

Reviews

The first step of oxidation of alkylbenzenes by permanganates in acidic aqueous solutions

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Data on the kinetics, kinetic isotope effects, substrate selectivity, and activation parameters for the first step of oxidation of alkylbenzenes by permanganate in acidic aqueous solutions are surveyed. The MnO_4^- , HMnO_4 , and MnO_3^+ species serve as oxidants at different acidities. The increase in the positive charge in this series enhances the electrophilicity of the reagent, which manifests itself as an increase in the reaction rate and a change in the site of attack on the alkylbenzene molecule (either the aromatic ring or C-H bond in the alkyl group). The oxidation of the alkyl C-H bonds in alkylbenzenes and in alkanes follows similar mechanisms, while the attack on the aromatic ring proceeds via the electrophilic aromatic substitution mechanism with a transition state intermediate between the charge transfer complex and σ -complex.

Key words: alkylbenzenes, permanganates, aqueous acid solutions, oxidation, kinetics, kinetic isotope effects, selectivity, activation parameters, mechanisms.

Introduction

Permanganates are widely used as oxidants for organic compounds, including hydrocarbons. Alkanes are oxidized to ketones and alkylbenzenes are converted into the corresponding benzenecarboxylic acids.^{1,2} However, the kinetics and mechanisms of the reactions and the nature of the reactive species are poorly understood; virtually no data on the oxidation in water or aqueous acids (except for the $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ system)² had been available prior to the publication of our studies,³⁻⁶ which is due to the low solubility of hydrocarbons.

Reactions with permanganates are normally studied either in aqueous solutions using substrates containing hydrophilic groups (COOH , SO_3H , OH , etc.) with extrapolation of the kinetic data to unsubstituted hydro-

carbons,⁷⁻¹² or in aqueous organic solvents in the presence of phase transfer catalysts (quaternary ammonium salts,^{13,14} crown ethers¹⁵), or in organic media in which tetraalkylammonium permanganates are soluble.¹⁵⁻¹⁷ However, in each case, the process is complicated either by oxidation of the alkyl groups in R_4NMnO_4 ¹⁶ or by oxidation of the solvent.^{13,14}

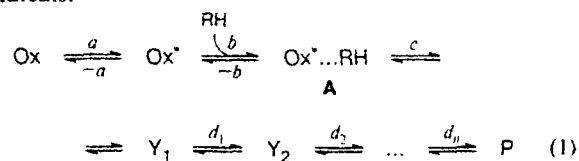
Meanwhile, in aqueous media, the step of involvement of the substrate in the reaction (the first step, see below) can be studied directly by the kinetic distribution method^{6,18} or the syringe reactor method,⁶ which provide reliable kinetic data for poorly soluble volatile substrates and, in combination with the study of the products, allow one to elucidate the mechanism of the whole reaction. These methods were employed in more than 200 publications of one of the authors of this

review with coworkers and provided vast information on the kinetics, kinetic isotope effects (KIE), substrate selectivity, and the mechanisms of the first steps of solvolysis of haloalkanes and their reactions with metal aquaions;¹⁹ oxidation of alkanes,⁶ dihydrogen,²⁰ benzene,²¹ alkylbenzenes,^{4,5,22} and thiophene²³ by various oxidants and metal complexes including Pd^{II}, Hg^{II}, Pt^{II}–Pt^{IV}, and Cr^{VI}; and electrophilic aromatic substitution reactions.^{24–26} A modification of the distribution method has been developed to study the kinetics of isobutylene hydration.²⁷

Aqueous solutions of permanganates provide a unique possibility of investigating the mechanisms of oxidation of hydrocarbons by MnO₄[−], HMnO₄, and MnO₃⁺, which have different charges (−1, 0, +1) and differ in electrophilicity. Oxidation of alkanes by permanganates has been considered in detail previously.⁶ In this review, we summarize the data on the kinetics, kinetic isotope effects, substrate selectivity, and activation parameters of the first step of oxidation of alkylbenzenes by permanganates in acidic aqueous media. The natures of the active species for different acidities, the sites of the attack on alkylbenzene molecules by these species (either the nucleus or the alkyl C–H bond), and the reaction mechanisms are discussed. The reactions of hydrocarbons with permanganates in alkaline media, which involve the ·OH radicals arising upon oxidation of the solvent,^{28–30} and oxidation of olefins in alkaline and organic media, which include nucleophilic attack by the MnO₄[−] anion on the double bond with intermediate formation of manganese(v) diester,^{31–33} are beyond the scope of this review.

Approaches to the study of the first step of oxidation and electrophilic aromatic substitution

In the general case, the reaction of hydrocarbons (alkanes RH or arenes ArH) with oxidative (electrophilic) reagents (Ox) is a multistep and often multipathway process giving rise to a broad range of products. Thus the final products of permanganate oxidation of *n*-pentane are pentan-2-one and pentan-3-one in 2 : 1 ratio; traces of propionic acid and pentan-2-ol and pentan-3-ol are formed as intermediate products.² According to the data published previously,^{6,34} the activation of the substrate is preceded by reversible or irreversible pre-activation of the oxidant (reaction (1), step *a*) due to a change in its composition, structure, or spin state or to the formation of a coordination vacancy or radicals.



The reagent Ox should be transformed into a species (Ox^{*}) that would enable cleavage of the strong C–H or

C–C bond in the subsequent elementary step. The species Ox^{*} reacts with the substrate to form complex A, which is converted into intermediate product Y₁ in elementary step *c* of reaction (1). Species A can be either a π-complex or encounter complex in a solvent cage. The species Ox^{*} is called direct reagent and the set of transformations *b* and *c* is referred to as substrate activation ("the first step").

A direct and reliable method, and the most general one, for the investigation of the first step is determination of the rate (−d[RH]/dτ) of involvement of the substrate in the reaction, which is measured based on the consumption of the substrate. In uncomplicated cases where steps *a* and *b* are fast and reversible, reaction *c* is slow (*k_c* ≪ *k_{−b}*) and irreversible, and concentrations Ox^{*} and A are low, we have^{6,34}

$$-d[\text{RH}]/d\tau = k[\text{RH}][\text{Ox}] = k_{+1}[\text{RH}][\text{Ox}^*] \quad \text{for } [\text{RH}] \ll [\text{Ox}], \quad (2)$$

where *k*₊₁ = *k_bk_c*/*k_{−b}* is the rate constant for the first step and *k* = *k*₊₁[Ox^{*}]/[Ox] is the measured rate constant.

Let us compare the approach described by Eq. (2) with traditional methods of kinetic measurements, which are based on the oxidant consumption when the substrate is present in excess, for example,^{2,35}

$$-d[\text{Ox}]/d\tau = k_{\text{Ox}}[\text{RH}][\text{Ox}] \quad \text{for } [\text{RH}] \gg [\text{Ox}],$$

or on the accumulation of products (P_{*i*}), for example,^{36,37}

$$d[\text{P}_i]/d\tau = k_{\text{P}}[\text{RH}][\text{Ox}] \quad \text{for } [\text{RH}] \gg [\text{Ox}].$$

The rate constants denoted by *k*_{Ox} and *k*_P (unlike *k* in Eq. (2)) are usually regarded as characteristics of the reactivity of hydrocarbons. However, in multistep oxidation processes, the reagent can be consumed not only in the first step but also in subsequent steps; in the general case, the relation *k*_{Ox} ≥ *k* should hold. Meanwhile, *k*_P ≤ *k* because the first step is not necessarily the slowest one in the *d*₁ → *d*_{*n*} sequence of transformations leading to the final products P_{*i*} (see reaction (1)); in this case, the constants *k*_P do not refer to the first step. This analysis gives the following inequalities for the rates and the relative rates^{6,34}

$$k_{\text{Ox}} \geq k \geq k_{\text{P}}, \quad k_{\text{Ox}}''/k_{\text{Ox}}' \geq k''/k' \geq k_{\text{P}}''/k_{\text{P}}'$$

Here *k*'' refers to a substrate with a more complex structure containing several C–H or C–C bonds of different types (for example, toluene relative to benzene). As the number of reaction sites increases, secondary reactions and the product composition become more diverse and, hence, the deviations of *k*_{Ox} and *k*_P from *k* increase. Analysis showed that the *k*_{Ox} and *k*_P values can substantially (by a factor of 10 or more) differ from *k* and depend in different fashions on the substrate structure and the medium.³⁸

Two methods for direct investigation of the first step of reactions have been developed;^{6,18} these are the kinetic distribution method (KDM) and the syringe reactor method. These techniques are required in all

cases to measure precisely the kinetics of reactions occurring in solution provided that a substantial portion of the volatile substrate (or reagent) is located in the gas phase above the solution, does not participate in the process at a given instant, and passes from one phase to the other during the process. In accordance with the KDM method, the first step of the reaction is studied with vigorous stirring of the phases, which ensures an equilibrium distribution of a poorly soluble volatile substrate between the gas and liquid phases.^{6,39} In this case, the k value in Eq. (2) should be replaced by

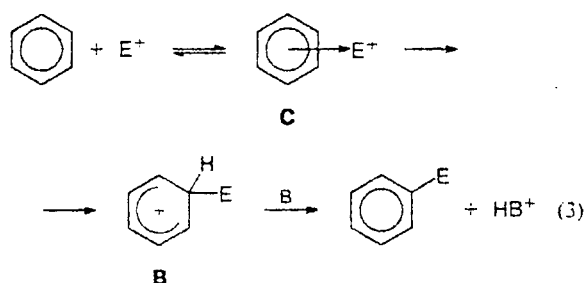
$$k_2 = k/(1 + \alpha\lambda),$$

where $\lambda = V_g/V_{liq}$ is the ratio of the gas-phase and solution volumes in the reactor and $\alpha = [RH]_g/[RH]_{liq}$ is the equilibrium coefficient of partition of the substrate between these two phases in the limit $[RH]_{liq} \rightarrow 0$. The variation of the gas-phase concentration of the substrate is usually monitored by GLC; this can also be done by other methods such as pressure gage and conductometric methods, "internal titration," or mass spectrometry.^{18,40,41} Recently, modifications of the KDM for reactions proceeding simultaneously in solution and in the gas phase above the solution⁴² and for reactions proceeding at gas—solid (catalyst) interfaces have been developed.⁴³ The syringe reactor method⁶ implies that the reaction is carried out in the absence of a gas phase ($\lambda = 0$).

