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The Dependence of the Mechanism of the Hydrolysis, Trans-esterification, and Trans-etherification of α,β-Alkenyl Ethers and Esters on Their Structure

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New experimental data obtained in the study of the mechanism of the hydrolysis of ethers and esters formed by enols and the related trans-esterification and trans-etherification of these compounds are collected in the present review.
Recent studies have confirmed the early views that the hydrolysis of the ethers formed by enols passes through a stage involving hydration of the ethylene bond, have made it possible to describe this reaction scheme in considerable detail, and have shown that an analogous mechanism can be extended to the hydrolysis of the esters formed by enols, in the discussion of which, until recently, schemes involving nucleophilic substitution at the carbonyl group were used.
The large amount of data on the alkaline hydrolysis of enol acylates indicates that the mechanism of this reaction is similar to, but not identical with that of the alkaline hydrolysis of alkyl esters.

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1. INTRODUCTION

Modern theories of equilibrium and the kinetics of chemical reactions are based on the classical studies of Menshutkin, carried out in the eighteen-hundreds. The object of these studies was the formation and hydrolysis of esters. Fifty years later, Polanyi and Szabo, using ^{18}O, determined the point of fission of the bonds in the hydrolysis of esters of carboxylic acids. This work became a classical example of the use of tracers to investigate reaction mechanisms. Since that time, a large number of workers, including a number of outstanding chemists of the present time, have taken part in the study of the details of the mechanism of esterification and etherification and the hydrolysis of ethers and esters. It is therefore not surprising that the hydrolysis, trans-esterification, and formation of esters are among the processes which have been studied most fully and in greatest detail, in both preparative and theoretical aspects.

The foregoing is only partly true of ethers and esters with characteristic structure in which the ether oxygen atom is next to an ethylenic bond. These are the $\alpha\beta$-alkenyl ethers and esters, which are often also called enol ethers and enol acylates or carboxylates. Studies of the chemistry of this group of ethers and esters have been chiefly of a practical nature, and the mechanism of their transformations has been little studied. Until recently, there was very little published information on the kinetics of the hydrolysis of vinyl ethers and esters, and no direct data on the point of fission of the bonds. In the discussion of the mechanism of the hydrolysis of these compounds, the authors restricted themselves to the analogy with the well-studied processes involving the corresponding alkyl ethers and esters[1-3].

Interest in the mechanism of the transformation of $\alpha\beta$-alkenyl ethers and esters began to increase in the late nineteen-fifties, when the intensive development of the theory of polymerisation brought to the forefront the problem of the dependence of the reactivity of monomers on their structure. The study of the mechanism of hydrolysis of vinyl ethers and esters from this viewpoint has extended in the last ten years to such an extent that the main regular features have now been outlined. It can therefore be regarded an appropriate time to summarise the results. A summary on this basis is also of interest in connection with the theory of the other reactions of these compounds.

The chemical properties of $\alpha\beta$-alkenyl ethers and esters, which have been studied in detail and described in reviews and monographs[1-7], show a similarity in the behaviour of ethers and esters of this type in reactions with acidic reagents, and demonstrate the high reactivity of their ethylenic bond in electrophilic addition, which obeys Markovnikov's rule.

The activation of the double bond can be attributed to conjugation of the π-electrons with the unshared pairs of electrons of the ether oxygen atom:

$$CH_2=CH-\ddot{O}-R\,.$$

According to Wheland's calculations[8], the conjugation energy in methyl vinyl ether is 3.6 kcal mole^{-1}. In accordance with this, the signal of the β-hydrogen atoms of the vinyl group in the proton magnetic resonance (PMR) spectra of enol ethers is displaced towards higher fields compared with the signal of the hydrogen atoms of the ethylene group in simple alkenes[9], and the frequency of the out-of-plane bending vibrations of the $=CH_2$ group† in the infrared spectrum of enol ethers is lower than that for alkenes[10].

In enol acylates, the conjugation of the vinyl group with the ether oxygen should be weakened by the influence of the electron-accepting carbonyl group. The extent to which this decreases the polarisation of the ethylenic bond can be estimated from spectroscopic data (Table 1), which indicate that in alkenyl carboxylates the C=C bond is less extensively polarised than that in methyl vinyl ether, but more extensively polarised than that in propene. Thus conjugation of the ether oxygen with the ethylenic bond still plays an important part.

Table 1. Spectroscopic data characterising the polarisation of the double bond.

Compound	Chemical shift δ of the β-hydrogen atoms in the PMR spectrum	References	Frequencies of the out-of-plane bending vibrations of the CH_2 group in the infrared spectra, cm^{-1} (Ref.10)
Ethylene	5.33	14	—
Propene	4.96	14	912
Methyl vinyl ether	4.05	9	811
Vinyl acetate	4.67	12	870
Isopropenyl acetate	4.62	13	
Vinyl benzoate	4.75	13	870
Methyl vinyl ketone	6.09	14	955

Enol ethers are stable in alkaline media, but are readily hydrolysed in weakly acidic and even neutral aqueous solutions, and this distinguishes them sharply from dialkyl ethers. For example, the rate of the acid hydrolysis of ethyl vinyl ether is greater than that of diethyl ether by a factor of 10^{13}.[15] The increase in the rate of hydrolysis of ethers when an ethylene bond is introduced in the α-position relative to the oxygen has been attributed to hydration of the C=C group, preceding the splitting of the bonds in the ether, as shown in the scheme:

$$CH_2=CH-OR+\overset{+}{H_3O}\rightarrow CH_3CH\begin{matrix}OR\\ \diagup\\ \diagdown\\ \overset{+}{O}H_2\end{matrix}\rightarrow ROH+CH_3CH=\overset{+}{O}H\,. \qquad (1)$$

The hydrolysis of $\alpha\beta$-alkenyl acylates, like the hydrolysis of the esters of saturated alcohols, is catalysed by both acids and alkalis. The rates of the acid and alkaline hydrolysis of alkenyl and alkyl acylates differ by not more than two orders of magnitude. The outward similarity in the stoichiometry of the reaction, which for the hydrolysis of vinyl esters can be represented by the equation

$$CH_2=CH-OCOR+H_2O\rightarrow CH_3=CH-OH+RCOOH \qquad (2)$$

† The change in this quantity can give information on the change in the π-charge on the carbon atom[11].

together with their identical catalytic behaviour, suggest that in the hydrolysis of acylates the introduction of the ethylenic group in the α-position to the ester oxygen atom does not alter the reaction mechanism[1-3]. This justifiable assumption probably also explains why almost no experimental studies were made of the mechanism of the hydrolysis of $\alpha\beta$-alkenyl esters until recently.

The molecule of an alkenyl carboxylate, however, contains two reactive centres—the carbonyl group and the vinyl group. The latter, as shown above, is activated by its proximity to the oxygen, so that the hydrolysis of enol acylates can take place in at least two ways: by electrophilic addition to the C=C bond or by nucleophilic addition to the C=O bond. The actual mechanism will depend to a considerable extent on the reaction conditions, in particular the acidity of the medium. In an alkaline medium, in which enol ethers are inactive, primary attack by hydroxide ions at the carboxyl group is most probable. In acidic solutions, attack by protons at the nucleophilic vinyl group becomes equally probable.

$\alpha\beta$-Alkenyl ethers and esters in anhydrous media readily undergo trans-etherification (3) and trans-esterification (4), which in this instance are also described as vinyl exchange:

$$CH_2=CH-OR+XOH\rightleftarrows CH_2=CH-OX+ROH\,, \qquad (3)$$

$$CH_2=CH-OCOR+XOH\rightleftarrows CH_2=CH-OX+RCOOH\,, \qquad (4)$$

where XOH is a compound with a labile hydrogen atom.

Reactions (3) and (4) undergo specific catalysis by the mercury salts of strong acids, whereas in the presence of mineral acids the addition of the reagent XOH takes place chiefly at the ethylenic bond. The mechanism of these reactions will be examined later; here it is important to note the following: (1) catalysis by mercury salts makes it possible to exclude the carbonyl group from consideration as an active centre of the molecule in reaction (4); (2) if the reagent XOH is water, the products of the trans-etherification or trans-esterification are identical with the hydrolysis products, as can be seen from the equation

$$CH_2=CH-OR+HOH\rightarrow ROH+CH_2=CH-OH\rightarrow CH_3CHO \qquad (5)$$

and (3) catalysts for vinyl exchange have also been found to be active in the hydrolysis of vinyl ethers and esters[16-18].

All this leads to the conclusion that in acid hydrolysis and possibly in aqueous hydrolysis the analogy between enol ethers and esters is as valid as that between the esters of enols and the esters of saturated alcohols.

The results of the study of the mechanism of hydrolysis of $\alpha\beta$-alkenyl ethers and esters, given below, have confirmed and refined existing theories of the mechanism of hydrolysis of enol ethers and have shown that existing theories of the mechanism of hydrolysis of enol esters are erroneous.

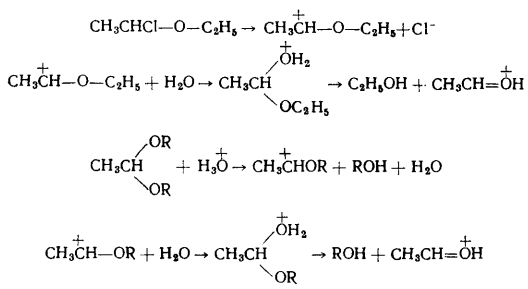
To avoid repetition, we begin with data on the point of fission of the bonds, since this information is necessary in a discussion of any mechanism of hydrolysis of ethers and esters.

