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KINETICS AND MECHANISM OF THE ALKALINE HYDROLYSIS OF VINYL ESTERS

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The mechanism of hydrolysis of vinyl esters is considered in the literature on the basis of ideas about the similarity in the behavior of vinyl and ethyl esters of carboxylic acids (^{1,2}). The use of the isotope method (O^{18}), however, showed that vinyl acetate and vinyl benzoate behave differently from the corresponding ethyl esters with respect to the site of bond cleavage (^{3,4}). Thus, under catalysis by electrophilic reagents (H_2SO_4, $HgSO_4$), cleavage of bonds occurs only between the vinyl group and oxygen; data obtained for alkaline saponification indicate a mixed mechanism of hydrolysis, with cleavage of the acyl-and vinyl-oxygen bonds.

Table 1

Ester	Hydrolysis solution	Isotopic-analysis results in excess, at. % O^{18}: ester CH_2=CHÖ CÖ R	Isotopic-analysis results in excess, at. % O^{18}: ester CH_2=CHÖCOR	Isotopic-analysis results in excess, at. % O^{18}: acid	Fraction of O^{18} transfer into the acid
Vinyl acetate		0.73		0.36	0.50
Vinyl acetate		0.62*		0.30	0.49
Vinyl acetate		0.73		0.36	0.50
Vinyl acetate			1.20	0.35	0.29
Vinyl benzoate		1.37		0.67	0.49

Ester	Hydrolysis solution	Isotopic-analysis results in excess, at. % O^{18}: ester CH_2=CHÖ CÖ R	Isotopic-analysis results in excess, at. % O^{18}: ester CH_2=CHÖCOR	Isotopic-analysis results in excess, at. % O^{18}: acid	Fraction of O^{18} transfer into the acid
Vinyl benzoate			1.52	0.52	0.34
Vinyl anisate	1.07			0.55	0.52
Vinyl anisate	3.81			1.83	0.48
Vinyl anisate			1.38	0.36	0.26
Vinyl anisate			1.41	0.36	0.25
Vinyl *p*-nitrobenzoate	2.42			1.09	0.45
Vinyl *p*-nitrobenzoate			1.04	0.29	0.28
Vinyl *p*-chlorobenzoate			0.98	0.17	0.17
Vinyl *p*-chlorobenzoate			0.63	0.12	0.19

* The ester isolated from the reaction mixture after hydrolysis of no less than half of the amount taken contained 0.63 at. % O. During hydrolysis of vinyl acetate, benzoate, and anisate in H_2O^{18}, the esters isolated under incomplete hydrolysis retained their natural isotopic composition.

In the present article we set forth the results of a further investigation of the hydrolysis of vinyl esters in an alkaline medium by isotopic and kinetic methods. To determine the site of bond cleavage, vinyl acetate, vinyl benzoate and its *p*-chloro-, nitro-, and methoxy-derivatives were prepared, containing O^{18} only in the ester oxygen, as well as vinyl acetate and vinyl benzoate labeled with O^{18} in both oxygen atoms of the OCOOH group. The methods of synthesis of these esters, and the determination of the position and content of O^{18} in them, are described in (^{5}).

Saponification of labeled esters was carried out either in homogeneous aqueous-alcoholic and aqueous-dioxane solutions, or under heterogeneous conditions with shaking of the ester with an alkaline aqueous solution. The acid salts formed during hydrolysis were isolated, purified, and analyzed for O^{18} content, as described in (^{3}); the melting points of the benzoic acids agreed with reference data. Samples of the initial vinyl esters were also subjected to isotopic analysis; their purity was checked by boiling point (or melting point) and refractive index. To ascertain the presence of exchange during hydrolysis, in a number of cases the reaction was not brought to completion; the unreacted ester was regenerat-

was purified and subjected to isotopic analysis. Experiments were also carried out on the hydrolysis of vinyl anisate and vinyl *p*-nitrobenzoate in H_2O^{18}. The O^{18} content in the initial hydrolyzing solution was determined from the isotopic composition of CO_2 after establishment of isotopic equilibrium between a large excess of H_2O^{18} and gaseous carbon dioxide. The results obtained are presented in Table 1.

