

Kinetics and Mechanism of Acetoxymercuration and Acid-Catalysed Hydration of α -Alkylstyrenes

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Dedicated to Professor Marvin Charton on the occasion of his significant anniversary

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Abstract: Nine α -alkylstyrenes carrying the following substituents have been synthesised: methyl, ethyl, propyl, butyl, pentyl, *isobutyl*, *isopropyl*, *sec-butyl* and *tert-butyl*. Kinetics has been measured for the reaction of these compounds with mercuric acetate in anhydrous acetic acid at 25 °C. The rate constants are very sensitive to inductive effects ($\rho_1 = -49.5$ in AISE theory) and steric effects ($\psi = -1.59$ according to Charton). These results support the presumed existence of an intermediate with an asymmetrically bound acetylmercuric cation to carbon atoms of the vinyl group of styrene. The kinetics of an acid-catalysed hydration of the above-mentioned α -alkylstyrenes were also measured in aqueous sulphuric acid at 25 °C. The derivatives exhibited kinetically a consecutive isomerisation reaction giving the more stable substituted styrenes. The values of the slope $m^{\ddagger}m^*$ of the dependence upon the excess acidity function (X) were evaluated, and exceptionally low values were found for the butyl and pentyl substituents (1.02 and 0.73, respectively), while on the other hand *tert-butyl* showed an exceptionally high value (3.28). On the basis of the facts, a mechanism has been suggested for the acid-catalysed hydration, involving the reaction of

a relatively stable and sterically hindered carbocation with water as the rate-limiting step of the reaction.

Keywords: Styrenes, methoxymercuration, hydration, substituent effects.

Introduction

Styrenes and their derivatives are often studied compounds. Besides their industrial applications, particular attention has been focused on electrophilic addition reactions to the double bond in the side chain of the aromatic ring. In the present paper, attention has been paid mostly to the oxymetallation reaction and acid-catalysed hydration.

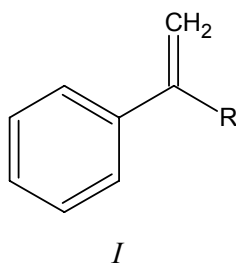
The most frequently studied oxymetallation reaction is methoxymercuration [1-6] with mercuric acetate in methanol, while other oxymetallation reactions are rather exceptional (for example, argentation with silver nitrate in water [7]). Solvent effects on alkoxymercuration of styrenes were dealt with in several papers [3-5]; however, in all the cases they referred to alcohols or their mixtures with other solvents. Within their research work on kinetics and mechanism of methoxymercuration of styrenes [1-8] and other alkenes [8-16], the authors have focused their attention especially on substituent effects [2, 3, 6, 8, 10, 12], including the steric ones [10, 12]; furthermore, to salt effects [14, 15], temperature dependences of the reaction rate constant [1, 2, 6] and in the context with the above-mentioned areas, also to the structure of the addition intermediate [3, 4, 8-10, 13-16]. From these studies it follows that methoxymercuration is an electrophilic reaction, whose rate-limiting step involves formation of an intermediate with an acetylmercuric cation asymmetrically bound to the carbon atoms of the styrene vinyl group. The structure of the adduct probably depends on that of the alkene [16, 17]. With respect to high sensitivity to changes in composition (polarity) of solvent, the high negative reaction constant for the substitution in aromatic ring ($\rho^+ \sim -3$), and the high negative activation entropy (~ -30 e.u.) it can be claimed with high certainty that the activated complex of this elementary step is both polar and highly ordered compared with the educts. Obviously, in the reaction with mercuric acetate the predominant electrophilic reagent is $\text{CH}_3\text{COOHg}^+$ cation and, depending on the substrate structure, the non-dissociated mercuric acetate can also make itself felt as an electrophile [14, 16].

The second most frequently investigated reaction of styrenes is their acid-catalysed hydration. The fundamental approach here consists in analysis of relationships between reactivity and acidity of medium; for a summary of both older and more recent results see refs. [22-26] and [27], respectively. Much less attention was paid to substituent effects on this reaction, and again mostly in the context of the acidity of the medium [25, 27-31]. There exist several potentially possible mechanisms of acid-catalysed hydration of styrenes; for a detailed analysis see [25]. The discussed reaction also exhibits a significant solvent kinetic isotope effect [27, 30]. On the basis of results published so far, the preferred mechanism consists in electrophilic addition with proton transfer to styrene in the rate-limiting step of reaction (general catalysis) and concomitant formation of the carbocation. The carbocation formed reacts rapidly with water (or other nucleophiles present) in the subsequent step giving the products. The energies of educts, intermediates and products of this reaction and those of the transition states of

individual elementary reactions are dealt with by means of quantum-chemical calculations in ref. [32]. According to the results of this paper, the sum of relative energies (referenced to the carbocation-water complex as the starting point of the scale) of styrene and hydroxonium ion is distinctly higher ($46.4 \text{ kcal}\cdot\text{mol}^{-1}$) than the energy of their complex ($15.7 \text{ kcal}\cdot\text{mol}^{-1}$). This result indicates that the formation of styrene-hydroxonium ion complex is really possible. Transformation of this complex into the carbocation-water complex ($0.0 \text{ kcal}\cdot\text{mol}^{-1}$) is connected with only small energy demands (relative energy of the transition state is $17.6 \text{ kcal}\cdot\text{mol}^{-1}$) as compared with the reverse process. Therefrom it follows that elimination of a proton from the carbocation obviously represents a step with distinctly the lowest rate constant.

For judging the reactivities of styrene derivatives in the reactions given, important results are contained in the studies dealing with the stabilities of the geometry isomers [33-35], electron structure [36, 37] and the therewith connected conformation of alkenyl group and benzene nucleus [37, 38]. In accordance to the general premises, more stable phenylalkenes are those with the conjugated alkenyl group and the benzene nucleus and the isomers with *E* configuration at the double bond. The energy barrier against rotation around the arene-alkene bond is low for styrenes ($< 4\text{-}5 \text{ kcal}\cdot\text{mol}^{-1}$), but it is increased with substitution especially at the α -carbon atom [38].

