

Kinetics and Mechanism of Reactions of Arenes in the HVO_3 –Sulfuric Acid System: Extended Compensation Effect

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Abstract—Kinetics, activation parameters, and the kinetic isotope effect (KIE) of hydrogen have been determined for the first rate-limiting step of the reactions of benzene, monoalkylbenzenes, dimethylbenzenes, and trimethylbenzenes in HVO_3 –sulfuric acid (54–70 wt % H_2SO_4) solutions. The effects of solution acidity on the rate constants (k) and KIE have been studied. The reactions begin with electron transfer from the arene to VO_2^+ and end with oxidative coupling:



$\log k$ is a linear function of the ionization potential of the arene (I_{ArH}). A three-parameter correlation is for the first time established between the activation energy (E), the logarithm of the preexponential factor ($\log A$), and I_{ArH} : $\log A = 0.15E - 0.058I_{\text{ArH}} + 49.1$ (E and I_{ArH} are expressed in kJ/mol). The reactions of arenes with VO_2^+ , NO_2^+ , and Co^{3+} are intercompared.

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Our laboratory has carried out extensive studies of hydrocarbon activation with oxidizers, metal complexes, electrophilic reagents, and free radicals in aqueous and sulfuric acid media [1–3]. In particular, we have determined the rate at which hydrocarbons enter into the reaction (the first, rate-limiting, or activation step) from hydrocarbon consumption data measured in the solution or in the solution–overlying gas system. Conventional kinetic methods, which are based on reactant consumption or product accumulation measurements, may lead to large errors in rate constants and in relationships between substrate reactivity and substrate structure and between substrate reactivity and the composition of the medium [1–4]. Hydrocarbons are poorly soluble in aqueous media and are distributed between the solution and the gas phase because of their high volatility. For this reason, special experimental methods were developed for determining the reaction rate. These are the syringe reactor method, which allows kinetics to be studied in the absence of a gas phase, and the kinetic distributive method, which enables the researcher to measure the true (liquid-phase) rate constant along with determining the solution–gas distribution coefficient for the substrate [1]. Use of these methods in combination with data avail-

able on intermediate and ultimate products provides deeper insight into reaction mechanisms.

This approach has made it possible to divide the reactions of benzene, methylbenzene, dimethylbenzene, and polymethylbenzenes (ArH) with electrophilic and oxidizing reagents (E^+) into groups according to the nature of the rate-limiting step [2, 5, 6]. Group I reactions begin with electron transfer; group II reactions, with the formation of a σ -complex. Although the

existence of $\left\{ \begin{array}{c} \text{H} \\ \diagup \\ \text{Ar} \\ \diagdown \\ \text{E} \end{array} \right\}^+$ charge-transfer complexes and

of the σ -complex $\left\{ \begin{array}{c} \text{H} \\ \diagup \\ \text{Ar} \\ \diagdown \\ \text{E} \end{array} \right\}^+$ as transition states or

intermediates is universally accepted [7–11], it was only in our works [5, 6] that the rate of group I reactions was demonstrated to be determined by the arene ionization potential I_{ArH} ,

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

and the rate of group II reactions was shown to be determined by the arene basicity $\log K_B$,

$$\Delta \log k = a \Delta \log K_B. \quad (2)$$

Here, b and a are coefficients depending on temperature and the nature of the arene. Group I includes nitration reactions in various media [12, 13] and substrate oxidation with cobalt(III) [14]. Group II includes most electrophilic aromatic substitution reactions (halogenation, alkylation, mercurization, oxymethylation, etc.) [6, 7, 15]. Furthermore, there are reactions whose rate is determined by both $\log K_B$ and I_{ArH} . In methylbenzene hydroxylation [16] and ArH oxidation with $HMnO_4$ or MnO_3^+ [2], the transition state is an entity intermediate between a charge-transfer complex and a σ -complex, as follows from the rate equation

$$\Delta \log k = b' \Delta I_{ArH} + a' \log K_B. \quad (3)$$

At the same time, the reaction between ArH and nitric acid [17] proceeds via two parallel pathways, one controlled by the ionization potential and the other by the basicity:

$$k = c_1 10^{b'' I_{ArH}} + c_2 K_B^{a''}. \quad (4)$$

In order to gain deeper insight into the mechanisms of the interaction between ArH and E^+ , we applied the above approach to arene oxidation with the metavanadic acid–sulfuric acid system. Vanadium(V) has been extensively studied as an oxidizer and catalyst [18–27] and has found commercial application [28, 29]. It is a component of phosphomolybdo vanadic 12-heteropolyacids, which are capable of activating dioxygen under mild conditions, thereby making oxidation on metal complexes a catalytic reaction [30–32]. However, no systematic information concerning the rates and mechanisms of arene–vanadium(V) reactions has been reported in the literature. Here, we report kinetics, the kinetic isotope effects (KIE) of hydrogen, and rate-versus-temperature dependences for the reactions of benzene, alkylbenzenes, dialkylbenzenes, and polyalkylbenzenes with metavanadic acid in sulfuric acid media; the effect of acidity on these reactions; and the composition of the product of toluene coupling in the HVO_3 –sulfuric acid system (see also preliminary brief communications on this subject [33, 34]).

EXPERIMENTAL PROCEDURES

Kinetic measurements. The following equation is used in the kinetic distributive method [1] involving the GLC monitoring of substrate consumption in the gas phase over the solution at $[ArH] \ll [HVO_3]$:

$$-(d[ArH]_g/dt) = k [ArH]_g [HVO_3] / (1 + \alpha \lambda), \quad (5)$$

where k is the rate constant of the second-order liquid phase reaction, $\lambda = V_g/V_{sln}$ is the gas-to-solution volume ratio in the reactor, and $\alpha = [ArH]_g/[ArH]_{sln}$ is the gas–liquid distribution coefficient of the substrate. We used the competition variant of the kinetic distributive method [1]: the rates of the reactions of two substrates $Ar'H$ and $Ar''H$ (not benzene) were simultaneously

measured in one solution. In the case of two parallel reactions,

$$-(d[Ar'H]_g/dt) = k' [Ar'H]_g [HVO_3] / (1 + \alpha' \lambda), \quad (6)$$

$$-(d[Ar''H]_g/dt) = k'' [Ar''H]_g [HVO_3] / (1 + \alpha'' \lambda). \quad (7)$$

By eliminating time and $[HVO_3]$ from Eqs. (6) and (7), we obtain, after integration,

$$\Delta \log [Ar'H]_g = \{k'(1 + \alpha'' \lambda)/k''(1 + \alpha' \lambda)\} \Delta \log [Ar''H]_g. \quad (8)$$

