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Kinetics, Substrate Selectivity, and Mechanisms of Alkane and Alkylbenzene Reactions with Peroxynitrous Acid in the Gas Phase and Solution

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Abstract—Specific features of the kinetics of alkane and alkylbenzene oxidation with HOONO formed in the H_2O_2–$NaNO_2$ system (pH 4.27) are quantitatively explained assuming the simultaneous occurrence of reactions in the gas and liquid phases. A model of the kinetic distribution method is developed and verified that accounts for the equilibrium distribution of a substrate and a reagent between phases and their interaction in both phases. Relative rate constants for the oxidation of *n*-alkanes (C_3–C_8), isobutane, cyclopentane, cyclohexane, benzene, and alkylbenzenes are measured over a wide range of the volume ratios of the gas and liquid phases ($\lambda = V_g/V_l$). Relative rate constants for the oxidation of alkanes in the gas phase and alkylbenzenes in gas and solution were determined. Similarity in substrate selectivities and kinetic isotope effects of the gas-phase reactions of alkanes and arenes with peroxynitrous acid and $^{\bullet}OH$ radicals suggest that hydroxyl radical or the $^{\bullet}OH \cdots NO_2$ radical pair is an active species in the gas phase. In solution, alkylbenzenes react nonselectively with HOONO, as well as with $^{\bullet}OH$ radicals. In contrast to the liquid-phase oxidation of arenes, the liquid-phase oxidation of all alkanes under study insignificantly contribute (5–15%) to the overall rate of the substrate consumption.

INTRODUCTION

Peroxynitrous acid (HOONO) is an intermediate in the oxidation of nitrites to nitrates with hydrogen peroxide in acidic media [1]:

$$HNO_2 + H_2O_2 \xrightarrow[-H_2O]{} NOONO \longrightarrow HNO_3. \qquad (I)$$

Being a strong oxidant ($E^0 = 1.4$ V [2]), it easily oxidizes organic compounds in aqueous solutions. However, no information was available until recently on the interaction of alkanes with HOONO; only one paper [3] irrelevant to kinetics was published on the reaction of arenes with HOONO in the H_2O_2–HNO_2 system at $[H^+] = 0.03$ g-ion/l with the formation of the mixture of nitro derivatives, phenols, and nitrophenols. Halfenny and Robinson [3] assumed that HOONO formed under these conditions rapidly decomposed into $^{\bullet}OH$ and NO_2 radicals, which immediately attacked the arene.

We have found earlier [4], using the kinetic distribution method, that alkanes and alkylbenzenes interact with aqueous HOONO solutions and with a model H_2O_2–HNO_2 system that generated HOONO *in situ*. In the case of alkanes, alcohols and ketones were formed as main products. A study of effective relative rate constants for the oxidation of a number of alkanes and alkylbenzenes in the system ($NaNO_2$–H_2O_2)/acetate buffer solution (pH 4.27) led to unexpected results. The dependence of the substrate selectivity on the volume ratio of the liquid and gas phases in the reactor was revealed. This fact had no precedent in hydrocarbon oxidation reactions [5]. It was explained by the simultaneous oxidation of hydrocarbons by HOONO in the aqueous solution and in the gas phase over the solution.

The goal of this work was to elucidate the mechanisms of reactions and the nature of active species in the gas and liquid phases by studying the substrate selectivity of the first step of oxidation (the step of entering substrates into reaction) for a wide range of normal, isostructured, and cyclic alkanes, as well as alkylbenzenes. For this purpose, an extended model of the kinetic distribution method, which took into account the equilibrium distribution of a substrate and a reagent between phases and the simultaneous occurrence of reactions in the gas and solution, was developed; the relative rate constants for the oxidation of 18 hydrocarbons in the system of (H_2O_2–HNO_2)/acetate buffer solution (pH 4.27) was studied over a wide range of volume ratios between the phases in a reactor; and the contributions from reactions in the gas and solution were identified. The information on the chemistry of peroxynitrous acid and reactions in the H_2O_2–HNO_2 system was briefly considered.

