KINETICS AND MECHANISM OF ACID CATALYSED HYDRATION OF α-METHYLSTYRENES

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*This work is dedicated to Professor Štefan Toma on the occasion of his 70th birthday.*

Twelve *para*-substituted α-methylstyrenes with substituents H, CH_3, CF_3, CH_3O, CH_3S, F, Cl, Br, CH_3CO, CH_3SO_2, CN a NO_2 were synthesised; additionally, the acid catalysed hydration kinetics of these compounds were measured in sulfuric acid in a concentration range *c* from 0.017 to 9.58 mol l^{-1}, at 25.0 °C. The observed rate constants obtained were used to construct the kinetic acidity function and calculate the catalytic rate constants. Based on the evaluation of the acidity function kinetic dependence on acid medium concentration, and the substituent effects of acid catalysed hydration of α-methylstyrenes on the catalytic rate constants, the mechanism of acid catalysed hydration was verified. The mechanism involves the addition of a proton to the double bond of α-methylstyrene in the rate-limiting reaction step denoted as A-S$_E$2. No evident difference was found between the effects of the acid medium on the acid catalysed hydration of styrenes and α-methylstyrenes, which indicates very similar activity coefficients of the reactants, and of the transition state of both substrates. The substituent effects evaluation shows that the rate-limiting step of the reaction consists in the addition of a proton to the substrate. The carbocation formation in the transition state of this reaction step proceeds roughly half-way compared with the extent of the carbocation formation by cumyl chloride hydrolysis. The obtained carbocation is in particular stabilised by the substituents with +*M* effect, while the influence of the substituents with –*M* and *I* effects is significantly smaller.
Keywords: Styrenes; Kinetics; Mechanism; Substituent effects; Kinetic acidity functions; Hammett equation; Carbocations.

The acid catalysed hydration kinetics of several ring-substituted α-methylstyrenes is discussed only in two previous papers[1,2]; the latter[2] suggests a reaction mechanism involving a slow proton transfer to styrene and the subsequent fast reaction with water. The mechanism is shown in Scheme 1.
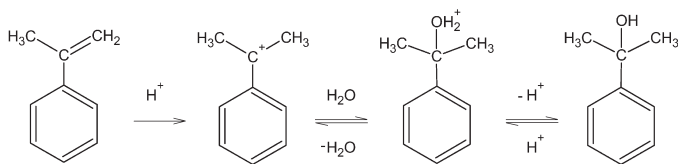
SCHEME 1

Three basic factors are decisive in the evaluation and verification of the α-methylstyrenes acid catalysed hydration mechanism: (i) the dependence on the concentration of the acid, (ii) the stability of 2-phenylpropan-2-yl carbocation as the expected intermediate formed in the rate-limiting step, and (iii) the operation of isotope effects.

The acid concentration dependence is characterised particularly by the activity of the solvated proton (or general acid), water and other components of the medium, substrate and the carbocation as the intermediate.

The A-S$_E$2 mechanism for the acid catalysed hydration was confirmed by evaluating the dependence of the observed rate constants on the acidity of the medium, characterised by Hammett and excess acidity functions[8,9]. The results were compared with similar studies for styrenes[3–6] and α-(trifluoromethyl)styrenes[7]. The dependence of the observed rate constant logarithm on the acidity function H_0 was found to be linear with a slope close to 1 (1.08–1.28 (ref.[3]), 1.03 (ref.[5])). The observed slopes of dependences of the rate constants logarithms, evaluated by means of the Cox–Yates excess acidity function for sulfuric acid ($m^{\ddagger}m^*$) with individual substituted α-methylstyrenes, were found to vary within the range of 1.154–1.660 (with styrenes, the range is 1.332–1.490). According to the author's[8] interpretation, these values indicate an advanced proton transfer on styrene in the transition state of the first reaction step.