The values of k' and k'' were determined using Eqs. (6) and (7), and the relative rate constant $k_{rel} = k'/k''$ was derived from relationship (8). The α values necessary for these calculations were measured in earlier studies [33, 34]. The rate constants determined in this study are listed in Tables 1 and 2. The errors in α and in the rate constants do not exceed $\pm 10\%$. KIEs were studied in two reactors with a common temperature-control jacket. This technique allowed us to measure, in one run, k_{rel} for alkylbenzenes containing hydrogen H and deuterium D and to determine the KIE value by the formula

$$(k_H/k_D) = k_{H, rel}/k_{D, rel}. \quad (9)$$

Reaction solutions and products. In our experiments, we used reagent-grade metavanadic and sulfuric acids and twice distilled water. For the reactions of low-reactivity arenes in solutions with $[HVO_3] \geq 10^{-3}$ mol/kg, the rate constant was independent of the solution storage time (up to 1 month) within the experimental error and did not change in a series of repeated measurements in the same solution. The reactions of active dimethylbenzenes and trimethylbenzenes were studied at $[HVO_3] \leq 10^{-4}$ mol/kg using freshly prepared solutions. In order to identify the toluene coupling products, 1.5 ml of toluene was added to 2.5 ml of a solution containing 0.048 mol/kg HVO_3 and 70.0 wt % H_2SO_4 . After 1 h, the reaction products that had formed in the organic phase at 30°C under stirring were analyzed on a chromatograph with a flame-ionization detector by comparing their retention times with the retention time of authentic compounds. The columns were packed either with 5% SE-30/Chromaton NAW (column length 1 m) or with INNOWAX (column length 30 m, i.d. 0.5 mm).

EXPERIMENTAL DATA

Kinetics. In aqueous sulfuric acid ($[H_2SO_4] > 50$ wt %), metavanadic acid oxidizes benzene and alkylbenzenes. This reaction is first-order with respect to substrate and HVO_3 (Eq. (5) is valid up to an ArH conversion of 90% and above). The toluene and *m*-xylene oxidation constants at 30°C are the following:

| Arene | [H ₂ SO ₄], wt % | [HVO ₃] × 10 ³ , mol/kg | <i>k</i> × 10 ² , kg mol ⁻¹ s ⁻¹ |
|------------------|---|--|---|
| Toluene | 59.9 | 3.83–35.1 | 3.4 ± 0.3 |
| <i>m</i> -Xylene | 53.7 | 1.18–36.4 | 14 ± 2 |

Effect of acidity. The reaction rate increases exponentially as the sulfuric acid concentration is raised. This is clear from experimental data for the oxidation of toluene with HVO₃ solutions in sulfuric acid (57–65 wt % H₂SO₄) and for the competing oxidations of the substrate couples toluene/ethylbenzene and toluene-d₈/ethylbenzene in a wider H₂SO₄ concentration range of 56.9–68.0 wt % (Table 1). Figure 1 plots log *k* as a function of the acidity function *H*₀ for (1) toluene, (2) toluene-d₈, and (3) ethylbenzene. log *k* increases linearly with decreasing *H*₀ in the H₂SO₄ concentration range 57–65 wt % and then plateaus. A similar behavior is shown by log *k* as a function of the acidity function *H*_R, which characterizes the ability of acid solutions to convert alcohols into carbocations. Numerical *H*₀ and *H*_R data are presented elsewhere [35, 36]. The slopes $-(\Delta \log k / \Delta H_0)$ and $-(\Delta \log k / \Delta H_R)$ of the linear portions of the log *k* curves for toluene, toluene-d₈, and ethylbenzene are equal to 1.6 ± 0.1 and 0.8 ± 0.1 , respectively.

Kinetic isotope effects. Replacing the ordinary substrate with a substrate containing deuterium in its aromatic ring does not change the rate of the reaction in the H₂SO₄–H₂O–HVO₃–ArH system at 30°C: KIE = 1 for

the C₆H₆/C₆D₆ and C₆H₅CH₃/C₆D₅CH₃ couples in 70 and 60 wt % H₂SO₄, respectively. For fully deuterated methylbenzenes, KIE > 1. For the *p*-xylene/*p*-xylene-d₁₀ couple in 59.7% H₂SO₄, *k*_H/*k*_D = 1.4. As for the toluene/toluene-d₈ couple, KIE increases from 1.2 to 1.5 as the sulfuric acid concentration is raised from 57 to 65 wt % and does not change as [H₂SO₄] is further increased to 68 wt % (Table 1).

Substrate selectivity. Table 2 illustrates the effect of the arene structure on the rate of arene conversion in 59.7 and 58.6% H₂SO₄. The *k* value for benzene, the least reactive substrate, was measured between 60 and 93°C. For dimethylbenzenes and trimethylbenzenes, the most active substrates, *k* was measured at 4–50°C. ArH sulfonation does not proceed to any significant extent under these conditions. For example, at [HVO₃] = 2×10^{-4} mol/kg and 30°C, the rate of mesitylene oxidation with vanadium(V) in 60% sulfuric acid is ~4000 times as high as the mesitylene sulfonation rate. The oxidation rate depends only slightly on the nature of the alkyl group (*tert*-BuPh < MePh ≈ EtPh ≈ *i*-PrPh) and increases markedly with increasing number of methyl substituents in ArH. Benzene is oxidized 100–400 times less rapidly than toluene.

