

Kinetics and Mechanism of Aromatic Electrophilic Substitution Reactions: VII. Temperature Dependence of Substrate Selectivity of Methylbenzene Hydroxylation in the System $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$

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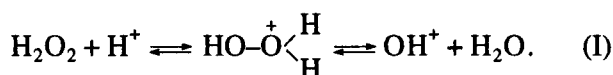
Received June 19, 1998

Abstract—The relative rates of the hydroxylation of toluene, *ortho*-, *meta*-, and *para*-xylenes, mesitylene, and pseudocumene are measured by the kinetic distribution method in the $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$ (70.0 wt %) system at 15 to 55°C. The activation entropies correlate with the basicities of arenes and the activation enthalpies correlate with both the basicities and ionization potentials of ArH . Substrate selectivity is described with a high accuracy by the general equation with three variables (basicity, ionization potentials, and temperature) and implies the compensation effect between changes in standard entropies and enthalpies for the basicity constants of ArH . The structure of the transition state of the slow step of hydroxylation is intermediate between the structure of a charge-transfer complex and that of a σ -complex.

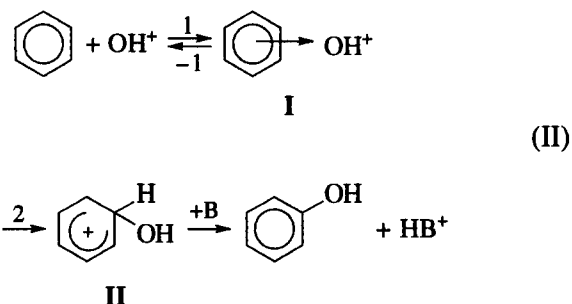
INTRODUCTION

Several groups of reagents are known as capable of hydroxylating arenes by the mechanism of aromatic electrophilic substitution; among them are the systems $\text{H}_2\text{O}_2\text{--strong acid}$ (H_2SO_4 [1], HF [2], $\text{HSO}_3\text{F--SO}_2\text{ClF}$ [2]), the solutions of peroxy acids (CH_3COOOH and CF_3COOOH [3–5]), peroxy complexes of metals, for example $\text{V}^{(V)}\text{O}_5$ [6], oxygen atoms $\text{O}(^3P)$ [7], and

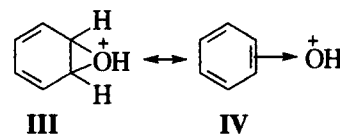
hydroxyl radicals $\cdot\text{OH}$ [8]. An OH^+ cation is an active species in the systems $\text{H}_2\text{O}_2\text{--strong acid}$ [1, 2, 9]. Hydrogen peroxide is a stronger acid ($K_a = 2 \times 10^{-12}$ mol/l) than H_2O , and its basicity is $\sim 10^6$ times lower [10]. In strongly acidic solutions, hydrogen peroxide may exist in a protonated form (H_3O_2^+ or H_5O_3^+), which may be considered as a hydrated OH^+ hydroxyl cation:



The hydroxylation by an OH^+ cation is usually described by the mechanism of aromatic electrophilic substitution



with the intermediate formation of a charge-transfer complex I and a σ -complex II [11]. The data on the regioselectivity of hydroxylation in the $\text{H}_2\text{O}_2/(\text{HSO}_3\text{F--SO}_2\text{ClF})$ system agree with the assumption on the existence of the protonated intermediate III, which can be presented as a localized π -complex IV formed by the electrophilic attack on to one of the π -bonds in a benzene ring [9]



However, because fast transformations of hydroxylation products (rearrangement of σ -complexes or further oxidation of phenols) are possible, the distribution of final products may not provide a correct picture of the selectivity at the first step. The study of intermediates

may not suggest the correct mechanism either because, due to fast transformations of intermediates, direct observations are often impossible or their interpretation is unambiguous: a species observed can be formed by a side pathway or after a rate-determining step.

