ortho-EFFECT ON THE ACID-CATALYZED HYDRATION OF 2-SUBSTITUTED α-METHYLSTYRENES

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Dedicated to the memory of Professor Otto Exner.

α-Methylstyrene and nine *ortho*-substituted analogs have been synthesized and the kinetics of their acid-catalyzed hydration in aqueous solutions of sulfuric acid at 25 °C have been investigated. The kinetic acidity function H_S has been constructed from the dependence of the observed rate constants k_{obs} on the sulfuric acid concentration. The catalytic rate constants of the acid-catalyzed hydration k_{ortho} have been calculated as well. The identical shape of the kinetic acidity functions for *ortho*- and *para*-derivatives confirms what the consistent mechanism A-SE2 of the acid-catalyzed hydration has already proved for the corresponding *para*-derivatives. The A-SE2 mechanism involves a rate-determining proton transfer of the hydrated proton to the substrate. From the dependence of the catalytic rate constants of the *ortho*-derivatives on the catalytic rate constants of the *para*-derivatives, it is seen that the logarithm of the catalytic rate constant for hydrogen as a substituent is markedly out of the range of the other substituents and, simultaneously, that the *ortho*-derivatives react significantly slower than the corresponding *para*-derivatives. In correlation with the substitent constants σ_p^+, a reaction constant of $\rho^+ = -1.45$ have been found. The constant is, in absolute value, considerably smaller than that for *para*-derivatives ($\rho^+ = -3.07$). In parallel, the steric effects are enforced more significantly for the monoatomic substituents (slope of the Charton's constants 3.92) than for substituents including more atoms (slope of the Charton's constants 2.09). A small value of the reaction constant ρ^+ has been elucidated due to the lower conjugation between the reaction centre and the benzene ring as a consequence of the geometric twist of the reaction centre out of the main aromatic plane accompanied by fading mesomeric interaction between the reaction centre and the substituents attached to the benzene ring. The isopropyl group in the carbocation is twisted less out of the aromatic plane for the monoatomic substituents and, therefore, also a small difference in the bulk of substituents has considerable steric influence on the conjugation between the carbocation and the benzene ring bearing substituents. On the contrary, the isopropyl group in the carbocations with polyatomic substituents is twisted to such a degree that changes in the bulk of substituents affect the resonant stabilization negligibly. Similar conclusions were also deduced from the correlations of the substitution constants σ_I and σ_R^+.

Keywords: Styrene; Acidity function; Substituent effects; *ortho*-Effect; Kinetics; Hydration.

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The study of the kinetics and mechanisms of the acid-catalyzed hydration of 4-substituted α-methylstyrenes based on the evaluation of kinetic acidity functions and substitution effects has recently been reported[1]. The mechanism referred to as A-SE2 involves an addition of the proton to the double bond of α-methylstyrene and the formation of the cumyl cation in the rate-determining step. As has been shown, the stability of a cumyl cation[1–5], or generally substituted benzyl carbocation[2–4,6–8], plays an important role in this reaction. The stability of such carbocations is determined by the substrate structure and depends in particular on the substitution at the α-position[6,8], the substitution of the benzene ring[1–4,7,8], and also on the solvation. The influence of the substitution of the aromatic ring on the carbocation stability is certainly considerable. For such reactions, the substitution constants σ_p^+ are the most suitable correlative variables, whereas the reaction constants ρ^+ range from –3.21 to –4.51 (refs[1,11–16]). The reaction constants and their dependence on the substitution constants σ_p^+ indicate a significant degree of proton transfer to the styrene in the transition state of the rate-determining step of the reaction.

The physicochemical properties of *ortho*-substituted α-methylstyrenes, in comparison with the *meta*- and *para*-substituted analogs, so far have not been systematically investigated. Most attention has been paid to the 2-methyl derivatives (UV/Vis[17,18], fluorescence[19,20], IR[17,21], Raman[21], NMR[22–24] spectroscopy; kinetics[25,26], dipole moment[27], refractometry[28], basicity in the gas phase[29] as well as quantum-chemical calculations[20,21,26]) and less to the 2-fluoro derivatives (kinetics[30,31], dipole moment[27] and isotope labeling[32]), 2-hydroxy derivatives (UV/Vis[33] and IR[33,34] spectroscopy), 2-methoxy derivatives (kinetics[25,30] and dipole moment[27]), 2-chloro derivatives (IR spectroscopy[34], kinetics[30] and dipole moment[27]), 2-bromo derivatives, 2-iodo derivatives (dipole moment[27]), and 2-nitro derivatives (IR spectroscopy[34]). All of the mentioned reports imply that the physicochemical properties of the *ortho*-derivatives of the α-methylstyrene differ from those observed for *meta*- and *para*-derivatives. A size of the difference depends particularly on the bulkiness and structure of the appended substituent.