Table 1. Effect of the sulfuric acid concentration on the oxidation rate of alkylbenzenes in the H₂SO₄–H₂O–HVO₃ solution and on KIE = *k*_{C₆H₅CH₃/*k*_{C₆D₅CD₃ at 30°C}}

| [H ₂ SO ₄], wt % | <i>k</i> × 10 ² , kg mol ⁻¹ s ⁻¹ | | | <i>k</i> _H / <i>k</i> _D (Eq. (9)) |
|---|---|---|---|---|
| | C ₆ H ₅ CH ₃ | C ₆ D ₅ CD ₃ | C ₆ H ₅ C ₂ H ₅ | |
| 56.9 | 1.4 | 0.9 | 1.4 | 1.2 |
| 57.2 | 1.9 | – | – | – |
| 57.3 | 3.0 | 1.9 | 3.5 | 1.2 |
| 58.2 | 2.7 | – | – | – |
| 59.7 | 5.7 | – | – | – |
| 59.7 | 3.8 | 3.3 | 4.5 | 1.2 |
| 61.8 | 16 | – | – | – |
| 61.8 | 11 | 8.0 | 13.0 | 1.3 |
| 62.5 | 20 | – | – | – |
| 63.5 | 40 | – | – | – |
| 63.6 | 39 | – | – | – |
| 64.1 | 58 | 42 | 61 | 1.3 |
| 64.5 | 89 | – | – | – |
| 65.1 | 130 | – | – | – |
| 66.2 | 130 | 84 | 152 | 1.5 |
| 68.0 | 140 | 110 | 190 | 1.4 |

Table 2. Rate constants (k , $\text{kg mol}^{-1} \text{ s}^{-1}$) for the reactions of benzene, monoalkylbenzenes, and polyalkylbenzenes with HVO_3 in 59.7 wt % H_2SO_4 and for the reactions of xylenes with HVO_3 in 58.6 wt % H_2SO_4 at various temperatures

| Benzene | | | | | | | |
|---------------------------|----------------------------|----------------------|----------------------|----------------------|----------------------|------|-----|
| $T, ^\circ\text{C}$ | 30 | 60 | 70 | 80 | 90 | 93 | |
| Benzene* | $0.63 \times 10^{-3}^{**}$ | 2.4×10^{-3} | 3.9×10^{-3} | 5.2×10^{-3} | 9.1×10^{-3} | | |
| Monoalkylbenzenes | | | | | | | |
| $T, ^\circ\text{C}$ | 20 | 30 | 40 | 50 | 65 | 80 | 95 |
| Toluene | 0.018 | 0.054 | 0.093 | 0.28 | 0.82 | 1.8 | 4.2 |
| Ethylbenzene | 0.015 | 0.061 | 0.112 | 0.33 | 0.89 | 2.05 | 5.7 |
| Isopropylbenzene | 0.016 | 0.054 | 0.10 | 0.25 | 0.97 | 3.0 | 6.9 |
| <i>tert</i> -Butylbenzene | 0.006 | 0.032 | 0.055 | 0.14 | 0.40 | 1.1 | 1.6 |
| Polymethylbenzenes | | | | | | | |
| $T, ^\circ\text{C}$ | 4 | 10 | 20 | 30 | 40 | 50 | |
| <i>o</i> -Xylene | 0.33 | 0.61 | 1.20 | 2.1 | 3.8 | | |
| <i>m</i> -Xylene | 0.32 | 0.46 | 1.28 | 1.9 | 5.3 | | |
| <i>p</i> -Xylene | 3.3 | 5.1 | 10.8 | 12 | 29 | | |
| Mesitylene | 2.4 | 3.4 | 9.8 | 18 | 51 | | |
| Pseudocumene | 20 | 29 | 52 | 68 | 180 | | |
| Xylenes | | | | | | | |
| $T, ^\circ\text{C}$ | 4 | 10 | 20 | 30 | 40 | 50 | |
| <i>o</i> -Xylene | 0.15 | 0.31 | 0.72 | 1.65 | 2.5 | 4.3 | |
| <i>m</i> -Xylene | 0.12 | 0.22 | 0.60 | 1.0 | 2.4 | 5.1 | |
| <i>p</i> -Xylene | 1.9 | 2.9** | 3.8 | 6.8 | 13 | 16 | |

*The rate constants of reactions involving benzene were determined in one solution containing 0.029 mol/kg HVO_3 at $\lambda = 1.8$.

**Estimated using Eq. (10).

Table 3. Activation parameters for arene– HVO_3 reactions in H_2SO_4 solutions and ionization potentials of arenes [37]

| Entry | Arene | $\log A$ [$\text{kg mol}^{-1} \text{ s}^{-1}$] | E , kJ/mol | I_{ArH} , kJ/mol |
|-------|---------------------------|--|--------------|---------------------------|
| 1 | Benzene | 3.6 ± 0.5 | 40 ± 3 | 890.7 |
| 2 | Toluene | 9.9 ± 0.4 | 65 ± 2 | 851.1 |
| 3 | Ethylbenzene | 10.6 ± 0.5 | 70 ± 3 | 845.3 |
| 4 | Isopropylbenzene | 11.3 ± 0.3 | 73 ± 2 | 839.6 |
| 5 | <i>tert</i> -Butylbenzene | 9.7 ± 0.7 | 66 ± 4 | 837.6 |
| 6 | <i>o</i> -Xylene | 8.5 ± 0.3 | 47 ± 2 | 826.0 |
| 6' | <i>o</i> -Xylene | 9.4 ± 0.5 | 54 ± 3 | |
| 7 | <i>m</i> -Xylene | 9.8 ± 0.7 | 55 ± 4 | 826.0 |
| 7' | <i>m</i> -Xylene | 10.3 ± 0.4 | 60 ± 2 | |
| 8 | <i>p</i> -Xylene | 8.1 ± 0.8 | 40 ± 5 | 814.5 |
| 8' | <i>p</i> -Xylene | 7.3 ± 0.4 | 38 ± 3 | |
| 9 | Mesitylene | 11.8 ± 0.6 | 61 ± 4 | 810.6 |
| 10 | Pseudocumene | 9.0 ± 0.8 | 41 ± 5 | 798.1 |

Note: Data 1–10 refer to 59.7 wt % H_2SO_4 ; data 6'–8', to 58.6 wt % H_2SO_4 .