Structure and properties of substituted benzylium cation as the most important common intermediate in the acid-catalysed hydration of styrenes and the reverse dehydration of the corresponding alcohols, or in various solvolytic reactions, were studied in a number of papers [28, 32, 34, 35, 39-45]. The rate of formation and, hence, also the stability of benzylium cation depends on substitution of the benzene nucleus; however, the reaction constants ρ^+ are large and negative [27, 39, 41, 45], and the Yukawa-Tsuno equation appears to be more satisfactory for evaluating the correlation dependence. An alkyl substitution at the α -carbon atom causes a lowering of the reaction constant mentioned due to the stabilisation of the cation by a positive inductive effect of the alkyl group [39-41]. Sensitivity to the α -substitution is higher than that to a substitution in an aromatic nucleus [32, 40, 41, 45], and the stabilities of the respective carbocations are also affected by steric effects [34, 35, 45]. Studies of carbocations in gas phase and solvents [32, 41, 45] showed that the solvation of the carbocations plays a significant role in their stabilisation. Competitive kinetic measurements of reactions of 1-phenylethyl carbocations with nucleophiles indicate a higher selectivity of the more stable substrates [43, 44], and a general base catalysis was proved in the reactions with alcohols [44]. In the set of papers oriented to styrene derivatives, the portion dealing with α -alkylstyrenes of general formula *I* is very small.



The experiments described concern syntheses [46-59] and spectral properties [7, 37, 60]; the above-mentioned argumentation was studied kinetically [7]. The theoretical approach includes calculations oriented to the electron properties [37] and an effect of α -substitution on the stability of the respective carbocation [40]. The survey given shows that there are not many experimental results concerning α -alkylstyrenes, and the reaction mechanisms described for styrene have not been verified

for α -alkylstyrenes. Therefore, the aim of this paper is, on the basis of kinetic measurements and evaluation of substituent effects, to verify and/or suggest mechanisms of acetoxymercuration and acid-catalysed hydration of the title α -alkylstyrenes, and to compare the results obtained here with those obtained elsewhere for other styrene derivatives.

Results and Discussion

Acetoxymercuration

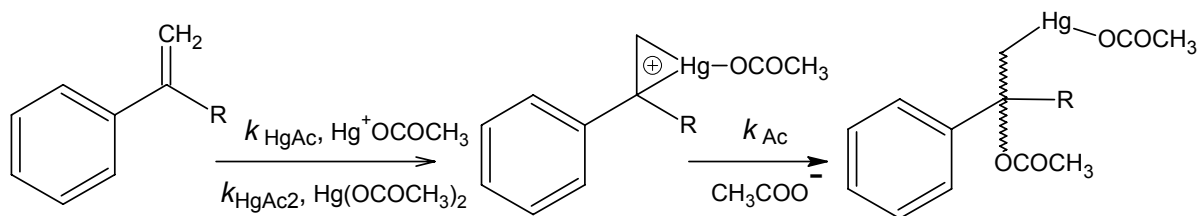
The mean values (from 3 measurements) of the observed rate constants k_{obs} of the reactions of α -alkylstyrenes with mercuric acetate depending on the concentration of the latter are presented in Table I.

Table I. Mean values (from three measurements) of observed rate constants k_{obs} (s^{-1}) of acetoxymercuration of α -alkylstyrenes depending on mercuric acetate concentration c ($\text{mol}\cdot\text{dm}^{-3}$) in acetic acid at 25.0 °C; the values in the second line are the wavelengths λ (nm) at which the measurements were carried out.

c	Me	Et	Pr	Bu	Pe	isoBu	isoPr	sec-Bu	tert-Bu
	262	270	268	269	268	270	268	262	260
$5.00 \cdot 10^{-3}$	$9.90 \cdot 10^{-5}$	$3.12 \cdot 10^{-4}$	$1.88 \cdot 10^{-4}$	$2.19 \cdot 10^{-4}$	$2.66 \cdot 10^{-4}$	$6.90 \cdot 10^{-5}$	$2.47 \cdot 10^{-5}$	$2.24 \cdot 10^{-5}$	$6.07 \cdot 10^{-5}$
$6.67 \cdot 10^{-3}$	$1.44 \cdot 10^{-4}$	$4.01 \cdot 10^{-4}$	$2.40 \cdot 10^{-4}$	$2.86 \cdot 10^{-4}$	$3.33 \cdot 10^{-4}$	$8.83 \cdot 10^{-5}$	$3.20 \cdot 10^{-5}$	$2.86 \cdot 10^{-5}$	$9.00 \cdot 10^{-5}$
$7.67 \cdot 10^{-3}$	$1.51 \cdot 10^{-4}$	$4.83 \cdot 10^{-4}$	$2.84 \cdot 10^{-4}$	$3.29 \cdot 10^{-4}$	$3.73 \cdot 10^{-4}$	$9.80 \cdot 10^{-5}$	$3.77 \cdot 10^{-5}$	$2.66 \cdot 10^{-5}$	$1.08 \cdot 10^{-4}$
$8.33 \cdot 10^{-3}$	$1.72 \cdot 10^{-4}$	$5.24 \cdot 10^{-4}$	$2.96 \cdot 10^{-4}$	$3.52 \cdot 10^{-4}$	$4.08 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	$4.00 \cdot 10^{-5}$	$3.60 \cdot 10^{-5}$	$1.04 \cdot 10^{-4}$
$9.00 \cdot 10^{-3}$	$1.88 \cdot 10^{-4}$	$5.62 \cdot 10^{-4}$	$3.18 \cdot 10^{-4}$	$3.84 \cdot 10^{-4}$	$4.44 \cdot 10^{-4}$	$1.19 \cdot 10^{-4}$	$4.30 \cdot 10^{-5}$	$3.88 \cdot 10^{-5}$	$1.10 \cdot 10^{-4}$
$1.00 \cdot 10^{-2}$	$2.02 \cdot 10^{-4}$	$5.75 \cdot 10^{-4}$	$3.39 \cdot 10^{-4}$	$4.15 \cdot 10^{-4}$	$4.87 \cdot 10^{-4}$	$1.27 \cdot 10^{-4}$	$5.43 \cdot 10^{-5}$	$3.65 \cdot 10^{-5}$	$1.21 \cdot 10^{-4}$
$1.17 \cdot 10^{-2}$	$2.26 \cdot 10^{-4}$	$6.73 \cdot 10^{-4}$	$3.88 \cdot 10^{-4}$	$4.84 \cdot 10^{-4}$	$5.73 \cdot 10^{-4}$	$1.46 \cdot 10^{-4}$	$6.30 \cdot 10^{-5}$	$4.25 \cdot 10^{-5}$	$1.35 \cdot 10^{-4}$
$1.33 \cdot 10^{-2}$	$2.63 \cdot 10^{-4}$	$7.22 \cdot 10^{-4}$	$4.42 \cdot 10^{-4}$	$5.46 \cdot 10^{-4}$	$6.67 \cdot 10^{-4}$	$1.60 \cdot 10^{-4}$	$6.80 \cdot 10^{-5}$	$4.79 \cdot 10^{-5}$	$1.55 \cdot 10^{-4}$
$1.43 \cdot 10^{-2}$	$2.77 \cdot 10^{-4}$	$7.49 \cdot 10^{-4}$	$4.58 \cdot 10^{-4}$	$5.71 \cdot 10^{-4}$	$8.25 \cdot 10^{-4}$	$1.71 \cdot 10^{-4}$	$7.50 \cdot 10^{-5}$	$5.18 \cdot 10^{-5}$	$1.78 \cdot 10^{-4}$
$1.50 \cdot 10^{-2}$	$2.87 \cdot 10^{-4}$	$7.96 \cdot 10^{-4}$	$4.88 \cdot 10^{-4}$	$5.84 \cdot 10^{-4}$	$8.35 \cdot 10^{-4}$	$1.75 \cdot 10^{-4}$	$8.37 \cdot 10^{-5}$	$5.76 \cdot 10^{-5}$	$1.69 \cdot 10^{-4}$
$1.60 \cdot 10^{-2}$	$2.96 \cdot 10^{-4}$	$8.55 \cdot 10^{-4}$	$5.16 \cdot 10^{-4}$	$6.38 \cdot 10^{-4}$	$8.93 \cdot 10^{-4}$	$1.87 \cdot 10^{-4}$	$8.90 \cdot 10^{-5}$	$6.07 \cdot 10^{-5}$	$1.67 \cdot 10^{-4}$
$1.67 \cdot 10^{-2}$	$3.13 \cdot 10^{-4}$	$8.86 \cdot 10^{-4}$	$5.23 \cdot 10^{-4}$	$6.44 \cdot 10^{-4}$	$9.04 \cdot 10^{-4}$	$1.91 \cdot 10^{-4}$	$9.63 \cdot 10^{-5}$	$6.62 \cdot 10^{-5}$	$1.73 \cdot 10^{-4}$
$1.80 \cdot 10^{-2}$	$3.32 \cdot 10^{-4}$	$9.08 \cdot 10^{-4}$	$5.57 \cdot 10^{-4}$	$6.92 \cdot 10^{-4}$	$1.08 \cdot 10^{-3}$	$2.04 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	$8.16 \cdot 10^{-5}$	$1.90 \cdot 10^{-4}$
$2.00 \cdot 10^{-2}$	$3.73 \cdot 10^{-4}$	$9.93 \cdot 10^{-4}$	$6.03 \cdot 10^{-4}$	$7.46 \cdot 10^{-4}$	$1.20 \cdot 10^{-3}$	$2.18 \cdot 10^{-4}$	$1.04 \cdot 10^{-4}$	$1.26 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$