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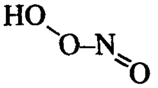
PEROXYNITROUS ACID AND REACTIONS IN THE HNO_2–H_2O_2 SYSTEM

Peroxynitrous acid and peroxynitrite exist as two isomers:


cis-HOONO (pK_a 6.8)


trans-HOONO (pK_a 7.9)

cis-HOONO is a stronger acid, which is by 1–2 kcal/mol more stable than *trans*-HOONO [2, 6–8].

HOONO is formed by the reaction between nitrogen oxide and hydrogen peroxide [9] or the superoxide anion $O_2^{\cdot-}$ [10], between alkylnitrites and hydroperoxide anion [11], between a triplet anion NO^- and oxygen [12], and by the radiolysis or photolysis of nitrates in solutions or crystals [13, 14]. The conventional method of HOONO synthesis [6] is based on reaction (I) in which HOONO is formed by the following mechanism [15]:

$$\begin{gathered} NO_2^- + 2H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO^+ + H_2O, \\ NO^+ + H_2O_2 \xrightarrow{k_2} HOONO + H^+ \end{gathered} \qquad \text{(II)}$$

which is described by the rate law

$$\frac{d[HOONO]}{dt} = \frac{k_1k_2[NO_2^-][H_2O_2][H^+]^2}{k_{-1}[H_2O] + k_2[H_2O_2]}. \qquad (1)$$

It was found that $k_1 = 5.8 \times 10^6$ l^2 mol^{-2} s^{-1} and $k_2/k_{-1}[H_2O] = 2.4$ l/mol (phosphate buffer solution, pH 4–6, 25°C) [15].

In alkaline solutions at pH > 10, peroxynitrous acid is in the form of the ^-OONO anion and is rather stable, but it rapidly decomposes in neutral and acidic media:

$$^-OONO + H^+ \overset{K_a}{\rightleftharpoons} HOONO \xrightarrow{k_d} NO_3^- + H^+. \qquad \text{(III)}$$

The rate of HOONO decomposition measured from a decrease in the absorbance of peroxynitrite at 302 nm ($\varepsilon = 1670$ l mol^{-1} cm^{-1} [6]) follows the rate law [2]:

$$\begin{gathered} -d[HOONO]/dt \\ = k_d[HOONO]_\Sigma[H^+]/(K_a + [H^+]), \end{gathered} \qquad (2)$$

where $[HOONO]_\Sigma = [HOONO] + [^-OONO]$; $k_d = 1.3$ s^{-1} at 25°C. The decomposition of HOONO in the HNO_2–H_2O_2 system at pH < 7 is much faster than its formation, and a quasi-stationary concentration is established with time according to equations (1) and (2)

$$[HOONO]_\Sigma^* = \frac{k_1k_2[NO_2^-][H_2O_2][H^+](K_a + [H^+])}{k_d(k_{-1}[H_2O] + k_2[H_2O_2])}. \qquad (3)$$

The decomposition of HOONO proceeds via the intermediate formation of radicals NO_2 and $^{\cdot}OH$ or a radical pair $NO_2 \cdots {}^{\cdot}OH$ [3, 16]. The high activity of HOONO in the nitration and hydroxylation of arenes [3] and in the oxidation reactions catalyzed by metal ions [7] is assumed to be due to the above species and the NO_2^+ cation. However, there is evidence [2] that HOONO intramolecularly isomerizes into HNO_3. The direct interaction of HOONO or ^-OONO with a substrate is assumed, for example, in the oxidation of sulfhydryl groups [17], dialkyl sulfides [18], dialkyl sulfones [18], and in the nitration of phenols [7]. A drastic decrease in reaction rates observed in many reactions at pH > 7.5 is related to the fact that *trans*-HOONO or its excited form is active [2, 7, 8].