A key point of the acid catalysed hydration kinetics and mechanism is the stability of the 2-phenylpropan-2-yl cation. In the case that stable products are formed in the subsequent rapid reaction step, the low carbocation concentration in the reaction medium results in a higher observed rate constant. According to quantum chemical calculations[10], the energy of the solvated 1-phenylethan-1-yl carbocation is lower than that the energy of the styrene complex with hydrated proton, being only slightly higher than the energy of protonated 1-phenylethan-1-ol. The stability of 2-phenylpropan-2-yl carbocation[11–14] and, generally, of substituted benzyl carbocation[11–13,15–17] depends on the substitution at α-position[15,17], the substitution in the ring[11–14,16,17], and on the solvation[18,19].

Hydration rate dependence studies of the ring-substituted α-methylstyrenes on substitutent constants were undertaken. For correlation of the measured rate constants, the σ^+ substituent constants are more appropriate. The reaction constants ρ^+ vary in the range from –3.21 to –4.51 (refs[1,3,4,6,8,20]). The magnitude of the reaction constant and the dependence on the σ^+ substituent constants indicate a significant extent of proton transfer to styrene in the transition state of the rate-limiting step. Generally, the reaction constant in acid catalysed hydration of styrenes is lower than in solvolytic reactions (SN1) with the same carbocation intermediates[12,13,20]. This is obviously due to the difference in the electron density deficit at the reaction centre in the transition state of the hydration and solvolysis and the extent of solvation stabilisation of this transition states.

The existence of kinetic isotope effect in acid catalysed hydration of α-methylstyrene[2,8] forms another piece of evidence in favour of the proton transfer to the substrate as the rate-limiting step of the reaction. The reactions using α-deuterated or β,β-dideuterated styrenes did not reveal any isotope exchange of deuterium[21], hence the carbocation cannot be formed in a rapid pre-equilibrium.

The mechanism of acid catalysed hydration of styrenes can be considered experimentally well based and verified. Although it is possible to accept the same mechanism also in the case of α-methylstyrenes, there is not sufficient experimental evidence for this conclusion. Therefore, the aim of this paper is to evaluate the effect of the acid medium and substitution on the acid catalysed hydration of α-methylstyrenes as well as to confirm the existence of the A-SE2 mechanism for these substrates.

EXPERIMENTAL

Syntheses of α-Methylstyrenes

The α-methylstyrenes with *para*-substituents H, CH$_3$, CF$_3$, CH$_3$O and NO$_2$ were prepared by known procedures[22–25]. The α-methylstyrenes with *para*-substituents F, CN, CH$_3$S, CH$_3$CO and CH$_3$SO$_2$ were synthesised by dehydration of the corresponding 2-phenylpropan-2-ols in the presence of phosphoric acid (procedure *A*) or phosphorus pentoxide (procedure *B*). 4-Bromo-α-methylstyrene was prepared by the Wittig reaction (procedure *C*). 2-(4-Chlorophenyl)propene was obtained by purification of a commercial sample.

Procedure A: A 10-ml flask was filled with 0.03 mol of the respective alcohol and 0.4 ml (0.006 mol) of 85% trihydrogenphosphoric acid. The reaction mixture was refluxed under reduced pressure for 30 min. Then the product was distilled off through a column.

Procedure B: The same as procedure *A*, but using a catalytic amount of phosphorus pentoxide instead of trihydrogenphosphoric acid.

Procedure C: A 500-ml three-necked flask equipped with an inlet of inert gas (argon) was filled with 18.4 g (0.16 mol) of potassium *tert*-butoxide and 57.4 g (0.16 mol) of methyltriphenylphosphonium bromide. Then 60 ml of phenetol was added while stirring. The components partially dissolved, whereupon 10 ml of dry toluene was added, and the solution was stirred at room temperature for 1 h. Then, the stirred reaction mixture was treated with a solution of 10 g (0.05 mol) of 4-bromoacetophenone in 30 ml of dry toluene, added dropwise within 40 min, keeping the temperature at 20–25 °C. The reaction was monitored by TLC (silica gel; benzene–ethyl acetate 95:5), using detection with iodine vapour. After the reaction was complete (about 2 h), the reaction mixture was quenched by pouring onto a solution of 45 g of ammonium chloride in 150 ml of water. The organic phase was separated, diluted with 50 ml of benzene, and extracted with water several times. After drying the organic phase with anhydrous sodium sulfate and concentrating it in vacuum evaporator, phenetol was removed by vacuum distillation. The crude product was purified by column chromatography (silica gel; benzene–ethyl acetate 95:5). The pure product was obtained by fraction distillation. Yield 4.2 g (42%).