The kinetic model of the reaction was derived on the basis of the presumed reaction mechanism [2-5, 8] described in Scheme 1.

Scheme 1



The first approximation presumed a reaction of α -alkylstyrenes with both reagents given in Scheme 1. The observed rate constant is then given by the relationship:

$$k_{\text{obs}} = k_{\text{HgAc2}} [\text{Hg}(\text{OCOCH}_3)_2] + k_{\text{HgAc}} [\text{Hg}^+ \text{OCOCH}_3], \quad (1)$$

where k_{HgAc2} is the rate constant of reaction with non-dissociated mercuric acetate $\text{Hg}(\text{OCOCH}_3)_2$ and k_{HgAc} is the rate constant of the reaction with $\text{CH}_3\text{COOHg}^+$ cation. The actual concentrations of the reagents are given by the following relationships:

$$[\text{Hg}^+ \text{OCOCH}_3] = \frac{-K_{\text{HgAc2}} + \sqrt{K_{\text{HgAc2}}^2 + 4K_{\text{HgAc2}} c_{\text{HgAc2}}}}{2}, \quad (2)$$

and

$$[\text{Hg}(\text{OCOCH}_3)_2] = c_{\text{HgAc2}} - [\text{Hg}^+ \text{OCOCH}_3], \quad (3)$$

where K_{HgAc2} is the dissociation constant of mercuric acetate giving acetate anion and $\text{CH}_3\text{COOHg}^+$ cation. The rate constants k_{HgAc2} and k_{HgAc} in Eq. (1) and the unknown value of the dissociation constant K_{HgAc2} in Eq. (2) were calculated by a non-linear regression. For all the α -alkylstyrenes studied by us, the constant k_{HgAc2} was statistically insignificant. The reaction with non-dissociated mercuric acetate as the electrophile did not significantly make itself felt kinetically, and the $\text{CH}_3\text{COOHg}^+$ cation obviously is the only electrophile, like in other mercurations [2-5, 9]. This conclusion is supported by the decrease of the observed reaction rate constant with the increase in concentration of added sodium acetate (the slope -0.0047 ± 0.0003) due to suppression of the dissociation of mercuric acetate [14, 15].

For these reasons, the constant k_{HgAc2} was deleted in Eq. (1), and thus the dependence of the observed rate constant reads as follows:

$$k_{\text{obs}} = k_{\text{HgAc}} [\text{Hg}^+ \text{OCOCH}_3], \quad (4)$$

where the actual concentration of the $\text{CH}_3\text{COOHg}^+$ cation is given by Eq. (2). A new calculation by the non-linear regression provided statistically significant constants k_{HgAc} for all the derivatives (see Table IV.). The value of unknown dissociation constant K_{HgAc2} obtained by calculation is 0.25 ± 0.08 .

