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KINETICS OF THE HYDROLYSIS OF VINYL ESTERS UNDER CATALYSIS BY MERCURY IONS

(Presented by Academician A. N. Frumkin on 17 VII 1963)

In our previous works, using O^{18}, it was shown that the hydrolysis of vinyl esters under catalysis by electrophilic reagents (acid, mercury sulfate) proceeds with cleavage of the vinyl-oxygen bond of the ester ([1,2]). This refuted the generally accepted scheme of hydrolysis, which had earlier been extended to vinyl esters by analogy with ethyl esters of carboxylic acids and was attributed by us to a primary attack of the electrophilic reagent on the double bond $C = C$.

In the present work, in order to clarify the dependence of the reaction rate on the structure of the ester and the details of the reaction mechanism, we investigated the kinetics of hydrolysis of five vinyl esters. The catalyst was a mixture of mercury acetate with sulfuric acid—a specific catalyst for vinyl-exchange reactions ([3]) and for the hydrolysis of vinyl esters ([1,2]). In the presence of mercury acetate alone or sulfuric acid alone at concentrations of 0.001–0.01 mole/liter and at 25°, hydrolysis practically does not occur, as shown by control experiments.

Kinetic experiments were carried out in aqueous-alcoholic solutions at 25°±0.05°. For each experiment two solutions were prepared: the first—weighed portions of mercury acetate and the vinyl ester in anhydrous ethanol; the second—a solution of sulfuric acid in aqueous alcohol. Immediately after mixing and stirring, the first control sample was taken. Then, at specified time intervals, 5.0 ml samples were taken from the reaction mixture and poured, to stop the reaction, into an ice-cooled mixture of 20 ml water with 10 ml CCl_4, to which several milliliters of a titrated alkali solution had previously been added. The sample was shaken and immediately titrated with alkali using phenolphthalein. The reaction rate was measured by the amount of acid formed.

Fig. 1. Dependence of the reaction rate on the concentration of vinyl esters. 1—acetate, 2—anisate, 3—benzoate, 4—*p*-chlorobenzoate, 5—*p*-nitrobenzoate

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Fig. 2

Figure 2: Fig. 2

The rate of hydrolysis of vinyl acetate and of four substituted vinyl benzoates was found. It turned out that in each case the course of the reaction is described by a first-order equation; however, the rate constant changes with the initial concentration of the ester. The dependence of the hydrolysis rate v on the initial concentration of the substrate C is shown in Fig. 1.

A change in the structure of the acyl radical has comparatively little effect on the rate of hydrolysis of substituted vinyl benzoates. Thus, replacement of the electropositive group CH_3O by the strongly electronegative p-nitro group slows the hydrolysis of vinyl benzoates by only a factor of 3. In terms of the rate of hydrolysis under comparable conditions, the esters studied are arranged—

are arranged in the order: acetate, anisate > benzoate, n-chlorobenzoate > n-nitrobenzoate. This sequence is the opposite of that observed for alkaline hydrolysis.

The relationship between the hydrolysis rate constants of vinyl benzoates and the Hammett substituent constants σ is shown in Fig. 2 for ester concentrations of 0.1 mole/l at 15°. The small value $\rho = -0.425$ reflects the weak sensitivity of the reaction to changes in the structure of the acyl residues of vinyl esters ([12]).

Fig. 2. Determination of the reaction constant for the hydrolysis of vinyl esters at 15°, 0.1 mole/l

The similarity in the behavior of the esters studied is also manifested in the very close values of the parameters of the Arrhenius equation, found from the temperature dependence of the reaction rate (see Table 1).

Table 1

Substituent	CH_3O	H	Cl	NO_2	Vinyl acetate
E, kcal	14.6	14.7	14.9	14.7	15.1
$\lg A$	8.3	8.3	8.3	8.0	8.4

The kinetics of hydrolysis of vinyl esters in the presence of a mercury catalyst was studied in greater detail using vinyl acetate as an example. The dependence of hydrolysis on the catalyst concentration, on the concentration of sulfuric

acid at a constant amount of mercury acetate, on the concentration of mercury acetate at a constant sulfuric acid content, and on the concentration of water was determined.

The reaction rate does not depend on the concentration of water if the concentration exceeds 7 mole/l. In the range from 7 to 2 mole/l, the hydrolysis rate increases as the water concentration decreases. The latter may be explained either by the occurrence, along with hydrolysis, under conditions of low water concentrations, of a faster reaction of substitution of the acid group of vinyl acetate by an alcohol group, or by the effect of a change in the polarity of the medium ([4]). To avoid the influence of small changes in water concentration, we carried out all the remaining kinetic experiments in alcoholic solutions containing about 11 mole/l of water.