An interest in the chemistry of HOONO and nitrogen oxides increased greatly in recent years. This is due to an important role of these substances in physiological processes (digestion, control of blood pressure and sexual functions, antibiotic effect, growth of tumor cells, etc.) [14, 19–21].[1] It is assumed [10, 14, 21] that HOONO is an intermediate in the reactions of nitrogen oxide in cells. Thus, peroxynitrite is formed by the fast recombination ($k = 6.7 \times 10^9$ l mol^{-1} s^{-1} [21]) of nitrogen oxide, the product of enzymatic oxidation of *L*-arginine [22], and superoxide anion, a usual product of cell metabolism under aerobic conditions [23]. Nitrogen oxide can transform *in vivo* into NO^- and NO^+, which are oxidized by oxygen or hydrogen peroxide to peroxynitrite [11, 12].

Information on the properties and reactions of HOONO in the gas phase is unavailable [24]. The chemistry of peroxynitrous acid was also considered in [14].

EQUILIBRIUM DISTRIBUTION OF A SUBSTRATE AND A REAGENT BETWEEN GAS AND SOLUTION FOR REACTIONS SIMULTANEOUSLY OCCURRING IN BOTH PHASES

Kinetic distribution method. The method was proposed, comprehensively studied, and used in various versions by one of us [5, 25]. A similar approach has been previously used to describe the kinetics of the hydration of gas-phase isobutylene [26]. The kinetic distribution method is unique in allowing kinetic studies of the reactions of volatile, poorly soluble substrates such as alkanes in aqueous or sulfuric acid solutions. This method provided much data on the kinetics, kinetic isotope effect, substrate selectivity, and mechanisms of the first step (the step of substrate activation) in the solvolysis of alkyl halides, including the reactions induced by metal ions [27], in the oxidation of alkanes [5] and electrophilic substitution of arenes [28, 29], and other reactions [30, 31]. A necessary condition for the application of the method is the intensive stir-

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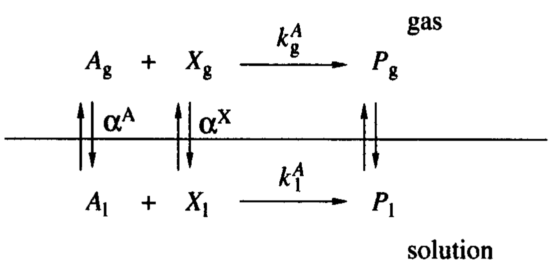
[1] In 1992, *Science* called nitrogen oxide "the molecule of the year" [19]. In 1997, the First International Conference on the Chemistry and Biology of Peroxynitrite was held in Ascona (Switzerland).



Scheme. Model of a two-phase system with the equilibrium distribution of substrate A and reagent X between gas and solution for reactions simultaneously occurring in two phases.

ring of phases. This is achieved by shaking the reactor at a high frequency and eliminating diffusion and mass transfer limitations [32].

A “simple” model for the kinetic distribution method [5] implies that substrate A distributed between the gas and liquid phases of a closed reactor is at equilibrium, but the reaction with reagent X occurs only in the solution. At [A] ≪ [X], the kinetics of the substrate consumption from the gas phase is described by the equation

$$-\mathrm{d}[\mathrm{A}]_g/\mathrm{d}t = k_\lambda^A[\mathrm{A}]_g[\mathrm{X}] = k_l^A[\mathrm{A}]_l[\mathrm{X}]/(1+\alpha^A\lambda),$$
$$\lambda = V_g/V_l, \quad \alpha^A = [\mathrm{A}]_g/[\mathrm{A}]_l, \tag{4}$$

where k_λ^A is the apparent constant for the substrate consumption from the gas phase at a given volume ratio of gas to solution (V_g/V_l) in the reactor; k_l^A is the true second-order rate constant for the reaction in the liquid phase; α^A is the coefficient of the equilibrium distribution of the substrate between the gas and solution at a dilution limit $[\mathrm{A}]_l \longrightarrow 0$, when the Henry law is valid. By varying λ, one can determine the values of k_l^A and α^A from the dependence of $1/k_\lambda^A$ on λ by the kinetic distribution method.