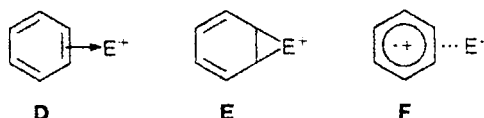
These methods made possible direct investigation of the kinetics of the first step of oxidation of saturated hydrocarbons in water and aqueous acids. Acid catalysis of this type of reactions was found; examples are the acid-catalyzed oxidative dehydrogenation of alkanes with Pd^{II} complexes^{6,44} and oxidation of alkanes on treatment with Pt^{II}—Pt^{IV}, Hg^{II}, Ru^{IV}, Mn^{III}, H₂S₂O₈, HOCl,^{6,45–49} or HOONO⁴² at temperatures below 100 °C. The selectivity (1^0 — 2^0 — 3^0) of these reactions,* kinetic isotope effects (KIE), and so-called 6/5 effects (the ratio of the rate constants for the oxidation of cyclohexane and cyclopentane) have been investigated. The temperature dependences of the KIE and the 6/5 values were studied for several systems;^{50,51} more than 1000 rate constants corresponding to the first step of reactions of saturated hydrocarbons with various oxidants were determined.⁶ Two factors accounting for the acid catalysis of these reactions were established. First, this is protonation of the oxidant to give more electrophilic and, as a consequence, more reactive species.^{6,52} This mechanism will be considered below in relation to permanganates. The second factor is the acid-salt assistance caused by desolvation of the transition state of reactions between the ionic reagent M⁺ and noncharged substrate RH.^{6,53}

* The notation 1^0 — 2^0 — 3^0 for the selectivity means the ratio of the rate constants for the oxidation of primary (1^0), secondary (2^0), and tertiary (3^0) C—H bonds in alkanes referred to one C—H bond.

Yet another class of reactions studied extensively by these methods is electrophilic substitution and oxidation of arenes. Oxidation of alkylbenzenes by salts of metals such as Co^{III},^{22,54–57} Mn^{III},^{57,58} Tl^{III},⁵⁹ Hg^{II},⁵⁹ Cr^{VI},⁶⁰ Mn^{VII},^{2,5} and Pd^{II}^{61,62} follows the electrophilic aromatic substitution (EAS) mechanism. According to modern views,^{63–66} reactions of arenes with electrophiles (E⁺) occur according to scheme (3) and include the formation of σ -complex **B**, which is preceded by the formation of charge transfer complex (CTC) **C**.



Apart from structure **C** (which is a complex with the benzene π -system), this intermediate has also been described as a complex with a localized double bond **D**,⁶⁷ complex **E**,⁶⁵ and radical ion pair **F**.^{66,68,69}



It is generally believed that reactions with high substrate and site selectivities are limited by the formation of the σ -complex⁷⁰ and those with low substrate selectivity and high site selectivity are limited by the CTC formation.⁶⁴

However, traditional approaches to the elucidation of the mechanisms of these reactions based on the study of intermediates^{69,71} or products^{72,73} do not always allow one to reach ones goal. Direct observations of intermediates are often either impossible, because these species are rapidly converted, or cannot be unambiguously interpreted because a given species could have formed *via* a side pathway or in post-limiting steps and the distribution of final products (site selectivity) is not always controlled by the first slow step.

In some studies, when choosing the mechanism for EAS reactions, researchers discussed the relationship between the reaction rates usually determined from the accumulation of isomeric products and the basicity ($\log K_B$)⁶⁹ and ionization potentials ($I_{A/H}$) of arenes.^{65,66} A method^{67,74} proposed for combined calculation of the substrate and site selectivities of EAS is based on the use of multiparametric equations including the ionization potentials of substrates, charge and orbital characteristics of the arene C—C bonds, and the σ -constants of

substituents. However, even simple one-parametric dependences of the rates on the basicity or ionization potentials of arenes are seldom used for two reasons. First, in the series of substrates considered in the majority of works,^{66,69} the $\log K_B^0$ and I_{ArH} values are correlated with each other; therefore, since the accuracy of measurements of the rate constants is relatively low, it is impossible to decide which of these two factors controls the reaction. Second, the relative rates determined by the product accumulation do not always serve as a criterion of the mechanism of the first slow step.

Studies of the first steps of the reactions of arenes with oxidative and electrophilic reagents in aqueous acid solutions made possible the first *kinetic classification*⁷⁵ of these reactions into several groups depending on what values correlate with the relative rate constants ($\Delta \log k$) in a broad range of methylbenzenes:

— ionization potentials of arenes (I_{ArH})

$$\Delta \log k = b \Delta I_{ArH} \quad (4)$$

— the basicity of arenes ($\log K_B^0$)*

$$\Delta \log k = a \Delta \log K_B^0 \quad (5)$$

— both of them

$$\Delta \log k = a \Delta \log K_B^0 + b \Delta I_{ArH} \quad (6)$$

This kinetic classification of the EAS mechanisms is, in principle, consistent with that outlined above. Dependences (4) and (5) indicate that the process occurs *via* the slow formation of the CTC or the σ -complex, respectively; when Eq. (6) holds, the transition state of the first slow step has a structure intermediate between the charge-transfer and σ -complexes.⁷⁵ As noted above, the $\log K_B^0$ and I_{ArH} values obey a mutual correlation. However, for the benzene—polymethylbenzenes series,^{67,76} the correlation score is relatively low (correlation coefficient $r = 0.902$). Therefore, when the rate constants are measured with a sufficient accuracy, one can draw a distinction between relations (4), (5), and (6) and distinguish the kinetics corresponding to Eq. (6) from the kinetics of the parallel reactions, $k = k_1 + k_{II}$, in which the pathways k_1 and k_{II} are controlled by the basicity and the ionization potentials, respectively.^{75,77}

The situation described by Eq. (4) was observed^{24,26,34,75} for the nitration of methylbenzenes in various systems. The substrate selectivities and the activation energies of these reactions are controlled only by the ionization potentials of the arenes and the activation entropies do not depend on the nature of the substrate. Equation (5) refers to most EAS reactions (halogenation, alkylation, mercuration, sulfuration).⁷⁵ Data on the activation parameters of this class of reaction for a broad range of substrates are not available now. Dependences (6) were found to hold^{75,78} for hydroxylation of methylbenzenes in the H_2O_2 — H_2SO_4 ,

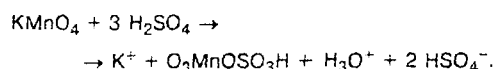
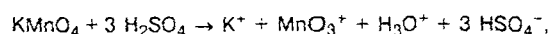
* The equilibrium constants for the protonation of arenes in liquid HF were used as $\log K_B^0$ for benzene and methylbenzenes.⁶⁷

CF_3COOOH — CCl_4 , and CF_3COOOH — $CHCl_3$ systems. It is shown below that Eq. (6) is also valid for reactions of alkylbenzenes with $HMnO_4$ and MnO_3^+ .

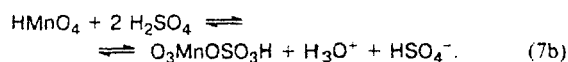
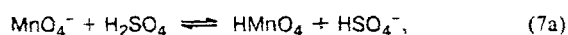
Active Mn^{VII} species and the oxidation kinetics

The state of permanganates in acidic aqueous media

In neutral, weakly acidic, and weakly alkaline solutions, permanganates exist as stable MnO_4^- ions. According to the data of cryoscopic and conductometric measurements, dissolution of $KMnO_4$ in 99.9% H_2SO_4 gives rise to six species including three HSO_4^- anions.⁷⁹ According to another study,⁸⁰ four species including two HSO_4^- anions are formed; this conforms to the stoichiometry of formation of the MnO_3^+ cation or its complex with HSO_4^-



It has been noted⁸¹ that in moderately acidic media, $HMnO_4$ is formed as an intermediate between MnO_4^- and MnO_3^+ ions. The most rigorous proof of the existence of the $HMnO_4$ species was obtained using spectrophotometric⁸² and kinetic studies^{4,5,83} (see below). The absorption spectra of permanganate in the UV and visible regions depend substantially on the concentration of H_2SO_4 . Three absorption bands and five isobestic points were found⁸² at 30320, 26000, and 20800 cm^{-1} for 0–10 M H_2SO_4 , at 22300 cm^{-1} for 10–17.5 M H_2SO_4 , and a common band at 15150 cm^{-1} . It was concluded that MnO_4^- and $HMnO_4$ are present in 0–10 M H_2SO_4 , while $HMnO_4$ and O_3MnOSO_3H exist in 11–17.5 M H_2SO_4 , in conformity with Eqs. (7a) and (7b), respectively.



The distribution of Mn^{VII} species in H_2SO_4 ⁸² implies the $pK_a = -4.5$ value for $HMnO_4$ in equilibrium (7a). A close value, $pK_a = -4.57$, has been obtained previously⁸⁴ for $[H_2SO_4] = 41.5$ – 97% (w/w). For solutions of $KMnO_4$ in 0–3 M $HClO_4$, $pK_a = -2.25$ was found.⁸¹

In aqueous solutions, permanganate acts as an efficient one-, three-, or five-electron oxidant.⁸⁵ In highly alkaline media, MnO_4^- is reduced to the manganate ion MnO_4^{2-} , which is then vigorously reduced to MnO_2 ; in weakly alkaline or neutral media, the reduction directly gives MnO_2 . In acidic media, permanganate is converted into MnO_2 or, in the presence of excess reducing agent, into Mn^{2+} . Acidic solutions of permanganates are unstable. The rate of its decomposition in sulfuric acid solutions increases as the concentration of H_2SO_4 increases to 12 mol L^{-1} and then decreases, reaching a

Table 1. Effect of the concentration of perchloric acid on the KIE and contributions of reactions with HMnO₄ (*k*₀') and MnO₃⁺ (*k*₊') to the overall rate of oxidation of toluene in the KMnO₄–HClO₄–H₂O system at 25 °C

[HClO ₄] /mol L ⁻¹	-H ₋ ⁹¹	-H ₀ ⁹¹	<i>a</i> _w ⁹²	<i>α</i>	<i>k</i> ₂ · 10 ⁻³ ^a /L mol ⁻¹ s ⁻¹	<i>k</i> ₂ ^H / <i>k</i> ₂ ^D	<i>k</i> ₀ ' · 10 ³ /L mol ⁻¹ s ⁻¹	<i>k</i> ₀ ^H / <i>k</i> ₀ ^D	<i>k</i> ₊ ' · 10 ³ /L mol ⁻¹ s ⁻¹	<i>k</i> ₋ ^H / <i>k</i> ₋ ^D
0	—	—	1.00	0.28	0.370	21.7 ^b	—	—	—	—
0.0011	—	—	1.00	0.28	0.378	—	—	—	—	—
0.01	—	—	1.00	0.28	0.383	—	—	—	—	—
0.1	-1.10	0	0.990	0.28	0.483	8.40	0.063	1.6±0.2	—	—
0.50	-0.33	0	0.980	0.28	0.637	3.93	0.260	1.6±0.2	—	—
1.00	0.19	0.30	0.957	0.28	1.25	2.16	0.870	1.5±0.1	—	—
1.28	0.44	0.44	0.946	0.27	1.90	1.86	1.55	1.7±0.2	—	—
1.50	0.58	0.56	0.931	0.27	2.35	—	2.14	—	—	—
1.60	0.66	0.60	0.925	0.26	2.69	1.56	2.57	1.5±0.1	—	—
2.00	0.93	0.80	0.902	0.25	4.90	1.50	4.78	1.6±0.1	—	—
2.15	1.00	0.86	0.893	0.25	6.98	1.48	5.18	1.6±0.1	1.45	1.0±0.6
2.24	1.10	0.92	0.890	0.25	9.00	—	6.40	—	2.25	—
2.50	1.28	1.05	0.867	0.25	15.9	1.41	9.45	1.6±0.1	6.08	1.1±0.3
2.74	1.46	1.16	0.845	0.25	28.8	1.37	13.6	1.7±0.1	14.9	1.1±0.2
3.00	1.69	1.30	0.826	0.24	45.0	1.36	17.9	1.6±0.1	26.8	1.2±0.2
3.50	1.93	1.56	0.783	0.24	105	—	31.8	—	73.0	—
4.00	2.25	1.80	0.724	0.24	337	—	49.5	—	287	—
4.50	2.58	2.04	0.662	0.24	1080	—	67.9	—	1010	—

^a The error in the determination of *k*₂ with allowance for the accuracy of the measurement of *α* is ±6%.