We have proposed earlier another method for the elucidation of the mechanism of aromatic electrophilic substitution reactions [1, 5, 12, 13]; this method was based on the study of the substrate selectivity (relative reaction rates) in the first step that was determined by the kinetics of hydrocarbon consumption in the reaction. The correlations between the respective relative rate constants ($\Delta \log k$) and arene basicities ($\log K_B$) or ionization potentials (I_{ArH}) for a wide range of methylbenzenes point to the occurrence of the reaction through the slow step of σ -complex or charge-transfer complex formation, respectively. The dependence of the selectivity on $\log K_B$ and I_{ArH}

$$\Delta \log k = a \Delta \log K_B + b \Delta I_{ArH}, \quad (1)$$

which was found and comprehensively analyzed for arene oxidation by HMnO_4 species [14] was explained by the transition state whose structure is intermediate between the structures of charge-transfer and σ -complexes. The correlation between $\Delta \log K_B$ and ΔI_{ArH} in the benzene-methylbenzenes series is weak (the correlation coefficient $r = 0.902$). However, if the measurements of reaction rate constants are rather accurate, this correlation reliably distinguishes between the dependence of substrate selectivity on the basicity or ionization potentials ($\Delta \log K_B$ or ΔI_{ArH}). This correlation also makes certain whether the kinetics is described by equation (1) or parallel reactions take place in which case $k = k_I + k_{II}$, $\Delta \log k_I = a \Delta \log K_B$, and $\Delta \log k_{II} = b \Delta I_{ArH}$ [15].

The important additional information on the mechanism can be obtained from the data on the temperature dependence of substrate selectivity and on the activation parameters. We recently demonstrated [16] that the substrate selectivity in the reactions of methylbenzenes with HMnO_4 species in the temperature range from 20 to 70°C can be described by the equation that involves the characteristics of substrates (basicities and ionization potentials) and temperature:

$$\begin{aligned} \Delta \log k &= \frac{T \Delta \Delta S^\ddagger - \Delta \Delta H^\ddagger}{2.3 RT} \\ &= \frac{a' T_0 \Delta \log K_B^0}{(c T_0 - 1)} \left(c - \frac{1}{T} \right) + \frac{b' \Delta I_{ArH}}{2.3 RT}, \end{aligned} \quad (2)$$

where a' , b' , and c are constants and $\Delta \log K_B^0 = \log K_B^0 - \log (K_B^0)_{st}$ is the relative basicity at $T = T_0$. Equilibrium constants for the protonation of arenes in liquid HF at 0°C were used as K_B^0 [17]. According to equation (2),

the entropies of activation for alkylbenzene reactions with HMnO_4 correlate with basicity:

$$\Delta \Delta S^\ddagger = \Delta S^\ddagger - \Delta S_{st}^\ddagger = \frac{2.3 RT_0 c a'}{(c T_0 - 1)} \Delta \log K_B^0. \quad (3)$$

The enthalpies of activation correlate with $\Delta \log K_B^0$ and ΔI_{ArH} :

$$\begin{aligned} \Delta \Delta H^\ddagger &= \Delta H^\ddagger - \Delta H_{st}^\ddagger \\ &= \frac{2.3 RT_0 a'}{(c T_0 - 1)} \Delta \log K_B^0 - b' \Delta I_{ArH}. \end{aligned} \quad (4)$$

Equation (2) is derived on the assumption that changes in standard entropies and enthalpies are related by the compensation equation for arene basicity [16]:

$$\Delta \Delta S_B = c \Delta \Delta H_B. \quad (5)$$

No direct evidence for relation (5) is available; however, equations (2), (3), and (4) for other aromatic electrophilic substitution reactions could serve as indirect evidence. While parameters a' and b' can be different for different reactions; parameter $c = \Delta \Delta S_B / \Delta \Delta H_B$, which, by definition, reflects only the properties of ArH , should not be dependent on the nature of the reagent in the series of substrates.

To obtain data on the activation parameters and additional information on the mechanism of reaction (II) based on them and to verify relation (5), we measured the relative reaction rates for the hydroxylation of methylbenzenes in the H_2O_2 - H_2SO_4 (70.0 wt %) system at 15 to 55°C. Earlier [13], we showed that the substrate selectivity of the hydroxylation of methylbenzenes in the H_2O_2 - H_2SO_4 , CF_3COOOH - CCl_4 , and CF_3COOOH - CHCl_3 systems at 25°C was controlled by both the basicities and ionization potentials of ArH . It might be expected that the temperature-dependent relative rate constants for these reactions are described by equation (2) and that the entropies and enthalpies of activation are described by equations (3) and (4), respectively.