2. POINT OF FISSION OF THE BONDS IN HYDROLYSIS

The hydrolysis of ethyl vinyl, n-butyl vinyl, isopropyl vinyl, allyl vinyl, and phenyl vinyl ethers[16], and also 3-ethoxy-2-cyclohexenone[19], in aqueous solutions of sulphuric acid enriched in $H_2{}^{18}O$, gave alcohols which did not contain ^{18}O. "Unlabelled" alcohols were also obtained in the hydrolysis of isopropyl vinyl and α-chlorodiethyl vinyl ethers in neutral solutions, in the hydrolysis of α-chlorodiethyl

ether by sodium carbonate solution[16], and in the acid hydrolysis of acetals[20]. The same result was obtained in the hydrolysis of isopropyl vinyl and n-butyl vinyl ethers, catalysed by mercury sulphate[16]. Thus in the hydrolysis of these alkenyl ethers, bond rupture takes place only between the unsaturated group and oxygen.

On the basis of independent data, the mechanism illustrated by schemes (6) and (7) has been established for the solvolysis of α-halogenoethers[21] and acetals[22]:



(6)

(7)

with the intermediate formation of hemiacetals and their decomposition into carbonyl compounds and alcohols. Data obtained using ^{18}O show that the decomposition of the hemiacetals involves the removal of alkoxy-groups, which during the reaction do not lose their bonds with their oxygen.

Thus the formation of alcohols which do not contain oxygen from the medium, observed in the hydrolysis of vinyl ethers, confirms scheme (1), which assumes the intermediate formation of hemiacetals.

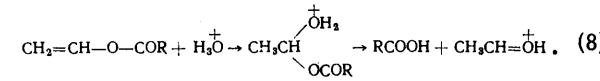
The fact that identical results were obtained regarding the point of fission of the bonds in the hydrolysis of vinyl ethers containing alcohol residues with different structures, such as the ethyl, allyl, and phenyl groups, indicates that the established features are general. This is also indicated by data on the mechanism of the formation of methyl α-naphthyl ether from [^{18}O]methanol and 1-naphthol, catalysed by sulphuric acid, in which the ether contains oxygen only from the methanol[23]. From this it follows that the back reaction in the acid decomposition of this ether should take place with fission of the bond between the unsaturated naphthyl group and oxygen, that is, like the hydrolysis of vinyl ethers.

Study of the acid hydrolysis of enol carboxylates in $H_2{}^{18}O$ showed that in this instance also the reaction involves vinyl–oxygen fission. This was established for the hydrolysis of the following esters: vinyl acetate in acidic and initially neutral media[17,24], vinyl formate, propionate, butyrate, pelargonate, adipate[25], and *p*-methoxybenzoate, isopropenyl acetate and benzoate, α-acetoxystyrene[26], and α-methoxyvinyl benzoate[27]. The same is true of the hydrolysis of vinyl acetate and benzoate[24] and the *p*-methoxy- and *p*-nitro-derivatives of the latter[18] with catalysis by mercury sulphate.

It can be seen from these data that neither the replacement of the alkyl residue by an acyl residue nor the introduction of substituents in the α-position of the vinyl group alters the point of fission of the vinyl group in acid hydrolysis. The point of fission of the bonds is apparently determined primarily by the presence of the ethylenic bond next to the ether oxygen atom.

Fission of the bond between the vinyl group and oxygen in the hydrolysis of enol acylates agrees with the idea that in the presence of electrophilic reagents the active reaction centre is not the carbonyl group but the vinyl group[17,24,27], since solvolytic processes at the carbonyl group are characterised by acyl–oxygen splitting[28,29]. This conclusion is also confirmed by the fact that mercury sulphate—a specific catalyst for electrophilic addition to multiple carbon–carbon bonds—although accelerating the hydrolysis of enol acylates (as will be shown later), does not alter the point of fission of the bonds.

On this basis, the mechanism proposed for the acid hydrolysis of enol esters was the same as that for the hydrolysis of alkenyl ethers[17,24] [see scheme (1)], that is, a mechanism involving hydration of the ethylenic bond [scheme (8)], later confirmed by kinetic data:



(8)

Preliminary addition at the ethylenic bond was also confirmed for the reaction of 1-methoxyvinyl benzoate with $C_6H_5C^{18}O^{18}OH$ without the addition of mineral acid. The ^{18}O is equally distributed between the two reaction products —methyl acetate and benzoic anhydride[30]. Vinyl–oxygen bond fission was also established in the exchange of acetate groups between vinyl acetate and acetic acid in the presence of mercury sulphate[31].

As noted above, enol ethers are stable in the presence of bases, but the ethers of nitrophenols undergo hydrolysis and trans-etherification fairly readily in concentrated alkali solutions. For the example of the alkaline hydrolysis of 2,4-dinitrophenetol, labelled with ^{18}O in the ether group, and the reaction of 2,4-dinitroanisole with $C_2H_5{}^{18}OH$ it was established that during the reaction the alkyl radicals do not lose their bonds with their oxygen atom, that is, only the bond between the aryl group and oxygen is broken[32].

Table 2. Relative* concentration of ^{18}O in the carboxyl group of the acid formed in the alkaline hydrolysis of vinyl esters in the systems: *I*) unlabelled ester + $H_2{}^{18}O$; *II*) ester labelled with ^{18}O in both oxygen atoms + H_2O; *III*) ester labelled with ^{18}O at the oxygen of the C–O–C group + H_2O**.

Vinyl ester	System			Theoretical concentration of ^{18}O for rupture of the bond					
				acyl–oxygen			vinyl–oxygen		
	I	II	III	I	II	III	I	II	III
Acetate	0.32—0.36	0.49—0.50	0.30						
Benzoate	0.39—0.42	0.49	0.34						
Anisate	0.48—0.52	—	0.25	0.50	0.50	0.00	0.00	1.00	1.00
p-Chlorobenzoate	—	—	0.18						
p-Nitrobenzoate	0.45	—	0.28						

* The concentration of ^{18}O in the original labelled compound was taken as unity.

** These esters were prepared by the action of the corresponding acyl chlorides on chloromercuracetaldehyde-^{18}O. It was confirmed for the example of vinyl acetate that the tracer is present only in the ether oxygen atom[35].

In the alkaline hydrolysis of vinyl esters, only part of the ether oxygen appears in the resulting salts of carboxylic acids (Table 2)[17,18,33,34]. At the same time the esters isolated from the reaction mixture after incomplete hydrolysis retain their original isotopic composition. This indicates that isotopic exchange between the ester and the medium does not take place during the reaction, and the results obtained must be attributed to a mixed hydrolysis

mechanism, with fission of the bonds formed by the oxygen atom with both the acyl group and the vinyl group.

The mechanism of the alkaline hydrolysis of enol acylates will be examined in more detail later, in connection with kinetic data. Here we would merely point out that the mechanism of the alkaline hydrolysis of vinyl acetate and vinyl benzoate differs significantly from the mechanism of the alkaline hydrolysis of the ethyl esters of the same acids, since in the hydrolysis of the latter, only acyl–oxygen bond splitting is observed[29].

3. ACIDIC HYDROLYSIS OF ETHERS

After the first systematic studies, which were carried out in Skrabal's laboratory[36–39] with the aim of obtaining quantitative data on the rates of hydrolysis of ethers with the most varied structures, the study of the kinetics of hydrolysis of $\alpha\beta$-alkenyl ethers developed along three directions: (1) investigation of the nature of the catalysis (specific or general acid catalysis); (2) determination of the kinetic isotopic effect of the solvent; and (3) determination of the dependence of the kinetic parameters of the reaction on the structure of the substrate.

With catalysis by mineral acids, the hydrolysis of $\alpha\beta$-alkenyl ethers is described by a first-order equation with rate constants proportional to the concentration of catalyst[40–46]. An exception is the hydrolysis of furan and 2,5-dimethylfuran, for which the kinetic equation contains the acidity function H_0.[47] It should be noted that in the experiments with cyclic ethers the acid concentration amounted to several moles per litre, whereas in the experiments with ethers with linear structure the acid concentration did not exceed 1×10^{-2} N, that is, it was below the limit at which the difference between C_{H^+} and H_0 becomes perceptible. The reaction rate depends to a marked extent on the composition of the solvent, and decreases when dioxan[40] or ethanol[47] are added to the aqueous solutions. The change in the rate of hydrolysis of isopropyl vinyl and n-butyl vinyl ethers with change in the concentration of water in aqueous dioxan solutions from 3 M to 22 M[44] is given by a curve with a minimum in the region of 10 M H_2O, characteristic of changes in H_0 with change in the composition of the medium[48].

The temperature dependence of the rate constants corresponds to the Arrhenius equation[40,43–45]. The activation parameters found from these data are given in Table 3. The values of $\Delta S^{\neq}$ (Table 3) vary from +4 e.u. to −28 e.u., and are linearly related to the activation energy values (only isopropenyl methyl ether does not show this regular feature). This compensation effect is observed if the reaction of the substrate with the solvent makes a significant contribution to the activation parameters of the reaction[49]. With this condition, changes in the value of $\Delta S^{\neq}$ cannot provide a criterion of change in the mechanism of acid catalysis.

The hydrolysis of ethyl vinyl ether[44], isopropenyl methyl ether[43], and 2-ethoxycyclopentene-1-carboxylic acid (ECA)[46] in buffer mixtures with varying concentrations of undissociated acids showed that this concentration appears in the kinetic equation for the reaction, that is, that the hydrolysis of enol ethers undergoes general acid catalysis. The catalytic constants for the proton donors studied are given in Table 4.

The values of k_{HA} given in Table 4 satisfy Brønsted's equation with $\alpha = 0.45$ for ethyl vinyl ether[44] and $\alpha = 0.50$ for isopropenyl methyl ether and isopropyl vinyl ether[43].