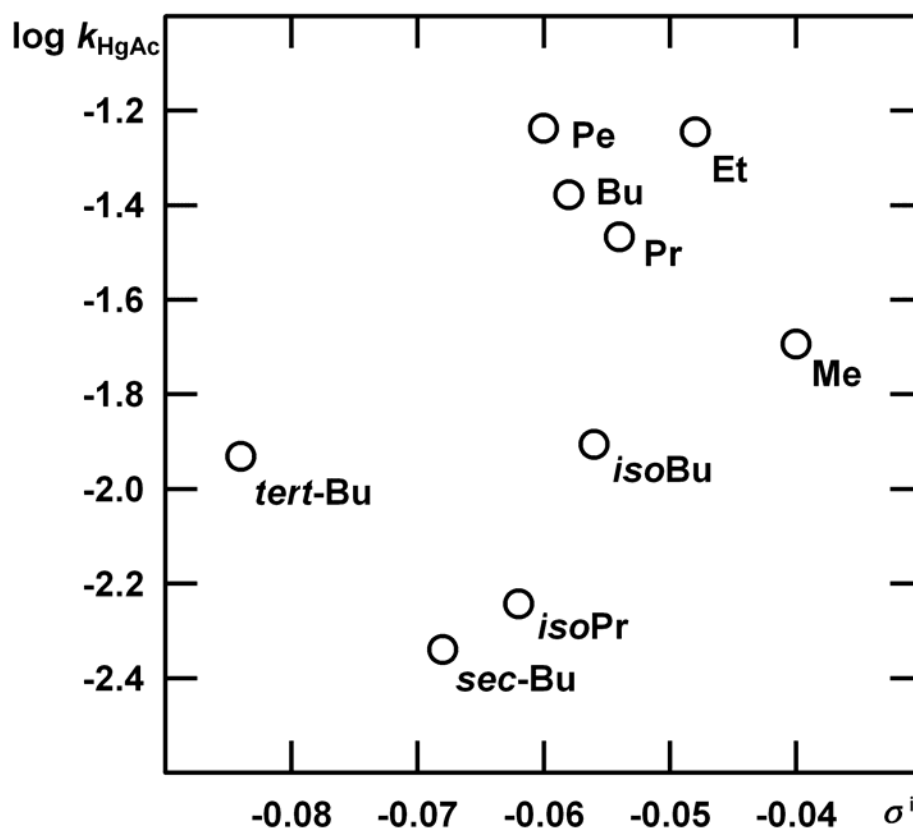
The evaluation of the inductive effect of the α -substituents in styrene made use of the substituent constants σ^i AISE theory, [63, 64]), which describe the inductive effects of substituents, and that of steric effects made use of Charton's substituent constants ν [65]. The dependence of logarithm of the rate constant k_{HgAc} upon the substituent constants σ^i is depicted in Fig. 1. At first sight, the placements of individual points in the picture do not evoke an unambiguous notion about the effects of individual substituents upon the given reaction; however, it is evident that both inductive and steric effects are operating. With application of an additional indicator variables $\text{Ind}_{\text{Me,Et}}$ ($= 1$ for methyl and ethyl, otherwise $= 0$) and $\text{Ind}_{\text{branched}}$ ($= 1$ for *isopropyl*, *sec-butyl* and *tert-butyl*, otherwise $= 0$), the

dependence of logarithm of the rate constant k_{HgAc} upon the substituent constants σ^i and υ can be described by the following equation:

$$\log k_{\text{HgAc}} = -(3.29 \pm 0.19) - (49.5 \pm 4.4)\sigma^i - (1.59 \pm 0.18)\upsilon + (0.328 \pm 0.066)\text{Ind}_{\text{Me,Et}} - (0.982 \pm 0.064)\text{Ind}_{\text{branched}} \quad (5)$$

$n = 9, s = 0.058, R = 0.995.$

Figure 1. Dependence of logarithm of rate constant k_{HgAc} of acetoxymercuration of α -alkylstyrenes upon the σ^i constant.



From Eq. (5) it follows that the reaction of α -alkylstyrenes with mercuric acetate is extremely sensitive to inductive effects of the substituents and is significantly slowed down by steric effects, inclusive of the branching of alkyl groups. From these facts it is possible to draw the conclusion that a positive charge is developed to a considerable extent on the α -carbon atom in the transition state of reaction, which is in accordance with the previously observed high sensitivity to substitution in the aromatic nucleus of styrene [2, 6-8, 12]. Obviously, the bulky mercuric electrophile assumes a position near to both α - and β -carbon atoms in the transition state of the reaction, which is in accord with the view that the intermediate being formed contains the acetylmercuric cation asymmetrically bound to the carbon atoms of the vinyl group in styrene [2, 3].

The value of the regression coefficient for the indicator variable $\text{Ind}_{\text{Me,Et}}$ in Eq. (5) shows that the derivatives with small substituents (methyl, ethyl) react twice as fast as those with the other linear alkyl groups ($\log 2 = 0.301$). This fact evokes a notion that this is a statistical factor. The reason can lie in the hindrance against the approach of reagent to the vinyl bond in styrene from that side to which the alkyl chain is conformationally deviated due to hydrophobic interactions in polar solvent. The regression coefficient for the indicator variable $\text{Ind}_{\text{branched}}$ shows that branching at the first carbon atom

of the alkyl group results in an almost tenfold decrease in the rate constant k_{HgAc} as compared with the other alkyl groups irrespective of the overall bulkiness of the substituents. In the context with the above discussion, this fact can be explained by steric hindrance against the approach of reagent towards the reaction centre with a branched alkyl substituent in the conformation minimising steric interactions with the benzene nucleus (above and below the nucleus, in an “astride” manner). Another possible explanation is a deviation of the vinyl group (as the reaction centre) out of the plane of the molecule, which is connected with a loss of the resonance energy due to conjugation between the cation being formed and the aromatic nucleus. However, with respect to the complexness of the substituent effects upon the reaction discussed, it is impossible to decide unambiguously which of the two variants is correct.

Acid-Catalysed Hydration of α -Alkylstyrenes

In the measurements of acid-catalysed hydration kinetics all the derivatives showed a decrease in absorbance with time, the dependences obeying the model of the first order in the substrate. Likewise, all the derivatives, except for α -*tert*-butylstyrene, exhibited a consecutive reaction connected with increase in the absorbance with time at higher concentrations of sulphuric acid. With the derivatives containing the ethyl, propyl, butyl, pentyl and *isobutyl* substituents, within the sulphuric acid concentration range of 2 – 6.5 mol·dm⁻³, the kinetics could be evaluated according to the model of the consecutive reactions. The values of the observed rate constants k_{obs} of the first step of acid-catalysed hydration measured for various sulphuric acid concentrations in water at 25 °C are presented in Table II., those of the subsequent step being given in Table III. With the k_{obs} values measured, we constructed a kinetic acidity function [61, 62] and calculated the rate constants k_{H1} and k_{H2} independent of the sulphuric acid concentration (see Table IV.).