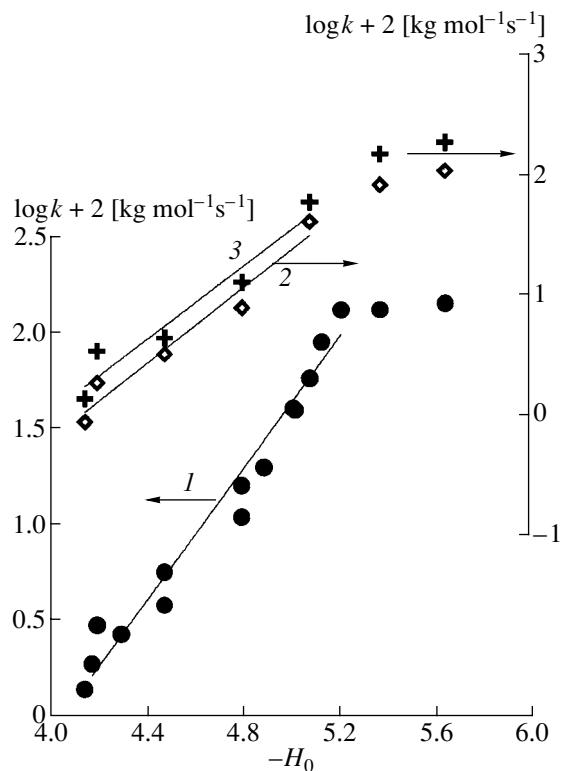


Fig. 1. Reaction rate constant versus the acidity function H_0 for (1) toluene, (2) toluene-d₈, and (3) ethylbenzene in $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HVO}_3$ solutions at 30°C.

Toluene oxidation yields coupling products, namely, methyldiphenylmethanes with the formula $\text{PhCH}_2\text{C}_6\text{H}_4\text{CH}_3$, and no ditolyls ($\text{CH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$) or dibenzyl ($\text{PhCH}_2\text{CH}_2\text{Ph}$).

Reaction rates and the ionization potential of arenes. The rate of the first, slow, stage of methylbenzene oxidation in the $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HVO}_3$ system is not correlated with the basicity of ArH (the correlation coefficient is $r = 0.6$). At the same time, in the benzene-methylbenzenes series, $\log k$ is linearly related to the ArH ionization potential (Fig. 2, line I), obeying Eq. (1) with a high correlation coefficient of $r = 0.998$. Ethylbenzene, isopropylbenzene, and *tert*-butylbenzene react at a lower rate and are outliers (open circles 3–5) apparently because of steric hindrance.

Activation parameters. Extended compensation effect. The Arrhenius equation is valid for the reactions of the substrates in $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HVO}_3\text{--ArH}$ solutions:

$$\log k = \log A - E/2.3RT. \quad (10)$$

The $\log A$ and E data obtained using this equation are listed in Table 3.

After we had plotted E as a function of A on the coordinates of the compensation effect equation [38, 39],

$$E = C_1 + C_2 \log A \quad (11)$$

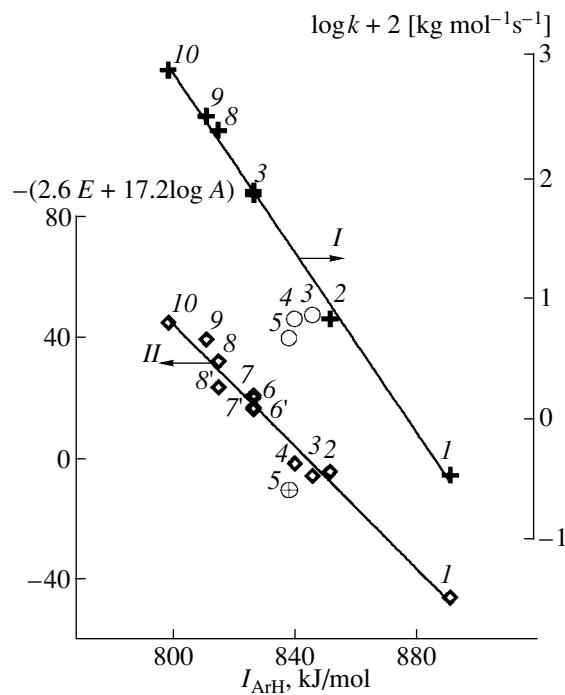


Fig. 2. (I) Rate constant and (II) activation parameters versus ionization potential for the reactions of arenes in $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HVO}_3$ solutions: (I) 30°C, 59.7 wt % H_2SO_4 ; (II) 59.7 and 58.6 wt % H_2SO_4 . The data points are numbered in the same way as in Table 3.

we first viewed the result as widely scattered experimental data. However, it was found in an earlier study [34] that the substrates can be divided into four groups according to the number of substituents in the benzene ring (n). The first group (at the extreme right of Fig. 3; points 9, 10) consists of trimethylbenzenes ($n = 3$); the second group (points 6–8 and 6'–8'), of dimethylbenzenes ($n = 2$); the third (points 2–5), of monoalkylbenzenes ($n = 1$); the fourth (point 1 at the left of Fig. 3), of benzene alone ($n = 0$). The rates of the reactions involving benzene depend weakly on temperature and are characterized by a small $\log A$ value (Table 3). The slopes of lines I–III in Fig. 3, which refer to the first three groups of substrates, are similar, and each indicates that there is a compensation effect, since $\log A$ and E vary symbatically.

It was assumed that, in our system, the activation energy depends not only on $\log A$, as in the case of an ordinary compensation effect (Eq. (11)), but also on the number of substituents in the benzene ring. In an earlier study [34], we found that the experimental data for this system can be fitted to the following empirical equation with a high degree of accuracy ($r = 0.993$; the significance level for each of the three coefficients is below 0.0001):

$$E = 7.0 \log A - 18.6n^{0.6} + 15.0. \quad (12)$$

This equation provides a good fit for all of the experimental data (Fig. 3, line IV). The isokinetic temperature is 367 K. Although the correlation equation (12) does not take into account steric factors explicitly, it covers not only benzene and methylbenzenes but also the sterically hindered arenes ethylbenzene, isopropylbenzene, and *tert*-butylbenzene.