General acid catalysis was not observed by Skrabal and coworkers, since they altered the concentration of only one of the components of the buffer mixture, and the increase in the concentration of undissociated acetic acid was proportional to the increase in the H_3O^+ concentration. Recalculation of Skrabal's data[43,44] led to good agreement in the values of $k_{H_3O^+}$ in aqueous solutions, obtained by different authors (Table 4).

Table 3. Kinetic characteristics of the hydrolysis of α,β-alkenyl ethers with catalysis by mineral acids.

No.	Substrate	Catalyst, solvent	$k_{25°}$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	$\frac{k_{H_2O}}{k_{D_2O}}$	References
1	t-Butyl vinyl ether	80% dioxan + $HClO_4$	0.386	7.3	—	—	—	42
2	Isopropyl vinyl ether	80% dioxan + $HClO_4$	0.156	3.0	—	—	—	42
		90% dioxan + H_2SO_4	0.160	—	17.6	−6.0	—	45
		H_2O + HCl	4.45	2.4	14.0	−10.7	—	43
3	Ethyl vinyl ether	80% dioxan + $HClO_4$	0.053	1	—	—	—	42
		40% dioxan + HCl	0.34	—	17.9	−2.6	—	40
		H_2O + $HClO_4$	2.13	—	14.4	−11.1	2.95	44
		H_2O + HCl	1.87	(1)	15.2	−8.2	—	43
4	Isobutyl vinyl ether	80% dioxan + $HClO_4$	0.041	0.8	—	—	—	42
		H_2O + HCl	2.25	(1.2)	15.9	−5.7	—	43
5	n-Butyl vinyl ether	80% dioxan + $HClO_4$	0.037	0.7	—	—	—	42
		80% dioxan + HCl	0.22	—	19.7	—	—	40
		40% dioxan + HCl	0.37	—	19.0	—	—	40
		90% dioxan + H_2SO_4	0.026	—	21.3	+3.9	2.8	45
		H_2O + HCl	2.00	(1.06)	16.2	−4.9	—	43
6	Divinyl ether	H_2O + HCl	0.008	0.004	—	—	—	15
7	2-Ethylbutyl vinyl ether	80% dioxan + $HClO_4$	0.023	0.64	—	—	—	42
8	Benzyl vinyl ether	80% dioxan + $HClO_4$	0.0081	0.15	—	—	—	42
9	β-Chloroethyl vinyl ether	80% dioxan + $HClO_4$	0.0044	0.08	—	—	—	42
		H_2O + HCl	0.165	(0.09)	16.6	−8.5	2.52	43
10	ECA	H_2O + HCl	37	(20)	14.2	−14.2	2.9	46
11	Monovinyl ether of bisethylene glycol	H_2O + HCl	0.40	(0.22)	10.1	−28.3	3.3	41
12	2,3-Dihydropyran	H_2O + HCl	0.27	(0.15)	14.7	−14.7	—	43
13	2,5-Dimethylfuran	H_2O + $HClO_4$	0.0003	$(1 \cdot 10^{-4})$	—	—	1.7	47
14	Vinyl formate	80% dioxan + H_2SO_4	$7 \cdot 10^{-4}$	0.013	15.8	−24.5	0.84	25
15	Ethyl n-propenyl ether	80% dioxan + $HClO_4$	0.0092	0.17	—	—	—	42
16	n-Butenyl ethyl ether	ditto	0.0091	0.17	—	—	—	42
17	Ethyl isobutenyl ether	» »	0.0009	0.017	—	—	—	42
18	β-Chlorovinyl ethyl ether	» »	$8 \cdot 10^{-5}$	0.0015	—	—	—	42
19	Isopropenyl methyl ether	H_2O + HCl	970	(515)	13.6	−1.1	—	43
20	Ethyl isopropenyl ether	80% dioxan + CH_3COOH + CH_3COONa	10000**	—	—	—	—	42

* The rate of hydrolysis of ethyl vinyl ether in 80% aqueous dioxan or in aqueous solution was taken as unity. $k_{rel.}$ values in aqueous solution are given in parentheses.

** The rate constant is too high by a factor of at least 100, since no allowance was made for the catalytic action of the undissociated acetic acid[43].

The general acid catalysis in the hydrolysis of enol ethers indicates unambiguously that the rate-determining stage is the transfer of a proton from the catalyst to the substrate[43], in agreement with the marked decrease in reaction rate in D_2O (Table 3).

In this connection it should be noted that re-examination of the theory of the isotopic effect of the solvent, completed in the early nineteen-sixties, showed that neither the value of $k_{H_2O} : k_{D_2O}$ nor the form of the dependence of the reaction rate on the atomic fraction of deuterium in the solvent

can serve, as was previously supposed, as an unambiguous criterion of the mechanism of acid–base catalysis[50–52]. With independent data on the kinetic role of the stage involving proton transfer, however, the results of the determination of the reaction rate in D_2O and its mixtures with H_2O under certain conditions, in particular for $k_{H_2O} : k_{D_2O} \geq 2$, nevertheless give information on the structure of the intermediate complex and the movement of the proton relative to the reaction coordinate[51,53]. The maximal value of the isotopic effect for reactions with slow proton movement from H_3O^+ is equal to 3.6; this value is reached when in the transition state the proton reacts equally strongly with the water molecule which it is leaving and with the nucleophilic centre of the substrate[53]. This structure of the transition state also corresponds to a value of the parameter α equal to 0.5 in Brønsted's equation[54]. This same parameter can be found from the form of the dependence of the reaction rate on the atomic fraction of deuterium in the solvent using the equation[43,44,55]

$$\frac{k_n}{k_H} = \frac{(1 - n + nl^{1+\alpha})^2 \cdot (1 - n + l^{1+2\alpha} n\, k_D : k_H)}{(1 - n + nl)^3} \qquad (9)$$

where n is the atomic fraction of deuterium and l the exchange coefficient of the ion L_3O^+‡, equal to 0.67.[55] The values of the parameter α found in this way for the hydrolysis of ethyl vinyl ether[44] and 2-chloroethyl vinyl ether[43] were 0.6 and 0.5 respectively, in good agreement with the value found from Brønsted's equation.

Table 4. Catalytic constants for various proton donors in aqueous solution at 25°C.

Substrate	H^+ donor	k_{HA}, litre mole^{-1} s^{-1}	Refs.
Ethyl vinyl ether	H_3O^+	2.13	44
		1.89	43
		2.35*	43
	HCOOH	$8.8 \cdot 10^{-3}$	44
	CH_3COOH	$1.8 \cdot 10^{-3}$	44
		$2.8 \cdot 10^{-3}$	43
Isopropyl vinyl ether	H_3O^+	4.43	43
	CH_3COOH	$8.6 \cdot 10^{-3}$*	
Isopropenyl methyl ether	H_3O^+	970	43
	$H_2PO_4^-$	0.16	43
	HCO_3^-	$8.4 \cdot 10^{-4}$	43
	H_2O	$1.44 \cdot 10^{-6}$	43
2-Ethoxy-1-cyclopentenecarboxylic acid (ECA)	H_3O^+	0.22	46
	$ClCH_2COOH$	0.0026	46

* Recalculated from Skrabal's data[43].

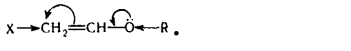
For proton transfer from formic acid to ethyl vinyl ether, $k_{HCOOH} : k_{HCOOD} = 6.8$, compared with 2.95 for catalysis by hydroxonium ions[44]. For the hydrolysis of ECA, the isotopic effect increases from 2.9 for catalysis by H_3O^+ to 8.0 for catalysis by the protons of the carboxyl group of the substrate itself[46]. The explanation of these facts according to modern theories is that the observed influence of the replacement of H by D in solution is made up of two isotopic effects operating in opposite directions: a primary effect leading to a decrease in the reaction rate in D_2O, and a secondary effect leading to an increase in the rate of the process. The secondary isotopic effect is absent if the proton donor contains only one labile H atom[53,56,57].

‡ Where L represents either H or D (Ed. of Translation).

The general acid catalysis in the hydrolysis of enol ethers provides evidence against primary attack by H^+ on the oxygen atom, since this is characterised by rapid attainment of prototropic equilibrium and specific catalysis. Examples of reactions of this type are provided by the hydrolysis of acetals[58] and the alkyl esters of carboxylic acids[29].

Further confirmation of primary attack by the protons on the unsaturated group is provided by the structural dependence of the reactivity of enol ethers in acid hydrolysis. The available kinetic data (Table 3) show that electron-donating substituents attached to the oxygen atom increase the reaction rate (ethers 1–9 in Table 3), whereas the same substituents attached to the β-carbon atom of the vinyl group decrease the reaction rate (ethers 15–18 in Table 3). In both instances, the changes in the hydrolysis rate constants with change in the structure of the substrate are described by the Hammett–Taft equation in the form[42] $\lg(k/k_0) = \sigma^*\rho^*$. An equation of this form indicates that the influence of polar factors predominates. For substituents attached to the oxygen atom, $\rho^* = -2.8$, and for substituents attached to the β-carbon atom of the vinyl group, $\rho^* = +1.5$.