^b Calculated from the temperature dependence of *k*₂^H/*k*₂^D.

minimum at [H₂SO₄] = 15 mol L⁻¹. The formation of O₂ upon decomposition of permanganate is catalyzed by manganese(vi). According to published data,^{82,86,87} H₃MnO₄⁺ and Mn^{VI}HMnO₄ are active in the formation of O₂. In both cases, the reaction involves a free water molecule occurring in the inner sphere of manganese.

Oxidation kinetics and the model for the influence of the medium acidity

The kinetics of oxidation of hydrocarbons in acidic aqueous solutions is described by a second-order equation^{2-5,38,83}

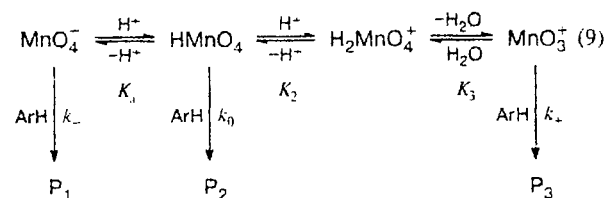
$$-d\ln[\text{ArH}]_g/d\tau = k_2 = k_2[\text{KMnO}_4]/(1 + \alpha\lambda). \quad (8)$$

The reduction of aqueous solutions of KMnO₄ affords colloidal MnO₂ · H₂O,^{17,88-90} which can, in principle, catalyze permanganate oxidation of organic substrates^{17,89,90} but in the case of alkanes and alkylbenzenes, judging by the published data,^{3,4} MnO₂ does not influence the oxidation rate. The *k*₂ values for methylcyclohexane³ and toluene^{4,83} in solutions of perchloric acid (10⁻⁶–4.5 mol L⁻¹) are constant in the range of [H⁺] = 10⁻⁶–10⁻³ mol L⁻¹, while at [H⁺] > 10⁻² mol L⁻¹, they increase exponentially as the acidity increases (Table 1).^{*} It was concluded that in the plateau region, the MnO₄⁻ anion serves as the reagent, while at higher acidity, more reactive HMnO₄ molecules and MnO₃⁺ cations appear. The former can exist

^{*}According to Eq. (2), *k*₂ = *k*₊₁[Ox^{*}]/[Ox] = (*k*_b*k*_c/*k*_{-b})[Ox^{*}]/[Ox]; however, kinetic data do not allow one to distinguish the contributions of *k*_c and *K*_b = *k*_b/*k*_{-b} to the *k*₂ value.

as the H₂O...H⁺...OMnO₃⁺ ion pair, while the latter exists as the ester O₃MnOCIO₃ or the MnO₃⁺...ClO₄⁻ ion pair (they are written below as HMnO₄ and MnO₃⁺, respectively).

Based on the data on the kinetics of oxidation of hydrocarbons and the state of manganese(vii) at various acidities,⁸³ the following kinetic model was proposed:



According to scheme (9) and with allowance for the additional relations

$$[\text{KMnO}_4] = [\text{MnO}_4^-] + [\text{HMnO}_4] + [\text{MnO}_3^+]$$

and

$$K_a = [\text{MnO}_4^-]a_{\text{H}^+} / ([\text{HMnO}_4] \gamma_0)$$

$$K_2 K_3 = [\text{HMnO}_4] a_{\text{H}^+} \gamma_0 / ([\text{MnO}_3^+] \gamma_+ a_w) \quad (10)$$

the kinetics of the consumption of hydrocarbons is described by the equation

$$-d\ln[\text{ArH}]/d\tau = k_2[\text{KMnO}_4] = k_-[\text{MnO}_4^-] + k_0[\text{HMnO}_4] + k_+[\text{MnO}_3^+], \quad (11)$$

where *k*₋, *k*₀, and *k*₊ are the rate constants for the reactions with MnO₄⁻, HMnO₄, and MnO₃⁺, respec-

tively: K_a is the acidity constant of HMnO_4 ; K_2K_3 is the product of the acidity constants of H_2MnO_4^+ (K_2) and the hydration constant of MnO_3^+ (K_3); γ_- , γ_0 , and γ_+ are the activity coefficients of MnO_4^- , HMnO_4 , and MnO_3^+ , respectively; and a_{H^+} and a_w are the activities of H^+ and water. The following dependence of k_2 on the acidity can be derived from Eqs. (10) and (11):

$$k_2 = \frac{k_-K_aK_2K_3 + (k_0K_2K_3a_{\text{H}^+\gamma_-/\gamma_0}) + [k_+a_{\text{H}^+}^2\gamma_-/(\gamma_+a_w)]}{[a_{\text{H}^+\gamma_-/\gamma_+}^2/(\gamma_+a_w)] + (K_2K_3a_{\text{H}^+\gamma_-/\gamma_0}) + K_aK_2K_3}$$

No data on the K_2 and K_3 values are available; however, the product K_2K_3 should be, at least, 2 or 3 orders of magnitude greater than K_a . Hence, when $\text{p}K_a = -2.25$, the inequality

$$(K_aK_2K_3 + K_2K_3a_{\text{H}^+\gamma_-/\gamma_0}) \gg a_{\text{H}^+}^2\gamma_-/(\gamma_+a_w)$$

should hold in the acidity range studied. By introducing designations $h_- \equiv a_{\text{H}^+\gamma_-/\gamma_0}$ and $h_0 \equiv a_{\text{H}^+\gamma_0/\gamma_+}$, we obtain⁸³

$$k_2 = \frac{k_-K_a}{K_a + h_-} + \frac{k_0h_-}{K_a + h_-} + \frac{k_+h_0/a_w}{K_2K_3(K_a + h_-)} \quad (12)$$

The three terms on the right-hand side of Eq. (12) reflect the contributions of the reactions involving MnO_4^- , HMnO_4 , and MnO_3^+ to the experimental rate constant k_2 . In moderately acidic media at $K_a \gg h_-$, the contribution of the reaction with MnO_3^+ can be neglected and the following equation holds:

$$k_2 = k_- + k_0h_-/K_a$$

The following linear dependence can be written for this region:

$$\log k_0' = C_0 - H_- \quad (13)$$

where $C_0 = \log(k_0/K_a)$, $k_0' = (k_2 - k_-)$ is the contribution of the reaction with HMnO_4 at a given acidity and k_- is the rate constant k_2 in water at $\text{pH} = 5-7$ (for toluene, $k_- = 3.7 \cdot 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C). In the general case, when the three Mn^{VII} species contribute to the reaction, it follows from Eq. (12) that

$$\log[k_+'(K_a + h_-)] = C_+ - (H_0 + H_- + \log a_w) \quad (14)$$

where $k_+' = k_2 - (k_-K_a + k_0h_-)/(K_a + h_-)$ is the contribution of the reaction with the MnO_3^+ cation at a given acidity, $C_+ = \log[k_+/(K_2K_3)]$, $H_0 = -\log h_0$, and $H_- = -\log h_-$ are the acidity functions.

Comparison of the model with the experiment

According to published data,^{3,5,83} when $[\text{HClO}_4] \leq 2 \text{ mol L}^{-1}$, the theoretical linear correlation (13) is obeyed for alkylbenzenes and alkanes. The slope ratio of the corresponding straight line is 1.1 ± 0.1 for methylcyclohexane and 1.03 ± 0.03 for toluene. Thus, in this acidity range, MnO_4^- and HMnO_4 are the reagents.

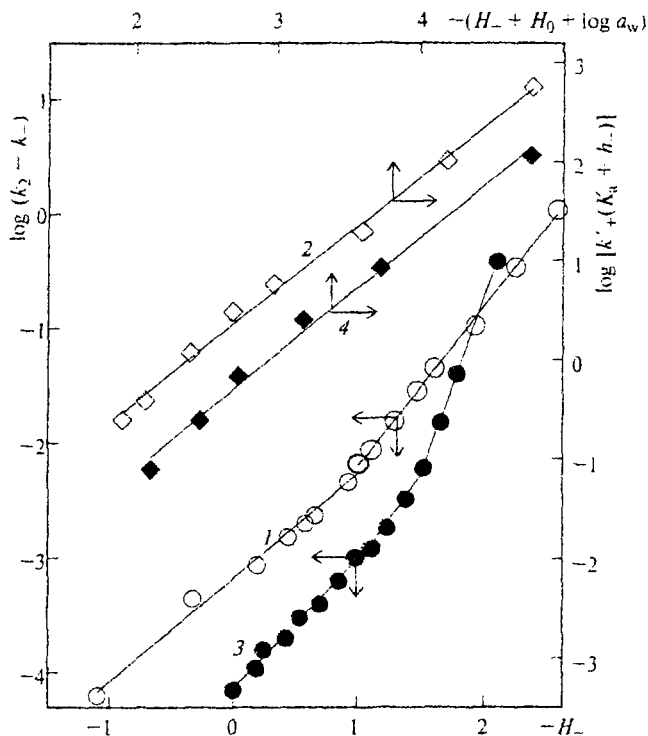


Fig. 1. Rate constants for the oxidation of toluene by permanganate in aqueous perchloric acid (1) and the oxidation of *n*-pentane by permanganate in trifluoroacetic acid (2) vs. acidity function (H_-). Fulfillment of Eq. (14) for the reactions of toluene (3) and *n*-pentane (4) with MnO_3^+ .

When $[\text{HClO}_4] > 2 \text{ mol L}^{-1}$, a steeper dependence of $\log(k_2 - k_-)$ on H_- is observed for toluene (the slope is $\Delta \log(k_2 - k_-)/\Delta H_- \approx -1.4$; Fig. 1, straight line 1), indicating that the reaction of MnO_3^+ makes a substantial contribution in this case.

The contributions of the reaction involving HMnO_4 , $k_0' = k_0h_-/(K_a + h_-)$, and the k_+' values for toluene were calculated⁸³ using $\text{p}K_a = -2.25$ for HClO_4 solutions (see Table 1). The $k_0 = 0.10 \pm 0.01$ value was found from dependence (12) for concentrations of HClO_4 ranging from 0.5 to 2.0 mol L^{-1} when the contribution of the reaction with MnO_3^+ can be neglected. When $[\text{HClO}_4] > 2 \text{ mol L}^{-1}$, relation (14) with a slope ratio of 1.1 ± 0.1 holds (see Fig. 1, straight line 2). This confirms quantitatively the fact that the permanganyl cation or its complex with ClO_4^- acts as the reagent at $[\text{HClO}_4] > 2 \text{ mol L}^{-1}$.