When the concentration of reagent X is unknown or varies during the reaction, a “competitive” version of the kinetic distribution method is to be used enabling the measurement of the relative rates for two substrates A and B [5]. In this case, the concentration of X is eliminated from the two rate laws

$$\left.\begin{aligned}-\mathrm{d}[\mathrm{A}]_g/\mathrm{d}t &= k_\lambda^A[\mathrm{A}]_g[\mathrm{X}]\\ -\mathrm{d}[\mathrm{B}]_g/\mathrm{d}t &= k_\lambda^B[B]_g[\mathrm{X}]\end{aligned}\right\}. \tag{5}$$

By integrating (5), we obtain

$$\ln[\mathrm{A}]_g = (k_\lambda^A/k_\lambda^B)\ln[B]_g + \mathrm{const}. \tag{6}$$

For reactions occurring only in solution, the relative liquid-phase rate constants k_l^A/k_l^B are related to the measured values of k_λ^A/k_λ^B by the equation [5]

$$k_l^A/k_l^B = k_\lambda^A(1+\alpha^A\lambda)/k_\lambda^B(1+\alpha^B\lambda). \tag{7}$$

Extended model of the kinetic distribution method. Let us consider the extended model of the kinetic distribution method. First, the model suggests that both volatile substrate A and reagent X have an equilibrium distribution between phases. Second, the model assumes a simultaneous reaction between A and X in both phases of a closed reactor (see the scheme).

Let us introduce the following designations: N_g^A, N_g^X, N_l^A, and N_l^X are the amounts of components A and X in gas and solution, respectively; $[\mathrm{A}]_g = N_g^A/V_g$, $[\mathrm{X}]_g = N_g^X/V_g$, $[\mathrm{A}]_l = N_l^A/V_l$, and $[\mathrm{X}]_l = N_l^X/V_l$ are the concentrations of components A and X in the gas phase and in the solution, respectively.

$$\begin{aligned}N^A &= N_g^A + N_l^A = [\mathrm{A}]_g V_g + [\mathrm{A}]_l V_l\\ &= [\mathrm{A}]_g V_g(1 + 1/\alpha^A\lambda),\end{aligned} \tag{8}$$

$$\begin{aligned}N^X &= N_g^X + N_l^X = [\mathrm{X}]_g V_g + [\mathrm{X}]_l V_l\\ &= [\mathrm{X}]_g V_g(1 + 1/\alpha^X\lambda).\end{aligned} \tag{9}$$

As in (4), α^A and $\alpha^X = [\mathrm{X}]_g/[\mathrm{X}]_l$ denote the equilibrium distribution coefficients of substrate between the phases; and $\lambda = V_g/V_l$. When the reaction simultaneously occurs in both phases, the overall rate of substrate consumption is

$$\begin{aligned}-\mathrm{d}N^A/\mathrm{d}t &= k_g^A[\mathrm{A}]_g[\mathrm{X}]_g V_g + k_l^A[\mathrm{A}]_l[\mathrm{X}]_l V_l\\ &= [\mathrm{A}]_g[\mathrm{X}]_g V_g(k_g^A + k_l^A/\alpha^A\alpha^X\lambda),\end{aligned} \tag{10}$$

where k_g^A and k_l^A are the true rate constants in the gas and solution, respectively.[2] At the same time, according to equation (8),

$$-\mathrm{d}N^A/\mathrm{d}t = -V_g(1 + 1/\alpha^A\lambda)\mathrm{d}[\mathrm{A}]_g/\mathrm{d}t. \tag{11}$$

It follows from equations (10) and (11) that

$$\begin{aligned}&-V_g\left(\frac{\alpha^A\lambda + 1}{\alpha^A\lambda}\right)\frac{\mathrm{d}[\mathrm{A}]_g}{\mathrm{d}t}\\ &= V_g[\mathrm{A}]_g[\mathrm{X}]_g\left(\frac{k_g^A\alpha^A\alpha^X\lambda + k_l^A}{\alpha^A\alpha^X\lambda}\right).\end{aligned} \tag{12}$$

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[2] Here, usual determination of the rate as –d[A]/d*t* or $-(1/V_l)(\mathrm{d}N^A/\mathrm{d}t)$ are unsuitable because substance A or X is present and reacts in two phases whose volumes are different.

