Corresponding Member of the Academy of Sciences of the USSR M. F. Shostakovskii, A. S. Atavin, B. V. Prokop' ev, B. A. Trofimov, V. I. Lavrov, N. M. Deriglazov

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR M. F. Shostakovskii, A. S. Atavin, B. V. Prokop' ev, B. A. Trofimov, V. I. Lavrov, N. M. Deriglazov

KINETIC DEUTERIUM ISOTOPE EFFECT IN THE HYDROLYSIS REACTION OF SIMPLE VINYL ETHERS

Despite the considerable number of studies devoted to the hydrolysis of α,β-unsaturated ethers, the mechanism of this reaction is still not entirely clear. In a series of recent works ([1], [2]), carried out with the aid of labeled oxygen O^{18}, experimental evidence was obtained for vinyloxygen (more precisely, ethylideneoxygen) cleavage of vinyl ethers in the case of hydrolysis catalyzed by protons or Hg^{2+} cations. Such a scheme of hydrolytic decomposition followed naturally from the previously advanced assumption of initial addition of water at the multiple bond and the intermediate formation of an unstable hemiacetal ([3–5]).

In the mechanism of hydrolysis of vinyl ethers, the question of the rate-determining stage of the process has remained unresolved up to the present. Although in some earlier works ([4], [6]) it was assumed that the slow step of hydrolysis is the formation of the hemiacetal, this was not sufficiently confirmed experimentally.

It is known that in the hydrolysis reaction of acetals ([7], [8]) or esters under the influence of protonic acids ([9]), the rate-determining stage is the corresponding transformation of the protonated form. This is manifested in a strong acceleration of the reaction in heavy water. As Kilpatrick showed ([8]), hydrolysis of acetals in the temperature interval 0–40° in deuterium oxide proceeds 2.6–3 times faster than in ordinary water. This effect is not purely kinetic; it is due to the different acid strengths of H_3O^+ and D_3O^+.

Analogously, for simple vinyl ethers one should expect acceleration of hydrolysis in heavy water if one assumes, according to ([2]), that the reaction begins with preliminary protonation without formation of a true C–H bond (π-complex). However, the entire course of our investigations did not confirm the indicated assumption ([2]).

To resolve the question of the limiting stage, we measured the rate of acid-catalyzed (HCl) hydrolysis of the monovinyl ether of diethylene glycol (MDEG) in ordinary and heavy water (D_2O). MDEG was chosen because of its solubility

in water, as well as its reduced tendency toward isomerization, in contrast to the monovinyl ethers of 1,2- and 1,3-glycols ([10]).

The kinetics was studied by the accumulation of acetaldehyde in the reaction mixture, the concentration of which was determined polarographically. (Polarograph LP-60; mercury dropping electrode; supporting electrolyte 0.1 N LiOH, simultaneously neutralizing the catalyst; differential recording; capillary characteristic: $m = 1.34$ mg/sec, $t = 0.6$ sec, at the half-wave potential for acetaldehyde reduction -1.98 V.) The calculation of k_1 and k_2 was carried out by the formulas:

$$k_1 = \frac{2.303}{t} \lg \frac{a}{a-x}; \qquad k_2 = k_1/b,$$

where a is the height of the acetaldehyde wave after complete hydrolysis, corresponding to the initial concentration of ether (mm); x is the height of the acetaldehyde wave at time t (mm); b is the catalyst concentration (g-mol/l).

For purposes of checking the polarographic measurements and improving the reliability of the results, the method of alkaline oximation was also used [5], but, unlike the method described, the titration was carried out potentiometrically with an automatic titrator, Jupiter type 7–77–1–1. The experiments were performed in a kinetic apparatus of type [5].