The above data cannot be explained if primary attack by the protons on the oxygen atom is assumed, since in this instance the direction of the influence of the substituents would be independent of their position in the molecule. The influence of substituents indicates that, among the factors determining the reactivity of enol ethers in electrophilic media, the most important part is played by the conjugation of the p-electrons of the oxygen atom with the π-electrons of the double bond. Electron-donating substituents attached to oxygen facilitate this conjugation and increase the reaction rate, but in the β-position of the vinyl group they hinder conjugation and decrease the rate of hydrolysis



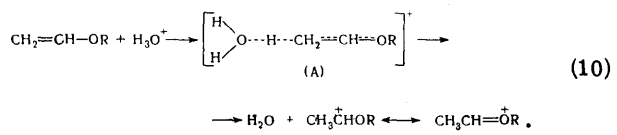
The decrease in the rate of hydrolysis of divinyl ether relative to that of ethyl vinyl ether, which surprised Skrabal, becomes understandable from this viewpoint. Each vinyl group of divinyl ether acts as an electron-accepting substituent relative to the other and weakens its conjugation with oxygen. Comparison of the hydrolysis rate constants for ethyl vinyl ether and divinyl ether, and also for ethyl vinyl ether and vinyl formate, shows that the retarding action of the vinyl group is stronger than that of the carbonyl group, the reaction rate being decreased by a factor of 240 in the first instance and only 80 in the second. Allyl and benzyl groups also show a retarding action, but this is much weaker than that of the vinyl group. The reaction of vinyl ethyl ether is about ten times more rapid than that of 2-chloroethyl ether, but 700 times more rapid than that of β-chlorovinyl ethyl ether. In the first instance the inductive effect of chlorine on the ethylenic bond is shown, whereas in the second instance the effect of conjugation of the free pairs of electrons of the chlorine with the π-electronic system becomes more marked. The chlorine acts as electron donor and hinders the conjugation of the electrons of the oxygen with the double bond.

Not only kinetic data, but also other physicochemical data indicate that electrophilic reagents attack the double bond, and not oxygen. Thus the results of a study of the dielectric constants of solutions of tin(IV) chloride in inert solvents indicate the formation of complexes of two different types on the addition of furan, 2-methylfuran, and thiophen, or the saturated analogues of these compounds[59]. In the first instance, complexes involving the C=C group are

formed, whereas in the second instance complexes involving the oxygen or sulphur atoms are formed. This conclusion was confirmed by spectroscopic data[60] for the example of the complexes of thiophen with tin(IV) chloride.

The analogous study using vinyl ethers was unsuccessful, since these compounds polymerised rapidly in the presence of tin(IV) chloride[59]. Polymerisation itself, however, indicates activation of the double bond, that is, reaction of the complex-forming species with this reactive centre.

The above data provide convincing justification for the mechanism accepted at present for the acid hydrolysis of $\alpha\beta$-unsaturated ethers, according to which the first, rate-determining stage of the reaction involves the transfer of protons from the catalyst to the β-carbon atom of the vinyl group with the formation of carbonium ions[41-47], scheme (10):

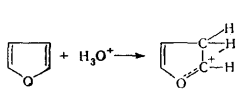


(10)

In the transition complex (A) the proton occupies a central position between the molecules of water and the substrate.

The partial oxonium character of the ions formed, that is, their stabilisation by interaction of the p-electrons of the oxygen with the positive centre, explains the important part played by conjugation and the high reactivity of enol ethers in the presence of electrophilic reagents. In the original state, conjugation of the π-electrons of the multiple bond with the p-electrons of the oxygen leads to localisation of the negative charge on the β-carbon atom of the vinyl group. The corresponding increase in the energy of the original state was recently confirmed experimentally in a determination of the thermodynamic characteristics of the original and final states in the acid hydrolysis of ethyl vinyl ether[61]. The results of this work made it possible to construct the energy profile of the reaction. The presence of the negative charge on the carbon of the vinyl group facilitates attack by protons and the formation of a transition state with structure approaching that of a σ-complex, and not a π-complex. On the other hand, the possibility of displacement of the electrons of the oxygen to the vacant p-orbitals of the neighbouring carbon atom of the carbonium ions leads to delocalisation of the positive charge, and this increases the stability of the ions and makes this reaction path energetically favourable.

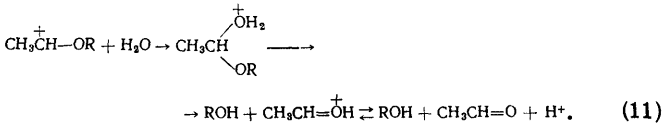
In derivatives of the cyclic vinyl ether furan, the conjugation of the unshared pair of electrons of the oxygen with the π-electrons of the ring does not lead to localisation of the negative charge and an increase in the energy of the original state as a result of the aromaticity of the system produced. The formation of the carbonium ions



is accompanied by loss of aromaticity and a decrease in the conjugation energy. These factors explain the increased stability of furan derivatives in acid hydrolysis, compared with other vinyl ethers, including 2,3-dihydropyran[43]. On the other hand, the increased reactivity of isopropenyl ethers relative to vinyl ethers can be attributed to the increased stability of the carbonium ions with increase in the degree of branching of the carbon chain attached to the positive centre. Carbonium ions with structures similar to those formed in the hydrolysis of enol ethers are formed in the hydrolysis of acetals[58]. In agreement with this, a linear relationship was found between the rate constants for the two reactions with analogous structural changes in the substrate[43].

Kinetic data cannot give information on the subsequent course of the reaction, since the rate-determining stage is the first stage. This gap can be partly filled by using isotopes.

In the hydrolysis of ethyl vinyl ether in D_2O, the acetaldehyde formed contained only one deuterium atom, indicating that the proton transfer is irreversible[44] and that the subsequent transformation undergone by the carbonium ions is more rapid than the isotopic exchange of hydrogen in these ions§. The analogy with the hydrolysis of acetals, and also the results of a study of the mechanism of the acid hydration of alkenes[65], styrene[66], acetylenic ethers, and sulphides[67-69]¶ indicate that the carbonium ions are subjected to nucleophilic attack by water and are converted into the protonated forms of the hemiacetals, which decompose to give the aldehyde and alcohol. The formation of alcohols which do not contain oxygen from the medium in the hydrolysis of both alkenyl ethers and acetals confirms the scheme:



(11)

An interesting feature is that even for allyl vinyl ether, stabilisation of the carbonium ion by attachment of water is more favourable than rupture of the allyl–oxygen bond with the formation of the aldehyde retaining the oxygen of the substrate. This indicates that the $CH_3\overset{+}{C}H-O-CH_2CH=CH_2$ ion is more stable than the allyl cation.

Schemes (10) and (11), based on the results of kinetic and isotopic studies, confirm and give the details of views on the mechanism of the hydrolysis of enol ethers developed on the basis of chemical intuition more than thirty years ago. This now represents one of the few examples where it has been possible to characterise reliably and in sufficient detail the structure of the intermediate complex in the rate-determining stage of the reaction.

4. ACID HYDROLYSIS OF ESTERS

Kinetic data have been published on the acid hydrolysis of esters of four structural types: the vinyl and isopropenyl esters of aliphatic and benzoic acids. It was shown above that change in the structure of enol acylates does not lead to a change in the point of fission of the bonds, which corresponds to the replacement of the anion of the carboxylic acid by hydroxide.

As with the ethers, the acid hydrolysis of enol esters is described by a first-order equation, but it takes place under slightly more severe conditions[25,26,45,70]. The rate constants for the hydrolysis of the alkenyl esters of aliphatic acids in aqueous dioxan solutions are linearly dependent on the analytical concentration of mineral acid. The kinetic equation for the hydrolysis of vinyl and isopropenyl benzoates contains the acidity function H_0 instead of C_{H^+}.[26,45] The problem of whether the acid catalysis is

§ The rapid exchange of the hydrogen of the C–H bonds in carbonium ions is dealt with in papers by Setkina and Kursanov[62,64].

¶ For all these reactions it has been proved that the rate-determining stage is the transfer of H^+ from the catalyst to the substrate with the intermediate formation of carbonium ions.

specific or general has not been studied. The fact that the observed rate constants remain constant with time, that is, as the carboxylic acid accumulates in the reaction system, can be attributed either to the absence of general catalysis or to low values for the catalytic constants of the acids formed, compared with $k_{H_3O^+}$.

The temperature dependence of the rate constants in all instances obeys the Arrhenius equation. The kinetic characteristics of the hydrolysis of the compounds studied are given in Tables 5 and 6.

Table 5. Kinetic characteristics of the hydrolysis of αβ-alkenyl esters of aliphatic acids in aqueous dioxan solutions.

Substrate	Catalyst, solvent	$10^3 k_{80°}$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	k_{H_2O}/k_{D_2O}	Refs.
Vinyl formate	80% dioxan + H_2SO_4	35.5	18.6	15.0	—24.5	0.84	25
	99% dioxan + H_2SO_4	36.7	19.2	13.6	—29.5	1.0	25
Vinyl acetate	80% dioxan + H_2SO_4	4.19	2.19	17.8	—21.0	0.74	45
	99% dioxan + H_2SO_4	1.91	1.0	12.1	—39.6	1.22	45
	50% dioxan + HCl	5.57	2.9	16.2	—25.2*	—	70
Vinyl propionate	80% dioxan + H_2SO_4	1.59	0.83	16.9	—25.8	—	45
	50% dioxan + HCl	3.71	1.9	13.9	—32.5*	—	70
Vinyl butyrate	80% dioxan + H_2SO_4	0.81	0.42	17.5	—25.1	0.70	45
	99% dioxan + H_2SO_4	0.62	0.32	13.8	—32.5	1.3	45
	50% dioxan + HCl	2.43	1.2	15.5	—28.9*	—	70
Vinyl monochloro-acetate	80% dioxan + H_2SO_4	1.43	0.75	14.8	—31.7	—	45
Vinyl adipate	80% dioxan + H_2SO_4	0.90	0.47	18.5	—22.0	—	45
Vinyl phenylacetate	80% dioxan + H_2SO_4	0.71	0.37	19.1	—17.4	—	45
Vinyl trimethylacetate	50% dioxan + HCl	0.41	0.21	23.4	—9.6	—	70
Isopropenyl acetate	80% dioxan + H_2SO_4	1.33	0.70	18.9	—11.7	0.78	26
	50% dioxan + HCl	4.68	2.45	17.5	—21.9	—	70
α-Acetoxystyrene	98% dioxan + H_2SO_4	1.85	0.97	20.0	—16.8	1.06	26

* The rate of hydrolysis of vinyl acetate in 99% aqueous dioxan was taken as unity.