In the UV/Vis spectra of the *ortho*-substituted α-methylstyrenes, the longest-wavelength band is shifted hypsochromically[17,33] whereas one older report states that no absorption band appears in this range[18]. The IR[17,21,33,34] and Raman[21] spectra differ considerably while the substitution effects are fairly seen for the valence vibration ν_{O-H} of 2-hydroxy derivative. From the recorded ^{13}C NMR spectra, it has been shown that the *ortho*-substitution in α-methylstyrenes tends to reduce the deshielding effect on the

vinyl group at C-1 (ref.[22]). The ^{13}C NMR chemical shifts of 4- and 5-substituted 2-methylcumyl cations measured in the presence of $SbF_5/FSO_3H/SO_2ClF$ at –80 °C correlate significantly with the substitution constants. When comparing the reaction constants to other derivatives, the *ortho*-methyl substitution does not affect the stabilization of the carbocation. The influence of the *ortho*-substitution is kinetically important in particular for those reactions in which the rate of an intermediate formation in the rate-determining step depends on the stabilization of the reaction centre through resonance effects. When comparing *ortho*- and *para*-derivatives, the relative rate of the dichlorocarbene addition to α-methylstyrene[25] decrease for the methoxy derivative 5.5 times and for the *para*-methyl derivative even 11.7 times. Similar relations were also found for the reactions with peroxyl radicals[26].

The described substitution effects in the *ortho*-position of α-methylstyrenes are frequently explained as a twist of the double bond placed in the side chain from the main aromatic plane. This supposition is further supported by the observed dipole moments[27,28] and the steric hindrance of resonance, particularly seen in the UV/Vis spectra[17,18,33], in the measured gas-phase basicity[29] as well as in the chemical reactions[25,26]. The dihedral angle between the substituted benzene ring and the vinyl group estimated from the dipole moment of 2-α-dimethylstyrene, amounts to 71–75° (ref.[27]). Quantum-chemical calculations of the same compound give the dihedral angles of 30–60° (ref.[20]), 112° (C_2C_1–$C_\alpha C_\beta$, ref.[21]), and 73° (ref.[26]). According to ab initio calculations, the vinyl group is twisted out of the benzene plane already for α-methylstyrene (two energetic minima around 40 and 140°, respectively) as well as for 2-methylstyrene (two energetic minima around 150 and 210°, respectively)[35]. Even the styrene itself is not a planar molecule[36]. Theoretical calculations predict the dihedral angle to be 27°. The related torsion vibrations of the *core-en* bond for *ortho*- and *meta*-substituted styrenes have already been reported[37].

According to the above statements is it clear that from the whole spectrum of effects referred[38–68] to as the *ortho* effect, the acid-catalyzed hydration of 2-substituted α-methylstyrenes involves, in particular, the twist of the isopropenyl group or the respective cation of the isopropyl group from the benzene plane. The corresponding dihedral angle depends on the bulkiness of the appended substituent. A twist of the side group bearing the reaction centre affects in particular the resonant stabilization of the π-electron system, the mesomeric interaction between the *ortho*-substituents and the reaction centre, and also the solvation of the reaction centre. The above-mentioned effects will surely have different impacts on either

the alkene as a reactant or on the carbocation as an intermediate. According to the Hammond postulate, the transition-state energy in the rate-determining step is given by the energy of the carbocation and, therefore, the rate constant will depend in particular on its stabilization.

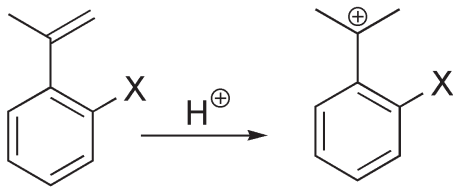
With respect to the specific character of the interaction between the reaction centre and the *ortho*-substituents in concrete molecules and reactions, a quantitative interpretation of the *ortho*-substitution effects seems to be difficult. However, two standard approaches based on the similarity principle are already known. The first, older and less commonly approved approach involves the Hammett correlations in order to propose universal substitution constants σ_{ortho} (refs[42,45]). The second uses combinations of the substitution constants describing the electronic effects separately[42,69,70] (inductive or mesomeric), whereas a description of the additional effects, in particular the description of the steric effects, is realized by adding other terms to the correlation equation. Recently, quantum-chemical approaches are also increasingly applied for the description of such experimental data[61,62,65].