EXPERIMENTAL

The kinetics of toluene hydroxylation in the H_2O_2 - H_2SO_4 (70.0 wt %) system was studied by the kinetic distribution method [18] from the consumption of the substrate from the gas phase at $[\text{H}_2\text{O}_2] \gg [\text{ArH}]$

$$\begin{aligned} -d[\text{ArH}]_g/d\tau &= k_\lambda [\text{ArH}]_g \\ &= k [\text{ArH}]_s [\text{H}_2\text{O}_2] / (1 + \alpha \lambda), \end{aligned} \quad (6)$$

where k_λ is the observed first-order rate constant for the consumption of arene from the gas phase at a given volume ratio between gas and solution in a reactor ($\lambda = V_g/V_s$); k is the second-order rate constant in the liquid phase; $\alpha = [\text{ArH}]_g/[\text{ArH}]_s$ is the coefficient of the equi-

Table 1. Distribution coefficients α and kinetic parameters of toluene hydroxylation in the system $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$ (70.0 wt %)

$T, ^\circ\text{C}$	$[\text{H}_2\text{O}_2] \times 10^2, \text{ mol/kg}$	λ	α	$k_\lambda \times 10^4, \text{ s}^{-1}$	$k \times 10^2, \text{ kg mol}^{-1} \text{ s}^{-1}$
15	5.70	1.77	0.44	1.56	0.49
25	2.96	1.80	0.61	2.30	1.6
35	2.96	1.80	0.84	7.38	6.3
45	2.06	1.75	1.08	14.60	21

librium distribution of arene between the gas and solution.

Relative rate constants for the oxidation of methylbenzenes were measured by the competitive version of the kinetic distribution method [18]. This method eliminates the complications related to a possible change in the concentration of a reagent caused by its decomposition in the course of reaction. This is important at low concentrations of hydrogen peroxide and high temperatures. In this case, in the simultaneous oxidation of the substrates ArH^A and ArH^B , the concentration of the reagent and time are eliminated from two kinetic equations (6), and, after integrating, we obtain

$$\log[\text{ArH}^A]_g = \frac{k^A(1 + \alpha^B\lambda)}{k^B(1 + \alpha^A\lambda)} \log[\text{ArH}^B]_g + \text{const.} \quad (7)$$

The concentrations of arenes in the gas phase in both versions of the kinetic distribution method were determined by GLC using methane as an internal standard. The values of α required for the calculation of k were found by the method described in [18]. The average error of determining k^A/k^B was $\pm 6\%$, taking into account the errors in measuring α .

Doubly distilled water and chemically pure sulfuric acid transparent in the UV region were used for the preparation of 70.0% H_2SO_4 solution. Working solutions of hydrogen peroxide in sulfuric acid of the required concentration were prepared before use by gravimetry.

RESULTS AND DISCUSSION

Kinetics of toluene hydroxylation. The oxidation of toluene in the $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$ (70.0 wt %) system is the first-order reaction with respect to the substrate. Equation (6) was usually verified when arene conversion was up to 90% and when the reaction order was assumed to be first with respect to the initial concentration of H_2O_2 . The results obtained are illustrated by the following data ($\lambda = 1.80$; $\alpha = 0.61$; 25°C):

$[\text{H}_2\text{O}_2] \times 10^2, \text{ mol/kg}$	1.15	2.96	4.30	6.47
$k_\lambda \times 10^4, \text{ s}^{-1}$	0.82	2.30	3.30	4.60
$k \times 10^2, \text{ kg mol}^{-1} \text{ s}^{-1}$	1.5	1.6	1.6	1.5

Table 1 presents the rate constants for the oxidation of toluene in the temperature range from 15 to 45°C calculated from equation (6) and the values of k_λ , α , λ , and $[\text{H}_2\text{O}_2]$. Under the experimental conditions, sulfuration does not make a significant contribution to the apparent rate constant for the consumption of ArH . Thus, at 25°C , the rate constant for the sulfuration of toluene in 70.0% sulfuric acid is $k_s = 4.5 \times 10^{-8} \text{ s}^{-1}$ [19], which is $\sim 10^4$ times lower than the rate constant of hydroxylation ($k[\text{H}_2\text{O}_2] = 4.7 \times 10^{-4} \text{ s}^{-1}$ at $[\text{H}_2\text{O}_2] = 2.96 \times 10^{-2} \text{ mol/kg}$).

We failed to measure reaction rate constants at higher temperatures because of a considerable decrease in the concentration of hydrogen peroxide caused by its decomposition during the reaction. In the temperature range studied, the Arrhenius equation holds with the correlation coefficient $r = 0.999$. The values of preexponential factors ($\log A = 14.9 \pm 0.3$), energies ($E = 95 \pm 2 \text{ kJ/mol}$), enthalpies ($\Delta H^\ddagger = E_a - RT = 92 \pm 2 \text{ kJ/mol}$), and entropies ($\Delta S^\ddagger = 19.15 \log(A/T) - 205.9 = 32 \pm 1 \text{ J mol}^{-1} \text{ K}^{-1}$) of activation for the oxidation of toluene were found from this equation.