The rate of hydrolysis increases proportionally to the concentration of sulfuric acid at a constant concentration of mercury acetate. When the concentration of mercury acetate is varied and the H_2SO_4 content is kept constant, the reaction rate is proportional to $HgAc_2^{1/2}$. The dependence of the hydrolysis rate of vinyl acetate on the catalyst concentration is shown in Fig. 3.

Fig. 3. Dependence of the reaction rate on the catalyst concentration

The totality of all the kinetic data agrees well with the scheme proposed by R. M. Flid and O. N. Temkin ([5,6]) for catalytic reactions of acetylene in the presence of mercury salts, which assumes the intermediate formation of a complex of both reacting substances with the catalyst:

$$\text{a) } A + K \underset{k_2}{\overset{k_1}{\rightleftarrows}} M_1; \qquad \text{b) } M_1 + B \underset{k_4}{\overset{k_3}{\rightleftarrows}} M_2; \qquad \text{c) } M_2 \xrightarrow{k_5} P + K,$$

where in our case A is water, B is vinyl acetate, K is the catalyst, and P is the reaction products.

The kinetic equation for the rate of a reaction proceeding according to such a scheme, in the case where the rate of the process is determined by the transformation of M_2,

$$v = \frac{k_1 k_3 k_5 [\mathrm{A}][\mathrm{B}][\mathrm{K}]}{(k_2 + k_1[\mathrm{A}])(k_4 + k_3[\mathrm{B}])} \tag{1}$$

when $k_1[\mathrm{A}] \gg k_2$, is transformed into

$$v = \frac{k_2 k_5 [\mathrm{B}][\mathrm{K}]}{k_4 + k_3[\mathrm{B}]} = \frac{k_5[\mathrm{B}][\mathrm{K}]}{K_\mathrm{n} + [\mathrm{B}]}, \tag{2}$$

where K_n is the instability constant of the complex M_2.

The great affinity of mercury ions for water, corresponding to the condition $k_1 > k_2$, is confirmed by the extremely easy hydrolysis of all ionized mercury salts (*). In our experiments, in addition, water was present in large excess, i.e., [A] was large. Thus, it may be assumed that the condition $k_1[A] \gg k_2$ was fulfilled, as a result of which the concentration of water does not enter into the kinetic equation, in agreement with the experimental data given above.

Table 2

Results of calculating k_5 by means of equation (2) from experimental data

Ether	ether	$HgAc_2$	H_2SO_4	K_n, min^{-1}	k_5	k_5, average
Vinyl acetate	0,108	0,0050	0,0050	0,0036	6,7	6,2
Vinyl acetate	0,216	0,0050	0,0050	0,0032	6,9	6,2
Vinyl acetate	0,323	0,0050	0,0050	0,0027	6,7	6,2
Vinyl acetate	0,216	0,0200	0,0174	0,0160	5,0	6,2
Vinyl acetate	0,216	0,0140	0,0122	0,0115	6,1	6,2
Vinyl acetate	0,216	0,0100	0,0087	0,0031	5,4	6,2
Vinyl acetate	0,216	0,0050	0,0043	0,0022	5,5	6,2
Vinyl acetate	0,216	0,0050	0,0021	0,0011	5,6	6,2
Vinyl acetate	0,216	0,0050	0,0087	0,0042	5,2	6,2
Vinyl acetate	0,216	0,0011	0,0084	0,0025	6,9	6,2
Vinyl acetate	0,216	0,0022	0,0084	0,0036	6,9	6,2

Ether	ether	$HgAc_2$	H_2SO_4	K_n, min^{-1}	k_5	k_5, average
Vinyl acetate	0,216	0,0050	0,0084	0,0052	6,5	6,2
Vinyl acetate	0,216	0,0066	0,0084	0,0062	6,9	6,2
Vinyl acetate	0,216	0,0100	0,0084	0,0069	6,3	6,2
Vinyl anisate	0,050	0,0050	0,0050	0,0051	3,8	3,5
Vinyl anisate	0,100	0,0050	0,0050	0,0037	3,3	3,5
Vinyl anisate	0,200	0,0050	0,0050	0,0029	3,4	3,5
Vinyl anisate	0,300	0,0050	0,0050	0,0023	3,4	3,5
Vinyl benzoate	0,050	0,0050	0,0050	0,0036	1,2	1,3
Vinyl benzoate	0,100	0,0050	0,0050	0,0026	1,3	1,3
Vinyl benzoate	0,200	0,0050	0,0050	0,0016	1,3	1,3
Vinyl benzoate	0,300	0,0050	0,0050	0,0012	1,3	1,3
Vinyl *p*-chlorobenzoate	0,050	0,0050	0,0050	0,0032	1,3	1,3
Vinyl *p*-chlorobenzoate	0,100	0,0050	0,0050	0,0023	1,2	1,3
Vinyl *p*-chlorobenzoate	0,200	0,0050	0,0050	0,0016	1,3	1,3
Vinyl *p*-chlorobenzoate	0,300	0,0050	0,0050	0,0012	1,3	1,3