From the above discussion it is clear that the substitution effects on the acid-catalyzed hydration of 2-substituted α-methylstyrenes can be immensely complex and their evaluation and interpretation may be quite complicated. To the best of our knowledge, no effort has been made to solve the above problems and thus this topic is the challenge and aim of this work.

RESULTS AND DISCUSSION

Kinetic Acidity Function

The dependence of the observed rate constants k_{obs} for the acid-catalyzed hydration of 2-substituted α-methylstyrenes (Scheme 1) on the sulfuric acid concentration are summarized in Table I. Using these values, we con-



SCHEME 1

structed[71] the kinetic acidity function H (ref.[72]). Figure 1 depicts the constructed H-function versus the concentration of the sulfuric acid used, as well as the kinetic acidity function for 4-substituted α-methylstyrenes

TABLE I
Wavelengths λ used for the kinetic measurements, number of the experimental measurements n, range of molar concentrations c of catalytic sulfuric acid, the catalytic rate constants log k_{ortho} of the acid-catalyzed hydration of *ortho* substituted α-methylstyrenes and their standard deviations s_k

Compd	2-X	λ, nm	n	c, mol l^{-1}	log k_{ortho}	s_k
1a	H	254	18	0.65–4.71	–3.842	0.030
1b	CH_3	228	15	2.03–5.70	–4.698	0.039
1c	CF_3	232	14	5.70–8.77	–6.598	0.024
1d	OH	238	15	0.40–3.88	–3.317	0.029
1e	OCH_3	236	17	0.51–4.16	–3.544	0.019
1f	OC_2H_5	238	17	0.51–4.16	–3.628	0.029
1g	SCH_3	252	12	2.51–5.45	–4.624	0.024
1h	F	234	15	2.76–6.67	–5.207	0.032
1i	Cl	208	13	5.23–8.09	–6.317	0.026
1j	Br	246	11	6.18–8.55	–6.602	0.038

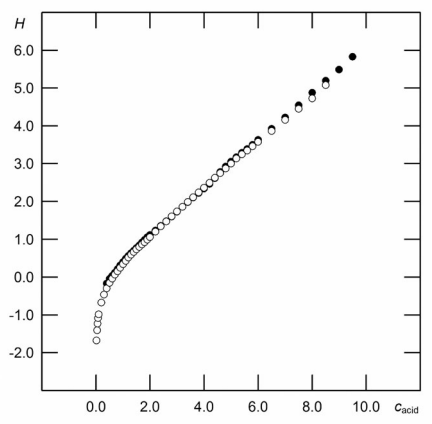


FIG. 1
Comparison of the kinetic acidity functions for 4-substituted (○) and 2-substituted (●) α-methylstyrenes, respectively, in aqueous sulfuric acid at 25 °C

obtained under the same reaction conditions. The almost identical shape of the dependence for both kinetic acidity functions implies that the conclusions made for the A-SE2 (refs[73,74]) mechanism of the acid-catalyzed hydration for *para*-derivatives[1] hold true also for *ortho*-derivatives. The mechanism A-SE2 involves the rate-determining transfer of a hydrated proton to the substrate – 2-substituted α-methylstyrene.

The Relationship Between ortho- and para-Substitution for α-Methylstyrenes

An analysis of the relationship between *ortho*- and *para*-substitution on a uniform substrate[51], in the same reaction and under the same conditions, seems to be a proper tool to evaluate the *ortho*-effect. An advantage of this approach is its simply defined physical model without external parameters (substitution constants with unequal reliability). Nevertheless, the experimental errors of both variables (random quantities) remain a limitation. The relationship between logarithms of both catalytic rate constants of the acid-catalyzed hydration of the *ortho*- and *para*-substituted α-methylstyrenes is illustrated in Fig. 2. This picture demonstrates that the logarithm of the catalytic rate constant for hydrogen as a substituent is markedly out of the range of the other substituents and, simultaneously, that the *ortho*-