Linear dependences of $\log k_2$ on the acidity function (H_R) with the slope $-(\Delta \log k_2/\Delta H_R) = 0.8-1.2$ were found² for reactions of permanganate with alkanes and arenes in trifluoroacetic acid (70–84 and 33–67% CF_3COOH , respectively). These kinetic data, together with the data of cryoscopic and spectrophotometric measurements for the same media,⁹³ were interpreted² as evidence for the fact that the MnO_3^+ cation or the

O_2MnOCF_3COO complex acts as the reagent under these conditions. However, the method used² for kinetic measurements, namely, determination of the consumption of the oxidant at $[Mn^{VII}] \ll [RH]$ without allowance for the expenditure of permanganate for the oxidation of the solvent and the primary reaction products can result, as noted above, in substantial errors in the determined rate constants.^{6,38} More precise plots for $\log k_2$ vs. $-H_R$, derived from the rate of consumption of hydrocarbons at $[Mn^{VII}] \gg [RH]$ in a wider range of acidity (0–86% CF_3COOH) proved to be nonlinear; the slope ratio for them varied from 0.3 to 0.7.³⁸ In the case of reactions of *n*-pentane with permanganate in trifluoroacetic acid,³⁸ relation (13) with a slope equal to unity is obeyed, as in the case of oxidation of arenes in solutions of $HClO_4$, up to $H_- = -1.0$, which corresponds to $[CF_3COOH] \approx 50\%$. When $[CF_3COOH] > 50\%$, a steeper dependence of $\log(k_2 - k_-)$ on H_- is observed (see Fig. 1, straight line 3). For CF_3COOH concentrations ranging from 50 to 86%, Eq. (14) with a slope ratio of the corresponding curve equal to 1.1 ± 0.1 is fulfilled (see Fig. 1, straight line 4). The $k_0 = 0.10 \pm 0.01$ value was found from relation (12) for CF_3COOH concentrations of 10 to 50%. These data indicate that the same Mn^{VII} species, MnO_4^- , $HMnO_4$, and MnO_3^+ , as in $HClO_4$, act as the reagents in trifluoroacetic acid at various acidities.

Kinetic isotope effects; differentiation of the attacks on the benzene ring and on the alkyl group

Experimental kinetic isotope effects

In the case of alkylbenzenes, a complicated problem of differentiating the reaction pathways in which the reagent attacks the alkyl group and the benzene ring arises. This problem was solved by a study of kinetic isotope effects as functions of the medium acidity and by determination of "individual KIE" related to the reactions with MnO_4^- , $HMnO_4$, and MnO_3^+ . First, let us consider experimental data.

In the oxidation of arenes, replacement of a light substrate by a substrate deuterated at the aromatic ring does not influence the reaction rate; for the C_6H_6/C_6D_6 and $C_6H_5CH_3/C_6D_5CH_3$ pairs in 0–4.5 *M* solutions of $HClO_4$ ^{4,5,83} and in 32.7–66.7% solutions of CF_3COOH ,² the ratio $k_2^H/k_2^D = 1$. However, for the $C_6H_5CH_3/C_6D_5CD_3$ pair at $[HClO_4] = 0-1.5$ mol L^{-1} , the KIE observed at 70 °C decreases from 13.6 to 1.45;⁴ that at 25 °C at $[HClO_4]$ of 0.1 to 3.0 mol L^{-1} decreases from 8.40 to 1.36⁸³ (see Table 1). This indicates that reactions involving MnO_4^- , $HMnO_4$, and MnO_3^+ are characterized by different individual KIE. At 25 °C and $[HClO_4] = 0$, the KIE cannot be measured directly because the rate of oxidation of toluene-*d*₈ is very low. The $k_-^H/k_-^D = 21.7$ value for 25 °C was found from the data presented below on the temperature dependence⁴ of k_-^H/k_-^D in the 25–90 °C range:

$T/^\circ C$	25	50	60	70	80	90
k_-^H/k_-^D	21.7	16.4	14.6	13.6	11.9	10.8

which satisfy the equation

$$\log(k_-^H/k_-^D) = \log(A^H/A^D) + (E_2^D - E_2^H)/(2.3RT), \quad (15)$$

for $A_-^H/A_-^D = 0.40$ and $(E_2^D - E_2^H) = 9.9$ kJ mol^{-1} . The toluene/toluene-*d*₈ pair in CF_3COOH solutions (32.7–66.7%) has the KIE = 1.03 ± 0.05 .²

The experimental KIE values for the *m*-xylene/*m*-xylene-*d*₁₀ and *p*-xylene/*p*-xylene-*d*₁₀ pairs in the $KMnO_4-H_2O$ system ($pH = 5-7$) at 70 °C are 11.3 and 16.8, while those in the $KMnO_4-HClO_4$ system (0.5 mol L^{-1}) are 1.18 and 1.23, respectively⁴ (Table 2).

High KIE values were found for the oxidation of substrates such as $PhCH(OH)CF_3/PhCD(OH)CF_3$ (15–16),^{12,94} $PhCH(Me)(CH_2)_2CO_2H/PhCD(Me)(CH_2)_2CO_2H$ (11.5),⁹⁵ and $CF_3CH(OH)O^-/CF_3CD(OH)O^-$ (14),⁸⁴ with MnO_4^- ; this was attributed¹² to the substantial contribution of tunneling.

The k_2^H/k_2^D values for alkanes, unlike alkylbenzenes, depend slightly on the acidity. Thus the KIE for the cyclohexane/cyclohexane-*d*₁₂ pair at 25 °C in $1 \cdot 10^{-4}$ *M* and 1 *M* $HClO_4$ are 7.6 and 5.0, respectively.⁵⁰ In both systems, dependence (15) holds with $A^H/A^D = 0.72 \pm 0.07$ and 0.32; $(E_2^D - E_2^H) = 5.8 \pm 2.9$ and 6.8 kJ mol^{-1} for $1 \cdot 10^{-4}$ *M* and 1 *M* $HClO_4$, respectively. In 50–84% solutions of CF_3COOH at 25 °C for the same substrates, KIE = 4.2.²

Individual KIE for the reactions of toluene/toluene-*d*₈ with MnO_4^- , $HMnO_4$, and MnO_3^+

Equations (13) and (14) were used to determine^{5,83} the KIE for each of the above-listed three reagents

$$MnO_4^-: k_-^H/k_-^D = 21.7,$$

$$HMnO_4: k_0^H/k_0^D = (k_2^H - k_-^H)/(k_2^H - k_-^D) = 1.6 \pm 0.1,$$

$$MnO_3^+: \frac{k_2^H}{k_2^D} = \frac{k_2^H(K_3 + h_-) - (k_2^H K_3 + k_0^H h_-)}{k_2^D(K_3 + h_-) - (k_2^D K_3 + k_0^D h_-)} = 1.1 \pm 0.1.$$

Table 2. KIE for the reactions of hydrocarbons with MnO_4^- (k_-^H/k_-^D) and $HMnO_4$ (k_0^H/k_0^D) at 70 °C and relationship of the oxidation of the side chain (k^{CH}) and the ring (k^R) in alkylbenzenes

Compound	k_-^H/k_-^D	k_0^H/k_0^D	k^{CH}/k^R	
			MnO_4^-	$HMnO_4$
Benzene	1.0	1.0	0	0
Toluene	13.6	1.45	≥ 200	0.5
<i>m</i> -Xylene	11.3	1.17	≥ 80	0.2
<i>p</i> -Xylene	16.8	1.13	≥ 70	0.14
Ethylbenzene	—	—	≥ 1700	3.8
Isopropylbenzene	—	—	≥ 1400	3.4
Cyclohexane	5.6	3.5	—	—

The values used for the calculation were $k_{-D} = 1.7 \cdot 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ for toluene- d_8 , $k_0^H = 0.10 \pm 0.01$, and $k_0^D = (6.2 \pm 0.3) \cdot 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. As was to be expected, the k_0^H/k_0^D and k_{+H}/k_{+D} ratios depend on the acidity (see Table 1). These individual KIE refer to the overall reaction of toluene with these species and, when combined with experimental KIE, allow one to consider separately the attacks on the aromatic nucleus and on the C—H bond of the alkyl substituent.^{5,82}

Differentiation between the attacks on the benzene ring and on the methyl group in toluene

Each species, MnO_4^- , HMnO_4 , and MnO_3^+ can attack toluene both at the benzene ring (k^R) and at the C—H bonds of the methyl group (k^{CH}).^{2,4,5} In accordance with experimental data, the KIE for the first pathway can be considered to be 1 (for example, for the $\text{C}_6\text{H}_5\text{CH}_3/\text{C}_6\text{D}_5\text{CH}_3$ pair). Therefore, the decrease in the observed k_2^H/k_2^D values following an increase in the acidity (see Table 1) implies that the contribution of the attack on the methyl C—H bonds decreases in the series MnO_4^- , HMnO_4 , and MnO_3^+ , while the contribution of the attack on the aromatic ring simultaneously increases. The decrease in the yield of benzoic acid (the product of oxidation of the methyl group) upon an increase in the concentration of HClO_4 ^{4,5} is consistent with this conclusion.

The ratio of the contributions of the two pathways k^{CH}/k^R was estimated^{5,83} from the k_{-H}/k_{-D} , k_0^H/k_0^D , and k_{+H}/k_{+D} values determined above based on the following statements:

1. The KIE values for the attack on the C—H bond by the three species are close, as in the case of alkanes^{3,38,50}

$$k_{-H}^{\text{CH}}/k_{-D}^{\text{CH}} = k_0^{\text{CH}}/k_0^{\text{CD}} = k_{+H}^{\text{CH}}/k_{+D}^{\text{CH}} \quad (16)$$

2. Oxidation involving the benzene ring with each of the three Mn^{VII} species has a KIE equal to 1. Since for each species

$$k^H = k^R + k^{\text{CH}} \quad \text{and} \quad k^D = k^R + k^{\text{CD}} \quad (17)$$

it follows from Eqs. (16) and (17) that

$$\frac{k^{\text{CH}}}{k^R} = \frac{k^{\text{CH}}}{k^{\text{CD}}} \cdot \frac{k^H/k^D - 1}{k^{\text{CH}}/k^{\text{CD}} - k^H/k^D} \quad (18)$$

where k^H/k^D is the overall KIE observed in the reaction of toluene with MnO_4^- (k_{-H}/k_{-D}), HMnO_4 (k_0^H/k_0^D), or MnO_3^+ (k_{+H}/k_{+D}); $k^{\text{CH}}/k^{\text{CD}}$ is the KIE for the attack on the C—H alkyl bond. For each Mn^{VII} species, this was assumed to be equal to the $k_{-H}^{\text{CH}}/k_{-D}^{\text{CH}}$ ratio, which is roughly equal to the k_{-H}^H/k_{-D}^D ratio. The k^{CH}/k^R values calculated using Eq. (18) assuming that $k_{-H}^{\text{CH}}/k_{-D}^{\text{CH}} = 22$, $k_0^H/k_0^D = 1.6$, and $k_{+H}^H/k_{+D}^D = 1.1$

for MnO_4^- , HMnO_4 , and MnO_3^+ are ≥ 200 , 0.6, and 0.1, respectively.*

Differentiation between the attacks on the benzene ring and on the C—H bond of the substituent for other alkylbenzenes

An estimate⁵ of the k_0^{CH}/k_0^R values using Eq. (18) and k_0^H/k_0^D and k_{-H}^H/k_{-D}^D with the assumptions made for toluene shows that the predominant pathway in the reactions of *p*- and *m*-xylenes with HMnO_4 is the attack on the aromatic ring (see Table 2). The k_0^{CH}/k_0^R values for ethyl- and isopropylbenzenes were roughly estimated⁵ from the $(k_0 - k_0^R)/k_0^R$ values assuming that the rates of oxidation of the aromatic rings in these substrates are close to that in toluene, as in the case of known electrophilic aromatic substitution reactions.^{2,24,34} According to this estimate (see Table 2), oxidation of ethyl- and isopropylbenzene by HMnO_4 molecules, unlike oxidation of methylbenzenes, involves predominantly the C—H bonds in the alkyl group.