From the data obtained it is clear that in all cases the ester oxygen atom partially passes into the carboxylic acid formed. This confirms the assumption of a mixed mechanism for the alkaline hydrolysis of vinyl esters. The fraction of vinyl-oxygen cleavage changes only slightly with changes in the structure of the acyl residue of the ester. The preservation of the isotopic composition of the unreacted ester in incomplete hydrolysis indicates that in our case, as also in the hydrolysis of phenyl benzoates (^{6}) and lactones (^{11}), the rate of saponification exceeds the rate of exchange.

To obtain additional data on the reaction mechanism, we studied the kinetics of alkaline hydrolysis of the esters listed. The experiments were carried out in aqueous-ethanolic solutions containing 5-20 mol/liter of water at 15, 25, and 35°. In most experiments, equimolar amounts of alkali and ester were taken (0.03-0.30 mol/liter). The reaction rate was determined from the decrease in the alkali content in the solution. For this purpose, 5.0-ml samples were poured into a slight excess of cooled 0.10 *N* HCl solution, which was then titrated with alkali. In each series of experiments, the experimental data obeyed a second-order kinetic equation; the rate constant increased in proportion to the increase in the concentration of water in the initial solution, as is seen from Fig. 1.

Fig. 1. Dependence of the hydrolysis rate constant on the concentration of water in solution: 1—vinyl anisate, 2—vinyl benzoate, 3—vinyl *p*-chlorobenzoate, 4—vinyl acetate.

Table 2 gives the rate constants for solutions containing 13 mol/liter of water and the parameters of the Arrhenius equation for such solutions.

Table 2

Ester	$k_{25} \cdot 10^3$, liter/mol • sec^{-1}	E, kcal	lg A
Vinyl anisate	0.23	18.0	9.57
Vinyl benzoate	1.17	16.9	9.44

Fig. 2

Figure 1: Fig. 2

Ester	$k_{25} \cdot 10^3$, liter/mol · sec^{-1}	E, kcal	lg A
Vinyl p-chlorobenzoate	3.71	15.8	9.17
Vinyl p-nitrobenzoate	92.50	15.8	10.55
Vinyl acetate	13.10	13.0	7.67

There is no unified view in the literature on the kinetic role of water in ester saponification reactions. Ingold believes that the proportionality observed in these cases between the reaction rate and the water content in the solution gives the true reaction order and does not reflect the influence of changes in the polarity of the medium ([7]). Participation of water in the transition complex during alkaline hydrolysis is also assumed by Syrkin and Moiseev ([8]) and by Koivisto ([9]). For the hydrolysis of vinyl esters, it is difficult to imagine vinyl-oxygen bond cleavage without simultaneous addition of water to the vinyl group. We believe that this is manifested kinetically in the observed dependence of the second-order rate constant on the concentration of water, i.e., it leads to an overall third order of the reaction.

In order of increasing rate of alkaline hydrolysis, the esters studied are arranged as follows: anisate $<$ benzoate $<$ p-chlorobenzoate $<$ acetate $<$ p-nitrobenzoate, from which it follows that in the series of esters of benzoic acids electron-donating substituents retard, while electron-accepting-

···accelerate the reaction. On going from vinyl anisate to vinyl p-nitrobenzoate, the reaction is accelerated by more than 400 times.

The quantitative relation between the hydrolysis rate constants and the Hammett substituent constants σ is shown in Fig. 2. The reaction constant ρ found from the data obtained is 2.48. A close value, $\rho^* = 2.67$, was also found by us for esters of aliphatic acids, using the kinetic data of Ushakov and co-workers (10) and applying Taft’ s equation (12)

$$\lg k/k_0 = \sigma^* \rho^* + E_s + \psi,$$

where k_0 is the hydrolysis rate constant of vinyl acetate, $\sigma^* \rho^*$ characterizes the polar effect, E_s the steric effect, and ψ the resonance effect of the substituents (see Fig. 3).