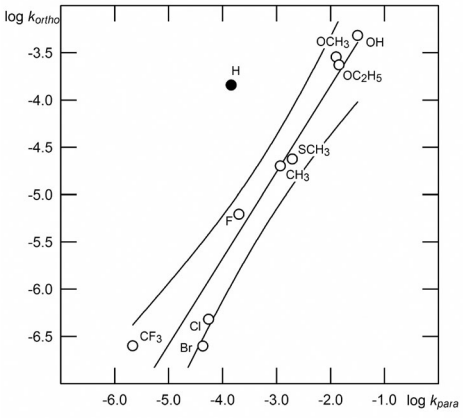


FIG. 2

Relationship between the logarithms of the catalytic rate constants of the acid-catalyzed hydration of 2-substituted (log k_{ortho}) and 4-substituted (log k_{para}) α-methylstyrenes in aqueous sulfuric acid at 25 °C. The points except hydrogen are fitted by weighted linear regression with marked 95% confidence region the regression line

derivatives react significantly slower than the corresponding *para*-derivatives. The apparently inhomogeneous results are most likely caused by the superposition of many factors, which affect both the reactant and also predominantly the carbocation formed within the reaction. The following factors are probably the most crucial ones: (i) a decrease in the conjugation between the reaction centre and the benzene ring caused by the geometric twist of the reaction centre from the benzene plane, (ii) a change in the mesomeric interaction of the reaction centre and the substituent depending in particular on the extent of such a twist, (iii) steric hindrance preventing the access of the reagent to the reaction centre, (iv) steric hindrance of the solvation stabilization of the carbocation evolving in the rate-determining step of the reaction, (v) specific interactions of the reaction centre with the substituent. The weighted linear regression of logarithms of the catalytic rate constants for *ortho*-substituted α-methylstyrenes (excluding outliers for hydrogen) on the logarithms of catalytic rate constants for *para*-derivatives and on Charton's steric constants υ (ref.[43]) provided the following relationship (*1*)

$$\log k_{ortho} = -(2.0 \pm 0.3) + (0.91 \pm 0.09) \log k_{para} \qquad (1)$$

$$n = 9,\ s = 0.375,\ R = 0.964,\ F(1,7) = 92.4\ .$$

The regression coefficient for Charton's steric constants was statistically not significant and, therefore, it is not stated in Eq. (*1*). On the other hand, from the statistical insignificance of the regression coefficient for the constants υ, we cannot deduce that steric effects were not involved. The outlier log k_{ortho} for the monatomic substituent – hydrogen and the frontier value log k_{ortho} for Br as a substituent on the other side of the 95% confidence region of the regression line (Fig. 2) strongly indicate the significance of steric effects. Since *ortho*-substitution involves a wide range of the above-mentioned factors, the steric effects in Eq. (*1*) could not be simply described by adding the steric constants υ or other related constants to the correlation relationship.

Interpretation of ortho-Substitution Through the Constants σ_p^+

The substitution constants σ_p^+ (refs[3,4,75]) are best suited[1] for a quantitative description of the substitution effects in the reactions involving carbocations as intermediates. Figure 3 illustrates the dependence of logarithms of the catalytic rate constants of the acid-catalyzed hydration for 2-sub-

stituted α-methylstyrenes on the substitution constants σ_p^+. The relationships depicted in Figs 2 and 3 correspond to each other – with the hydrogen substituent as an outlier, whereas the Br and CH_3S substituents lie within the limits of the confidence region of the regression line. The linear regression of logarithms of the catalytic rate constants for *ortho*-substituted α-methylstyrenes on the substitution constants σ_p^+, including the values for hydrogen, provided the following relationship (*2*)

$$\log k_{ortho} = -(5.45 \pm 0.26) - (2.28 \pm 0.48)\sigma_p^+ \qquad (2)$$

$$n = 10,\ s = 0.702,\ R = 0.859,\ F(1,8) = 22.5$$

and relationship (*3*) excluding the hydrogen values

$$\log k_{ortho} = -(5.70 \pm 0.15) - (2.52 \pm 0.26)\sigma_p^+ \qquad (3)$$

$$n = 9,\ s = 0.373,\ R = 0.965,\ F(1,7) = 93.4\ .$$

In comparison with the corresponding relationship for the *para*-derivatives[1], the relationships in Eqs (*2*) and (*3*) are not as close (*para*: $s = 0.242$, $R = 0.990$). The reaction constant in its absolute value is smaller for