Table II Values of observed rate constants k_{obs} (s⁻¹) of the first kinetically measurable step of acid-catalysed hydration of α -alkylstyrenes depending on sulphuric acid concentration c (mol·dm⁻³) in water at 25 °C; the values in the second line are the wavelengths λ (nm) at which the measurements were carried out.

c	Me	Et	Pr	Bu	Pe	<i>iso</i> Bu	<i>iso</i> Pr	<i>sec</i> -Bu	<i>tert</i> -Bu
	250	242	242	246	250	240	238	240	226
1.00	2.64 10 ⁻⁴		2.44 10 ⁻⁴	5.39 10 ⁻⁵		1.13 10 ⁻⁴	1.46 10 ⁻⁴	1.15 10 ⁻⁴	
1.50	6.16 10 ⁻⁴	5.59 10 ⁻⁴	4.93 10 ⁻⁴	1.21 10 ⁻⁴		2.68 10 ⁻⁴	3.90 10 ⁻⁴	2.50 10 ⁻⁴	
2.00	1.34 10 ⁻³	1.19 10 ⁻³	9.26 10 ⁻⁴	2.50 10 ⁻⁴		5.62 10 ⁻⁴	7.26 10 ⁻⁴	4.96 10 ⁻⁴	
2.50	2.61 10 ⁻³	2.24 10 ⁻³	1.83 10 ⁻³	5.59 10 ⁻⁴		1.10 10 ⁻³	1.40 10 ⁻³	1.03 10 ⁻³	
3.01	6.59 10 ⁻³	4.95 10 ⁻³	3.82 10 ⁻³	1.41 10 ⁻³		2.94 10 ⁻³	3.26 10 ⁻³	2.65 10 ⁻³	
3.08					1.57 10 ⁻³				
3.39					1.36 10 ⁻³				
3.50	1.11 10 ⁻²	9.84 10 ⁻³	6.85 10 ⁻³			4.60 10 ⁻³	6.64 10 ⁻³	4.27 10 ⁻³	
3.56	1.21 10 ⁻²	9.92 10 ⁻³	9.18 10 ⁻³			4.62 10 ⁻³	6.55 10 ⁻³	6.72 10 ⁻³	
3.89					2.63 10 ⁻³				
4.09	2.62 10 ⁻²	1.83 10 ⁻²	1.68 10 ⁻²	6.19 10 ⁻³		1.06 10 ⁻²	1.39 10 ⁻²	8.49 10 ⁻³	6.28 10 ⁻⁵

Table II. Cont.

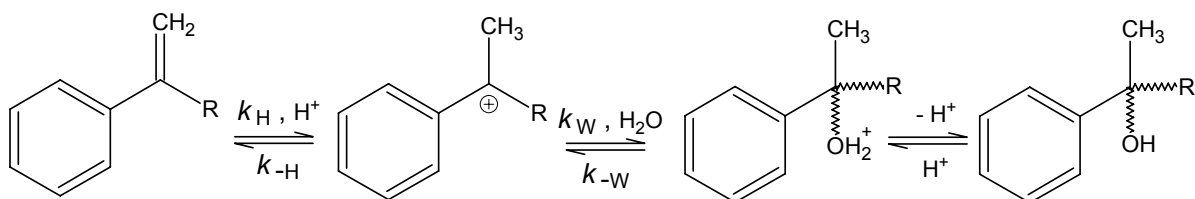
4.44		$3.04 \cdot 10^{-2}$	$3.08 \cdot 10^{-2}$						
4.51	$4.21 \cdot 10^{-2}$	$3.62 \cdot 10^{-2}$	$2.79 \cdot 10^{-2}$	$9.68 \cdot 10^{-3}$		$1.89 \cdot 10^{-2}$	$2.03 \cdot 10^{-2}$	$1.92 \cdot 10^{-2}$	$1.08 \cdot 10^{-4}$
4.82		$4.24 \cdot 10^{-2}$	$4.16 \cdot 10^{-2}$				$2.93 \cdot 10^{-2}$		
5.00	$9.78 \cdot 10^{-2}$	$6.88 \cdot 10^{-2}$	$4.36 \cdot 10^{-2}$	$1.13 \cdot 10^{-2}$		$3.42 \cdot 10^{-2}$	$5.55 \cdot 10^{-2}$	$3.39 \cdot 10^{-2}$	$2.28 \cdot 10^{-4}$
5.10					$8.38 \cdot 10^{-3}$				
5.56					$7.89 \cdot 10^{-3}$				
5.97					$1.72 \cdot 10^{-2}$				
6.89									$5.12 \cdot 10^{-3}$
7.33									$2.02 \cdot 10^{-2}$

Table III Values of observed rate constants k_{obs} (s^{-1}) of the second kinetically measurable step of acid-catalysed hydration of α -alkylstyrenes depending on sulphuric acid concentration c ($\text{mol} \cdot \text{dm}^{-3}$) in water at 25 °C, for the wavelengths λ (nm) at which the measurements were carried out, see Table II.

c	Et	Pr	Bu	Pe	isoBu
2.00	$1.16 \cdot 10^{-4}$	$1.87 \cdot 10^{-4}$			
2.06				$1.35 \cdot 10^{-3}$	
3.01	$6.24 \cdot 10^{-4}$				
3.50	$9.08 \cdot 10^{-4}$	$1.06 \cdot 10^{-3}$			
4.09	$2.31 \cdot 10^{-3}$	$3.59 \cdot 10^{-3}$	$2.30 \cdot 10^{-3}$		$1.57 \cdot 10^{-2}$
4.51	$3.33 \cdot 10^{-3}$	$4.86 \cdot 10^{-3}$	$5.89 \cdot 10^{-3}$		$2.09 \cdot 10^{-2}$
5.00	$1.24 \cdot 10^{-2}$	$1.28 \cdot 10^{-2}$	$2.50 \cdot 10^{-2}$		$3.74 \cdot 10^{-2}$
5.56				$3.34 \cdot 10^{-2}$	
5.97				$5.48 \cdot 10^{-2}$	
6.50				$9.66 \cdot 10^{-2}$	