Effects of the structure of hydrocarbons

Reactions with MnO_4^-

In aqueous solutions of permanganates at $\text{pH} = 5$ – 7 , the MnO_4^- anion is the only reagent species; the kinetics of the consumption of ArH , like that for toluene, is described by Eq. (8), where $k_2 = k_{-}$.⁴ The kinetic data for 20–70 °C⁹⁶ are listed in Table 3. For each hydrocarbon, the Arrhenius equation $\lg k_{-} = \lg A - E_a/(2.3RT)$ is fulfilled with the correlation coefficient $r = 0.994$ – 0.999 . The activation enthalpy ($\Delta H^\ddagger = E_a - RT$) and entropy (ΔS^\ddagger) found are given in Table 4. The reactivity of alkylbenzenes increases with an increase in the number of methyl groups and also in the sequence $\text{Bu}^i\text{Ph} \ll \text{MePh} \ll \text{EtPh} \leq \text{Pr}^i\text{Ph}$. At 70 °C, benzene is oxidized ~2000 times more slowly than toluene. The activation enthalpies for the oxidation of alkylbenzenes decrease in the series $\text{MePh} > \text{EtPh} > \text{Pr}^i\text{Ph}$ and those for methylbenzenes decrease with an increase in the number of methyl groups. The correlation between the activation energy and the energy of homolysis of the C—H bond (D_{CH}), $E_a = \text{const} + 0.3D_{\text{CH}}$, which is common for alkylbenzenes and alkanes, holds to within the experimental error⁹⁷ (Fig. 2, straight line 1). It was concluded^{4,96} that MnO_4^- attacks arenes both at the benzene ring and at the alkyl C—H bonds. Naturally, benzene undergoes attack at the nucleus, while methyl-, ethyl-, isopropyl-, and polymethylbenzenes are mainly attacked at the alkyl groups.

* Note that the deviations from the accepted value, $k_0^{\text{CH}}/k_0^{\text{CD}} = 22$, does not affect much the result. Even when the deviation is $\pm 50\%$, the k_0^{CH}/k_0^R ratio changes by only 15%.

Table 3. Rate constants^a for the oxidation of alkylbenzenes by the MnO_4^- anions ($k_- = k_2$)^b in the $\text{KMnO}_4\text{--H}_2\text{O}$ system and by the HMnO_4 molecules ($k_0' = k_2 - k_-$) in 0.5 M HClO_4 at different temperatures

Compound	20 °C		30 °C		40 °C		50 °C		60 °C		70 °C	
	$k_- \cdot 10^3$	$k_0' \cdot 10^2$	$k_- \cdot 10^3$	$k_0' \cdot 10^2$	$k_- \cdot 10^3$	$k_0' \cdot 10^2$	$k_- \cdot 10^3$	$k_0' \cdot 10^2$	$k_- \cdot 10^3$	$k_0' \cdot 10^2$	$k_- \cdot 10^3$	$k_0' \cdot 10^2$
Benzene ^c (1)	—	—	—	—	—	—	—	—	—	$1.6 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$
Toluene (2)	0.23	0.027	0.61	0.079	1.39	0.21	2.97	0.50	6.33	0.17	11.7	0.36
<i>o</i> -Xylene (3)	0.89	0.36	2.05	1.0	4.81	2.7	8.97	6.6	17.2	1.6	37.8	3.5
<i>m</i> -Xylene (4)	0.60	2.4	1.49	6.0	2.65	13	6.27	27	13.4	6.6	26.5	13.4
<i>p</i> -Xylene (5)	1.15	0.86	2.94	2.5	6.44	5.4	13.6	13	26.9	4.7	47.4	5.9
Mesitylene (6)	1.01	100	2.50	180	5.04	460	10.3	784	21.8	—	40.5	260
Pseudocumene (7)	2.28	22	4.11	51	11.6	120	18.6	237	31.0	48	88.9	—
Durene ^d (8)	—	330	—	740	—	1500	—	3220	—	—	—	—
Ethylbenzene (9)	—	—	11.3	0.45	23.5	0.91	45.3	2.0	83.9	0.28	140	0.58
Isopropylbenzene (10)	—	—	12.3	0.38	24.3	0.95	43.3	2.0	80.1	0.49	141	0.95

^a The constants are expressed in $\text{L mol}^{-1} \text{s}^{-1}$.^b The error in the determination of k_2 with allowance for the accuracy of the measurement of α is $\pm 6\%$.^c At 80 °C, $k_0' = 1.2 \cdot 10^{-3}$; at 90 °C, $k_- = 7 \cdot 10^{-5}$ and $k_0' = 3.7 \cdot 10^{-3}$.^d At 10 °C, $k_0' = 1.8$.**Table 4.** Activation parameters for the oxidation of hydrocarbons by MnO_4^- and HMnO_4 at different temperatures

Compound	MnO_4^-				HMnO_4				$-\log K_B$ ⁶⁷	I_{ArH} ⁷⁶ /eV
	$\log A$	E_a kJ mol ⁻¹	ΔH^\ddagger [*]	$-\Delta S^\ddagger$ [*] /J mol ⁻¹ K ⁻¹	$\log A$	E_a kJ mol ⁻¹	ΔH^\ddagger [*]	$-\Delta S^\ddagger$ [*] /J mol ⁻¹ K ⁻¹		
1	-12.9	-120	-118	-6	12.5±0.5	104±3	101±3	14±1	9.2	9.25
2	8.2±0.1	66±1	64±1	96±2	11.4±0.3	84±2	81±2	35±1	6.3	8.82
3	8.0±0.3	62±2	60±2	100±3	11.2±0.3	76±2	74±2	39±1	5.3	8.56
4	8.0±0.3	63±2	61±1	100±4	10.5±0.2	68±1	65±1	52±1	3.2	8.56
5	8.0±0.2	61±1	59±2	100±2	11.3±0.7	75±4	72±4	37±2	5.7	8.44
6	7.9±0.3	61±2	59±4	101±4	10.0±0.3	56±2	53±2	62±2	0.4	8.40
7	7.9±0.7	60±4	58±4	101±9	10.5±0.2	62±1	60±1	52±1	2.9	8.27
8	—	—	—	—	10.6±0.5	56±3	53±3	50±2	2.2	8.02
9	7.5±0.1	55±1	53±1	108±1	7.8±0.2	57±1	54±1	104±2	—	8.76
10	7.2±0.2	53±1	51±1	115±3	7.0±0.3	52±2	50±2	119±5	—	8.69
Cyclopentane (11) ⁵¹	8.8±0.6	70±4	68±4	85±6	—	—	—	—	—	7.8
Cyclohexane (12) ⁵¹	9.2±1.0	75±8	73±8	77±9	—	—	—	—	—	7.7

* At 25 °C

Reactions with HMnO_4

The substrate selectivity in the oxidation of alkylbenzene by HMnO_4 molecules was studied in 0.5 M HClO_4 .^{5,98} In this system, alkylbenzenes, like toluene, react with two Mn^{VII} -containing species, namely, MnO_4^- (k_-) and HMnO_4 (k_0').⁵ The k_0' values were calculated from k_2 and k_- (see Table 3).^{5,98} Under the given conditions, the contribution of the reaction with HMnO_4 to the overall rate of the process (k_0'/k_2) predominates for all substrates, except for ethyl- and isopropylbenzenes. The k_0' constant for each ArH satisfies the Arrhenius equation ($r = 0.994\text{--}0.999$) in the 20–70 °C temperature range.⁹⁸ The activation enthalpies and entropies found in this way (see Table 4) are effective parameters because the temperature dependences of the h_- and K_a values, which appear in k_0' , are unknown. However, the

true parameters of activation with respect to the standard state can be determined taking into account that $\Delta \log k_0' = \Delta \log k_0$.

The substrate selectivities and the activation parameters of the oxidation of alkylbenzenes by MnO_4^- and HMnO_4 are substantially different.^{4,5,96,98} Thus, at 70 °C, toluene is oxidized by HMnO_4 95 times as fast and with MnO_4^- 2000 times as fast as benzene. On passing from toluene to mesitylene, the k_0' value increases 700-fold and k_- increases only 3.5-fold. The preexponential factor for the reaction with HMnO_4 decreases in the same series 25-fold, and the activation energy decreases by 28 kJ mol⁻¹ (see Table 4). In the case of reactions with MnO_4^- , these values change by a factor of 3 and by 5 kJ mol⁻¹, respectively. The structure of the alkyl group does not have a pronounced effect on the rate of oxidation of monoalkylbenzenes by HMnO_4 , as ob-

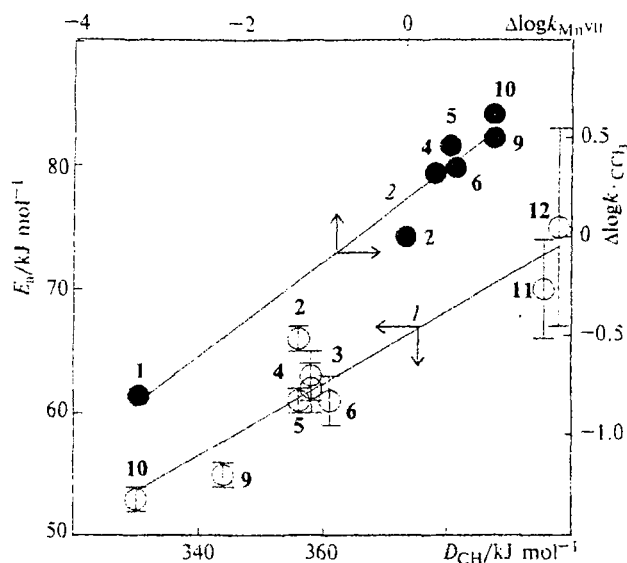


Fig. 2. Activation energies (E_a) of reactions of alkylbenzenes and cycloalkanes with the MnO_4^- anions vs energy of homolysis (D_{CH}) of the α -C-H bonds (1) and correlation between $\Delta \log k$ values for the reactions with the MnO_4^- anions and the $\cdot CCl_3$ radicals (2). The numbering of points corresponds to the numbers of compounds in Tables 3 and 4.

served in the case of MnO_4^- . The ratios of the rate constants k_0' in the series of MePh, EtPh, PrⁱPh at 70 °C are 1.0 : 1.5 : 2.5, and those for k_- are 1 : 12 : 12, respectively. The isotope effects for the oxidation of deuterated methylbenzenes by $HMnO_4$, unlike those for the reaction with MnO_4^- , are low (see Table 2). It was concluded^{4,5,96,98} that reactions of alkylbenzenes with MnO_4^- and $HMnO_4$ involve simultaneously the alkyl group and the aromatic nucleus; however, the ratios of the contributions of these pathways (k^{CH}/k^R) are different. In the case of benzene and methylbenzene, the predominant reaction pathway involves the aromatic ring, whereas for ethyl- and isopropylbenzenes, oxidation of the alkyl C-H bond predominates (see Table 2).