Relative rates and activation parameters for the oxidation of methylbenzenes. Table 2 presents relative rate constants for the oxidation of methylbenzenes at 15 to 55°C calculated with respect to toluene by equation (7) using the measured values of α . Under these conditions, benzene oxidation is very slow; therefore, we failed to measure the relative rates of the reactions with its participation. For all the substrates studied, the Arrhenius equation

$$\log(k^A/k^B) = \log(A^A/A^B) - (E_a^A - E_a^B)/2.3RT \quad (8)$$

holds with the correlation coefficients $r = 0.997\text{--}0.999$. The relative enthalpies ($\Delta\Delta H^\ddagger = \Delta E_a$) and entropies ($\Delta\Delta S^\ddagger = 19.15 \log(A^A/A^B)$) of activation found by equation (8) are given in Table 2.

Temperature dependence of substrate selectivity. As mentioned above, the relative constants for the hydroxylation of methylbenzenes in the $\text{H}_2\text{O}_2\text{--H}_2\text{SO}_4$ system at 25°C depend on both the basicities and the ionization potentials of ArH . We found that equation (1) is valid in the entire range of experimental temperatures (Fig. 1). According to equations (1) and (2), the absolute values of parameters $a = aT_0(cT - 1)/(cT - 1)T$ and $b = b/2.3RT$ decrease with an increase in temperature (Table 3). At the same time, the dimensionless coefficients $a' = 0.38 \pm 0.05$ and $-b' = 0.085 \pm 0.003$ remain constant within the experimental error in the entire temperature range. The value of c equal to $(2.5 \pm 0.2) \times 10^{-3} \text{ K}^{-1}$ was found from the Arrhenius dependence of the parameter a . It turned out that generalized equation (2) in the form of equation (9) describes the whole set of experimental data on substrate selectivity at any changes in the basicity, ionization potentials, and temperature:

Table 2. Distribution coefficients α^* , relative rate constants**, and activation parameters for the hydroxylation of methylbenzenes with hydrogen peroxide in 70.0% H_2SO_4 solution

No.	Arene	15°C		25°C		35°C		45°C		55°C		$-\Delta\Delta S^\ddagger$, $\text{J mol}^{-1} \text{K}^{-1}$	$-\Delta\Delta H^\ddagger$, kJ/mol	$-\log K_B^0$, [17]	I_{ArH} , eV [20]
		α	$\Delta\log k$	α	$\Delta\log k$	α	$\Delta\log k$	α	$\Delta\log k$	α	$\Delta\log k$				
1	Toluene	0.44	0	0.61	0	0.84	0	1.08	0	1.30	0	0	0	6.3	8.82
2	<i>ortho</i> -Xylene	0.28	0.72	0.39	0.66	0.56	0.62	0.75	0.55	0.98	0.51	20 ± 1	9.8 ± 0.3	5.3	8.56
3	<i>meta</i> -Xylene	0.45	1.42	0.65	1.30	0.92	1.15	1.24	1.00	1.66	0.90	55 ± 2	24 ± 1	3.2	8.56
4	<i>para</i> -Xylene	0.59	0.76	0.73	0.73	0.93	0.67	1.17	0.63	1.44	0.60	12 ± 1	7.5 ± 0.3	5.7	8.44
5	Mesitylene	0.31	2.46	0.48	2.17	0.72	1.92	1.15	1.70	1.70	1.49	104 ± 4	43 ± 1	0.4	8.40
6	Pseudo-cumene	0.21	1.84	0.35	1.72	0.58	1.55	0.81	1.39	1.35	1.30	53 ± 3	26 ± 1	2.9	8.27

* The average error of measuring α is $\pm 3\%$.** k is in $\text{kg mol}^{-1} \text{s}^{-1}$.**Table 3.** Satisfiability of equations (1) and (2) for the hydroxylation of methylbenzenes in the system H_2O_2 – H_2SO_4 (70.0 wt %)

$T, ^\circ\text{C}$	a	$-b, \text{eV}^{-1}$	r	a'	$-b'$
15	0.32 ± 0.02	1.50 ± 0.03	0.998	0.38 ± 0.05	0.086 ± 0.002
25	0.28 ± 0.01	1.47 ± 0.03	0.999	0.38 ± 0.04	0.087 ± 0.002
35	0.24 ± 0.01	1.39 ± 0.02	0.999	0.37 ± 0.04	0.085 ± 0.001
45	0.21 ± 0.01	1.31 ± 0.03	0.999	0.37 ± 0.04	0.083 ± 0.002
55	0.19 ± 0.01	1.27 ± 0.04	0.998	0.39 ± 0.05	0.083 ± 0.003
Mean value				0.38 ± 0.05	0.085 ± 0.003

$$\begin{aligned} \Delta\log k = & -(1.0 \pm 0.1)\Delta\log K_B^0 \\ & + (380 \pm 20)(\Delta\log K_B^0)/T \\ & - (0.089 \pm 0.010)\Delta I_{\text{ArH}}/2.3RT. \end{aligned} \quad (9)$$