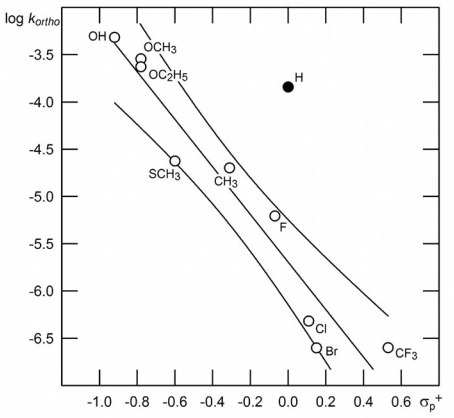


FIG. 3

Dependence of the logarithms of the catalytic rate constants of the acid-catalyzed hydration for 2-substituted α-methylstyrenes log k_{ortho} on the substitution constants σ_p^+ in aqueous sulfuric acid at 25 °C. The points except hydrogen are fitted by weighted linear regression with marked 95% confidence region the regression line

ortho-derivatives (*para*: $\rho^+ = -3.07$). This implies that the substituent effects are not perfectly described and that the influence of the *ortho*-substitution is lower than that for the *para*-position. However, an inclusion of the steric constants υ into Eq. (*2*) leads to a tighter relationship (*4*)

$$\log k_{ortho} = -(4.34 \pm 0.41) - (1.90 \pm 0.36)\sigma_p^+ - (2.14 \pm 0.71)\upsilon \qquad (4)$$

$$n = 10,\ s = 0.494,\ R = 0.942,\ F(2,7) = 27.3\ .$$

The regression coefficient for the steric constant υ is, in contrast to Eq. (*1*), statistically significant. Its large negative value (e.g. the steric constant for the alkaline hydrolysis of phenyl-2-substituted benzoates[76] amounts to 1.4) indicates an important steric retardation of the reaction as a consequence of the steric effects. The reaction constant ρ^+ is smaller in comparison with Eqs (*2*) and (*3*), respectively. The large residual standard deviation *s* and, on the contrary, the little explained variability ($100R^2 = 89\%$) hinder a relevant physicochemical interpretation of the obtained relationship. Hence, a systematic analysis was performed in order to extract the statistically most accurate explanatory variables based on the substitution constants. The following relationship has been found (*5*)

$$\log k_{ortho} = -(3.97 \pm 0.16) - (1.45 \pm 0.15)\sigma_p^+ - \\ - (3.92 \pm 0.38)\upsilon_{(1)} - (2.09 \pm 0.26)\upsilon_{(>1)} \qquad (5)$$

$$n = 10,\ s = 0.186,\ R = 0.993,\ F(3,6) = 144$$

where the variables $\upsilon_{(1)}$ and $\upsilon_{(>1)}$ refer to Charton's steric constant for the monatomic and polyatomic substituents (for others 0), respectively. Having statistically significant regression coefficients, no outliers, and normal residue distribution, Eq. (*5*) is also statistically valid. The residual standard deviation *s* is even smaller than those for the *para*-substitution (see above). The small reaction constant ρ^+ (e.g. compare with the following data[4] for *para*-substitution: 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, $\rho^+ = -2.26$, $s = 0.118$ and also refs[11–16]) implies that interaction in *ortho*-derivatives between the reaction centre and the substituent is significantly decreased compared to those observed for *para*-substitution. This could be explained due to a lower degree of conjugation between the reaction centre and the benzene ring as a consequence of the geometric twist of the reaction centre out of the main aromatic plane, accompanied by the vanishing of the

mesomeric interaction between the reaction centre and the substituent, depending on the extent of such a distortion. Regression coefficients for $\upsilon_{(1)}$ and $\upsilon_{(>1)}$ both have negative signs, hence the catalytic rate constant decreases with the increasing bulkiness of substituent. The regression coefficient for $\upsilon_{(1)}$ in Eq. (*5*) is almost five-times higher than those for $\upsilon_{(>1)}$. This further implies that the monoatomic substituents affect the rate constant more considerably than the polyatomic ones. This is most likely due to a small twist of the isopropyl group in the carbocation generated from the monoatomic-substituted α-methylstyrenes, where even small differences in the nature of substituents distinctively affect the entire conjugation between the carbocation and the substituents attached to the benzene ring. On the contrary, the isopropyl groups in the polyatomic-substituted α-methylstyrenes are twisted to such an extent that changes in the bulkiness of the substituents affect the resonance stabilization to a negligible extent.