The relative rates of the reaction pathways involving the attacks on the aromatic nucleus for benzene and methylbenzene at the temperatures studied are poorly correlated with the basicity ($r = 0.94-0.95$) or with the ionization potentials of arenes ($r = 0.96-0.97$). The two-parametric equation (6), which takes into account both factors is much better fulfilled ($r = 0.993-0.997$) (Fig. 3). This makes it possible to consider this reaction pathway as an EAS reaction, similar to electrophilic hydroxylation.^{34,72}

Reactions with MnO_3^+

The influence of the structure of hydrocarbons on the rate of their oxidation by MnO_3^+ cations was studied at $[HClO_4] = 3.5 \text{ mol L}^{-1}$ and at 25 °C.⁸³ Alkylbenzenes, like toluene, react with MnO_4^- , $HMnO_4$, and MnO_3^+ in 3.5 M $HClO_4$ according to reaction (9).

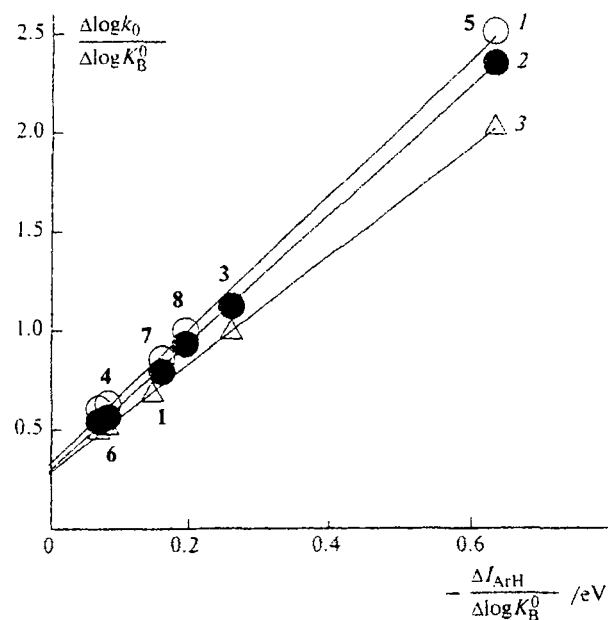


Fig. 3. Fulfillment of Eq. (6) for the oxidation of methylbenzenes by $HMnO_4$ at 20 (1), 40 (2), and 70 °C (3). The numbering of points corresponds to the numbers of compounds in Table 3.

The rates of oxidation in water and in 0.5 M $HClO_4$ (see Table 3) with allowance for Eq. (12) were used to calculate⁸³ the contributions of reactions with MnO_4^- ($k_- = k_- K_3 / (K_3 + h_-)$) and $HMnO_4$ ($k_0' = k_0 h_- / (K_3 + h_-)$) in 3.5 M $HClO_4$ and then to calculate $k_+ = k_2 - k_- - k_0'$, which are proportional to the k_+ values at a given acidity (Table 5). Now we compare the reactivities of methylbenzenes in the oxidation by $HMnO_4$ molecules^{5,98} and MnO_3^+ cations.⁸³ The similarity of the mechanisms of these two groups of reactions is indicated by the linear correlation (Fig. 4, straight line 1)

$$\log(k_+/k_+^{PhH}) = (0.75 \pm 0.01) \log(k_0/k_0^{PhH}).$$

However, the substrate selectivity of reactions with MnO_3^+ is markedly lower than that in the case of $HMnO_4$ (the slope ratio of the corresponding straight line is 0.75); the structure of the alkyl group in the series MePh, EtPh, and PrⁱPh does not influence much the reaction rate; the ratios of the rate constants for the reactions with MnO_3^+ at 25 °C are 1.0 : 1.1 : 1.2 (see Table 5), while those for $HMnO_4$ are 1.0 : 6.4 : 5.1, respectively (see Table 3). It was concluded⁸³ that the MnO_3^+ cations, unlike $HMnO_4$ molecules, attack ethyl- and isopropylbenzenes, as well as methylbenzenes, mostly at the aromatic nucleus. The substrate selectivity of this pathway, as in the case of reactions with $HMnO_4$, is described ($r = 0.990$) by Eq. (6) (see Fig. 4, straight line 2).

The substrate selectivity in the oxidation of alkanes, unlike the oxidation of alkylbenzenes, does not depend substantially on the acidity.^{3,38} The rate constants for

Table 5. Overall rate constants for the oxidation of alkylbenzenes by permanganate in 3.5 M HClO₄ at 25 °C (k_2)^{*} and rate constants for their oxidation by MnO₄⁻ (k_{-}), HMnO₄ (k_0), and MnO₃⁺ (k_{+})

Arene	k_2	$k_{-} \cdot 10^{-3}$	k_0	k_{+}
	L mol ⁻¹ s ⁻¹			
Benzene	$1.8 \cdot 10^{-3}$	$< 10^{-4}$	$2.2 \cdot 10^{-4}$	$(1.6 \pm 0.1) \cdot 10^{-3}$
Toluene	0.105	0.36	0.032	$(7.3 \pm 0.6) \cdot 10^{-2}$
Ethylbenzene	0.483	7.8	0.35	$(8 \pm 3) \cdot 10^{-2}$
Isopropylbenzene	0.509	8.7	0.41	$(9 \pm 4) \cdot 10^{-2}$
<i>o</i> -Xylene	1.42	1.3	0.73	0.69 ± 0.07
<i>m</i> -Xylene	7.01	0.89	4.4	2.6 ± 0.3
<i>p</i> -Xylene	3.01	2.0	1.8	1.3 ± 0.2

* The error in the determination of k_2 with allowance for the accuracy of the measurement of α is $\pm 6\%$.

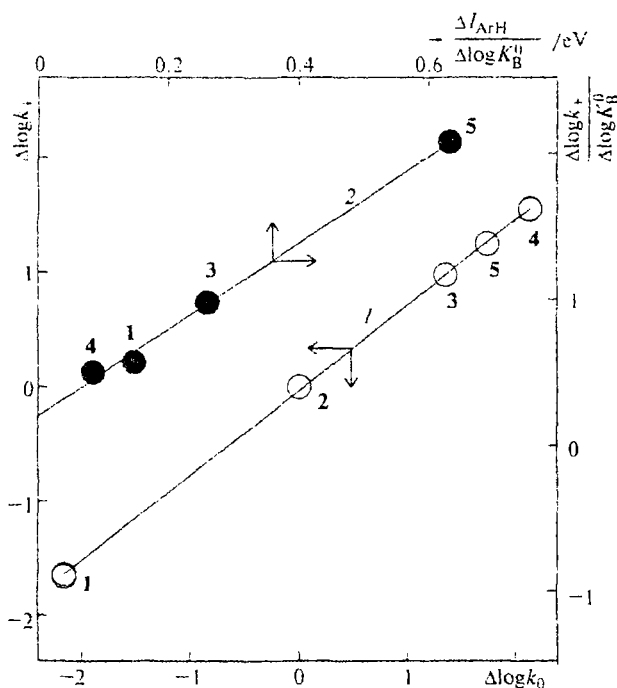


Fig. 4. Mutual correlation between $\log(k/k^{\text{PhH}}) = \Delta \log k$ for the reactions of alkylbenzenes with MnO₃⁺ and HMnO₄ (1); fulfillment of Eq. (8) for the oxidation of methylbenzene by MnO₃⁺ (2). The numbering of points corresponds to the numbers of compounds in Table 3.

n-alkanes, starting with ethane, increase linearly as the number (*n*) of the CH₂ groups increases; the slopes of the straight lines $k_2 = k_{\text{C}_3\text{H}_6} + (n-2)k_{\text{CH}_2}$ for reactions in 10⁻⁴ M HClO₄ and in 50 and 70% CF₃COOH are approximately equal.^{3,38} The k_2 value in the series of alkanes with tertiary C—H bonds increases linearly with an increase in the number of secondary C—H bonds; the slope of the corresponding straight lines is the same as in the case of *n*-alkanes. The reagents MnO₄⁻, HMnO₄, and MnO₃⁺ follow a normal type of bond

selectivity, $1^0 < 2^0 < 3^0$. The ratios of the rates of oxidation for the isobutane/*n*-pentane pair in 1 M HClO₄ and in 20–40% CF₃COOH are approximately equal (~2.9) but starting from a concentration of CF₃COOH equal to 50%, this ratio decreases (to 1.2 in 80% CF₃COOH).³⁸ This indicates that the MnO₃⁺ cation (whose contribution becomes significant at [CF₃COOH] > 50%) is less selective than MnO₄⁻ or HMnO₄.

According to published data,⁶ the relative rates of reactions of cycloalkanes (C_{*n*}H_{2*n*}), the k_6/k_5 and k_7/k_6 ratios, bear information on the positive charge on the central atom of the oxidant: as the electrophilicity increases, the k_6/k_5 ratio increases and k_7/k_6 decreases. The values $k_6/k_5 = 0.48, 0.88, 1.04$ and $k_7/k_6 = 3.7, 4.3, 1.7$ found^{3,38} for MnO₄⁻, HMnO₄, and MnO₃⁺, respectively, comply with this criterion.

Activation parameters

The activation parameters were studied for the reaction pathway involving the attack on the aromatic ring in the oxidation of alkylbenzenes by HMnO₄. It was found⁹⁸ that the activation entropies of the reactions of benzene and methylbenzene by HMnO₄ (see Table 4) correlate with the basicity of arenes (Fig. 5, straight line 1)

$$\Delta(\Delta S^\ddagger) = -(5.4 \pm 0.4) \Delta \log K_B^0 \quad (r = 0.983), \quad (19)$$

while the activation enthalpies correlate with both the basicity and the ionization potentials of ArH (see Fig. 5, straight line 2)

$$\Delta(\Delta H^\ddagger) = -(3700 \pm 300) \Delta \log K_B^0 + (0.20 \pm 0.02) \Delta I_{\text{ArH}} \quad (20) \\ (r = 0.973).$$

where $\Delta(\Delta S^\ddagger) = \Delta S^\ddagger - \Delta S^\ddagger_{\text{st}}$, $\Delta(\Delta H^\ddagger) = \Delta H^\ddagger - \Delta H^\ddagger_{\text{st}}$, $\Delta \log K_B^0 = \log K_B^0 - (\log K_B^0)_{\text{st}}$ and $\Delta I_{\text{ArH}} = I_{\text{ArH}} - I_{\text{st}}$. Toluene was taken to be the standard state (st).