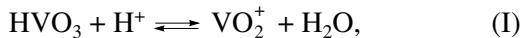
Since the ionization potentials of the arenes examined and of higher polymethylbenzenes correlate with $n^{0.6}$ ($r = 0.976$), which varies between 0 for benzene and 2.93 for hexamethylbenzene, our data can be fitted to a three-parameter equation interrelating the activation parameters and the temperature-independent parameter I_{ArH} :

$$\log A = 0.15E - 0.058I_{\text{ArH}} + 49.1. \quad (13)$$

None of these parameters alone is correlated with another parameter. Equation (13) is valid for the arene series consisting of benzene, methylbenzenes, ethylbenzene, isopropylbenzene, dimethylbenzenes, and trimethylbenzenes ($r = 0.995$; the significance level for each of the three coefficients is below 0.0001). *tert*-Butylbenzene is an outlier (Fig. 2, curve II). The isokinetic temperature is 335 K. The three-parameter equations (12) and (13) can be called extended compensation effect equations.

DISCUSSION

Active species. In aqueous acid solutions, HVO_3 exists as a mononuclear complex of the singly charged dioxo cation VO_2^+ or the doubly charged cation V(OH)_3^{2+} , which result from the reactions



and undergo interconversion [40–42]. Furthermore, it is believed that the singly charged cations $[\text{V(OH)}_4(\text{H}_2\text{O})]^+$ and $[\text{V(OH)}_4(\text{H}_2\text{O})_2]^+$ [42] exist in aqueous media and the complexes $[\text{V(OH)}_3(\text{HSO}_4)]^+$ and $[\text{VO}(\text{H}_2\text{O})\text{SO}_4]^+$ [41] exist in sulfuric acid. We will represent the vanadium reagent as VO_2^+ for the reason that we cannot make a well-founded choice among the above species. As the sulfuric acid concentration is raised from 57 to 65 wt %, the concentration of active species in the $\text{H}_2\text{SO}_4\text{--H}_2\text{O}\text{--HVO}_3$ solution and, possibly, the composition of these species vary. However, some limit is reached as $[\text{H}_2\text{SO}_4]$ is further increased to 68 wt %. It is this trend that determines the effect of solution acidity on k and KIE (Table 1, Fig. 1).

Mechanism of the reaction. According to Beletskaya et al. [8, 9], possible products of the first step of the reaction between an aromatic hydrocarbon and a variable-valence metal (Ag(II), Cu(II), Pd(II), Co(III), Mn(III), Fe(III), Tl(III), Pb(IV), or Ce(IV)) complex are radicals, radical cations, and cations. Our

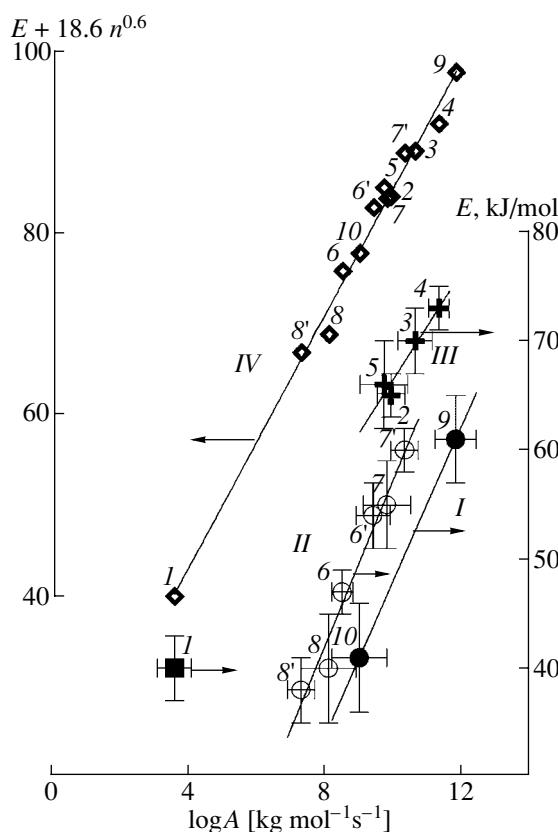
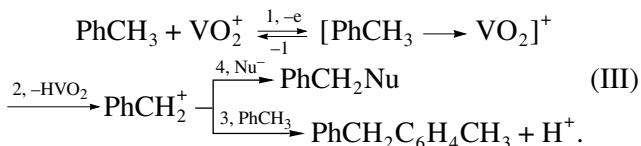


Fig. 3. E as a function of $\log A$ for the reactions of arenes with HVO_3 in 59.7 and 58.6 wt % H_2SO_4 : (I) trimethylbenzenes, (II) dimethylbenzenes, (III) monoalkylbenzenes, and (IV) the general relationship given by Eq. (12). The data points are numbered in the same way as in Table 3.

data are consistent with this view. The mechanism of the reaction for toluene can be represented as follows:



The reaction begins with electron transfer from toluene to VO_2^+ to yield a charge-transfer complex or an ion-radical pair (step 1). Step 2 is the abstraction of an H atom, which yields the benzyl carbocation PhCH_2^+ . Next, this carbocation attacks a PhCH_3 molecule (step 3) to produce the coupling product $\text{PhCH}_2\text{C}_6\text{H}_4\text{CH}_3$ or reacts with the nucleophile Nu^- (HSO_4^- or H_2O). A similar mechanism was earlier suggested for reactions of arenes with other metal complex oxidizers [8, 9] and with vanadium heteropolyacids [43, 44]. It was reported that step 2 may consist of two individual reactions, namely, H^+ abstraction yielding a PhCH_2^+ radical and the abstraction of the second electron [9, 43–45]. The absence of dibenzyl in the reaction products and the validity of correlation (1) are evidence

that the benzyl radical is not the first intermediate under the conditions examined. Applying the steady-state concentration method to mechanism (III), we obtain the following expression for the toluene disappearance rate:

$$\frac{d[\text{PhCH}_3]}{d\tau} = \frac{k_1 k_2 [\text{PhCH}_3][\text{VO}_2^+]}{(k_{-1} + k_2)} \times \frac{(2k_3[\text{PhCH}_3] + k_4[\text{Nu}^-])}{(k_3[\text{PhCH}_3] + k_4[\text{Nu}^-])} \quad (14)$$

According to this equation, the reaction must be first-order with respect to both the substrate and the reagent at both $k_4[\text{Nu}^-] \gg k_3[\text{PhCH}_3]$ and $k_4[\text{Nu}^-] \ll k_3[\text{PhCH}_3]$, and experiments have demonstrated that this is really the case. The numerical values of k_3 and k_4 have not been determined as yet.