As in the hydrolysis of enol ethers, a compensation effect is observed in the changes in the energy and entropy of activation. The experimental points on the plot of $\Delta S = f(E)$ for vinyl benzoates, the esters of aliphatic acids, and isopropenyl benzoates lie on three parallel straight lines arranged one above the other in the order indicated. Only vinyl formate and isopropenyl acetate do not fit into the general scheme.

In the series of vinyl and isopropenyl benzoates, electron-donating substituents in the *para*- and *meta*-positions of the benzene ring increase the reaction rate, whereas electron-accepting substituents decrease the reaction rate. An exception is vinyl *p*-nitrobenzoate, which reacts more rapidly than vinyl anisate by a factor of several tens. In this example, a departure from simple kinetic orders with respect to substrate and catalyst is also observed. The deviation of vinyl *p*-nitrobenzoate from the general relationship was attributed to a change in reaction mechanism. It is not excluded that the kinetic complications in this instance represent a manifestation of the catalytic activity of the comparatively strong *p*-nitrobenzoic acid.

The logarithms of the hydrolysis rate constants for the benzoates show a correlation with the Hammett constants σ. For the vinyl esters, ρ in the equation $\lg(k/k_0) = \sigma\rho$ is equal to −1.30,[45] whereas for the isopropenyl esters ρ = 1.1.[26]

These correlations indicate that the rate of the acid hydrolysis of αβ-alkenyl benzoates is determined chiefly by polar factors. The nature of the influence of substituents is the same as that in the acid hydrolysis of enol ethers, and opposite to that observed in the acid hydrolysis of alkyl benzoates[71].

Table 6. Kinetic characteristics of the hydrolysis of vinyl and isopropenyl benzoates in 99% dioxan at 80°C with catalysis by sulphuric acid.

Substrate,	$10^3 k$, litre mole^{-1} s^{-1}	$k^*_{rel.}$	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	$\frac{k_{H_2O}}{k_{D_2O}}$	Refs.
Vinyl anisate	0.76	3.5	19.4	—20.5		45
Vinyl benzoate	0.22	1	17.8	—27.0	1.5	45
Vinyl *p*-fluorobenzoate	0.17	0.8	18.6	—25.3	—	45
Vinyl *p*-chlorobenzoate	0.12	0.55	21.4	—18.1	—	45
Vinyl *m*-nitrobenzoate	0.03	0.013	29.0	—3.1	—	45
Isopropenyl anisate	28.8	130	16.1	—22.4	—	26
Isopropenyl benzoate	13.4	60	19.2	—15.1	2.0**	26
Isopropenyl *p*-chlorobenzoate	8.2	37	20.4	—12.5	—	26
Isopropenyl *m*-nitrobenzoate	2.0	9	—	—	—	26
Isopropenyl *p*-nitrobenzoate	2.5	11	22.8	—7.9	—	26

* The rate constant for the hydrolysis of vinyl benzoate in 99% dioxan was taken as unity.

** In 90% dioxan, $k_{H_2O}/k_{D_2O} = 1.80$.

In the series of αβ-alkenyl esters of aliphatic acids, the rate of acid hydrolysis decreases with increase in the length of the hydrocarbon chain of the acid component and with increase in its degree of branching (Table 5). The fact that the decrease in reaction rate is almost the same on going from vinyl acetate to vinyl propionate and vinyl monochloroacetate, in which the acyl residues differ considerably in polarity but have very similar dimensions, and the marked decrease in reaction rate on going to vinyl trimethylacetate[70] indicate that in the acid hydrolysis of these compounds, as in that of the ethyl esters of aliphatic acids, the chief part is played not by polar factors, but by steric factors[25,71].

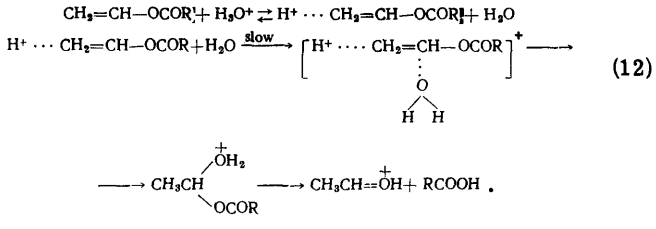
In accordance with the foregoing, the introduction of a methyl group into the α-position of the vinyl group produces different effects on reaction rate in the benzoates and the esters of aliphatic acids. The change from vinyl acetate to isopropenyl acetate is accompanied by a slight decrease in the rate of hydrolysis, but the corresponding change in structure in the benzoate series leads to an increase in reaction rate by a factor of 40–70. The influence of substituents in the benzene ring is weakened slightly, as can be seen from the decrease in the absolute magnitude of ρ from 1.30 to 1.10.[26]

The esters of aliphatic and benzoic acids also show different behaviour when the H_2O medium is replaced by D_2O. In the first instance, the sign of the isotopic effect of the solvent depends on the concentration of water in the solution. At relatively high concentrations of water (10–20 wt. % in dioxan) the reaction rate in D_2O increases by a factor of 1.2–1.4. Decrease in the water concentration to 1.0–2.0% leads either to the disappearance of the isotopic effect or to a slight decrease in reaction rate in D_2O. The rate of hydrolysis of vinyl and isopropenyl benzoates in heavy

water decreases by a factor of 1.5–2.0, and the retarding influence of D_2O is apparently independent of the concentration of water in the solution[26].

These data show that the kinetic features of the acid hydrolysis of $\alpha\beta$-alkenyl benzoates and ethers are extremely similar and differ significantly from the kinetic features of the hydrolysis of the alkenyl esters of aliphatic acids (influence of substituents, acidity of the medium, and isotopic effect of the solvent). On this basis, the mechanism proposed for the hydrolysis of alkenyl benzoates is the same as that for the hydrolysis of enol ethers[26], with rate-determining transfer of protons from the catalyst to the substrate.

The predominance of not the polar influence but the steric influence of the substituents, the increase in reaction rate in D_2O, and the linear dependence of the rate on the analytical concentration of mineral acid in the hydrolysis of the esters of aliphatic acids can be explained by assuming the A-2 mechanism of acid catalysis, represented by the scheme[26]

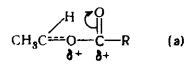


(12)

Although the increase in reaction rate in heavy water does not provide unambiguous proof of rapid reversible protonation in the first stage of the reaction, in the present instance evidence in support of scheme (12) is provided by the fact that the isotopic effect of the solvent (Table 5) has the same magnitude as that in other reactions in which the pre-equilibrium stage has been established independently (these values have been summarised[72]). Moreover, the values of $k_{H_2O}:k_{D_2O}$ for the hydrolysis of the esters of aliphatic acids agree with the results of a calculation[72] carried out on the basis of theories regarding a change in the reaction rate constants for acid catalysis in D_2O following the A-2 mechanism[52].

The decrease in the reaction rate in D_2O at low concentrations of water in the solution was attributed[45] to conversion of the open form of the activated complex into the ring form. The marked decrease in the energy and entropy of activation under these conditions (Table 5) agrees with this explanation. It may be assumed that at water concentrations equal to or slightly greater than the concentration of mineral acid, all the water molecules are bound in the solvate sheaths of the protons. This creates stereochemical conditions for the formation of an intermediate complex with a cyclic structure, since it ensures approach of the electrophilic and nucleophilic reagents, joined by hydrogen bonds, from the same direction towards the substrate molecule.

Thus in the acid hydrolysis of enol ethers and enol benzoates, the reaction rate is limited by the first electrophilic stage, leading to the formation of carbonium ions. For this mechanism, steric factors should not influence the reaction kinetics, as was found in the hydrolysis of vinyl and isopropenyl benzoates. The decrease in reaction rate on going from the ethers to the benzoates is in accordance with the weakening of the conjugation of the p-electrons of the C=C bond and the ether oxygen atom under the influence of the carbonyl group. It might have been expected that a carbonyl group situated next to the ether oxygen would make hydrolysis of the enol ethers through carbonium ions energetically unfavourable, since the stabilisation of the carbonium ions as a result of displacement of the p-electrons of the oxygen to the carbonium centre would have led to an improbable structure with two neighbouring electron-deficient atoms.



(a)

If, however, R is a benzene ring, the positive charge on the carbonyl carbon atom is reduced considerably as a result of the interaction with the π-electrons of the aromatic system. Data confirming the high stability of the benzoyl cations $C_6H_5\overset{+}{C}=O$, compared with acetyl and propionyl cations, were obtained in a study of the infrared spectra and NMR spectra of complexes of the corresponding fluorides with Lewis acids[73].

For the alkenyl esters of aliphatic acids, a decrease in the positive charge on the carbonyl carbon atom can take place only as a result of the relatively weak inductive effect and hyperconjugation, and the formation of ions of type (a) becomes unfavourable, and the nucleophilic character of the β-carbon atom of the vinyl group in the original state is decreased. As a result, the electrophilic attack of the protons in the first stage of the reaction does not proceed as far as the formation of a new covalent C–H bond. This process becomes possible only after or at the same time as nucleophilic attack by the water molecules on the α-carbon atom of the vinyl group. Thus the second, nucleophilic stage becomes the rate-determining stage, and this, as indicated above, should be sensitive to steric factors, since it requires movement out of the plane of the bulky acyl and other groups joined to the α-carbon atom, as confirmed experimentally.