As the temperature increases, the substrate selectivity (see Table 3) and the parameters *a* and *b* in Eq. (6) (Table 6) decrease. The general dependence of $\Delta \log k_0$ on $\log K_B^0$, I_{ArH} , and *T* was elucidated⁹⁸ with allowance for the fact that the basicity constants $\log K_B^0$ in Eq. (6)

Table 6. Fulfillment of relations (6) and (25) for the oxidation of methylbenzenes by HMnO₄

<i>T</i> /°C	<i>a</i>	$-b/\text{eV}^{-1}$	<i>r</i>	<i>a</i> ' *	<i>b</i> ' **
20	0.36 ± 0.02	3.38 ± 0.08	0.998	0.41 ± 0.02	0.196 ± 0.005
30	0.32 ± 0.01	3.27 ± 0.08	0.999	0.38 ± 0.01	0.203 ± 0.005
40	0.32 ± 0.02	3.05 ± 0.10	0.998	0.41 ± 0.03	0.189 ± 0.006
50	0.29 ± 0.03	3.03 ± 0.16	0.993	0.40 ± 0.04	0.194 ± 0.009
60	0.28 ± 0.02	2.91 ± 0.14	0.997	0.40 ± 0.03	0.192 ± 0.009
70	0.28 ± 0.01	2.62 ± 0.05	0.999	0.42 ± 0.02	0.178 ± 0.003

$$* a' = \frac{aT(cT_0 - 1)}{(cT - 1)T_0}, \quad ** -b' = -b \cdot 2.3RT.$$

vary as functions of temperature and the ionization potentials do not depend on T by definition:

$$2.3RT\Delta\log k = a' \cdot 2.3RT\Delta\log K_B + b' \Delta I_{ArH}. \quad (21)$$

Unlike the coefficients a and b in Eq. (6), the dimensionless parameters a' and b' in relation (21) do not depend on T . By expressing $\Delta\log k$ in terms of the changes in the activation enthalpy and entropy

$$2.3RT\Delta\log k = -\Delta(\Delta G^\ddagger) = T\Delta(\Delta S^\ddagger) - \Delta(\Delta H^\ddagger),$$

and $\Delta\log K_B$, in terms of the changes in the standard enthalpy and entropy

$$2.3RT\Delta\log K_B = -\Delta(\Delta G_B) = T\Delta(\Delta S_B) - \Delta(\Delta H_B), \quad (22)$$

we obtain that

$$\begin{aligned} T\Delta(\Delta S^\ddagger) - \Delta(\Delta H^\ddagger) &= \\ &= a' T\Delta(\Delta S_B) - a' \Delta(\Delta H_B) + b' \Delta I_{ArH}. \end{aligned} \quad (23)$$

The $\Delta(\Delta S_B)$ and $\Delta(\Delta H_B)$ values are unknown but they are presumably connected by the compensation dependence

$$\Delta(\Delta S_B) = c\Delta(\Delta H_B); \quad (24)$$

therefore, $\Delta\log K_B$ can be expressed in terms of $\Delta\log K_B^0$ for $T_0 = \text{const}$. From Eqs. (22) and (24), it follows that

$$\begin{aligned} \Delta(\Delta H_B) &= \frac{2.3RT}{cT-1} \Delta\log K_B = \frac{2.3RT_0}{cT_0-1} \Delta\log K_B^0, \\ \Delta(\Delta S_B) &= \frac{2.3RT_0c}{cT_0-1} \Delta\log K_B^0. \end{aligned}$$

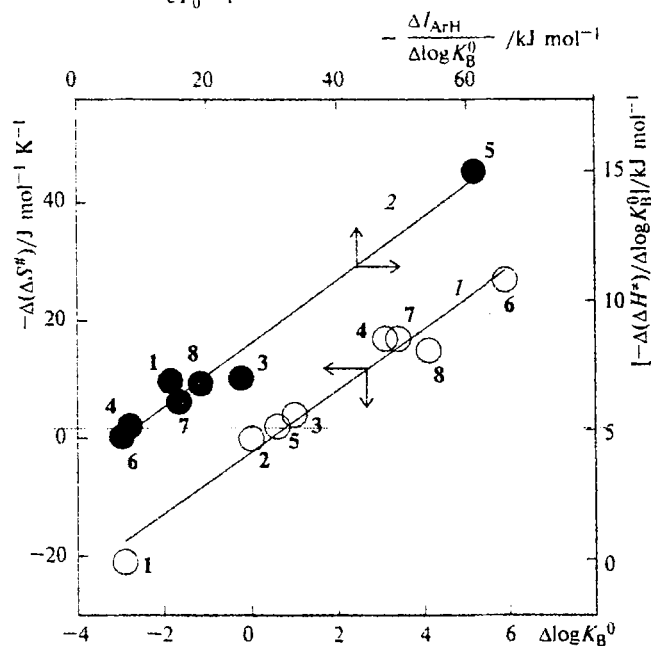


Fig. 5. Fulfillment of Eq. (19) (straight line 1) and (20) (straight line 2) for the oxidation of methylbenzenes by HMnO_4 . The numbering of points corresponds to the numbers of compounds in Table 3.

By substituting these expressions into Eq. (23), we have

$$\begin{aligned} \Delta\log k &= \frac{T\Delta(\Delta S^\ddagger) - \Delta(\Delta H^\ddagger)}{2.3RT} = \\ &= \frac{a' T_0 \Delta\log K_B^0}{cT_0 - 1} \left(c - \frac{1}{T}\right) + \frac{b' \Delta I_{ArH}}{2.3RT}. \end{aligned} \quad (25)$$

Grouping of the terms containing and not containing the factor $1/T$ in the second equality of Eq. (25) shows that the relative activation entropies should correlate with the basicity of arenes ($\Delta\log K_B^0$) and the activation enthalpies should correlate simultaneously with the basicities and the ionization potentials of ArH

$$\Delta(\Delta S^\ddagger) = 2.3RT_0ca' \Delta\log K_B^0 / (cT_0 - 1), \quad (26)$$

$$\Delta(\Delta H^\ddagger) = 2.3RT_0a' (\Delta\log K_B^0 - b' \Delta I_{ArH}) / (cT_0 - 1) \quad (27)$$

in conformity with empirical relations (19) and (20). Comparison of expressions (26), (27) and (19), (20) gave the following values of the parameters ($T_0 = 273 \text{ K}$):

$$2.3RT_0ca' / (cT_0 - 1) = -5.4 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$2.3RT_0a' / (cT_0 - 1) = -3700 \pm 300 \text{ J mol}^{-1},$$

Equation (25) in the form

$$\begin{aligned} \Delta\log k_0 &= -(0.16 \pm 0.04) \Delta\log K_B^0 + \\ &+ (157 \pm 26) \frac{\Delta\log K_B^0}{T} - (0.185 \pm 0.004) \frac{\Delta I_{ArH}}{2.3RT} \end{aligned}$$

reflects with high accuracy ($r = 0.999$) the whole set of experimental data on the substrate selectivity in the oxidation of methylbenzenes with HMnO_4 molecules on the variation of the basicity, ionization potentials, and temperature. The parameters $a' = 0.42 \pm 0.08$, $c = (1.0 \pm 0.6) \cdot 10^{-3} \text{ K}^{-1}$, and $b' = -0.185 \pm 0.004$ found from this equation are close to those presented above.

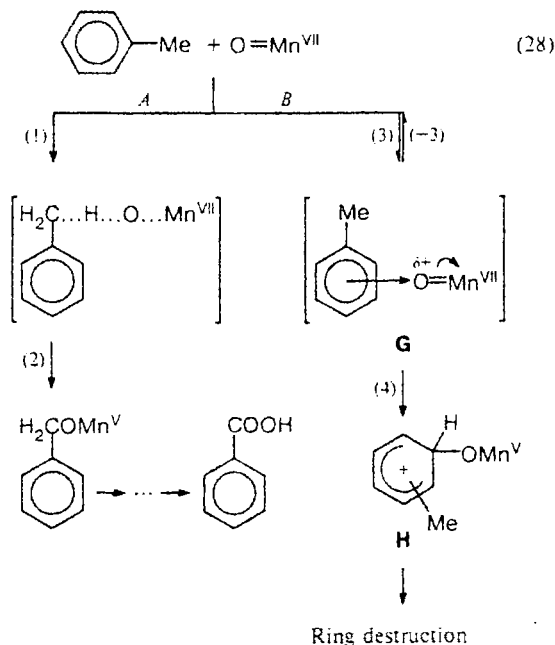
Correlation (25) is also fulfilled ($r = 0.990$) for the reactions of methylbenzenes with the MnO_3^+ cations.⁸³ In this case, the parameters $a' = 0.21 \pm 0.05$ and $-b' = 0.156 \pm 0.18$ calculated for $c = (1.0 \pm 0.6) \cdot 10^{-3} \text{ K}^{-1}$ are much lower than the corresponding values for the reaction with HMnO_4 ($a' = 0.42 \pm 0.08$ and $-b' = 0.185 \pm 0.004$). The fact that the substrate selectivities for the reactions of methylbenzenes with HMnO_4 and MnO_3^+ follow the same dependences on the basicities and ionization potentials allow the conclusion that oxidation of the aromatic nucleus in these two cases occurs by the same mechanism.

Oxidation mechanisms and catalytic effects

Mechanisms

Data on the kinetics, the KIE, and the substrate selectivity indicate that oxidation of alkylbenzenes by permanganate in aqueous acid solutions follows two parallel pathways; one of them assumes the attack by

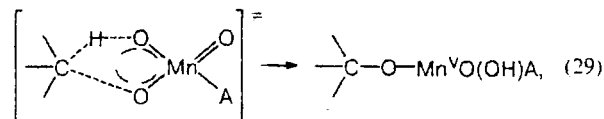
the reagent $O^{\delta+}=Mn^{VII}$ on the alkyl C—H bond and the other involves the attack on the aromatic ring (pathways *A* and *B* in reaction (28), respectively).



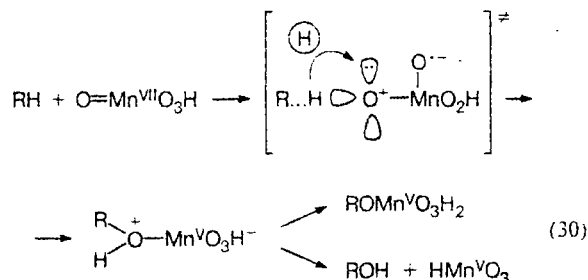
Pathway *A* involving the direct attack on the alkyl C—H bond, similar to that considered above for the oxidation of alkanes by the MnO_4^- anion,^{3,6,38} is confirmed by the following data: (1) high KIE observed for arenes deuterated at the alkyl groups (see Table 2), as for deuterioalkanes; (2) nearly quantitative formation of benzoic acid in the $KMnO_4-H_2O$ system;⁴ (3) low oxidation rate observed for benzene; (4) the agreement between the reactivity series of monoalkylbenzenes $PhCH_3 \ll PhCH_2Me \ll PhCHMe_2$ and the series of energies of the homolysis of the $\alpha-C-H$ bonds (D_{CH}); (5) the same type of bond selectivity, $1^0 < 2^0 < 3^0$, for the oxidation of alkylbenzenes and alkanes^{2,38} by the MnO_4^- anion; (6) the correlation between the activation energies and the energies of homolysis of the C—H bond common to alkylbenzenes and alkanes (see Fig. 2, straight line 1). It should also be noted that the substrate selectivity in the oxidation of alkylbenzenes by the MnO_4^- anion is similar to that for the abstraction of H atoms by radicals, for example, $\cdot CCl_3$ (cf. Ref. 99, see Fig. 2, straight line 2). The radicals, like MnO_4^- , attack alkylarenes according to two pathways involving the alkyl substituent and the aromatic ring (e.g., in the case of benzene).

