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Abstract

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MECHANISM OF HYDROLYSIS OF VINYL ESTERS

HYDROLYSIS OF VINYL ACETATE AND VINYL BENZOATE

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Hydrolysis of vinyl esters, in contrast to the hydrolysis of esters of saturated alcohols, has been insufficiently studied. In particular, there are no direct experimental data on the sites of bond cleavage. By analogy with the hydrolysis of alkyl esters of carboxylic acids in alkaline and acidic media, an acyl-oxygen scheme is assumed for the corresponding vinyl esters ([1,2,13]). However, the similarity in the behavior of simple and complex vinyl ethers in acidic media makes it very likely that hydrolysis proceeds in the vinyl-oxygen direction, as we recently found for simple vinyl ethers ([3]). Described below are experiments with vinyl acetate and vinyl benzoate in aqueous solutions enriched with H_2O^{18}, which showed a fundamental difference in the behavior of alkyl and vinyl esters of carboxylic acids.

We carried out the hydrolysis of the esters in acidic and alkaline solutions, in neutral KCl solutions, and also in dilute aqueous solutions of $HgSO_4$. The latter was used as a catalyst on the basis of Edel' man' s data ([4]) that this salt specifically catalyzes exchange of the acetate group of vinyl acetate for the acid residues of other carboxylic acids. The experiments were carried out both under heterogeneous conditions with vigorous shaking of the ester with water, and in homogeneous aqueous-ethanolic or aqueous-dioxane solutions. The direction of bond cleavage during hydrolysis was determined from the isotopic composition of the acids or their salts formed. It is known that salts of acetic and other carboxylic acids do not exchange oxygen with H_2O^{18}, while the acids themselves do so only under severe conditions in the presence of strong acidic reagents ([5,6]).

In all experiments, acetic acid was isolated from the hydrolysate as the potassium or sodium salt. For this purpose the reaction mixture was alkalized, repeatedly extracted with ether, the aqueous layer was boiled with activated carbon, and the colorless filtrate was evaporated on a water bath. The acetates were purified from inorganic salts by dissolution in ethanol and then dried in vacuum. Benzoic acid, which precipitated during hydrolysis of vinyl benzoate in the presence of $HgSO_4$, was filtered off, dried, and sublimed in vacuum. In alkaline-hydrolysis experiments the hydrolysate was diluted with water, extracted with ether, the aqueous layer was boiled with activated carbon, and then acidified with H_2SO_4. The precipitated C_6H_5COOH was purified as described above. The substances studied had melting points corresponding to reference data. Isotopic analysis of acetates and benzoic acid was carried out by a mass-spectrometric method after conversion of the substances studied into CO_2 by Rittenberg' s method (^{7}), or by pyrolysis (^{8}), but in platinum ampoules; analysis of water from the hydrolyzing solutions was carried out by exchanging it with CO_2 (^{9}). The total error of the isotopic analysis of oxygen in organic substances did not exceed 2–3% of the measured value.

To check for possible exchange in acetic acid, experiments on exchange of acetic acid with H_2O^{18} were set up in parallel with the experiments on acidic and neutral hydrolysis of vinyl acetate, over the same time and with the same additives. The conditions and results of the experiments with vinyl acetate and vinyl benzoate are given in Table 1.

Table 1

Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	B/A, %
medium	duration of hydrolysis	temp., °C	molar ratio ester : water	in the medium	in acid: from hydrolysis experiment **	in acid: from exchange experiment **	in unreacted ester	B/A, %
Vinyl acetate	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**	**Vinyl acetate**
0.8% aqueous-alcoholic solution H_2SO_4*	30 min.	25	1 : 2.6	1.14	0.06—0.10	0.03—0.04	—	

Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	B/A, %
2% aqueous solution $HgSO_4$	60 min.	25	1 : 10	1.17	0.05	0.09–0.10	–	
4% aqueous-alcoholic solution KCl*	30 min.	100	1 : 2.6	1.17	0.05	0.09–0.11	–	
25% aqueous solution KOH	1 min.	25	1 : 10	1.18	0.38–0.42	–	–	33.3
25% aqueous solution KOH	1 min.	25	1 : 10	2.71	0.92–1.02	–	–	35.8
7% aqueous-alcoholic solution NaOH*	instantaneous	25	1 : 10	1.22	0.38–0.39	–	–	32.1
Vinyl benzoate	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**	**Vinyl benzoate**

Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Hydrolysis conditions	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	Excess content of O^{18}, mol. %	B/A, %
2% aqueous solution $HgSO_4$	6 h	25	1 : 10	1.22	0	–	–	
20% aqueous solution NaOH	5 h	25	1 : 10	1.22	0.51	–	–	41.8
8% aqueous-alcoholic solution NaOH*	instantaneous	25	1 : 10	1.22	0.51	–	–	41.8
2.6% aqueous-dioxane solution KOH*	15 min.	100	1 : 25	2.72	1.09–1.10	–	0	40.5
6% aqueous-dioxane solution KOH*	50 min.	100	1 : 25	2.72	1.03–1.06	–	0	39.0

* Hydrolysis was carried out under homogeneous conditions. The solution contains, per 1 volume of water, 2 volumes of absolute alcohol in the case of an aqueous-alcoholic solution, or 3–4 volumes of absolute dioxane in the case of aqueous-dioxane solutions.
** Extreme values of not fewer than 4 determinations are given.