Comparing reactions whose rate is determined by the ionization potential. This group of reactions includes reactions of arenes with NO_2^+ , Co^{3+} , and VO_2^+ . The rate of these reactions is determined by the ionization potential according to Eq. (1).

Reaction mechanism. Among these reactions, electrophilic aromatic nitration has been studied in greatest detail [7, 46–49]. Esteves et al. [48], who have systematized the results of a long-term investigation of this process, consider three intermediates in the reaction coordinate–potential energy diagram. The first intermediate is an unoriented donor–acceptor π -complex with strong Coulomb interaction. The second is an oriented π -complex in which charge is transferred from the π -electron system of the arene to NO_2^+ (intimate $\text{ArCH}_3^+/\text{NO}_2$ pair). The decomposition of this complex yields the third intermediate, which is a σ -complex. The abstraction of a proton from this intermediate produces a nitrated arene.

Alkylbenzene oxidation with cobalt(III) occurs mainly via the abstraction of a hydrogen atom from the α -carbon of the alkyl group. For example, the formation of the benzyl radical PhCH_2^\cdot can occur either in a single step or in two steps [50]. In the latter case, the process includes electron transfer resulting in the radical cation PhCH_3^{+*} and subsequent deprotonation. The abstraction of another electron yields the carbocation PhCH_2^+ . This species enters either into substitution reactions at the alkyl group or into oxidative coupling [9, 41–54]. This mechanism is similar to the mechanism of the reaction involving VO_2^+ (scheme (III)). Thus, oxidative substitution yields products in which the new group is either in the aromatic ring (in the case of nitration) or in the side chain (in the case of the reactions with Co^{3+} or VO_2^+).

Similarity between the reactions involving different reactants. With anyone of the three reactants (NO_2^+ , Co^{3+} , and VO_2^+), the reaction is first-order with

respect to substrate; that is, the preactivation step (the formation of a reactive species) does not determine the overall reaction rate. Furthermore, the reaction is first-order with respect to HNO_3 (nitration [12, 13]) and HVO_3 . The reaction involving Co^{3+} is of the order 1.34 with respect to the oxidizer [14]. This fact is believed to be due to the participation of cobalt(III) complex dimers in the reaction. The reaction rate increases with increasing solution acidity. The reactivity of cobalt(III) acetate in acetic acid can be substantially increased by adding a small amount (up to 1 mol/l) of a strong acid [51]. In the reactions of arenes with NO_2^+ and VO_2^+ , $\log k$ is a linear function of the acidity function H_R . However, in the reactions involving NO_2^+ , $\log k$ passes through a maximum at $[\text{H}_2\text{SO}_4] \sim 90$ wt % [1]; in the reactions involving VO_2^+ , it plateaus at $[\text{H}_2\text{SO}_4] \geq 65$ wt %. Comparing the C–H bond dissociation rates for the primary carbon atom in toluene (1^0), the secondary carbon atom in ethylbenzene (2^0), and the tertiary carbon atom in isopropylbenzene (3^0) allows the one- and two-step alkylbenzene oxidation mechanisms to be distinguished [50]. In the one-step mechanism, reactivity always increases in the order $1^0 < 2^0 < 3^0$, following the decreasing order of C–H bond dissociation energies. In the two-step mechanism, in which the rate-limiting step is electron transfer, the strength of the C–H bonds is insignificant and the order of reactivities is mainly determined by the standard oxidation potential of the substrate (E_{ArH}^0).¹ Toluene, ethylbenzene, and isopropylbenzene are characterized by similar E_{ArH}^0 values [55] and, accordingly, similar C–H bond dissociation rates: $1^0 \approx 2^0 \approx 3^0$. In nitration at 25°C [13] and oxidation with VO_2^+ at 20–95°C (Table 2), the MePh, EtPh, and *i*-PrPh substrate selectivity is low. This finding is in agreement with the view that the rate-determining step is electron transfer. For the reactions of arenes deuterated only in their aromatic ring with Co^{3+} [14], NO_2^+ [13], and VO_2^+ , $\text{KIE} = 1$.

Distinctions between the reactions: compensation effect. In toluene nitration, KIE is $k_{\text{H}}/k_{\text{D}} = 1$ or 1.2 [13, 47]. Therefore, the rate-limiting step is electron transfer and the abstraction of a proton is a rapid step. A large KIE value of 5.6 [14] and a small KIE value of 1.08 [52] are reported for toluene oxidation with Co^{3+} . Since the latter value was obtained using a somewhat incorrect method based on oxidizer consumption measurements, we will accept the KIE value of 5.6 [14]. This large KIE value in the reaction involving Co^{3+} and

¹ The linear correlation $E_{\text{ArH}}^0 = 0.71I_{\text{ArH}} - 3.68$ was reported for arenes [55]. Here, E_{ArH}^0 is the standard oxidation potential in trifluoroacetic acid (in volts vs. Ag/AgClO_4 standard electrode) and I_{ArH} is the ArH ionization potential in the gas phase (in electron-volts).