Summarising the discussion of the experimental data at present available on the acid hydrolysis of enol ethers and esters leads to the conclusion that a donor–acceptor scheme is applicable in all instances for the mechanism of hydration of the ethylenic bond.

Other conditions being equal, the nature of the limiting stage is related to the structure of the substrate as follows: when structural factors facilitate the stabilisation of carbonium ions, rupture of the double bond and formation of a new C–H bond take place in the first electrophilic stage, which thus determines the rate of the process. Here the chief part is played by factors favouring conjugation of the p-electrons of the ether oxygen and the ethylenic bond. If this conjugation is suppressed, the fission of the old bonds and the formation of new bonds takes place under the simultaneous influence of both the electron acceptor and the electron donor, and the nucleophilic stage of the reaction becomes the limiting stage.

The extension of these ideas to other reactions involving electrophilic addition across the ethylenic bond of vinyl ethers and esters shows that the structure of the latter is not the only factor determining the composition of the intermediate complex and the nature of the limiting stage. Thus the addition of ethanol to butyl vinyl ether and also to vinyl acetate, catalysed by p-toluenesulphonic acid, is described by a second-order equation, in which the concentration of the nucleophile does not appear[74]; this is in accordance with slow transfer of the proton in both instances and is confirmed by the decrease in reaction rate on replacement of C_2H_5OH by C_2H_5OD.

The addition of acetic acid to the same ether and ester is described by a third-order equation, including the concentrations of substrate, catalyst, and acetic acid[74,75].

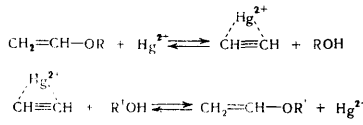
These data, together with the marked isotopic effect for the addition of CH_3COOD, indicate that the reaction mechanism is termolecular.

5. TRANS-ESTERIFICATION AND TRANS-ETHERIFICATION OF VINYL ESTERS AND ETHERS (TRANS-VINYLATION)

The trans-esterification of vinyl esters or the trans-etherification of vinyl ethers formally consists of the transfer of a vinyl group from one alcoholic or acid residue to another—see Eqns. (3) and (4). These reactions are therefore also described as vinyl exchange or trans-vinylation.

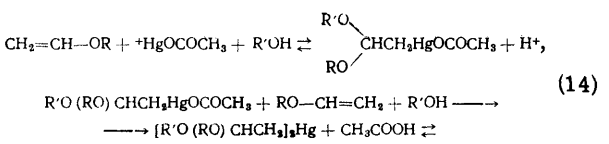
This reaction was first described in the patent literature[1]. Adelman[76] studied vinyl exchange in detail and showed that the mercury salts of strong acids, and also the addition to the reaction mixture of mercury(II) oxide and boron trifluoride, which catalyse the addition of alcohols and carboxylic acids to vinyl ethers and esters, under milder conditions act as specific catalysts for vinyl exchange. It was subsequently established that not only alcohols and acids, but also other organic compounds with a labile hydrogen atom, can take part in this reaction, that the reaction is an equilibrium reaction, and that side-reactions involving addition and polymerisation can be reduced to a minimum if equimolar mixtures of mercury acetate and sulphuric acid are used as catalyst.

For the mechanism of vinyl exchange, Adelman proposed the scheme



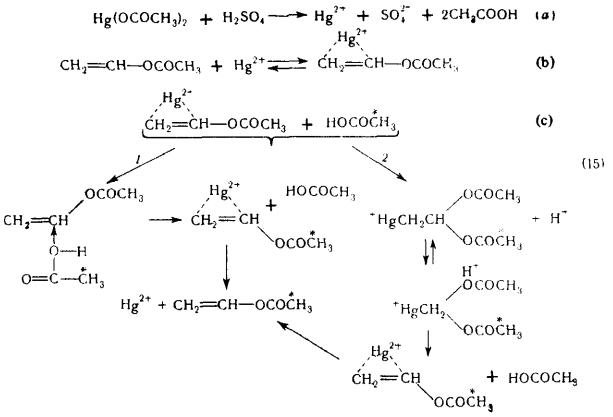
(13)

In 1962 it was established that acid solutions of palladium(II) chloride and salts of other platinum group metals can also catalyse the exchange of acyl residues between vinyl acetate and carboxylic acids and increase the rate of hydrolysis of vinyl acylates[77]. Without giving details of the proposed mechanism, the authors cited suggested that these reactions involve attack on the vinyl ester–metal ion complex by carboxylate ions or water molecules. On prolonged heating, vinyl ethers exchange their alcohol groups for the alkoxy-groups of any alcohols present under the influence of small quantities of mercury acetate in neutral anhydrous media[78]. Good yields of the exchange products could be obtained by removing them by distillation as they were formed. To confirm the suggestion that the reaction involves an organomercury compound, the authors cited showed that the latter catalyse the exchange in the same way as mercury acetate, and proposed the scheme:



(14)

Study of the reaction of vinyl acetate with the two isotopic forms of deuterio-acetic acid CD_3COOH and CH_3COOD at 25°C in the presence of Adelman's catalyst showed that in the reaction with CH_3COOD, deuterium does not enter the vinyl acetate molecule within the time required for the attainment of isotopic equilibrium between vinyl acetate and CD_3COOH.[30] Thus the hydrogen atoms of the vinyl group remain bound to their carbon atoms in the reaction, contrary to scheme (13). This conclusion was also confirmed in a PMR study of the formation of vinyl benzoate from deuterio-vinyl acetate and benzoic acid, catalysed by mercury acetate and BF_3.[12]



(15)

These data unambiguously refute Adelman's mechanism, and also prove that intermediate formation of acylals does not take place in the reactions studied.

Thus for the trans-vinylation of alcohols and carboxylic acids under the influence of the mercury salts of strong acids there remain two possible mechanisms: reversible addition of the cation of the mercury salt and the RO^- or $RCOO^-$ anion across the ethylenic bond, that is, an oxydeoxymercuration mechanism (scheme *15*, *2*) and a mechanism involving direct replacement of one ester group by another in ester molecules activated by coordination to mercury ions, analogous to that proposed by Smidt and coworkers[77] (scheme *15*, *1*).

Both mechanisms assume the formation of ionic complexes of mercury with the vinyl esters (stage *b*) and exchange of ester groups as a result of attack on these complexes by nucleophiles, and both mechanisms show agreement with vinyl–oxygen splitting of the bonds in the ester, confirmed experimentally (see section *2*). According to mechanism (*15*, *2*), the nucleophilic attack is complete with the formation of an organomercury compound. Mechanism (*15*, *1*) makes it possible to avoid this stage. The reaction path is apparently determined by the relative stability of the organomercury compounds and the mercury complexes in each specific instance.

Study of the kinetics of exchange between vinyl acetate and deuterio-acetic acid CD_3COOH under the influence of Adelman's catalyst[79] and the kinetics of the formation of vinyl benzoate from vinyl acetate and benzoic acid with catalysis by mercury acetate and BF_3 [80] showed that the overall order of the reaction with respect to the catalyst depends on the relative concentrations of the mercury salt and the acid. Subsequently, it was found[79] that there is a linear relationship between the reaction rate and the acetic acid concentration (1–10 M) but the initial rate of formation of vinyl benzoate increased more slowly than the benzoic acid concentration (0.3–1.0 M). The reaction with benzoic acid was found to be of first order with respect to vinyl acetate, whereas the exchange with deuterio-acetic acid was found to be of zero order with respect to vinyl acetate. The values found for the Arrhenius activation energy were 9.4 kcal $mole^{-1}$ and 11.0 kcal $mole^{-1}$ respectively.

The kinetic data on the exchange of vinyl acetate with acetic and benzoic acids were obtained under conditions which are not strictly comparable. Firstly, in the works

cited the solvents and acidic reagents used were not identical; secondly, for the exchange with acetic acid the data given were obtained after steady-state conditions had been established, whereas for the exchange with benzoic acid the initial rates of the process were given. Moreover, the ranges of change in the original concentrations in the works cited are narrow and do not always coincide with one another.

The kinetic data on the exchange between vinyl acetate and deuterio-acetic acid were interpreted on the basis of a direct replacement mechanism[78] (scheme *15*, *1*). The chief evidence in support of this scheme was provided by the dependence of the reaction rate on the ratio of the quantities of mercury acetate and sulphuric acid taken; this dependence was incompatible with an oxy-deoxymercuration mechanism. Application of the principle of steady-state concentrations to the corresponding kinetic scheme shows that the reaction rate in this instance would be independent of the acidity of the medium. If, however, the acetoxymercury derivative were formed in concentrations comparable with the concentration of mercury acetate, we would expect the rate to be linearly dependent on the acidity of the medium. The experimental data do not correspond to either situation.

The facts that the reaction rate is independent of the vinyl acetate concentration and that the reaction is of first order with respect to acetic acid do not contradict either of the mechanisms being considered. The linear dependence of the reaction rate on the acetic acid concentration was attributed[79] to rate-determining attack by this reagent on vinyl acetate molecules coordinated to mercury ions. The concentration of the activated substrate, in view of the large excess of substrate relative to the mercury salt, depends only on the latter, so that the concentration of ester does not appear in the kinetic equation.