Turning to the apparent rate constant k_λ for the consumption of the substrate from the gas phase given a value of λ, we obtain

$$-\frac{1}{[A]_g}\frac{d[A]_g}{dt} = k_\lambda^A[X]^* = \frac{[X]^*}{(1+\alpha^X\lambda)}\left(\frac{k_g^A\alpha^A\alpha^X\lambda + k_l^A}{1+\alpha^A\lambda}\right), \tag{13}$$

where $[X]^* = N^X/V_l = [X]_g(1+\alpha^X\lambda)/\alpha^X$ is the concentration of the reagent in the liquid phase with no regard of its distribution between phases.

By studying the kinetics of the competitive simultaneous consumption of two substrates A and B, we obtain equation (14) instead of equation (13) for the relative rate constants k_λ^A/k_λ^B. Equation (14) is convenient in that it does not contain the concentration of reagent X whose nature may be unknown and whose concentration may change substantially during the reaction:

$$\frac{k_\lambda^A}{k_\lambda^B} = \frac{(k_g^A\alpha^A\alpha^X\lambda + k_l^A)(1+\alpha^B\lambda)}{(k_g^B\alpha^B\alpha^X\lambda + k_l^B)(1+\alpha^A\lambda)}. \tag{14}$$

The relative rate constants for substrates A and B in the gas phase k_g^A/k_g^B and in the solution k_l^A/k_l^B, as well as the values of $k_g\alpha^X/k_l$ for each substrate, can be calculated from equation (14) rearranged as follows:

$$L + (L/\lambda)C_1 = C_2 + (1/\lambda)C_3. \tag{15}$$

This has three variables $L = k_\lambda^A(1+\alpha^A\lambda)/k_\lambda^B(1+\alpha^B\lambda)$, L/λ, and $1/\lambda$ because, as comparison to equation (14) shows, $C_1 = k_l^B/k_g^B\alpha^B\alpha^X$, $C_2 = k_g^A\alpha^A/k_g^B\alpha^B$, and $C_3 = k_l^A/k_g^B\alpha^B\alpha^X$. Note that equations (4) and (7) of the simple version of the kinetic distribution method are special cases of equations (13) and (14), respectively, at $\alpha^X = 0$, when a reagent is present only in the solution, and the reaction does not occur in the gas phase.

EXPERIMENTAL

Relative apparent rate constants for the oxidation of alkanes and alkylbenzenes in the H_2O_2–HNO_2 system (pH 4.27) at 25°C were measured by the consumption of substrates A and B from the gas phase using the competitive version of the kinetic distribution method (equation (6)). Hydrocarbons A and B and the concentrations of reagents (H_2O_2 and $NaNO_2$) were chosen so that the rates were convenient to measure. Changes in the concentrations of two substrates in the gas phase were monitored by GLC (an LKhM-80 chromatograph equipped with a flame-ionization detector and a column (1000 × 2 mm) packed with Chromaton N-AW impregnated with the SE-30 stationary phase). Methane, which is hard to oxidize under our conditions, was used as an internal standard. The precision of k_λ^A/k_λ^B values determined in replicate measurements was ±3%. The distribution coefficients of the substrate between the gas and the solution necessary for the calculation of the true rate constants were determined by the technique described in [5].

Working solutions were prepared by reaction (I) before experiments. The mixture of hydrocarbons (RH) and the internal standard were introduced into the gas phase of a closed, shaken, temperature-controlled reactor [5] containing sodium nitrite in an acetate buffer solution with pH of 4.27 and an ionic strength of 0.1. When the equilibrium distribution of RH between the gas and the solution was attained, the required amount of 30% hydrogen peroxide solution was added. In all cases, initial concentrations of $NaNO_2$ and H_2O_2 were much higher than those of the substrates. The reactor shaking frequency was usually higher than 350 min^{-1}; this excluded the diffusion limitations.