The values of the coefficients $a' = 0.41 \pm 0.06$, $-b' = 0.089 \pm 0.10$, and $c = (2.6 \pm 0.3) \times 10^{-3} \text{K}^{-1}$ can be found from equations (2) and (9).

Dependence of $\Delta\Delta S^\ddagger$ and $\Delta\Delta H^\ddagger$ on substrate properties. The entropies of activation found for the methylbenzenes under study correlate with their basicities (Fig. 2, line I):

$$\Delta\Delta S^\ddagger = -(17.1 \pm 0.7)\Delta\log K_B^0, \quad (10)$$

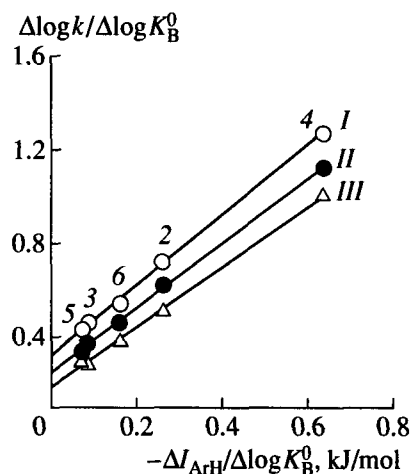
and the enthalpies of activation correlate with the basicities and ionization potentials of arenes (Fig. 2, line II):

$$\begin{aligned} \Delta\Delta H^\ddagger = & -(6700 \pm 400)\Delta\log K_B^0 \\ & + (0.096 \pm 0.013)\Delta I_{\text{ArH}}, \end{aligned} \quad (11)$$

which is in agreement with equations (3) and (4), respectively. Comparing equations (3) and (10) with equations (4) and (11), we obtain the following values of parameters ($T_0 = 273 \text{K}$): $a' = 0.40 \pm 0.06$, $b' = -0.096 \pm 0.013$, and $c = (2.5 \pm 0.3) \times 10^{-3} \text{K}^{-1}$. Within the error limits, these parameters coincide with the values of a' , b' , and c calculated from both equation (9) and the tem-

perature dependence of coefficients a and b in equation (1) (Table 3).

The closeness of the found value of $c = (2.5 \pm 0.3) \times 10^{-3} \text{K}^{-1}$ and its value $c = (1.5 \pm 0.2) \times 10^{-3} \text{K}^{-1}$ calculated in [16] from the data on the oxidation of methylbenzenes with permanganic acid is additional evidence for the validity of equations (2) and (5).

**Fig. 1.** Satisfiability of equation (1) for the hydroxylation of methylbenzenes in the system H_2O_2 – H_2SO_4 (70.0 wt %) at (I) 15, (II) 35, and (III) 55°C. Numbering of points is the same as in Table 2.

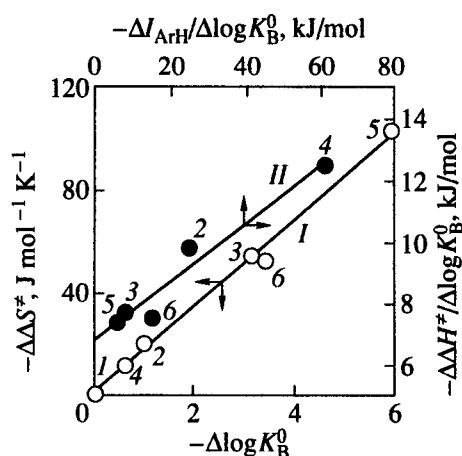


Fig. 2. Satisfiability of equation (line I) (10) and (line II) (11) for the hydroxylation of methylbenzenes. Reaction conditions and numbering points are the same as in Table 2.

Proceeding from the substrate selectivities and enthalpies of activation dependent on the basicities and ionization potentials of arenes and in accordance with the analysis in [16], we conclude that the hydroxylation of methylbenzenes in the H_2O_2 – H_2SO_4 system follows scheme (II), where step 1 is fast and irreversible and the structure of the transition state in step 2 is intermediate between the charge-transfer complex I and σ -complex II.

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