out in the absence of catalysts, by heating the ether with water in a sealed ampoule at 150° for 5 hr. We decided to try mercuric sulfate as a catalyst on the basis of Edelman' s data that this compound specifically catalyzes the exchange of alkoxy groups

of simple vinyl ethers for other groups [5]. It was also of interest to obtain direct experimental data on the direction of bond cleavage in α-chloroethyl ether, which, like other α-haloalkyl ethers, reacts according to the scheme

$$\mathrm{R{-}CHCl{-}O{-}R' + H_2O \rightarrow RCHO + R'OH + HCl.} \qquad \text{(II)}$$

It has been proposed that the hydrolysis of α-haloalkyl ethers proceeds with intermediate formation of oxonium compounds of simple vinyl ethers [1,9]. We hydrolyzed α-chloroethyl ether by the action of water without additives, and also with an aqueous solution of sodium carbonate.

The direction of bond cleavage during hydrolysis was determined from the isotopic composition of the alcohols formed, which, as is known ([6]), do not exchange oxygen with H_2O^{18}. Isotopic analysis of the alcohols was carried out by the method described in ([7]), but in platinum ampoules. Isotopic analysis of the water of the hydrolyzing solutions was carried out by the method of exchange with CO_2 ([8]).

The experimental conditions and results are presented in Table 1.

Table 1

Hydrolysis conditions medium	Hydrolysis conditions duration	Hydrolysis conditions temp., °C	Hydrolysis conditions molar ratio ether : water	Excess content of O^{18}, mol. % in the medium	Excess content of O^{18}, mol. % in the alcohol
Hydrolysis of vinyl ethyl ether					
0.2 M H_2SO_4	35 min.	35	1 : 3	0.98	0.02
0.2 M H_2SO_4	40 min.	35	1 : 3	0.88	0.03
Hydrolysis of vinyl-*n*-butyl ether					
0.2 M H_2SO_4	20 min.	80	1 : 11	1.10	0.01
0.2 M H_2SO_4	40 min.	80	1 : 11	1.10	0.03
1% $HgSO_4$	11 hr.	20–25	1 : 11	1.13	0.00
1% $HgSO_4$	12 hr.	20–25	1 : 10	1.13	0.03

Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %
Hydrolysis of vinyl isopropyl ether					
H_2O	5 hr.	140	1 : 6.4	1.22	0.03
H_2O	5 hr.	150	1 : 6.4	1.22	0.03
1% $HgSO_4$	10 min.	20–25	1 : 10	1.22	0.01
1% $HgSO_4$	10 min.	20–25	1 : 10	1.22	0.05
Hydrolysis of α-chloroethyl ether					
H_2O	Instantaneously	20–25	1 : 11	0.95	0.11
H_2O	»	20–25	1 : 6	0.95	0.05
8.5% Na_2CO_3	»	20–25	1 : 6	0.95	0.08

The data obtained show that the alcohols formed in the hydrolysis of vinyl ethyl, vinyl isopropyl, and vinyl-*n*-butyl ethers contain practically no excess O^{18}. It follows from this that the reaction proceeds with cleavage of the bond between the vinyl group and oxygen. Ethyl alcohol obtained in the hydrolysis of α-chloroethyl ether in both acidic and alkaline media contains 5–11% O^{18} of its content in the medium. The reason for the incorporation of a small amount of O^{18} into ethanol is unclear; however, whatever it may be, the data obtained leave no doubt that the principal reaction pathway is cleavage of the bond between the chlorinated alkyl group and oxygen.

The vinyl-oxygen direction of bond cleavage found by us in the hydrolysis of vinyl ethyl, vinyl isopropyl, and vinyl-*n*-butyl ethers in the presence of catalytic amounts of electrophilic reagents (sulfuric acid, mercuric sulfate), and also without addition of catalyst, agrees with the existing view concerning the intermediate formation of hemiacetals unstable in acidic media during the hydrolysis of simple vinyl ethers ([1], [10], [11]):

$$CH_2{=}CH{-}O{-}R + H_2O \longrightarrow CH_3CH\begin{pmatrix} OR \\ + \\ OH_2 \end{pmatrix} \qquad (a)$$

$$CH_3{-}CH\left(\begin{array}{c} OR \\ {}^{+} \\ O{-}H \\ H \end{array}\right) \longrightarrow CH_3CHO + ROH + H^+ \qquad \text{(b)}$$

(III)

Alcohols that do not contain the oxygen of the medium were also obtained in the work of Stassiuk et al., who studied the mechanism of acetal hydrolysis [12]. The data obtained are explained by these authors by the intermediate formation of hemiacetals and their decomposition according to a scheme analogous to (III b).

Regarding the details of the first stage of the reaction, the results of the present investigation make it possible to advance the following considerations: simple vinyl ethers have in the molecule two nucleophilic centers—the oxygen atom and the ethylenic bond. If the primary attack of electrophilic reagents—the catalysts—were directed at the oxygen atom with formation of oxonium ions, as Shostakovskii [1] believes, then one would expect an alkyl-oxygen direction of bond cleavage during hydrolysis, since in the oxonium ion (A), of the two carbon atoms adjacent to oxygen,

$$\begin{array}{c} CH_2 - R \\ CH_2 = CH - O^+ \\ \backslash H \end{array} \qquad \text{(A)}$$

the greatest positive charge should arise on the α-carbon atom of the alkyl group as a consequence of the mobility of the π-electrons of the ethylenic bond. Consequently, the attack of water molecules would be directed at the alkyl group and not at the vinyl group. Vinyl-oxygen bond cleavage thus indicates that the primary attack of electrophilic reagents is not on the oxygen atom, but on the π-electrons of the double bond, with subsequent addition of nucleophilic water molecules to the positive center that has formed.

In favor of this course of the reaction is the strong accelerating action of mercuric sulfate, which, as is known, is a specific catalyst in addition reactions at the $C = C$ double bond, as well as the formation of β-tropylideneacetaldehyde, and not tropyl ether, in the reaction of tropylium ions with vinyl ethyl ether [13]. The alcohol isolated by us in experiments on the hydrolysis of α-chlorodiethyl ether does not contain the oxygen of the medium, just as do the alcohols obtained in the hydrolysis of vinyl ethers and acetals [12].

These data are consistent with the known ideas that in all three reactions there is intermediate formation of hemiacetals [10,14].

The hydrolysis of α-halo ethers, however, differs substantially from the hydrolysis of simple vinyl ethers and acetals in that it does not require the addition of

a catalyst and proceeds at a rate exceeding the possibilities of ordinary kinetic measurements upon contact with water, as well as with an aqueous solution of Na_2CO_3. The differing reactivity of acetals, vinyl ethers, and α-halo ethers, increasing in this series from left to right, should apparently be attributed to the differing ease of formation of hemiacetals in the stage that determines the rate of all three hydrolytic processes.

The polarity of the $C—Cl$ bond in α-halo ethers and the stability of chloride ions greatly facilitate the displacement of the latter by water molecules, whereas nucleophilic substitution of alkoxyl groups in acetals proceeds with a considerable activation energy and requires prior addition of protons of the catalyst. As for the formation of hemiacetals from simple vinyl ethers, it most likely proceeds as a reaction of addition of water molecules to the ethylenic bond, which determines the kinetics of hydrolysis of these compounds.

The instantaneous hydrolysis of α-chlorodiethyl ether in solutions that do not contain electrophilic reagents (an aqueous solution of sodium carbonate) unequivocally rejects oxonium salts of vinyl ethers as obligatory intermediates in the hydrolysis of α-halo ethers [1].

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