The structure of all the products prepared was confirmed by ^{1}H NMR spectrometry (Bruker AMX-360 spectrometer). The purity was verified by liquid chromatography (HPLC Separon SGX c18, system methanol–water), and comparing the experimental physical characteristics with those given in literature (Tables I and II).

Kinetic Measurements

To a cell containing 2 ml of aqueous sulfuric acid (c = 0.017–9.58 mol l^{-1}), 2–5 µl of α-methylstyrene solution in methanol was added at 25 ± 0.1 °C. The cell content was mixed, and the absorbance decrease was monitored at suitable wavelengths (Tables I and II)

TABLE I
Synthesis, purity, physical properties and wavelengths of liquid *para*-substituted α-methylstyrenes used in kinetic runs

X	Synthesis	Purity[a]	B.p., °C/kPa		n_D^{20}		λ, nm
			Exp.	Ref.	Exp.	Ref.	
CH$_3$	ref.[23]	99.3	30–31/0.2	48–49/0.5[b]	1.5349	1.5352[c]	252
F	A	98.4	41–42/1.0	50–51/0.9[d]	1.5122	1.5120[e]	244
H	ref.[22]	99.4	56–58/2.4	69–69.2/3.6[f]	1.5380	1.5383[f]	246
Cl	–[g]	99.0	30–30.5/0.2	78–80/1.1[e]	1.5570	1.5559[e]	252
Br	C	98.6	75–76/0.5	77–79/0.5[h]	1.5816	1.5830[c]	254
CF$_3$	ref.[24]	99.3	68–68.5/2.0	63/2.0[i]	1.4685	1.4668[i]	250
CN	B	99.4	76–77/0.4	86–87.5/0.3[e]	1.5682	1.5680[e]	266

[a] HPLC Separon SGX c18, system methanol–water; [b] ref.[26]; [c] ref.[27]; [d] ref.[28]; [e] ref.[29]; [f] ref.[30]; [g] product of Aldrich; [h] ref.[25]; [i] ref.[31]

with UV-VIS spectrophotometer HP 8452A for a period of at least 5 half-lives. The kinetic dependences obtained were treated with a known algorithm[35] to calculate the observed rate constants, k_{obs}.

Construction of the Kinetic Acidity Function

The obtained dependences of the observed rate constants k_{obs} on the sulfuric acid concentration were treated with a known algorithm[36] to construct the kinetic acidity function.

TABLE II
Synthesis, purity, solvents used for recrystallisations, physical properties and wavelengths of solid *para*-substituted α-methylstyrenes used in kinetic runs

| X | Synthesis | Purity[a] | Solvent[b] | M.p., °C | | B.p., °C/kPa | | λ nm |
				Exp.	Ref.	Exp.	Ref.	
CH₃O	ref.[25]	98.9	h	30–32	32–34[c]	44–45/0.1	61–62/0.2[d]	256
CH₃S	A	98.8	w/e	48–49.5	51[e]	100–110/0.3	85/0.1–0.3[e]	278
CH₃CO	B	99.6	w/e	50–51	52–53[f]	83–87/0.4	125–126/1.3[g]	292
CH₃SO₂	B	99.7	w/e	70–71	–	–	–	262
NO₂	ref.[25]	99.6	e	49–50.5	51–53[c]	87–88/0.1	106–107/0.2[c]	328

[a] HPLC Separon SGX c18, system methanol–water; [b] solvents for recrystallisation: h heptane, w/e water–ethanol 1:1, e ethanol; [c] ref.[25]; [d] ref.[26]; [e] ref.[32]; [f] ref.[33]; [g] ref.[34]