RESULTS AND DISCUSSION

Selection of conditions for kinetic studies. We have found earlier [4] that, in a phosphate buffer solution (pH 7.05), the consumption of alkanes and arenes was observed only at the first moment after the addition of the alkaline (pH 12) solution of peroxynitrite, and then it immediately ceased. This is due to the fast decomposition of HOONO (at pH 7.1 and 25°C, according to equation (2), the rate constant for HOONO decomposition is 0.5 s^{-1}). At pH > 7.5, the oxidation of hydrocarbons did not occur. The rapid decomposition of HOONO at pH 7 prevented the kinetic study of alkane and arene oxidation under these conditions. To resolve the problem, we used the model H_2O_2–HNO_2 system where HOONO was generated *in situ* and, at certain values of pH, its quasi-stationary concentration was reached.

According to equation (3), [HOONO]* is proportional to $[H^+]$; therefore, in choosing pH, we proceeded from the requirements that the concentration of HOONO should be sufficiently high and reaction rates should be convenient to measure. The system ($NaNO_2$–H_2O_2)/acetate buffer solution (pH 4.27) was the most suitable and met these requirements. This system efficiently oxidizes alkanes and alkylbenzenes at 25°C by contrast to its individual components.

Kinetics. Changes in concentrations of hydrocarbons at $[NaNO_2] = [H_2O_2] \gg [A]$ did not obey the first-order equation (Fig. 1, curves *1*, *2*). This points to a decrease in the concentration of reagent X (HOONO) in the course of the reaction. In this case, using the competitive version of the kinetic distribution method, one can determine the relative constants (k_λ^A/k_λ^B) for the pair of substrates A and B (cyclohexane and cyclopentane in the particular case). Equation (6) is valid over the entire range where the substrate concentration

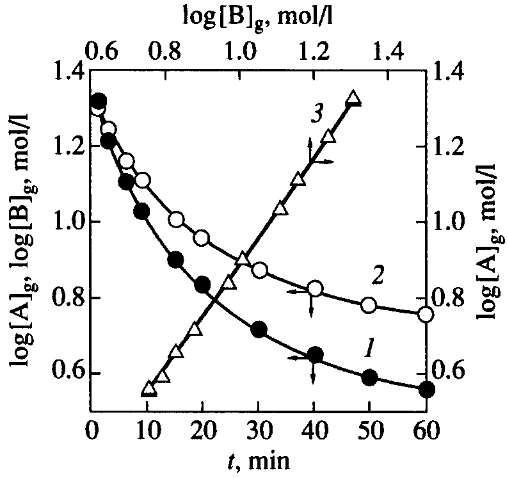


Fig. 1. Kinetic curves of (*1*) cyclohexane (A) and (2) cyclopentane (B) consumption in the system H_2O_2 (8.2×10^{-2} mol/l)–$NaNO_2$ (8.2×10^{-2} mol/l)/acetate buffer solution (pH 4.27), $\lambda = 2.31$; 25°C; (*3*) is the fit of equation (6) for the above pair of substrates.

decreases (Fig. 1, line *3*). This is indicative of the first-order reaction with respect to the substrate.

Inconsistency between kinetic data and the simple model of the kinetic distribution method. For reactions occurring only in solutions, the relative liquid-phase rate constants k_l^A/k_l^B are related to the measured quantities k_λ^A/k_λ^B by equation (7). Equation (7) is not valid for the oxidation of alkanes and arenes in the $NaNO_2$–H_2O_2 system over a wide range of λ. The calculated relative liquid-phase rate constants k_l^A/k_l^B changed by a factor of 1.2 to 8 for various pairs of substrates A and B in the λ range from 0.65 to 21. These changes were the most pronounced for the RH/ArH and $Ar'H^A/Ar''H^B$ pairs in which α was less than 1 for at least one substrate (Table 1). For the $R'H^A/R''H^B$ pairs, the deviations from equation (7) were insignificant; however, the calculations by equation (7) resulted in an unusual reversed order of the substrate selectivity