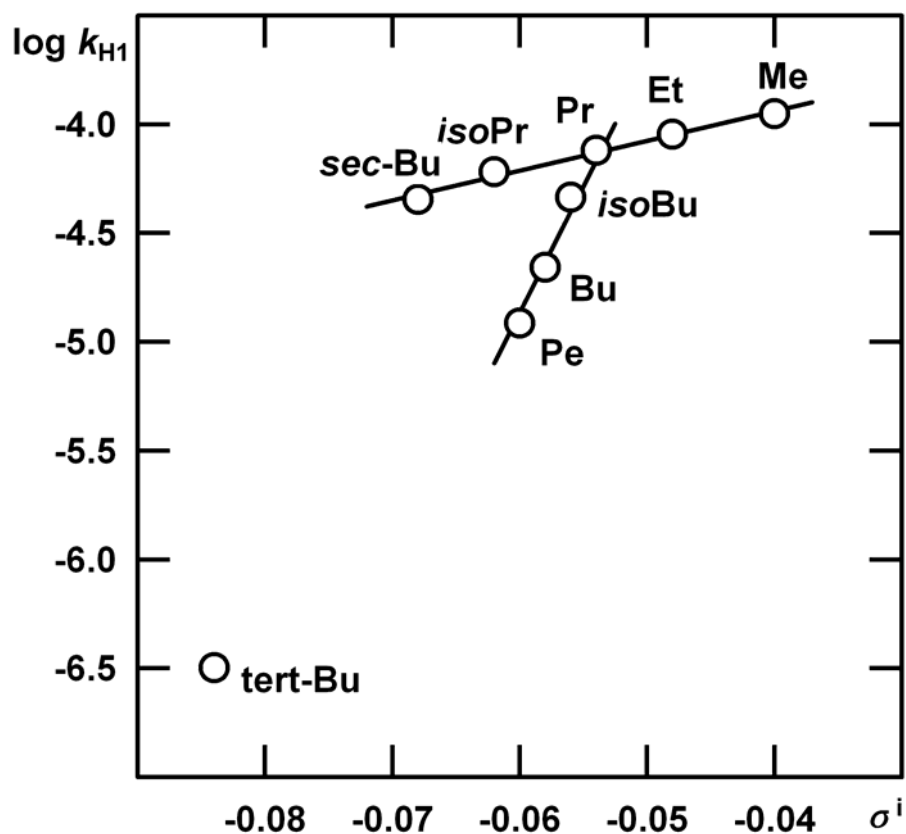
On the basis of known facts and literature data (see Introduction) we verified the reaction mechanism given in Scheme 2.

Scheme 2



The mechanism is composed of a sequence of three elementary reactions, involving addition of proton to the respective styrene, reaction of the carbocation formed with water, and subsequent splitting off of proton with concomitant formation of alcohol. In accordance with earlier studies [27], the effect of medium was evaluated by means of the excess acidity function, and the calculated values of a slope $m^{\ddagger}m^*$ for the first kinetic step are given in Table IV. For a majority of the substitution derivatives, these values agree with literature [27], exceptionally low values being found for butyl and pentyl substituents and an exceptionally high value for *tert*-butyl substituent. The decrease in the value of the slope $m^{\ddagger}m^*$ indicates a lower extent of proton transfer to the substrate in the transition state of the reaction, obviously due to the enhanced stability of the respective carbocation as an intermediate. On the other hand, the high value of the slope $m^{\ddagger}m^*$ found for α -*tert*-butylstyrene shows that in the transition state of the reaction the proton is transferred to the substrate to a high extent, because the respective carbocation is so little stable (the structure of the transition state is similar to that of the carbocation). Obviously, in the case of this substituent the stabilisation of the carbocation by a resonance with the benzene nucleus is impossible as a result of the sterically enforced deviation out of the plane of this nucleus [41, 45].

Figure 2. Dependence of rate constants k_{H1} of acid-catalysed hydration of α -alkylstyrenes upon substituent constants σ^i ; the points are interlaced by regression straight lines.



The dependence of logarithm of the catalytic rate constant k_{H1} upon substituent constants σ^i (AISE theory, [63,64]) is given in Fig. 2. From this diagram it can be seen that the values are divided into two dependences, the value for α -*tert*-butylstyrene occupying a special position. The different position of

this substituent and those of *isobutyl*, *butyl*, *pentyl* substituents corresponds with the different value of the slope $m^{\ddagger}m^*$, as mentioned above. In contrast to both the expectation and the results published about the substitution in the aromatic nucleus [24, 27, 31, 32, 45], the slopes are positive, i.e. the substituents with lower positive inductive effects accelerate the reaction. If Scheme 2 is valid, then the facts observed could be interpreted from two connected, though different, points of view – those of thermodynamics and kinetics.

The thermodynamic point of view is connected with the stability of the carbocation and the rate constants of its formation and decomposition; the kinetic point of view additionally takes into account the concentrations of the reacting components and, hence, the rate-limiting step of the reaction. According to the quantum-chemical calculations in ref. [32] as well as experimental observations [27], the rate constant k_H of the formation of the carbocation in Scheme 1 is lower than the rate constant k_W of the reaction of the carbocation with water as the nucleophile. The rate constant k_{-H} of elimination of proton with concomitant formation of alkene is the lowest among the rate constants given [32], which is connected with the differences in solvation of the uncharged alkene and charged carbocation. On the basis of the substituent effects at α -carbon atom [27, 32, 36, 37, 40, 41], it can justifiably be presumed that the energy of the carbocation decreases with increasing positive inductive effect of the substituent, and as a result, in accordance with the Hammond postulate, the value of the rate constant k_H increases and, on the contrary, the values of the rate constants k_W and k_{-H} decrease. These changes are manifested kinetically, too. In contrast to the solvolytic reactions, in which the carbocation is formed in the rate-limiting step by a monomolecular reaction, the rate of the formation of the carbocation in the acid-catalysed hydration depends not only on the styrene concentration but also on the proton activity, and the reaction is bimolecular. Similarly, the reaction of the carbocation with water is bimolecular, and its rate depends on water activity in the reaction medium. If the acid-catalysed hydration produces a stable cation and if the concentration of the catalysing acid is high, i.e. the proton activity a_H is high and the water activity a_w is low [22], then the $k_H a_H$ value can exceed the $k_W a_w$ value. As a result, the addition of proton to the substrate is faster than the reaction of carbocation with water, and there takes place a change in the rate-limiting step. In such case, the substituent effects are a sum of those for both kinetic steps. The dependence of logarithm of rate constant k_{H1} upon substituent constants σ^i (AISE, [63,64]) for the methyl, ethyl, propyl, *isopropyl* and *sec-butyl* substituents is described by the following equation:

$$\log k_{H1} = -(3.39 \pm 0.05) + (13.68 \pm 0.92)\sigma^i, \quad (6)$$

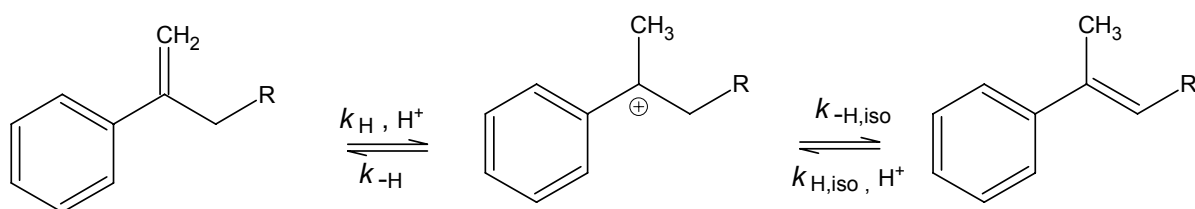
$$n = 5, s = 0.0204, R = 0.9933.$$

For the *butyl*, *isobutyl* and *pentyl* substituents, an estimate of the reaction constant ρ_I has a value of 144.5, the steric effects of the substituents being obviously not manifested (or at least they cannot be evaluated). The given values of the reaction constants exhibit marked differences, indicating differences in the reaction courses. From the relatively low value of the reaction constant ρ_I in Eq. (6) it can be deduced that there occurs superposition of the influence of the substitution on the formation of the carbocation (negative reaction constant [27, 32, 36, 37, 40, 41]) and on its reaction with water (positive reaction constant [43, 44]). Since Eq. (6) concerns such small substituents, and the sensitivity to steric effects described by parameter ψ is small, too, it is obvious that the structure of the carbocation is near to a planar arrangement [36, 41, 45], and the approach of a nucleophile to the reaction centre is not too sterically demanding. In the cases of *butyl*, *isobutyl* and *pentyl* substituents,

the stabilisation of the carbocation by alkyl groups is probably sufficiently efficient (see the discussion of the slope $m^{\ddagger}m^*$ value) and, at the same time, the formation of planar structure is so sterically unfavourable that the side chain is totally or distinctly deviated out of plane of the benzene nucleus. This situation results in the *ortho*-hydrogen substituents in the benzene nucleus becoming the dominant barrier against approach of the water molecule, and the sensitivity to the substitution is simultaneously increased. In the case of α -*tert*-butylstyrene, the alkenyl group is deviated out of plane both in the substrate and in the carbocation [41, 45], and the observed decrease in the rate constant k_{H1} , compared to other α -alkylstyrenes, is due to a steric hindrance to resonance.

The consecutive reaction observed with all the derivatives except α -*tert*-butylstyrene is almost certainly an isomerisation reaction producing more stable substituted styrenes [33-35] according to Scheme 3.

Scheme 3



Therefore, the values of rate constants k_{H2} given in Table IV are identical with the rate constants $k_{-H, iso}$ in Scheme 3. The above-given statements are especially supported by the absence of the consecutive reaction in the case of α -*tert*-butylstyrene, where the proposed isomerisation cannot take place, and also the increase in absorbance in the second step of the consecutive reaction, which indicates a formation of a new conjugated system. The faster the conjugated system formed is the more stable the isomeric styrenes are (Table IV). Therefrom it can be deduced that the structure of the transition state is very close to that of the products [32].

Table IV Rate constants and standard deviations of rate constants k_{HgAc} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), k_{H1} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) and k_{H2} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) and slope $m^{\ddagger}m^*$ for α -*R*-substituted styrenes; for details see the text.

<i>R</i>	k_{HgAc}	k_{H1}	$m^{\ddagger}m^*$	k_{H2}
Me	$(1.35 \pm 0.03) 10^{-2}$	$(1.12 \pm 0.06) 10^{-4}$	1.35 ± 0.01	Indiscernible
Et	$(3.80 \pm 0.07) 10^{-2}$	$(9.00 \pm 0.47) 10^{-5}$	1.13 ± 0.14	$(2.08 \pm 0.55) 10^{-5}$
Pr	$(2.27 \pm 0.05) 10^{-2}$	$(7.60 \pm 0.33) 10^{-5}$	1.32 ± 0.13	$(2.83 \pm 0.43) 10^{-5}$
Bu	$(2.79 \pm 0.05) 10^{-2}$	$(2.20 \pm 0.21) 10^{-5}$	1.02 ± 0.27	$(3.66 \pm 0.22) 10^{-5}$
Pe	$(3.86 \pm 0.07) 10^{-2}$	$(1.22 \pm 0.08) 10^{-5}$	0.73 ± 0.35	$(1.17 \pm 0.16) 10^{-4}$
<i>iso</i> -Bu	$(8.30 \pm 0.03) 10^{-3}$	$(6.04 \pm 0.06) 10^{-5}$	1.25 ± 0.11	$(1.21 \pm 0.12) 10^{-4}$
<i>iso</i> -Pr	$(3.81 \pm 0.03) 10^{-3}$	$(4.62 \pm 0.58) 10^{-5}$	1.27 ± 0.14	very slow
<i>sec</i> -Bu	$(3.05 \pm 0.03) 10^{-3}$	$(4.51 \pm 0.17) 10^{-5}$	1.31 ± 0.19	very slow
<i>tert</i> -Bu	$(7.83 \pm 0.03) 10^{-3}$	$(2.29 \pm 0.07) 10^{-8}$	3.28 ± 0.97	Insensitive