the fact that KIE in the reaction involving VO_2^+ increases from 1.2 to 1.5 as the acidity of the medium is raised (Table 1) are apparently explained by the competition between electron transfer and deprotonation in the two-step mechanism. The following factors are significant in this competition: the steric effect, the transfer of an electron forming the C–H σ -bond to the aromatic π -electron system [56], the nature of the base [57], and the energy of the breaking alkyl bond C–H. This is a plausible explanation of the fact that $\text{KIE} > 1$ and of the unusual reactivity order $2^0 > 3^0 > 1^0$ in the reactions of alkylbenzenes with Co^{3+} (the $2^0 : 3^0$ and $3^0 : 1^0$ ratios are not large, varying between 1.1 and 1.8) [50]. Since Co^{3+} in an acid medium is a strong one-electron oxidizer ($E_0 = 1.8$ V [58]), the aromatic radical cation forms at a high rate. The abstraction of H^+ is a significant factor in the reaction rate. Furthermore, cobalt(III) acetate is viewed not only as an oxidizer, but primarily as a free-radical reagent [9]. In this case, because the abstraction of an H atom is a slow step, the KIE value

is large. As compared to Co^{3+} , VO_2^+ is a weaker one-electron oxidizer ($E_0 = 1.0$ V [58]) and deprotonation in the reaction involving this reagent is a much less significant factor in the reaction rate. However, this factor increases as the acidity of the medium is raised. It is interesting that I_{ArH} correlates with the C–H bond dissociation energy [49, 59] in the benzene–toluene–ethylbenzene–isopropylbenzene–*p*-xylene–*m*-xylene series ($r = 0.980$). It is apparently because of this correlation that the arene ionization potential is so significant not only in the reactions involving NO_2^+ , which have a single rate-limiting step (electron transfer), but also in the reactions involving VO_2^+ and, particularly, Co^{3+} , in which the electron transfer and deprotonation rates are comparable.

The substrate selectivity is higher in the reactions of benzene and polymethylbenzenes with VO_2^+ than in the same reactions with Co^{3+} and, particularly, NO_2^+ , as is indicated by an increase in the coefficient b in Eq. (1):

| System | VO_2^+ , 59.7% H_2SO_4 , 30°C | $\text{Co}^{3+}-\text{CH}_3\text{COOH}$, 1.9 M CF_3COOH , 25°C [14] | NO_2^+ , 63.8% H_2SO_4 , 25°C [12] | NO_2^+ , 64.9% H_2SO_4 , 25°C [13] |
|--------------|---|---|--|--|
| b , mol/kJ | 0.056 ± 0.001 | 0.042 ± 0.001 | 0.031 ± 0.003 | 0.026 ± 0.001 |

There is no compensation effect in arene nitration or arene oxidation with cobalt. In the reactions with NO_2^+ , the preexponential factor is nearly independent of the nature of the substrate: $\log A = 12.2 \pm 0.2$ (isoentropic series) [12]. The activation energy of the oxidation of toluene, ethylbenzene, cumene, diphenylmethane, and triphenylmethane with cobalt(III) in acetic acid is 105.9 kJ/mol (isoenthalpic series) [53]. The reaction $\text{ArH} + \text{VO}_2^+$ is the first example of the extended compensation effect.

Thus, the arene– VO_2^+ reactions are controlled by the arene ionization potential and belong formally to the same group as the reactions of arenes with NO_2^+ and Co^{3+} (group I). At the same time, there are significant distinctions between the oxidizers. While arene nitration is controlled by electron transfer, the reactions involving VO_2^+ and, particularly, Co^{3+} are likely to have two slow steps, namely, electron transfer and deprotonation. In the first approximation, the rates of both steps are determined by the arene ionization potential. It is not impossible that the alkylbenzene oxidation reactions proceeding via single-step H transfer also belong to group I. Furthermore, reactions involving the above electrophiles differ markedly in terms of the compensation effect. Three-parameter compensation relationships are established for the reactions between ArH and VO_2^+ . The finding that the correlation equation (12) is

very precisely obeyed in wide ranges of variables requires further investigation.

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REFERENCES

1. Rudakov, E.S., *Reaktsii alkanov s okislitelyami, metal-lokompleksami i radikalami v rastvorakh* (Reactions of Alkanes with Oxidizers, Metal Complexes, and Free Radicals in Solutions), Kiev: Naukova Dumka, 1985.
2. Rudakov, E.S. and Lobachev, V.L., *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 5, p. 765.
3. Goncharuk, V.V., Kamalov, G.L., Kovtun, G.A., et al., in *Kataliz. Mekhanizmy gomogenogo i geterogenogo kataliza, klasternye podkhody* (Catalysis: Cluster Approaches to the Mechanisms of Homogeneous and Heterogeneous Catalysis), Kiev: Naukova Dumka, 2002.
4. Rudakov, E.S., Tishchenko, N.A., and Volkova, L.K., *Kinet. Katal.*, 1986, vol. 27, no. 5, p. 1101.
5. Rudakov, E.S. and Lobachev, V.L., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, 1987, vol. 9, no. 3, p. 25.
6. Rudakov, E.S. and Lobachev, V.L., *Kinet. Katal.*, 1990, vol. 31, no. 6, p. 1302.
7. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, Ithaca: Cornell Univ. Press, 1969.
8. Beletskaya, I.P. and Makhon'kov, D.I., *Usp. Khim.*, 1981, vol. 50, no. 6, p. 1007.