RESULTS AND DISCUSSION

The Kinetic Acidity Function

The log k_{obs} values of acid catalysed hydration of 4-substituted α-methylstyrenes at various concentrations of sulfuric acid were used for the construction[36] of the kinetic acidity function[37] H, whose dependence on the sulfuric acid concentration is presented in Fig. 1. For comparison, the same figure also presents the H_0 acidity function obtained with substituted anilines in the same medium[38]. The relation between the acidity functions H and H_0 is described by the equation:

$$H = (9.41 \pm 1.65) \times 10^{-2} + (1.24 \pm 0.01)H_0 \qquad (1)$$

$$n = 52, \ s = 8.27 \times 10^{-2}, \ R = 0.9993.$$

The slope of the dependence on the acidity function H_0 is close to the values given in literature for styrenes (1.08–1.28 (ref.[3]), 1.27–1.56 (ref.[4]),

1.26 (ref.[21])), α-methylstyrenes (1.20 (ref.[5])) and α-(trifluoromethyl)styrenes (1.02–1.51 (ref.[7])). More precise information about acid catalysed hydration of α-methylstyrenes is obtained by introducing additional quantities into the regression, characterising the reaction medium (logarithm of water activity, log a_w (ref.[9])) and the logarithm of hydrogensulfate ion concentration (log $c_{HSO_4^-}$, ref.[9]). The dependence of the acidity function is then described statistically by the tighter relation:

$$H = (0.577 \pm 0.124) + (1.22 \pm 0.02)H_0 -$$

$$- (0.327 \pm 0.069)\log a_w - (0.134 \pm 0.025)\log c_{HSO_4^-} \qquad (2)$$

$$n = 52, \; s = 2.97 \times 10^{-2}, \; R = 0.9999.$$

From Eq. (2) it follows, that the acidity function decreases with increasing concentration of the hydrogensulfate anion, which can be explained by the salt effect of this anion on proton as the reactant. The acidity function decreases with decreasing water activity, the slope being lower than the one usually (not quite correctly) given[4,5], see slope 1. From the standpoint of kinetics, the reaction of carbocation with water, giving alcohol and proton, can be considered as a fast consecutive equilibrium. The decreasing water activity and increasing proton activity shift the equilibrium in the direction of the starting compounds; the carbocation concentration in the reaction mixture increases. Due to that, the slow reverse reaction of carbocation de-
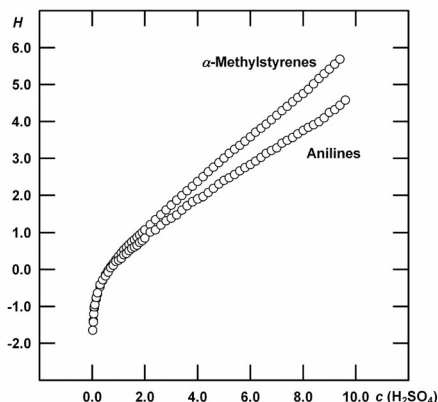

FIG. 1
Comparison of kinetic acidity function based on α-methylstyrenes with acidity function based on anilines in water at 25 °C

composition to styrene and proton becomes more kinetically significant and the observed rate constant decreases. However, from Eq. (*2*) it cannot be inferred whether the dependence of the observed rate constant on water activity is due to the reaction mechanism or lower carbocation stabilisation by water molecules[18].

The dependence of acidity function H on the Yates–Cox excess acidity function X (refs[39–41]) is:

$$H = (2.31 \pm 1.72) \times 10^{-2} + (0.996 \pm 0.020) \log c_{HSO_4^-} +$$

$$+ (1.39 \pm 0.01)X \tag{3}$$

$$n = 52, \ s = 7.29 \times 10^{-2}, \ R = 0.9995.$$

Statistically, the slope of the dependence of $\log k_{obs}$ on the proton concentration logarithm is significantly equal to 1. The slope $m^{\ddagger}m^*$ in Eq. (*3*) lies in the interval from 1.15 to 1.66 given for substituted α-methylstyrenes[1,2] in literature[8]. According to the literature studies[8], this validates the mechanism of acid catalysed hydration A-S$_E$2.

Catalytic Rate Constants

The construction of the acidity function by the algorithm[36] provides simultaneously logarithms of catalytic rate constants for all the substitution derivatives; the values are presented in Table III along with their standard deviations. The values of the standard deviations are lower than in the usual correlations for the evaluation of substituent effects (0.06 logarithmic units[42]).