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Experimental

Syntheses of Compounds Studied

The α -alkylstyrenes with methyl (Me), ethyl (Et), propyl (Pr), butyl (Bu), pentyl (Pe), *isobutyl* (*isoBu*), *isopropyl* (*isoPr*) and *sec-butyl* (*sec-Bu*) substituents were prepared by the Wittig reaction, under inert atmosphere of argon, from the respective alkylphenylketones and the methyltriphenylphosphonium ylide generated *in situ*. The starting alkylphenylketones were prepared by reactions of benzonitrile with the corresponding alkylmagnesium bromides. α -*tert*-butylstyrene (*tert-Bu*) was prepared by reaction of phenylmagnesium bromide with pinacolone and subsequent dehydration by means of vacuum distillation with phosphorus pentoxide. The styrenes were purified by *dry-flash* chromatography (silica gel/petroleum ether) with a subsequent vacuum distillation. The purity of the α -alkylstyrenes prepared was checked by HPLC (Ecom LCP4000.2 pump, Ecom LCD 2084.1 detector, 150x4.6 mm Kromasil 100-7 μ m column, C18, mobile phase ethanol/water 75:25 v/v, flow 1.0 cm³·min⁻¹) with UV detection and by comparing the refractive index with literature data; their identification was carried out by ¹H-NMR spectroscopy (Bruker AMX 360, 360.14 MHz for ¹H) in CDCl₃ at laboratory temperature: α -methylstyrene: δ 7.46 – 7.21 (m, 5H), 5.34 (s, 1H), 5.05 (s, 1H), 2.09 (s, 3H); α -ethylstyrene: δ 7.43 – 7.23 (m, 5H), 5.27 (s, 1H), 5.06 (dd, J = 2.9 Hz and 1.5 Hz, 1H), 2.51 (bm, J = 7.4 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H); α -propylstyrene: δ 7.46 – 7.38 (m, 2H), 7.37 – 7.23 (m, 3H), 5.26 (d, J = 1.7 Hz, 1H), 5.05 (dd, J = 2.9 Hz and 1.4 Hz, 1H), 2.46 (bt, J = 7.4 Hz, 2H), 1.48 (sextet, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); α -butylstyrene: δ 7.40 – 7.22 (m, 5H), 5.20 (d, J = 1.5 Hz, 1H), 5.05 (d, J = 1.5 Hz, 1H), 2.50 (t, J = 6.6 Hz, 2H), 1.43 (m, 2H), 1.35 (m, 2H), 0.88 (t, J = 7 Hz, 3H); α -pentylstyrene: δ 7.60 – 7.57 (m, 2H), 7.50 – 7.41 (m, 3H), 5.45 (d, J = 1.6 Hz, 1H), 5.24 (dd, J = 2.8 Hz and 1.4 Hz, 1H), 2.68 (td, J = 7.5 Hz and 1 Hz, 2H), 1.65 (m, 2H), 1.49 (m, 4H), 1.07 (t, J = 7 Hz, 3H); α -iso-propylstyrene: δ 7.37 – 7.19 (m, 5H), 5.13 (dd, J = 1.4 Hz and 0.6 Hz, 1H), 5.03 (t, J = 1.4 Hz, 1H), 2.84 (bseptet, J = 6.9 Hz, 1H), 1.11 (d, J = 6.9 Hz, 6H); α -iso-butylstyrene: δ 7.38 – 7.20 (m, 5H), 5.23 (d, J = 1.8 Hz, 1H), 5.00 (d, J = 1, 1 Hz, 1H), 2.36 (dd, J = 7.2 Hz and 0.8 Hz, 2H), 1.64 (nonet, J = 6.8 Hz, 1H), 0.85 (d, J = 6.6 Hz, 6H); α -sec-butylstyrene: δ 7.38 – 7.25 (m, 5H), 5.21 (s, 1H), 5.05 (s, 1H), 2.64 (septet, J = 7.2 Hz, 1H), 1.64 – 1.52 (m, 1H), 1.42 – 1.29 (m, 2H), 1.15 (dd, J = 6.9 Hz and 1.9 Hz 3H), 0.91 (td, J = 7.3 Hz and 2 Hz, 3H); α -tert-butylstyrene: δ 7.32 – 7.20 (m, 3H), 7.17 – 7.10 (m, 2H), 5.17 (d, J = 1.7 Hz, 1H), 4.76 (d, J = 1.7 Hz, 1H), 1.11 (s, 9H). The pure styrene derivatives were kept in sealed ampoules. The boiling points, refractive indexes and yields of the styrenes prepared are presented in Table V.

Table V. Physical properties of synthesised α -alkylstyrenes and yields of syntheses with respect to starting ketones.

<i>R</i>	b.p.[°C]/press[torr], exp.	b.p.[°C]/press[torr], lit.	n_D (20 °C), exp.	n_D (20 °C), lit.	Yield, %
Me	59-61/20	52-60/15 [47]	1.525	1.536 [53]	78
Et	76-79/20	73-74/15 [48]	1.525	1.527 [54]	60
Pr	78-82/10	77-78/10 [49]	1.514	1.521 [55]	68
Bu	80-85/05	89-90/10 [50]	1.523	1.523 [56]	83
Pe	65-70/ 1	93-95/10 [51]	1.511	1.510 [57]	90
<i>iso</i> -Pr	72-78/10	71-72/10 [49]	1.514	1.518 [57]	51
<i>iso</i> -Bu	74-79/ 5	83-84/10 [49]	1.511	1.510 [58]	48
<i>sec</i> -Bu	74-80/ 5	-	1.510	-	42
<i>tert</i> -Bu	84-90/10	73/10 [52]	1.502	1.499 [59]	14

Kinetic Measurements

The kinetics of methoxymercuration were measured in a solution of anhydrous acetic acid obtained by mixing one part of a $1.75 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ solution of the respective α -alkylstyrene (kept at the constant temperature of 25.0 °C) with two parts of the mercuric acetate solution with concentration ranging from $7.5 \cdot 10^{-3}$ to $3.0 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ at the same temperature. The cell containing the reaction mixture was placed in a thermostated block of a Beckman DU 7500 UV-VIS spectrophotometer, and the decreasing absorbance of styrene was measured at $25.0 \pm 0.1 \text{ °C}$ for a period of at least 5 reaction half-lives. The wavelengths used in these kinetic measurements are given in Table I for the individual α -alkylstyrenes. The kinetics of the reactions with added sodium acetate was measured in the same way. The water content in the acetic acid used (Sigma-Aldrich) was 0.06 % (determined by the Karl Fischer method).

The kinetics of acid-catalysed hydration was measured in 10% v/v methanol solutions (needed for dissolution of styrene) in aqueous sulphuric acid within the concentration range from 1.00 to 7.33 $\text{mol} \cdot \text{dm}^{-3}$. A glass cell was charged with the sulphuric acid solution at the above-mentioned temperature, and a 10 μl methanolic styrene solution of suitable concentration was added by means of a micro-syringe, whereupon the mixture was thoroughly shaken. The cell was placed in the block of a HP34556 UV-VIS spectrophotometer kept at constant temperature, and the absorbance decrease was followed at $25.0 \pm 0.1 \text{ °C}$ for a period of at least 5 reaction half-lives. The wavelengths used for the kinetic measurements of individual styrenes are given in Table II.

Mathematical-Statistical Treatment of Results

The observed rate constants were calculated for monotonous absorbance-time dependences (all the acetoxymercurations and some of the acid-catalysed hydrations) by standard procedures using the model of pseudo-first-order reaction. The observed rate constants in the reactions with two kinetically manifested steps (some of the acid-catalysed hydrations) were evaluated by a non-linear regression

using the model of the consecutive reactions. The catalytic rate constants of acid-catalysed hydration together with the corresponding acidity functions [23, 61] were calculated by a procedure described elsewhere [62]. All the other dependences presented in this paper were evaluated by linear or non-linear regressions using standard calculation procedures.

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