The heavy water had a purity of 99.77 mole %, d_{30}^{30} 1.10785, and a specific electrical conductivity of $0.4 \cdot 10^{-5}$ $\Omega^{-1} \cdot \mathrm{cm}^{-1}$. Solutions of DCl were prepared from

Table 1

Rate constants for hydrolysis of the monovinyl ether of diethylene glycol (MEDG) in H_2O and D_2O (polarography) (HCl concentration $8 \cdot 10^{-4}$ g-mol/l)

T, °C	Initial concentration of MEDG, g-mol/l	$k_1 \cdot 10^4$, sec^{-1}, H_2O,	$k_1 \cdot 10^4$, sec^{-1}, D_2O,	k_2, l · mol^{-1} · sec^{-1}, H_2O,	k_2, l · mol^{-1} · sec^{-1}, D_2O, DCl	Initial concentration of MEDG, g-mol/l	$k_1 \cdot 10^4$, sec^{-1}, H_2O,	$k_1 \cdot 10^4$, sec^{-1}, D_2O,	k_2, l · mol^{-1} · sec^{-1}, H_2O,	k_2, l · mol^{-1} · sec^{-1}, D_2O, DCl
20	0.008	2.16	1.90	2.88	2.53	0.076	3.26	2.86	0.404	0.354

T, °C	Initial concentration of MEDG, g-mol/l	$k_1 \cdot 10^4$, sec^{-1}, H_2O,	$k_1 \cdot 10^4$, sec^{-1}, D_2O,	k_2, l · mol^{-1} · sec^{-1}, HCl	k_2, l · mol^{-1} · sec^{-1}, D_2O, DCl	T, °C	Initial concentration of MEDG, g-mol/l	$k_1 \cdot 10^4$, sec^{-1}, H_2O,	$k_1 \cdot 10^4$, sec^{-1}, D_2O,	k_2, l · mol^{-1} · sec^{-1}, HCl	k_2, l · mol^{-1} · sec^{-1}, D_2O, DCl
20	0.01	2.52 2.21	2.49	2.15 0.276	2.13 0.186	20	0.01	5.38 35 determinations	5.23	4.57 of 35 determ. 0.650	4.56 0.644
25	0.008	3.24	3.42	2.96 0.124	2.93	25	0.008	av.			

17.42% deuterium chloride in D_2O, b.p. 107.5° at 713 mm. MEDG was obtained as described [11] and had the following constants: b.p. 104° (8 mm), n_D^{20} 1.4478, d_4^{20} 1.0269.

The reaction rate was measured at temperatures of 20, 25, and 30° in the acidity range $4 \div 8 \cdot 10^{-4}$ g-mol/l HCl (DCl) and at an initial ether concentration of $5 \cdot 10^{-3}$–$2 \cdot 10^{-2}$ g-mol/l.

Table 2

Rate constants for hydrolysis of MEDG (oximation) (HCl concentration $5.52 \cdot 10^{-4}$ g-mol/l)

T, °C	Initial concentration of MEDG, 10^{-2} g-mol/l	$k_1 \cdot 10^4$, sec^{-1}	k_2, l · mol^{-1} · sec^{-1}	T, °C	Initial concentration of MEDG, 10^{-2} g-mol/l	$k_1 \cdot 10^4$, sec^{-1}	k_2, l · mol^{-1} · sec^{-1}
20	1.03	1.73	0.53	20	1.04	2.16	0.61
25	1.04	2.21	0.40				

The results of the kinetic measurements for H_2O and D_2O are summarized in Table 1 (polarography). In Table 2, for comparison, rate constants for MEDG hydrolysis found by the oximation method are given.

Fig. 1. Dependence of k_1 on [HCl]

Figure 1: Fig. 1. Dependence of k_1 on [HCl]

In accordance with [3-6, 12], under conditions of constant acidity the hydrolysis of the vinyl ether studied proceeds as a pseudomonomolecular process. The first-order reaction rate constant k_1, at the same temperature and HCl concentration, does not depend on the initial concentration

ether (in the interval studied) and remains constant within the limits of measurement error. Variation of the acid concentration leads to a linear change in k_1 (Fig. 1). The constant of the bimolecular process k_2 does not depend on the HCl concentration and changes only with temperature. The temperature dependence of k_2, calculated by the method of least squares [13] from the data of Table 1, is expressed for H_2O as

$$k_2^H = 9.59 \cdot 10^6 \exp(-5050/T) \tag{1}$$

and for D_2O as

$$k_2^D = 1.68 \cdot 10^8 \exp(-6290/T). \tag{2}$$

The kinetic isotope effect (K.I.E.) is

$$k_2^H/k_2^D = 5.71 \cdot 10^{-2} \exp(1240/T). \tag{3}$$

Fig. 1. Dependence of k_1 on [HCl]

Table 3 gives, for comparison, the found rate constants of MED hydrolysis in H_2O and D_2O, as well as the values of the K.I.E. together with those calculated by formulas (1)–(3).