Fig. 2. Determination of the reaction constant ρ for the hydrolysis of vinyl benzoates

Fig. 3

Figure 2: Fig. 3

Before proceeding to a discussion of the reaction mechanism, it is of interest to compare the available kinetic and isotope data on the alkaline hydrolysis of vinyl and corresponding ethyl esters*: a) introduction of substituents into the acyl radical of both types of esters causes a change in the hydrolysis rate of the same direction and of similar magnitude; b) the values of ρ and of the activation energy of the reaction are very close for analogously constructed vinyl and ethyl esters; c) ethyl esters decompose during hydrolysis by the acyl-oxygen pathway, whereas vinyl esters do so by both the acyl- and the vinyl-oxygen schemes; d) for ethyl esters the hydrolysis rate is commensurate with the rate of oxygen exchange with the medium, whereas for vinyl esters k_{hyd} considerably exceeds k_{exch}. Thus, along with the similarity there is a substantial difference in the behavior of vinyl and ethyl esters in alkaline medium.

Fig. 3. Determination of the reaction constant ρ^* for the hydrolysis of aliphatic vinyl esters (from data of S. N. Ushakov and co-workers)

For cases in which $k_{\text{hyd}} \gg k_{\text{exch}}$, the step determining the rate of hydrolysis, according to Bender (11), is the addition of hydroxyl ions to the carboxyl carbon atom of the ester. Syrkin and Moiseev (8) consider that the potential barrier of this process is always higher than that of the remaining steps of hydrolysis. The results of the present work support the views of Syrkin and Moiseev, since the close values of ρ and E for vinyl and ethyl esters are difficult to explain otherwise than by a common limiting step, although the ratios $k_{\text{hyd}} : k_{\text{exch}}$ for ethyl and vinyl esters are different. This step is apparently the addition of OH^- to solvated ester molecules. For vinyl esters a form of the transition complex close to that depicted below is highly probable:

An interesting feature of complexes of such a structure is their ability, upon decomposition along different pathways, to give acetaldehyde and a carboxylic acid.

directions, as is evident from the scheme.

Scheme 1

It is possible that decomposition is preceded by abstraction of proton (a) or (b), which also determines the direction of cleavage of old bonds and formation of new ones.

Table 3 shows what relative fraction of O^{18} should be contained in the carboxylic acid formed for the three considered pathways of decomposition of the complex, depending on the position of the labeled atom in the system. As an example, the relative content of O^{18} in the carboxyl of the acid is given for equal probabilities

* For data on the kinetics of the alkaline hydrolysis of ethyl benzoates, see (13).

of pathways 1, 2, and 3. The results of this calculation agree with the isotopic composition of the acid oxygen found in the experiments. However, a simple calculation shows that significant changes in the relative role of each of the pathways lead only to a comparatively small change in the isotopic composition of the oxygen of the carboxyl group of the acids, of the same order as the total experimental error. Therefore, we regard the satisfactory agreement of the found and calculated values as evidence in favor of the occurrence of all three pathways, but not of their equivalence. Moreover, the experimental data can also be well explained by decomposition of the complex only along pathways 2 and 3, with predominance of the latter.

Table 3

Relative content of O^{18} in the carboxyl group of the acid for different positions of the labeled atom in the system

Direction of decomposition	Position of O^{18}: in the ether oxygen of the acid	Position of O^{18}: in the two O atoms of the carboxyl group of the ether	Position of O^{18}: in the hydrolyzing solution
1	1/3	2/3	1/3
2	0	1/2	1/2
3	1,2	1/2	1/2
With equal probability of the three pathways	5,18	5/9	4/9
Found in experiments	1/5–1/3	1/2	4/10–5/10*

* According to the data of the present and preceding (3) works.

Thus, the results of our experiments prove the presence of two directions of bond cleavage in the hydrolysis of vinyl esters in an alkaline medium, according to vinyl and acyl-oxygen schemes, but do not make it possible to elucidate the details of the process of decomposition of the intermediate complex.

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