According to the views of Flid and Temkin[81], the catalytic activity of mercury ions in the reactions of unsaturated compounds is due to the formation of termolecular complexes containing both reagents and the catalyst. From this viewpoint, the slow stage of the process may be the introduction of the reagent with the smaller affinity for the metal ion into its coordination sphere. The dependence of the rate of formation of vinyl benzoate from vinyl acetate and benzoic acid[80] agrees with these views. From published data[80] it can be seen that the initial reaction rate is related to the sum of the concentrations of acetic and benzoic acids†, as would be expected if the slow stage of the reaction is the displacement of one of the molecules of the unsaturated ester from the coordination sphere of the mercury ions by a carboxylic acid molecule.

The difference in the dependence of the reaction rate on the vinyl acetate concentration in the reactions with acetic and benzoic acids can apparently be attributed to the displacement of the equilibrium for complex formation by vinyl acetate with mercury ions towards the starting materials as a result of the lower concentrations of ester and the higher reaction temperature.

Thus although the available kinetic data are insufficient for a final choice to be made between mechanisms (*15*, *1*) and (*15*, *2*), they apparently show better agreement with the first mechanism.

Slinckx and Smets[80] adopted a reaction scheme including the formation of the acetoxy-mercury derivative (*b*) $CH_3COOHgCH_2CH(OCOCH_3)_2$, and they consider that the replacement of the acetate group by the benzoate group takes place in (*b*) as bimolecular substitution at the tertiary carbon atom. As justification for this improbable scheme, which is contrary to extensive experimental material on the behaviour of oxymercury derivatives in acid media[82-84], the authors cited give a kinetic equation of the form:

$$v = k[\text{ester}][C_6H_5COOH][BF_3][(CH_3COO)_2Hg],$$

which does not correspond to their own experimental data, and also the replacement of the acetate group in (*b*) by a benzoate group in the presence of BF_3.[12] This last fact merely confirms again the reversible nature of the deoxymercuration, and cannot serve as proof of the proposed mechanism.

In conclusion it should be emphasised that if the formation of oxymercury derivatives or coordination complexes as active intermediate species in vinyl exchange is determined by the relative stability of these compounds, the second version of the mechanism is more probable for the exchange between vinyl acylates and carboxylic acids, since the stability of organomercury compounds decreases considerably on going from the alkoxy- to the acyloxy-derivatives.

It is not excluded that in the exchange between enol ethers and alcohols the predominating mechanism is that involving the formation of organomercury compounds, as found for vinyl exchange in media not containing a strong acid[78], and also in the hydrolysis of vinyl ethers and esters in the presence of mercury salts, as will be shown below.

6. HYDROLYSIS OF ETHERS AND ESTERS, CATALYSED BY MERCURY SALTS

It was stated above that the addition of a mercury salt increases the rate of hydrolysis of vinyl ethers and esters without altering the point of cleavage of the bonds. Study of the hydrolysis of vinyl acetate and n-butyl vinyl ether in D_2O in the presence of mercury sulphate showed that the acetaldehyde formed contains only one D atom[29], as in the acid hydrolysis of ethyl vinyl ether[43]. The kinetic features of the reaction, which are the same for the hydrolysis of butyl vinyl ether and vinyl acetate[85,86], and also apparently for vinyl benzoates[87], differ significantly from those observed in both acid hydrolysis and vinyl exchange. It was established by a potentiometric method for the example of vinyl acetate and butyl vinyl ether that the addition of mercury perchlorate solution to an aqueous dioxan solution of the ether or ester leads to the formation of acid in quantities equivalent to the mercury salt content[85,86]; this corresponds to quantitative conversion of the mercury salt into an organomercury compound:

$$CH_2{=}CH{-}OR + HgX_2 + HOH \rightarrow XHgCH_2{-}CH(OR)(OH) + HX$$

or

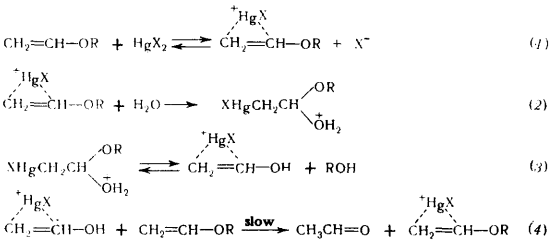
$$CH_2{=}CH{-}OR + HgX_2 + HOH \rightarrow X^- + XHgCH_2CH(OR)(\overset{+}{O}H_2) \rightarrow XHgCH_2CH{=}O + ROH + HX.$$

The rate of hydrolysis increases linearly with increase in the concentration of mineral acid and is independent of the ionic strength of the solution[85,86]. The order of the reaction with respect to the substrate and the mercury salt is fractional and changes with change in the pH of the medium. The ethers and esters can be arranged in the following order of reaction rates at 20°C (the relative rates

† The acetic acid was introduced into the reaction mixture with the mercury acetate solution. The relationship indicated was not noticed by the authors cited[80].

under comparable conditions are given in parentheses): n-butyl vinyl ether (~ 10^2) > vinyl acetate (1.0) > vinyl anisate (0.39) > vinyl benzoate (0.17) > vinyl *p*-chlorobenzoate (0.13) > vinyl *p*-nitrobenzoate (0.10). This order corresponds to an increase in reaction rate with increase in the electron-donating power of the substituent attached to the ether oxygen atom, and is the opposite of that which might have been expected if the reaction rate were determined by the deoxymercuration stage, since organomercury compounds containing acyl groups undergo solvolysis much more readily than their alkoxy-analogues[83,84].

The available experimental data have been explained using scheme (16),[85,86] which is the same for the hydrolysis of vinyl ethers and esters.



(16)

According to scheme (16), the coordination complexes of the ether or ester with mercury ions undergo rapid nucleophilic attack by water and are converted into the oxymercury derivatives. Acid hydrolysis of the oxymercury derivatives does not lead to liberation of the mercury ion catalyst, since the mercury ions remain bound in ionic complexes with the reaction product—the enol form of acetaldehyde. The slow stage of the process is the transfer of mercury ions from the product to the substrate, as shown by stage (4). The transfer of catalyst from the product to new molecules of ether or ester is more rapid, the more nucleophilic their ethylenic bond, in agreement with the observed dependence of the rate of hydrolysis on the structure of the substrate.

Scheme (16), on the one hand, is a detailed form of scheme (*15*, *2*) for aqueous solutions. On the other hand, it corresponds to scheme (*12*) for the acid hydrolysis of the alkenyl esters of aliphatic acids, since the splitting of the double bond takes place under the joint influence of electrophilic and nucleophilic reagents. The difference is that the mercury ions, unlike the protons in acid catalysis, are not regenerated at the end of the catalytic cycle. The greater catalytic activity of mercury ions compared with protons in the hydrolysis of vinyl ethers and esters agrees with the idea that the C=C bond is weakened by dative interaction when the unsaturated ether or ester is introduced into the coordination sphere of mercury ions[88,89].

7. ALKALINE HYDROLYSIS OF ESTERS

The first kinetic study of the alkaline hydrolysis of enol acylates was made in 1927, when Skrabal and Zachorka[90] established that vinyl acetate in alkaline aqueous solutions is hydrolysed much more rapidly than ethyl acetate. They showed that the reaction is described by an equation of second order and of first order with respect to ester and alkali, that is, it is analogous to the hydrolysis of ethyl acetate. The second-order rate constant was found to be 620 litre mole^{-1} min^{-1} at 25°C, which corresponds to an increase in reaction rate by a factor of 100 on going from ethyl acetate to vinyl acetate. The same authors determined the first-order rate constant for the "aqueous" hydrolysis of vinyl acetate, which is equal to 7.4×10^{-6} min^{-1} and is greater than the analogous constant for ethyl acetate by a factor of 1000. According to their data, the maximal stability of vinyl acetate corresponds to pH 4.44.

The vinyl esters of aliphatic acids can be arranged in the following order of rates of hydrolysis at 25°C in a 0.05 *N* solution of sodium hydroxide in 95.5% ethanol[91], analogous to the order for the ethyl and methyl esters[21] (the relative rates of hydrolysis are given in parentheses): monochloroacetate (600) > formate (350) > acetate (1) > butyrate (0.22) > isobutyrate (0.12) > isovalerate (0.085) > crotonate (0.078).

An interesting feature is that under these conditions the rates of hydrolysis of ethyl and vinyl acetates were found to be the same, whereas in the hydrolysis of vinyl acetate in aqueous alkali solution an increase in the reaction rate by more than two orders of magnitude was observed, which is much greater than the increase in the water concentration.

The rates of hydrolysis of the divinyl esters of saturated dibasic acids in aqueous ethanol solutions differ little from that for vinyl acetate. Increase in the length of the hydrocarbon chain leads to a decrease in the reaction rate and an increase in the activation energy[92].

Table 7. Comparison of the kinetic characteristics of the alkaline hydrolysis of vinyl and ethyl carboxylates at 25°C*.

Ester	10^5k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
Vinyl anisate	23.0	18.0	−16.7
Ethyl anisate	11.5	18.6	−15.9
Vinyl benzoate	114	16.9	−17.3
Ethyl benzoate	55.0	17.7	−15.9
Vinyl *p*-chlorobenzoate	371	15.2	−18.5
Ethyl *p*-chlorobenzoate	237	16.8	−16.1
Vinyl *p*-nitrobenzoate	9.25	15.8	−12.3
Ethyl *p*-nitrobenzoate	5.67	14.5	−16.5
Vinyl acetate	1.31	13.0	−26.2
Ethyl acetate	621	14.2	−23.0

* The data on the kinetics of hydrolysis of ethyl benzoate in 85% aqueous ethanol solutions are taken from Ingold and Nathan[93], and the data on the kinetics of the alkaline hydrolysis of ethyl acetate in a solvent with the same composition are taken from Evans and coworkers[94].