Interpretation of ortho-Substitution Through the Constants σ_I *and* σ_R^+

The relationship of log k_{ortho} on the substitution constants σ_I and σ_R^+ including the steric constants $\upsilon_{(1)}$ and $\upsilon_{(>1)}$ is given by Eq. (*6*)

$$\log k_{ortho} = -(3.93 \pm 0.21) - (2.25 \pm 0.67)\sigma_I - (1.51 \pm 0.20)\sigma_R^+ - \\ - (3.67 \pm 0.63)\upsilon_{(1)} - (2.00 \pm 0.36)\upsilon_{(>1)} \qquad (6)$$

$$n = 10,\ s = 0.233,\ R = 0.991,\ F(4,5) = 68.2\ .$$

When comparing Eq. (*6*) with (*5*), relationship (*6*) is much less tighter whereas regression coefficients for the variables $\upsilon_{(1)}$ and $\upsilon_{(>1)}$ are consistent having analogical interpretation as for Eq. (*5*). When comparing Eq. (*6*) with equation obtained for *para*-substitution[1], both regressions are statistically similar whereas the reaction constants ρ_I and ρ_R^+ for *ortho*-substitution are roughly half-size (*para*: $s = 0.227$, $R = 0.992$, $\rho_I = -4.16$, $\rho_R^+ = -2.94$), and the reaction constant ρ_R^+ has changed slightly more than ρ_I.

A systematic analysis of the statistically most accurate explanatory variables based on the substitution constants σ_I and σ_R^+ provided an even statistically tighter relationship (*7*)

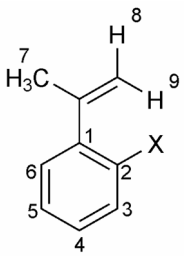
$$\log k_{ortho} = -(3.82 \pm 0.17) - (3.02 \pm 0.59)\sigma_I - (1.53 \pm 0.16)\sigma_R^+(\text{conjug}) - \\ - (3.21 \pm 0.55)\upsilon_{(1)} - (1.76 \pm 0.31)\upsilon_{(>1)} \qquad (7)$$

$$n = 10,\ s = 0.192,\ R = 0.994,\ F(4,5) = 101$$

where σ_R^+(conjug) is equal to σ_R^+ for the conjugating substituents and 0 for the others (H, CH_3, CF_3). The reason for such selection may be seen in an overestimated value of σ_R^+ for the substituent CH_3 (–0.29, ref.[68]) in Eq. (*6*). It is also worthwhile to notice that the reaction constant ρ_R^+ almost did not change, whereas the reaction constant ρ_I increased. When comparing the absolute values of ρ_I and ρ_R^+ constants for *ortho*- and *para*-substitutions, ρ_I and ρ_R^+ values for the *ortho*-substitution are lower within a factor of one-third and one-half, respectively. This is unambiguous evidence that the *ortho*-substitution of the acid-catalyzed hydrolysis of α-methylstyrenes acts as a steric hindrance-factor, affecting in particular, the resonant stabilization of the carbocation.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ (10% solutions) at 360 MHz with a Bruker AMX 360 instrument at 25 °C. Chemical shifts are reported in ppm relative to the signal of HMDS (0.05 ppm). Coupling constants (*J*) are given in Hz. The particular protons are marked as follows (X = *ortho*-substituent).



Preparation of *ortho*-Substituted α-Methylstyrenes. General Method

The general method involves an addition of Grignard reagents to the appropriate carbonyl compounds (ketones, esters, and acyl chlorides). The ethereal solution of the substrate was added dropwise to a stirred solution of the Grignard reagent (3 equiv.) in ether over the period of 1 h at 25 °C. The reaction mixture was refluxed for an additional 2 h, cooled and poured on ice. Upon acidification with sulfuric acid, the organic phase was separated, washed with Na_2SO_3 (10% aqueous solution) and water, dried (Na_2SO_4), and the solvent evaporated. The crude alcohol was purified by vacuum distillation accompanied by either spontaneous or P_2O_5-induced dehydration. This protocol provide a straightforward and general approach to the target compounds with simple methodology and easy work-up. No attempts were undertaken to further optimize the preparative yields.