9. Makhon'kov, D.I., Rodkin, M.A., and Beletskaya, I.P., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1987, vol. 9, no. 3, p. 4.
10. Galli, C. and Fornarini, S., *J. Chem. Soc., Perkin Trans. 2*, 1993, p. 1147.
11. Rosokha, S.V. and Kochi, J.K., *J. Org. Chem.*, 2002, vol. 67, no. 6, p. 1727.
12. Rudakov, E.S., Lobachev, V.L., and Tserkovnikov, S.A., *Kinet. Katal.*, 1993, vol. 34, no. 3, p. 439.
13. Rudakov, E.S., Lobachev, V.L., Ignatenko, V.M., and Velichko, L.I., *Kinet. Katal.*, 1986, vol. 27, no. 6, p. 1315.
14. Rudakov, E.S. and Lobachev, V.L., *Kinet. Katal.*, 1988, vol. 29, no. 5, p. 1056.
15. Lobachev, V.L., Zimtseva, G.P., and Rudakov, E.S., *Teor. Eksp. Khim.*, 2001, vol. 37, no. 1, p. 15.
16. Lobachev, V.L., *Teor. Eksp. Khim.*, 1999, vol. 35, no. 1, p. 39.
17. Lobachev, V.L., Rudakov, E.S., and Savsunenko, O.B., *Kinet. Katal.*, 1991, vol. 32, no. 1, p. 17.
18. Waters, W.A., *Mechanism of Oxidation of Organic Compounds*, London: Methuen, 1963.
19. Yatsimirskii, K.B. and Nikolov, G.S., *Zh. Fiz. Khim.*, 1970, vol. 44, no. 5, p. 1129.
20. Mimoun, H., Saussine, L., Daire, E., et al., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 10, p. 3101.
21. Singh, V.P. and Saxena, S.B., *J. Indian Chem. Soc.*, 1988, vol. 65, no. 12, p. 847.
22. Lindroor-Heinanen, R. and Virtanen, P.O.I., *Remiakemi*, 1988, vol. 15, no. 10B, p. 1038.
23. Moiseeva, N.I., Gekhman, A.E., Blyumberg, E.A., and Moiseev, I.I., *Kinet. Katal.*, 1988, vol. 29, no. 4, p. 970.
24. Mamedov, E.A. and Corberan, V.C., *Appl. Catal.*, A, 1995, vol. 127, nos. 1–2, p. 1.
25. Krylov, O.V. and Shub, B.R., *Nonequilibrium Processes in Catalysis*, Boca Raton: CRC, 1994.
26. Krylov, O.V. and Matyshak, V.A., *Usp. Khim.*, 1995, vol. 64, no. 2, p. 177.
27. Griesel, L., Bartley, J.K., Wells, R.P.K., and Hutchings, G.J., *J. Mol. Catal. A: Chem.*, 2004, vol. 220, p. 113.
28. Muzgin, V.N., Khamzina, L.B., Zolotov, V.L., and Bezrukov, I.Ya., *Analiticheskaya khimiya vanadiya* (Analytical Chemistry of Vanadium), Moscow: Nauka, 1981.
29. Satterfield, Ch. N., *Heterogeneous Catalysis in Practice*, New York: McGraw-Hill, 1980.
30. Matveev, K.I., *Kinet. Katal.*, 1977, vol. 18, no. 4, p. 862.
31. Matveev, K.I. and Kozhevnikov, I.V., *Kinet. Katal.*, 1980, vol. 21, no. 5, p. 1189.
32. Burton, H.A. and Kozhevnikov, I.V., *J. Mol. Catal. A: Chem.*, 2002, vol. 185, p. 285.
33. Volkova, L.K., Lobachev, V.L., and Rudakov, E.S., *Teor. Eksp. Khim.*, 1999, vol. 35, no. 6, p. 349.
34. Volkova, L.K., Rudakov, E.S., Lobachev, V.L., et al., *Teor. Eksp. Khim.*, 2003, vol. 39, no. 6, p. 341.
35. Vinnik, M.I., *Usp. Khim.*, 1966, vol. 35, no. 11, p. 1922.
36. Deno, N.C., Jaruzelski, J.J., and Schwiesheim, G., *J. Am. Chem. Soc.*, 1955, vol. 77, no. 11, p. 3044.
37. Fukuzumi, S. and Kochi, J.K., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 24, p. 7240.
38. Riche, C.D. and Sadger, U.F., in *Progress in Physical Organic Chemistry*, Cohen, S.G., Streitwieser, A., Jr., and Taft, R.W., Eds., New York: Wiley Interscience, 1963, vols. 1, 2.
39. Brown, M.E. and Galwey, A.K., *Thermochim. Acta*, 2002, vol. 387, p. 173.
40. Littler, J.S. and Waters, W.A., *J. Chem. Soc.*, 1959, no. 3, p. 1299.
41. Littler, J.S. and Waters, W.A., *J. Chem. Soc.*, 1959, no. 12, p. 4046.
42. Ivakin, A.A. and Fotiev, A.A., *Tr. Inst. Khim. Ural. Nauchn. Tsentr. Akad. Nauk SSSR*, 1971, vol. 24, p. 1.
43. Kozhevnikov, I.V., Kim, V.I., and Talzi, V.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 10, p. 2167.
44. Kozhevnikov, I.V., *Usp. Khim.*, 1993, vol. 62, no. 5, p. 510.
45. Gorodetskaya, T.A., Kozhevnikov, I.V., Matveev, K.I., et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, no. 5, p. 1010.
46. *Advances in Physical Organic Chemistry*, Gold, V., Ed., London: Academic, 1963.
47. Carey, F.A. and Sundberg, R.J., *Advanced Organic Chemistry*, part A: *Structure and Mechanisms*, New York: Plenum, 1984, 2nd ed.
48. Esteves, P.M., Carneiro, W.J., Cardoso, S.P., et al., *J. Am. Chem. Soc.*, 2003, vol. 125, no. 16, p. 4836.
49. Chen, L., Xiao, H., Xiao, J., and Gong, X., *J. Phys. Chem. A*, 2003, vol. 107, p. 11440.
50. Baciocchi, E., D'Acunzo, F., Galli, C., and Lanzalunga, O., *J. Chem. Soc., Perkin Trans.*, 1996, p. 133.
51. Hanotier, J., Hanotier-Bridoux, M., Raditzky, P., and Labofina, S.A., *J. Chem. Soc., Perkin Trans.*, 1973, no. 4, p. 381.
52. Kochi, J.K., Tang, R.T., and Bernath, T., *J. Am. Chem. Soc.*, 1973, vol. 95, no. 21, p. 7114.
53. Sakota, K., Kamiya, Y., and Ohta, N., *Can. J. Chem.*, 1969, vol. 47, no. 3, p. 387.
54. Nyberg, K. and Wistrand, L.-G., *Chem. Scr.*, 1974, no. 6, p. 234.
55. Howell, J.O., Goncalves, J.M., Amatore, C., et al., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 14, p. 3968.
56. Onopchenko, A. and Schulz, J.G.D., *J. Org. Chem.*, 1972, vol. 37, no. 16, p. 2564.
57. Baciocchi, E., Gabrielli, R., Giancaspro, C., et al., *Tetrahedron Lett.*, 1985, vol. 26, p. 4269.
58. *Svoistva neorganicheskikh soedinenii: spravochnik* (Properties of Inorganic Compounds: A Handbook), Rabinovich, V.A., Ed., Leningrad: Khimiya, 1983.
59. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu: spravochnik* (Bond Dissociation Energies, Ionization Potentials, and Electron Affinities: A Handbook), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974.