The identical influence of substituents in the acyl group of vinyl and ethyl acylates is also confirmed by data on the alkaline hydrolysis of vinyl benzoates with substituents in the *para*-position of the benzene ring in 77% aqueous ethanol solutions[17,34] (Table 7), which show that the similarity in the values of the rate constants for the hydrolysis of vinyl and ethyl benzoates is due to the similarity in the values of the energy and entropy of activation.

The changes in reaction rate in the series of ethyl benzoates, however, is due entirely to change in the activation energy at constant value of the entropy of activation, whereas in the vinyl benzoate series there is an appreciable change in the values of $\Delta S^{\neq}$, which partly compensates the influence of the change in activation energy.

The similarity in the kinetic characteristics of the alkaline hydrolysis of vinyl and ethyl esters (Table 7) apparently is not of great importance from the viewpoint of reaction mechanism, since the results were obtained under

conditions of different water concentration. The marked influence of this factor on the rate of hydrolysis of vinyl acetate was noted above. In the concentration range 5 to 20 M the rate of hydrolysis of vinyl acetate (and vinyl benzoates) is linearly dependent on the water concentration[34], but the influence of the composition of the solvent on the values of $E^{\neq}$ and $\Delta S^{\neq}$ has not been elucidated. Thus the similarity in the values of these parameters for the hydrolysis of vinyl and ethyl esters is possibly due to accidental coincidence. In aqueous solution, the values of $\Delta S^{\neq}$ for the alkaline hydrolysis of $\alpha\beta$-alkenyl and alkyl acetates in some instances differ considerably, although the activation energies are similar (Table 8). For vinyl and ethyl acetates the difference amounts to 17 e.u. The increase in reaction rate by a factor of 30 on going from cyclopentyl acetate to cyclopentenyl acetate is due chiefly to the increase in the entropy of activation.

Table 8. Kinetic parameters of the alkaline hydrolysis of various enol and alkyl acetates in aqueous solution at 20°C.[95]

Acetates	k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Acetates	k, litre mole^{-1} s^{-1}	$E^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
Vinyl	3.28	12.8	−12.7	Ethyl	0.006	11.0	−31.0
Isopropenyl	0.31	11.6	−21.2	Cyclopropyl	0.18	12.1	−20.8
Cyclopentenyl	0.85	10.5	−24.8	n-Butyl	0.06	10.6	−27.7
Cyclohexenyl	0.18	10.5	−26.5	Cyclopentyl	0.03*	11.8	−28.2

* At 21°C.

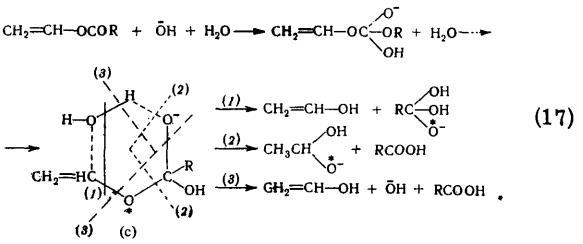
The dependence of the rate constant for alkaline hydrolysis in aqueous ethanol solutions on the structure of the acyl residue satisfies the Taft equation $\lg(k/k_0) = \rho^*\sigma^* + E_S + \psi$ for the vinyl esters of aliphatic acids and the Hammett equation $\lg(k/k_0) = \rho\sigma$ for the benzoates. The values $\rho^* = +2.67$ and $\rho = +2.48$ almost coincide with those established for the alkaline hydrolysis of ethyl carboxylates[17,34].

Change in the structure of the alkenyl radical has a fairly marked influence on the rate of alkaline hydrolysis of enol acylates (Table 8), the effect being apparently stronger than that of analogous changes in the structure of saturated alcohol radicals.

The reaction rate for isopropenyl acetate is smaller by a factor of 10 than that for vinyl acetate, whereas the rate of hydrolysis of isopropyl acetate is smaller than that of ethyl acetate by a factor of only 3.7–4.0;[22,94] according to data obtained by the same authors, the same difference in rates was observed for the hydrolysis of the acetates of primary and secondary butyl alcohols.

The available experimental data are contradictory, since, on the one hand, they indicate a similarity in the mechanism of the alkaline hydrolysis of enol esters and their analogues with a saturated alcoholic group (the stability of the enol ethers in alkaline media and the rapid hydrolysis of the esters, the similarity in the values of ρ in the Hammett–Taft equation for ethyl and vinyl acylates, and the marked similarity in the kinetic parameters for the hydrolysis of ethyl and vinyl benzoates in alcoholic solutions). On the other hand, the partial transfer of the ether oxygen to the carboxyl group in the absence of exchange between the esters and the medium during the reaction, the change in $\Delta S^{\neq}$ when substituents are introduced into the benzene ring of vinyl benzoates, the marked decrease in the reaction rate on going from aqueous to aqueous-alcoholic media, and the more marked influence of the structure of the alcohol component on the reaction rate indicate that the mechanisms of the alkaline hydrolysis of alkenyl and alkyl carboxylates are not the same.

An attempt was made to reconcile the accumulated data by the suggestion that the rate-determining reaction involves attack by hydroxide ions on the carbonyl group with the formation of a cyclic intermediate complex (*c*),[34] similar to that previously proposed by Hinshelwood[96] and by Syrkin and Moiseev[28] for the alkyl esters, scheme (*17*):



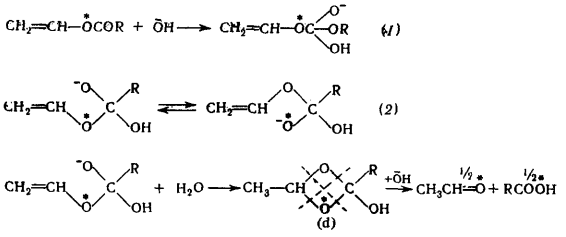
(17)

The authors cited based the proposed scheme on the following considerations: the slow addition of hydroxide ions to the carbonyl carbon atom corresponds to the observed values of ρ and the absence of exchange with the medium during the reaction; the formation of the complexes (*c*) for vinyl esters is facilitated by polarisation of the C=C bond; and decomposition of complex (*c*) in various directions, as shown in the scheme, can lead to the same reaction products with different isotopic compositions. In particular, decomposition in directions *1* and *2* or *3* and *2* at commensurate rates explains the partial transfer of the ether oxygen atom to the carboxyl group of the salt of the carboxylic acid formed.

To this it may be added that the attachment of the oxygen of water to the α-carbon atom of the vinyl group in the transition state agrees with the stronger influence of the structure of the alkenyl group, compared with the alkyl group, on the rate of hydrolysis.

Another possible interpretation of the experimental data appeared recently, since it was established that the hydrolysis of substituted benzhydryl benzoates, in which alkyl–oxygen splitting of the bonds takes place, is accompanied by intramolecular redistribution of ^{18}O between the ether and carbonyl oxygen atoms[97,98]. This was attributed to reversible breakdown of the ester molecule to form ion pairs, whose lifetime in the solvent cell is so great that extensive intramolecular isotopic exchange of oxygen can take place. This reaction path is possible if the structure of the alcohol radical ensures stability of the alkyl cations in the ion pairs.

The structure of the unsubstituted vinyl group does not satisfy this condition, but on the other hand it makes possible exchange between the ester and carbonyl oxygens without the formation of ion pairs, as can be seen from the schemes:



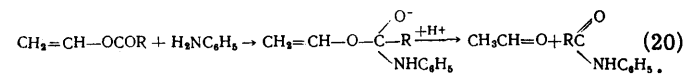
(18)

(19)

In the present instance, this reaction mechanism can be favoured by polarisation of the ethylenic bond. After the formation of the *ortho*-form of the ester, the polarisation

of the double bond should be intensified, and the polarisation is possibly no less than that in the molecules of vinyl ethers.

Evidence in support of schemes (*18*) and (*19*) is provided by the fact that in the acylation of aniline in anhydrous solution by vinyl acetate and benzoate labelled only in the ether oxygen atom, ~ 20% of the tracer was found in the anilides[35]. The following mechanism has been proposed for the acylation of amines by vinyl carboxylates[99]:



(20)

Since the yield of amides is quantitative[99], it is difficult to explain the partial transfer of ether oxygen to the anilide except by using a scheme analogous to scheme (*18*).

For hydrolysis according to scheme (*19*) in a medium enriched in $H_2{}^{18}O$, the concentration of ^{18}O in the anion of the acid formed would be half that in the medium, whereas in the hydrolysis of an ester labelled only in the ether oxygen the concentration would be half that in the original ester, and one-quarter of that in the vinyloxy-group. These relationships were found for the hydrolysis of vinyl anisate (Table 2). It may be assumed that the electron-donating methoxy-group in the *para*-position of the benzene ring facilitates the formation of the cyclic acylal (*d*), since it increases the negative charge on the carbonyl oxygen atom and intensifies the polarisation of the ethylenic bond in the required direction.

All that has been said above regarding the distribution of the tracer in the products of hydrolysis according to scheme (*19*) also applies to scheme (*18*) with the condition that the equilibrium in stage *2* can be established before the decomposition of the *ortho*-form of the ester into the reaction products.

It can be seen from scheme (*18*) that the intramolecular exchange of oxygen may also involve a third oxygen atom of the *ortho*-form. This may explain the data on the isotopic composition of acetic, benzoic, and *p*-chlorobenzoic acids, given in Table 2, particularly if slight exchange between the ester and the medium, which might remain unobserved, is assumed.

We do not yet have sufficient information to enable us to give preference to one of the above schemes. Any interpretation of the mechanism of the hydrolytic decomposition of vinyl esters in alkaline media, however, should take account of the fact that the rupture of the bonds between the vinyl group and oxygen plays a significant part.

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