α-*Methylstyrene* (**1a**) was synthesized from benzoyl chloride and methylmagnesium iodide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 41%, b.p. 48 °C/14 mbar (ref.[25], b.p. 57 °C/13 mbar), n_D^{20} = 1.5342 (ref.[25], n_D^{20} = 1.5330). ^{1}H NMR (360 MHz, $CDCl_3$): 7.44 d, 2 H, ^3J = 9.0 (H-2,6); 7.30 t, 2 H, ^3J = 9.0 (H-3,5); 7.24 t, 1 H, ^3J = 9.0 (H-4); 5.34 s, 1 H (H-8); 5.05 s, 1 H (H-9); 2.09 s, 3 H (H-7).

2-Methyl-α-methylstyrene (**1b**) was synthesized from acetone and 2-methylphenylmagnesium bromide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 10%, b.p. 47–50 °C/11 mbar (ref.[17], b.p. 172–173 °C/760 mbar), n_D^{20} = 1.5147 (ref.[17], n_D^{20} = 1.5152). ^{1}H NMR (360 MHz, $CDCl_3$): 7.08–7.15 m, 4 H (H-3,4,5,6); 5.16 s, 1 H (H-8); 4.82 s, 1 H (H-9); 2.29 s, 3 H (2-CH_3); 2.01 s, 3 H (H-7).

2-Trifluoromethyl-α-methylstyrene (**1c**) was synthesized from 2-(trifluoromethyl)benzoyl chloride and methylmagnesium iodide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 9%, b.p. 31 °C/6 mbar, n_D^{20} = 1.4512. ^{1}H NMR (360 MHz, $CDCl_3$): 7.60 d, 1 H, ^3J = 8.1 (H-3); 7.42 t, 1 H, ^3J = 8.1 (H-5); 7.29 t, 1 H, ^3J = 8.1 (H-4); 7.19 d, 1 H, ^3J = 8.1 (H-6); 5.17 s, 1 H (H-8); 4.84 s, 1 H (H-9); 2.03 s, 3 H (H-7).

2-Hydroxy-α-methylstyrene (**1d**) was synthesized from 2-hydroxyacetophenone and methylmagnesium chloride in THF following the general procedure and purified by vacuum distillation with spontaneous dehydration. Yield 63%, b.p. 55 °C/1 mbar (ref.[33], b.p. 92–93 °C/16 mbar), n_D^{20} = 1.5446 (ref.[33], n_D^{20} = 1.5463). ^{1}H NMR (360 MHz, $CDCl_3$): 8.20 s, 1 H (2-OH); 7.65 d, 1 H, ^3J = 7.8 (H-3); 7.24 t, 1 H, ^3J = 7.8 (H-5); 7.11 d, 1 H, ^3J = 7.8 (H-6); 7.01 t, 1 H, ^3J = 7.8 (H-4); 5.32 s, 1 H (H-8); 5.09 s, 1 H (H-9); 2.06 s, 3 H (H-7).

2-Methoxy-α-methylstyrene (**1e**) was synthesized from methyl 2-methoxybenzoate and methylmagnesium iodide following the general procedure and purified by vacuum distillation with spontaneous dehydration. Yield 45%, b.p. 77–79 °C/2–3 mbar (ref.[27], b.p. 56–60 °C/1 mbar), n_D^{20} = 1.5338 (ref.[27], n_D^{20} = 1.5296). ^{1}H NMR (360 MHz, $CDCl_3$): 7.15–7.21 m, 2 H (H-3,5); 6.83–6.89 m, 2 H (H-4,6); 5.13 s, 1 H (H-8); 5.04 s, 1 H (H-9); 3.80 s, 3 H (2-OCH_3); 2.10 s, 3 H (H-7).

2-Ethoxy-α-methylstyrene (**1f**) was synthesized from ethyl 2-ethoxybenzoate and methylmagnesium iodide following the general procedure and purified by vacuum distillation with spontaneous dehydration. Yield 22%, b.p. 55 °C/4 mbar, n_D^{20} = 1.5227. ^{1}H NMR (360 MHz, $CDCl_3$): 7.16–7.22 m, 2 H (H-3,5); 6.83–6.89 m, 2 H (H-4,6); 5.09 s, 1 H (H-8); 5.05 s, 1 H (H-9); 4.02 q, 2 H, ^3J = 7.8 (2-OC**H**$_2$$CH_3$); 1.57 s, 3 H (H-7); 1.38 t, 3 H, ^3J = 7.8 (2-OCH_2C**H**$_3$).