T{\scriptsize ABLE} III
Logarithms of catalytic rate constants, k_H, for *para*-substituted α-methylstyrenes

X	$\log k_H$	X	$\log k_H$	X	$\log k_H$	X	$\log k_H$
CH$_3$O	−1.895±0.021	F	−3.698±0.032	Br	−4.367±0.018	CN	−6.320±0.031
CH$_3$S	−2.709±0.032	H	−3.842±0.020	CH$_3$CO	−5.627±0.027	CH$_3$SO$_2$	−6.628±0.025
CH$_3$	−2.928±0.015	Cl	−4.261±0.029	CF$_3$	−5.668±0.030	NO$_2$	−6.778±0.024

Evaluation of Substituent Effects

The substituent effects on the addition of proton to styrene and its derivatives are interpreted by the Hammett equation with σ_p^+ constants[1,11,19] or by the Yukawa–Tsuno equation[12-14].

The dependence of catalytic rate constants on the substituent constants σ_p^+ is described by the relation:

$$\log k_{obs} = -(4.11 \pm 0.07) - (3.07 \pm 0.14)\sigma_p^+ \qquad (4)$$

$$n = 12, \; s = 2.42 \times 10^{-1}, \; R = 0.990$$

and, using the Yukawa–Tsuno equation, by the relation:

$$\log k_{obs} = -(3.75 \pm 0.06) - 3.75 \pm 0.11[\sigma_p + (0.46 \pm 0.06)(\sigma_p^+ - \sigma_p)] \quad (5)$$

$$n = 12, \; s = 9.65 \times 10^{-2}, \; R = 0.999$$

or with σ_p^0

$$\log k_{obs} = -(3.74 \pm 0.07) - (3.75 \pm 0.14)[\sigma_p^0 + (0.55 \pm 0.06)(\sigma_p^+ - \sigma_p^0)] \quad (6)$$

$$n = 12, \; s = 1.18 \times 10^{-1}, \; R = 0.998.$$

Comparing the equations, the first one (*4*) interprets the data with less accuracy and does not describe the substituent effects in a relevant way. An estimate of the reaction constant evaluated by means of the Hammett equation using the substituent constants σ_p^+ is –3.21 (ref.[1]). According to residual standard deviation *s*, Eqs (*5*) and (*6*) are closer than those given in ref.[13] for the same reaction ($\rho^+ = -2.92$, $s = 0.146$). The values of reaction constant ρ^+ depend on the substitution at α-carbon atom[13] (styrene, $H_2O–H_2SO_4$, $\rho^+ = -3.69$, $s = 0.21$; α-CF_3-styrene, $H_2O–H_2SO_4$, $\rho^+ = -5.36$, $s = 0.176$; α-MeO-styrene, $H_2O–H_2SO_4$, $\rho^+ = -2.26$, $s = 0.118$). Our measured reaction constants are somewhat higher than the above-mentioned ones, which can be due to the different selection of substituents in the correlation.

The values of reaction constants indicate the attack of an electrophile on the reaction path from the educts to the transition state of the rate-limiting step. Regarding the magnitude of the reaction constant, this step must be the first one in the mechanism given in Scheme 1: in this step, an electron deficit is developing at the α-carbon atom of the side chain. The value of *r* in Eq. (*5*) or Eq. (*6*) provides further data; it indicates a lower extent of carbocation formation in the transition state of the reaction, compared

with the reference value for solvolyses of cumyl chlorides. From the value of the parameter r in Eq. (5) or Eq. (6) follows that in the transition state of the reaction, proton transfer to α-methylstyrene occurs to about half of the extent compared with the splitting of C–Cl bond by solvolyses of cumyl chloride. The comparison[13] of the same value for α-(trifluoromethyl)-styrenes ($r = 1.00$) and α-methoxystyrenes ($r = 0.42$) shows that the extent of the proton transfer in the transition state of the reaction is markedly affected by the substitution at the α-carbon atom of styrene.