Ether	ether	$HgAc_2$	H_2SO_4	K_n, min^{-1}	k_5	k_5, average
Vinyl *p*-nitrobenzoate	0,050	0,0050	0,0050	0,0022	0,66	0,64
Vinyl *p*-nitrobenzoate	0,100	0,0050	0,0050	0,0013	0,56	0,64
Vinyl *p*-nitrobenzoate	0,200	0,0050	0,0050	0,0009	0,69	0,64

The value of K_n can be found graphically from the dependence of the hydrolysis rate on the ester concentration. It is known that in cases of reversible formation of substrate complexes with a catalyst, $1/v$ depends linearly on $1/C$ ([8]). The intercepts cut off by the straight lines on the ordinate axis of such plots are numerically equal to $1/v_{max}$, while the tangent of the angle of inclination of the straight lines to the abscissa axis determines the value K_n/v_{max}, where v_{max} is the maximum reaction rate, attained when the excess of substrate is so large that practically all of the catalyst is bound.

In the indicated manner, from Fig. 4 we found the following values of K_n for the investigated esters $CH_2 = CHOCO - X$:

X	$CH_3OC_6H_4$	C_6H_5	ClC_6H_4	$O_2NC_6H_4$	CH_3
K_n	0,21	0,073	0,092	0,057	0,54

The limited experimental material and the considerable errors usually introduced by the graphical method do not allow the numerical values of K_n to be determined with great reliability; however, the values given above apparently correctly reflect the order of magnitude and show relatively small changes in the instability constants of the complexes of the investigated esters with mercury ions.

To check the applicability of equation (2) to the hydrolysis of vinyl esters in the presence of a mercury catalyst, with its aid, knowing the values

K_H, the values of k_5 were calculated. The results are given in Table 2; they show that, for vinyl acetate in different series of experiments, the calculated values of k_5 are reproduced satisfactorily, which confirms the correctness of the adopted reaction scheme. Good agreement of the values of k_5 was also found for the other esters.

Fig. 4. Determination of the instability constants of vinyl esters with the catalyst. The curve designations are the same as in Fig. 1.

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Figure 3: Fig. 4. Determination of the instability constants of vinyl esters with the catalyst. The curve designations are the same as in Fig. 1

On the basis of all that has been said, we obtain the kinetic equation for the hydrolysis of vinyl esters under catalysis by $HgAc_2$ and H_2SO_4 in the form

$$v = \frac{k_5[\text{ester}]\,[H_2SO_4]\,[HgAc_2]^{1/2}}{K_H + [\text{ester}]}$$

$(\text{l/m})^{3/2} \cdot \text{min}^{-1}$.

The manifestation of catalytic activity by mercury acetate only in the presence of sulfuric acid shows that, under the conditions of our experiments, the active catalyst is mercury ions ([14]), and the role of the acid consists in the ionization of weakly dissociated mercury acetate ($K_{\text{diss}} = 2 \cdot 10^{-9}$ ([9])).

The hydrolysis scheme may be represented by the following sequence of reactions, analogous to the reactions of vinyl exchange ([13]):

$$Hg^{2+} + 2H_2O \rightleftharpoons Hg^{2+}(H_2O)_2 + CH_2{=}CHOCOR \rightleftharpoons$$

$$\rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ OCOR \end{matrix} \cdots Hg^{2+} \begin{matrix} OH_2 \\ \\ OH_2 \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ OH \end{matrix} + RCOOH + Hg^{2+}(OH_2)_2.$$

It may be thought that the exchange of acid residues for a hydroxyl group takes place within the coordination sphere of mercury aquo complexes with the ester, which explains the much greater catalytic activity of Hg^{2+} ions in comparison with protons.

The proportionality of the hydrolysis rate to the acid concentration can also be explained by the intermediate formation of the product of addition of mercury acetate at the ethylene bond,

$$AcHgCH_2 - CH\begin{matrix}/Ac \\ \backslash Ac\end{matrix}$$

and by the decomposition of this compound in the slow stage under the action of sulfuric acid ([10,11]).

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