2-Methylthio-α-methylstyrene (**1g**) was synthesized from methyl 2-(methylthio)benzoate and methylmagnesium iodide following the general procedure and purified by vacuum distillation with spontaneous dehydration. Yield 20%, b.p. 98 °C/12 mbar, n_D^{20} = 1.5781. ^{1}H NMR (360 MHz, $CDCl_3$): 7.15–7.23 m, 2 H (H-3,5); 7.06–7.09 m, 2 H (H-4,6); 5.23 s, 1 H (H-8); 4.94 s, 1 H (H-9); 2.40 s, 3 H (H-7); 2.08 s, 3 H (2-SCH_3).

2-Fluoro-α-methylstyrene (**1h**) was synthesized from 2-fluorobenzoyl chloride and methylmagnesium iodide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 23%, b.p. 49 °C/21 mbar (ref.[27], b.p. 62 °C/28 mbar), n_D^{20} = 1.5059 (ref.[27], n_D^{25} = 1.5031). ^{1}H NMR (360 MHz, $CDCl_3$): 7.31 t, 1 H, ^3J = 7.6 (H-5); 7.22–7.27 m, 1 H (H-3); 7.10 d, 1 H, ^3J = 7.5 (H-6); 7.01–7.06 m, 1 H (H-4); 5.24 s, 1 H (H-8); 5.04 s, 1 H (H-9); 2.16 s, 3 H (H-7).

2-Chloro-α-methylstyrene (**1i**) was synthesized from 2-chlorobenzoyl chloride and methylmagnesium iodide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 21%, b.p. 39–40 °C/5 mbar (ref.[30], b.p. 75 °C/14 mbar), n_D^{20} = 1.5337 (ref.[30], n_D^{25} = 1.5329). ^{1}H NMR (360 MHz, $CDCl_3$): 7.30 d, 1 H, ^3J = 7.6 (H-3); 7.11–7.28 m, 3 H (H-4,5,6); 5.20 s, 1 H (H-8); 4.94 s, 1 H (H-9); 2.07 s, 3 H (H-7).

2-Bromo-α-methylstyrene (**1j**) was synthesized from 2-bromobenzoyl chloride and methylmagnesium iodide following the general procedure and purified by vacuum distillation with added P_2O_5. Yield 30%, b.p. 56–57 °C/4 mbar (ref.[27], b.p. 55–65 °C/0.9 mbar), n_D^{20} = 1.5576

(ref.[27], n_D^{20} = 1.5530). ^{1}H NMR (360 MHz, $CDCl_3$): 7.49 d, 1 H, ^3J = 8.0 (H-3); 7.20 t, 1 H, ^3J = 7.6 (H-5); 7.15 d, 1 H, ^3J = 7.6 (H-6); 7.06 t, 1 H, ^3J = 7.6 (H-4); 5.18 s, 1 H (H-8); 4.89 s, 1 H (H-9); 2.05 s, 3 H (H-7).

Kinetic Measurements

A solution of respective α-methylstyrenes (2–5 μl) in methanol was added to a cell containing 2 ml of aqueous sulfuric acid (c = 0.017–9.58 mol l^{-1}) kept at 25 ± 0.1 °C. The cell content was mixed, and the absorbance decrease was monitored spectrophotometrically (UV/Vis spectrophotometer HP 8452A) at suitable wavelengths (Table I) for a period of at least 5 half-lives. The kinetic dependencies obtained were treated by a known algorithm[77] to calculate the observed rate constants k_{obs}.

Construction of the Kinetic Acidity Function

The obtained dependencies of the logarithm observed rate constants log k_{obs} on the sulfuric acid concentration were treated by a known algorithm to construct the kinetic acidity function[71]. Likewise, the catalytic rate constants log k_{ortho} were obtained this way.

Correlation Valuation

The substitution constants used were taken from the literature[43,69]. The dependence of logarithms of the catalytic rate constants log k_{ortho} on substitution constants were examined by multivariate graphical display methods and subsequently treated by multiple linear regressions (including *t*-test, *F*-test, assessing multicollinearity, and residual analysis). Residuals in all of the presented regressions had normal distribution and outliers were not detected. The OPstat Program[78] was employed for all statistical calculations.

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