The dependence of the logarithm of catalytic rate constants on the substituent constants σ_I and σ_R^+ is described by the relation:

$$\log k_{obs} = -(3.95 \pm 0.15) - (4.16 \pm 0.32)\sigma_I - (2.94 \pm 0.16)\sigma_R^+ \qquad (7)$$

$$n = 12, \; s = 2.27 \times 10^{-1}, \; R = 0.992.$$

The correlation is not as close as in Eq. (5), the deviating points being those for substituents CH_3S and CH_3O. Probably, this is due to a lower reliability of some of the substituent constants of the groups used in the calculation. According to Eq. (7), the influence of the inductive effect on the rate constant is higher than that of the mesomeric effect; this is the case even after omitting the deviating points. This conclusion does not quite agree with the idea of significant conjugation between the positively charged reaction centre at α-carbon atom and the substituents. Obviously, this type of correlation does not describe in an entirely relevant way the substituent effect on acid catalysed hydration of α-methylstyrenes.

The dependence of the catalytic rate constants logarithms on substituent constants, according to the AISE theory[43], is presented in Fig. 2 and described by Eq. (8):

$$\log k_{obs} = -(6.46 \pm 0.16) - (5.68 \pm 0.32)_I[\sigma^i - (0.521 \pm 0.027)] -$$

$$- (15.1 \pm 1.4)_N[\sigma^i - (0.521 \pm 0.027)] -$$

$$- (3.58 \pm 0.81)_E[\sigma^i - (0.521 \pm 0.027)] \qquad (8)$$

$$n = 10, \; s = 0.198, \; R = 0.995.$$

Considering the dependence on Fig. 2 and Eq. (8) it is clear, that the carbocation stability depends on the substituents denoted by AISE theory as inner nucleophiles (N, the IInd class including CH_3O, CH_3S, F, Cl and Br). The corresponding rate constant is roughly 2.5 times higher compared with

the rate constant for the substituents accompanied solely by inductive effect (I, the Ist class including CH_3, H and CF_3). The carbocation stabilisation by the substituents with $+M$ effect is certainly more significant (dominant) compared with the stabilisation by the substituents with I effect. The rate constant for the substituents denoted by AISE theory as inner electrofiles (E, the IIIrd class including CH_3CO, CH_3SO_2, CN and NO_2) is least, while this rate constant differs slightly (statistically significantly) from the constant of the substituents accompanied solely by inductive effect. A mesomeric interaction of these substituents with a reaction centre is therefore not significant.
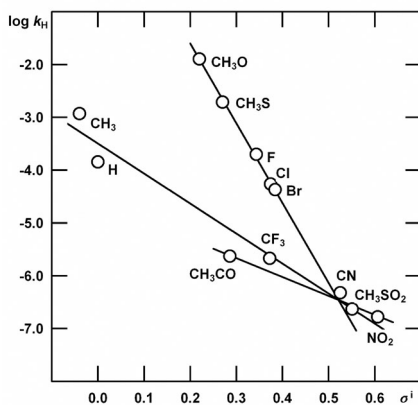

Fig. 2

Dependence of logarithm of catalytic rate constant, log k_H, on substituent constants σ^i, according to AISE theory

CONCLUSIONS

Based on the evaluation of the dependences of both the kinetic acidity function on the acid medium characteristics and the substituent effects on the catalytic rate constants of acid catalysed hydration of α-methylstyrenes, it is possible to confirm the mechanism suggested earlier for this reaction given in Scheme 1. No evident difference was found between the effect of the acid medium on acid catalysed hydration of styrenes and α-methylstyrenes, which indicates very similar activity coefficients of educts and transition states with both substrates. From the evaluation of substituent effects follows that the rate-limiting step of the reaction consists in the addition of proton to the substrate. The extent of the bond formation between proton and the β-carbon atom of α-methylstyrene in the transition

state of the proton-to-substrate transfer is about half of the extent of splitting of the C–Cl bond in solvolyses of cumyl chlorides. The reactivity is fundamentally affected by the electron density at the α-carbon atom of α-methylstyrene and by the mesomeric stabilisation of the electron deficit at the reaction centre of the transition state, exclusively provided by substituents with the +*M* effect.

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