From the data in Table 1 it is evident that the acetic acid formed during acid hydrolysis and during hydrolysis in the presence of salts contains only a small excess amount of O^{18}, corresponding to a slight exchange of the acid during the experiment. Benzoic acid obtained in the presence of mercuric sulfate contains no excess O^{18} at all, in accordance with the considerably slower exchange of benzoic acid as compared with acetic acid. These results prove unambiguously that, under the indicated conditions, cleavage of the bond between the vinyl residue and oxygen takes place. Thus, the direction of bond cleavage in the hydrolysis of vinyl acetate and vinyl benzoate under catalysis by sulfuric acid or salts is opposite to the direction of bond cleavage in esters of saturated alcohols, for example in ethyl acetate and ethyl benzoate, and is analogous to the hydrolysis of simple vinyl ethers. The alkyl-oxygen bond cleavage in esters of carboxylic acids, demonstrated in a number of examples, was observed with such a structure of the alcoholic radical as ensures the stability of the corresponding carbonium ion (carbinols of branched structure) (^{10}). Vinyl esters do not satisfy this condition. Consequently, the results of our experiments are difficult to explain on the basis of the known concepts of the mechanism of ester hydrolysis. The mechanism of hydrolysis of simple vinyl ethers (^{3}), on the contrary, can readily be extended, as is clear from the scheme, to the transformations of complex vinyl esters in acidic aqueous solutions:

$$\mathrm{CH_2{=}CH{-}O{-}CO{-}R + H^+ \longrightarrow CH_2\overset{H^+}{=}CH{-}O{-}CO{-}R}$$

$$\mathrm{CH_2\overset{H^+}{=}CH{-}O{-}CO{-}R + H_2O \longrightarrow CH_3{-}CH\left(\begin{matrix} O{-}COR \\ OH_2^+ \end{matrix}\right) \longrightarrow CH_3\overset{+}{C}HOH + RCOOH}$$

$$\mathrm{CH_3\overset{+}{C}HOH \longrightarrow CH_3CHO + H^+}$$

Such a course of the reaction is consistent with the ability of vinyl acetate and other vinyl esters to add reagents with a labile hydrogen atom, giving ethylidene derivatives (^{2}), and explains the catalytic effect of mercuric sulfate in our experiments. Scheme I is also supported by the formation of acetaldehyde mercurated in the methyl group when an excess of mercury salt acts on vinyl acetate (^{11}). Potassium (sodium) acetate and benzoate, obtained by alkaline saponification of the initial esters, contain, respectively, from 32 to 36 and from 39 to 42% O^{18} of its content in H_2O^{18}.

The incorporation of O^{18} into the $-\mathrm{COO}^-$ groups of acetic and benzoic acids, which are incapable of exchange in alkaline media, indicates attack by OH^- ions (or water molecules) on the carbonyl carbon atom of the esters. According to current views ($^{10,\ 12,\ 13}$), this attack leads to the formation of the ortho form of the ester (a):

$$\mathrm{CH_2{=}CH{-}O{-}CO{-}R + OH^- \longrightarrow CH_2{=}CH{-}O{-}C(OH)(O^-){-}R} \qquad \text{(a)}$$

II.

In the acyl-oxygen direction of decomposition of (a), the acid formed should contain 1 atom of oxygen from the medium. In fact, as Bender showed, somewhat more enters the acid, since the carbonyl group of the ester partially exchanges oxygen with water during hydrolysis. In the vinyl-oxygen decomposition of (a), an acid should be formed containing only 1/3 of its oxygen from the medium. Owing to exchange of the ester during the reaction, this value may become somewhat larger.

Obviously, our data for both vinyl acetate and vinyl benzoate (on average 33% O^{18} and 41% O^{18} of the O^{18} content in H_2O) could be explained by vinyl-oxygen decomposition of (a), assuming that vinyl acetate decomposes before it has time to exchange, whereas the decomposition of vinyl benzoate, which according to Ushakov' s data (^{2}) is ten times slower, is accompanied by exchange. However, such an interpretation is contradicted by the normal isotopic composition of the vinyl benzoate isolated by us from the reaction mixture in incomplete hydrolysis. The only possible explanation for the formation of benzoic acid containing less than 50 and more than 33% O^{18} from the medium remains a mixed mechanism of decomposition of vinyl benzoate, with cleavage of both vinyl-and acyl-oxygen bonds.

Schemes II and III, in our opinion, account for the totality of the data on alkaline saponification of complex vinyl esters:

$$\mathrm{CH_2{=}CH{-}O{-}C(OH)(O^-){-}R + H_2O}$$

$$\xrightarrow[2]{1}\begin{cases}\mathrm{CH_2{=}CH{-}O{-}C(OH)(O^-){-}R \longrightarrow RCOOH + CH_3CHO + OH^-}\\ \mathrm{CH_2{=}CH{-}O{-}C(OH)(O^-){-}R \longrightarrow R{-}C({=}\,O)OH + CH_3CHO + OH^-}\end{cases}$$

III

In the hydrolysis of vinyl acetate, pathway 1 strongly predominates; in the hydrolysis of vinyl benzoate, pathway 2 also acquires a significant role.

Path (a) of Scheme II, in Ingold' s terminology, corresponds to the $B_{\mathrm{Al}} - 2$ mechanism. The only established case of the manifestation of this mechanism up to now has been the hydrolysis of β-lactones (^{10}). The results of the present work show that alkaline saponification of complex vinyl esters represents yet another example of the manifestation of the $B_{\mathrm{Al}} - 2$ mechanism.

Our data on both the alkaline and the acid hydrolysis of vinyl esters make it necessary to revise the existing interpretations of the mechanism of these reactions (^{1}, ^{2}, ^{13}).

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