The mechanisms of oxidation of the C—H bonds in alkanes have been studied previously.^{3,6,38} The KIE values and their temperature dependences and the 6/5 effect led to the conclusion^{3,38,51} that oxo species such as $O=MnO_2A$ ($A = O^-, OH, ClO_4, \text{ or } OCOF_3$) are the reactive Mn^{VII} species in aqueous acidic solutions of

permanganate and that the C—H bond is cleaved either in a cyclic transition state

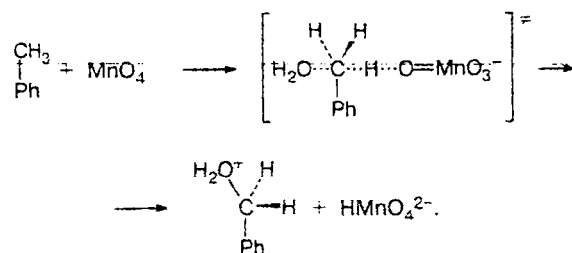


or in a "three-step elementary event,"⁶ which resembles the mechanism proposed^{100,101} for the insertion of singlet methylene into methane but is somewhat more complicated (includes the transfer of an electron onto the Mn atom and cleavage of two Mn=O bonds).



The transition states (see reactions (29) and (30)) contain a five-coordinate carbon atom. New facts supporting the formation of transition states with a five-coordinate carbon atom in the hydroxylation of C—H bonds with oxo reagents have been reported recently.¹⁰² According to the published data,⁶ in an alkaline medium, the MnO_4^{2-} anions themselves are not reactive toward the oxidation of alkanes, despite the high two-electron potential of Mn^{VI} . This result confirms the assumption that the charge of the reagent has a substantial influence on its activity, which decreases in the series $MnO_3^+ \gg HMnO_4 \gg MnO_4^- \gg MnO_4^{2-}$. This is consistent with mechanism (30) because the higher the positive charge of the $O=Mn^{\text{VI}}$ species, the easier the formation of the electrophilic reagent, O^+-Mn^{VI} , which attacks directly the C—H bond.

It has been suggested^{103–105} that pathway *A* of reaction (28), which involves the transfer of an H atom of the toluene methyl group on oxygen of the MnO_4^- anion, is valid only for toluene solutions, whereas in aqueous solutions, oxidation involves hydride transfer:



The high KIE values (>10) for the reaction pathway involving oxidation of the C—H bond in the alkyl

substituent have been interpreted¹² as being due to the substantial contribution of tunneling. Yet another opinion^{50,96} is that high KIE and $E_a^D - E_a^H$ values and low A^H/A^D ratios are due to the compensation effects for the KIE; when the structure of the reagent changes, systems with high and low KIE are described by a common compensation dependence.

Depending on the type of the transition state (TS) in the slow step of the reaction, the mechanism of electrophilic aromatic substitution including the successive formation of CTC (or radical ion pair) **G** and σ -complex **H** (see reactions (28), pathway *B*) can be realized as three variants.

(a) The TS is similar to the CTC; according to the published data,^{26,75} in this case, the substrate selectivity and the activation energy are controlled only by the ionization potentials of arenes, whereas the activation entropy remains constant in the series of methylbenzenes;

(b) the TS is similar to the σ -complex; in this case, irrespective of the presence of the pre-equilibrium step (3), the substrate selectivity should correlate only with the stability of the resulting σ -complexes, *i.e.*, with the basicity of ArH,^{34,75} and the activation energy (enthalpy) correlates with the enthalpy of formation of ArH₂⁺;

(c) The structure of the TS is intermediate between the CTC and the σ -complex. In this case, the substrate selectivity and the activation energy are expected to correlate with both the basicities and the ionization potentials of ArH. This dependence of the substrate selectivity and the activation enthalpy on two parameters cannot be interpreted within the framework of variants (a) and (b).

It can be concluded based on the foregoing that in the oxidation of benzene and methylbenzene by HMnO₄ and MnO₃⁺, step (3) of pathway *B* in reaction (28) is fast and reversible and the TS of step (4) has a structure intermediate between CTC **G** and σ -complex **H**.

Catalytic effects and reactions in the presence of halide ions

The data considered above indicate that oxidation of hydrocarbons by permanganates in aqueous solutions is catalyzed by Brønsted acids. Examples of catalysis by Lewis acids such as AlCl₃ and BF₃ are also known.¹⁰⁶ The reactions involving permanganate in nonaqueous and mixed solvents are accelerated in the presence of phase transfer catalysts, namely, tetraalkylammonium salts,^{13,14} crown ethers,¹⁵ or calixarenes.¹⁰⁷ Oxidative halogenation in the presence of permanganate is known. Thus, according to published data,¹⁰⁸ solutions of HCl and HBr in acetonitrile in the presence of KMnO₄ efficiently halogenate arenes, alkenes, and alkynes under mild conditions (25–60 °C).

Oxidative chlorination of toluene in aqueous media has been studied.¹⁰⁹ It was shown that the oxidation of toluene on treatment with MnO₄⁻ and HMnO₄ in the KMnO₄–0–0.4 *M* HClO₄–H₂O system in the pres-

ence of chloride ions at H⁺ > 0.02 mol L⁻¹ is accompanied by parallel chlorination giving rise to chlorotoluenes (*ortho/para* = 3.2). Provided that [ArH] ≪ [Cl⁻] ≪ [KMnO₄], the following kinetic equation is fulfilled

$$-d[\text{ArH}]/dt = (k_-[\text{MnO}_4^-] + k_0[\text{HMnO}_4] + k_{\text{Cl}}[\text{Cl}^-][\text{H}^+])[\text{ArH}].$$

Chlorination has the first order with respect to Cl⁻ and H⁺ and the zero order with respect to Mn^{VII}. The substrate selectivity in the series of benzene, toluene, *o*-, *m*-, and *p*-xylenes, and pseudocumene correlates with the basicity of ArH (see Eq. (5)); for the toluene/toluene-d₈ pair of substrates, KIE = 1.0. The data obtained are consistent with the mechanism of electrophilic chlorination; the reactive species H₂OCl⁺, arising upon permanganate oxidation of Cl⁻, attacks the arene at the aromatic nucleus to give the σ -complex in the slow step.

Comparison of the reactivities of MnO₄⁻, HMnO₄, and MnO₃⁺

Table 7 summarizes the characteristics of the reactions of hydrocarbons with the three Mn^{VII}-containing oxidative reagents, having different charges (-1, 0, +1). The oxidation rates for both classes of substrates increase appreciably as the positive charge of the oxidant increases, $k_- \ll k_0 \ll k_+$.

As shown above, the predominant pathway of the reactions of arenes, except for benzene, with the MnO₄⁻ anions is oxidation of the alkyl C–H bond. Conversely, the HMnO₄ molecules attack all substrates, except for ethyl- or isopropylbenzenes, mainly at the aromatic

Table 7. Comparison of the reactions of alicyclic and aromatic hydrocarbons with the three Mn^{VII} species (25 °C)

Characteristics of the reaction	MnO ₄ ⁻	HMnO ₄	MnO ₃ ⁺
	<i>Alkanes</i>		
$k_{c-C_6H_{12}}$ /L mol ⁻¹ s ⁻¹	6.5 · 10 ⁻⁵	4 · 10 ⁻²	>3
(KIE) _{c-C₆H₁₂} 6/5 Ratio	5.0 0.45	7.6 0.98	4.2 1.04
	<i>Arenes</i>		
k_{PhCH_3} /L mol ⁻¹ s ⁻¹	3.7 · 10 ⁻⁴	0.10	>10
(KIE) _{PhCH₃} Direction of the attack	21.7 The alkyl C–H bond, partially the nucleus	1.63 The nucleus and the alkyl C–H bond	1.1 The nucleus
($k^{\text{CH}}/k^{\text{R}}$) _{PhCH₃} The substrate selectivity correlates	200 With the energy homolysis of the C–H bond (D_{CH})	0.5 With log K_B and I_{ArH}	<0.1 With log K_B and I_{ArH}
Parameters of Eq. (25)	–	$a' = 0.42,$ $-b' = 0.185$	$a' = 0.21,$ $-b' = 0.156$

ring, and the MnO_3^+ cation attacks all alkylbenzenes without exception at the aromatic ring.

The change in the ratio of the contributions of the oxidation pathways involving the C—H bond of the alkyl group (k^{CH}) and the aromatic ring (k^{R}) in the series MnO_4^- , HMnO_4 , and MnO_3^+ results in lower KIE. Comparison of the rates of oxidation of toluene by the three Mn^{VII} species with allowance for the ratio of the rate constants for the pathways involving the attacks on the C—H bond and on the aromatic ring ($k^{\text{CH}}/k^{\text{R}}$) for MnO_4^- , HMnO_4 , and MnO_3^+ (see Table 7) leads to the conclusion that the rate of the attack on the ring increases much more rapidly upon an increase in the positive charge than the rate of the attack on the alkyl group. This is apparently due to the enhancement of the electrophilic properties of the reagent in this series. The lower substrate selectivity and the smaller magnitudes of the a' and $-b'$ parameters of Eq. (25) indicate that the MnO_3^+ cation is a stronger electrophilic reagent in the reactions with the aromatic ring than the HMnO_4 molecule.

Conclusion

The data presented here confirm the fact that the most exact information on the reactivity of alkylbenzenes and the mechanisms of their activation can be obtained by direct investigation of the first step of the reaction based on the consumption of the substrate. This method substantially supplements the traditional approaches to the study of EAS reactions; in the case of complex multistep reactions, this method has no alternative and is especially convenient when poorly soluble volatile substrates are involved. In this review, the efficiency of this method was illustrated in relation to the oxidation of alkylarenes by permanganates, which was found to proceed largely according to the EAS mechanism.

It was found that MnO_4^- , HMnO_4 , and MnO_3^+ act as the oxidative species in aqueous acid solutions at various acidities. The increase in the positive charge in this series enhances the electrophilic properties of the reagent; this is manifested as an increase in the rate of the reaction with the hydrocarbon and the change of the site of the attack on the alkylbenzene molecule. Study of the variation of the kinetics, the KIE, and the selectivity as functions of the acidity makes it possible to distinguish the contributions of the reactions of alkylbenzenes with the three manganese(VII) species and the attacks by these species on the C—H bonds of the alkyl groups and on the aromatic ring.

The data on the substrate selectivity for a broad range of alkylbenzenes led to the conclusion that the oxidation of the alkyl C—H bonds in alkylbenzenes follows the same mechanism as that in alkanes, while the benzene ring is attacked by the EAS mechanism. It was found that the substrate selectivity and the activation enthalpy for the latter pathway in benzene and methylbenzene are controlled simultaneously by the

basicities and the ionization potentials of arenes, while the activation entropy is controlled only by the basicity. It was concluded that the transition state of the pathway involving the attack by HMnO_4 or MnO_3^+ on the ring has a structure intermediate between the CTC and the σ -complex. In the presence of chloride ions, the oxidation by manganese(VII) is accompanied by the parallel electrophilic chlorination with the H_2OCl^+ cation, which attacks the arene at the benzene ring.

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