The decrease in the rate of hydrolytic decomposition of MED in D_2O agrees with data obtained for the hydrolysis of α,β-acetylene ethers [14], although in the latter case the kinetic isotope effect is not so significant ($k_{H_2O}/k_{D_2O} = 1.7$). The difficulty of the reaction in the heavy-water medium is reflected in the values of the activation energies ($E_{H_2O} = 10.1$, $E_{D_2O} = 12.5$ kcal/mol) and the pre-exponential factors.

Table 3

Average rate constants of MED hydrolysis in H_2O and D_2O and the kinetic isotope effect

T, °C	k_2^H, found	k_2^H, calculated (1)	k_2^D, found	k_2^D, calculated (2)	k_2^H/k_2^D, found	k_2^H/k_2^D, calculated (3)
20	0.276	0.314	0.076	0.081	3.64	3.93
25	0.408	0.419	0.124	0.114	3.30	3.66
30	0.650	0.554	0.186	0.163	3.50	3.42

The results obtained unambiguously indicate that the rate-limiting stage of the acid hydrolysis of simple vinyl ethers is protonation. This makes it necessary to reject assumptions about the intermediate formation of π-complexes or any other unstable associates of the substrate with protons.

On the basis of the presence of the kinetic isotope effect of hydrogen, it may be concluded that in the first stage of the reaction a new $C-H$ ($C-D$) bond is formed; thus, there is every reason to believe that the hydrolysis of simple vinyl ethers consists of electrophilic attack on the double bond and subsequent transformations of the carbocation (I).

$$CH_2{=}CHOR + H^+ \xrightarrow{\text{slow}} CH_3{-}C^+H{-}OR$$

(I)

$$CH_3{-}C^+H{-}OR + H_2O \xrightarrow{\text{fast}} CH_3{-}CH\begin{pmatrix} OR \\ O^+H_2 \end{pmatrix} \xrightarrow{\text{fast}} CH_3CHO + HOR + H^+.$$

The formation of the carbonium ion (I) should be favored by partial compensation of the electron deficiency at the α-carbon atom by the unshared electrons of the neighboring oxygen

$$CH_3{-}C^+H{-}\overset{\curvearrowleft}{O}{-}R.$$

(I)

In other words, some stabilization of I will occur owing to the tendency of the oxygen atom to form oxonium compounds

$$CH_3{-}C^+H{-}OR \rightleftarrows CH_3{-}CH{=}OR.$$

In view of the high polarity of the medium, one cannot disregard the possibility of simultaneous nucleophilic attack on the solvent molecules with a synchronous electron shift in four-center systems

In a comparative assessment of the rates of homogeneous hydrolysis of MED and simple vinyl ethers that do not contain oxygen atoms in the alkoxy radical ([4,6]), attention is drawn to the increased stability of MED toward hydrolytic cleavage.

Vinyl ethers	Hydrolysis rate constants at 25°, liter · mol^{-1} · sec^{-1}
CH_2=CHOC_2H_5	2.90([6]), 3.25([4])
CH_2=CHOi–C_3H_7	8.66([4])
CH_2=CHO$CH_2CH_2OCH_2CH_2OH$	0.41

Apparently, the influence of the oxygen atom located in the β-position to the vinyloxy group is similar in nature to the effect of the allyl radical in vinyl allyl ether, the hydrolysis rate of which is of the same order as that of MED ([4]).

At concentrations exceeding the solubility of vinyl alkyl ethers, the reaction acquires a heterogeneous character, and the hydrolysis rate is determined by the rate of transfer of the substrate into solution. Under these conditions water-soluble MED is hydrolyzed considerably faster than vinyl alkyl ethers.

Irkutsk Institute of Organic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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