$$n\text{-RH} > iso\text{-RH} > cis\text{-RH} > \text{AlkPh}.$$

An obvious correlation between relative rate constants and the solubility of substrates α was observed [4]. This fact has no precedent among the known liquid-phase reactions of hydrocarbon oxidation [5]. These facts allowed us to assume that, in our case, the simultaneous oxidation of hydrocarbons occurred in the solution and in the gas phase of the reactor.

Verification of the extended model of the kinetic distribution method. The supposed model quantitatively describes experimental data on the oxidation of alkanes and arenes in the system (H_2O_2–HNO_2)/acetate buffer solution with an accuracy of ±10% (Table 1). Table 2 presents the relative gas-phase rate constants for the oxidation of alkanes under study calculated by equation (15) using the least-squares method. Table 3 summarizes relative rate constants for the oxidation of arenes in the gas and solution and the values of $k_l/k_g\alpha^X$ for each substrate. Note that the values of $k_l/k_g\alpha^X$ for the same substrate obtained from the k_λ^A/k_λ^B relationships for different pairs of hydrocarbons A/B are close, as is illustrated by an example of toluene:

$\frac{\text{A}}{\text{B}}$	$\frac{n\text{-Pentane}}{\text{Toluene}}$	$\frac{n\text{-Hexane}}{\text{Toluene}}$	$\frac{\text{Cyclopentane}}{\text{Toluene}}$	$\frac{\text{Cyclohexane}}{\text{Toluene}}$	$\frac{\text{Benzene}}{\text{Toluene}}$	$\frac{ortho\text{-Xylene}}{\text{Toluene}}$
$k_l^B/k_g^B\alpha^X$	0.34	0.40	0.39	0.38	0.32	0.42

This is further evidence for the extended KDM model.

Reactions of alkanes in the gas phase. Rate constants with respect to *n*-pentane for the oxidation of test hydrocarbons in the gas phase are presented in the third column of Table 2. The rate of *n*-alkane oxidation linearly increases with an increase in their chain length, and the values of k_g^{RH} are proportional to the number of secondary C–H bonds in a hydrocarbon molecule (n_{CH}^{sec}); that is, the equality

$$6\log k_g^{RH}/n_{CH}^{sec}k_g^{n\text{-}C_5H_{12}} \simeq 1$$

is valid. The similarity of the substrate selectivity for the oxidation of hydrocarbons by peroxynitrous acid and $^{\bullet}OH$ radicals [5, 33, 34] in the gas phase is striking: for all alkanes under study, linear correlations exist between the values of $k_g^{RH}/k_g^{n\text{-}C_5H_{12}}$ for two reactions with the correlation coefficient of 0.998 and the slope $c \simeq 1.0$ (Fig. 2, line *1*):

$$(k_g^{RH}/k_g^{n\text{-}C_5H_{10}})_{HOONO} = c(k_g^{RH}/k_g^{n\text{-}C_5H_{12}})_{^{\bullet}OH} \qquad (16)$$

The values of $k_g^{cyclo\text{-}C_6H_{12}}/k_g^{cyclo\text{-}C_5H_{10}}$ and the kinetic isotope effect in the gas phase $(KIE)_g$ obtained for the cyclo-C_6H_{12}/cyclo-C_6D_{12} pair in reactions with HOONO were compared with the corresponding values found in reactions with $^{\bullet}OH$ radicals. This comparison also confirmed the closeness of the kinetic characteristics

Table 1. Relative rate constants for the oxidation of pairs of substrates *n*-hexane/toluene and *ortho*-xylene/toluene in the H_2O_2–$NaNO_2$ system and the parameters of equation (15) (pH 4.27; $T = 25°C$)

λ	*n*-Hexane (A)/toluene (B) (RH/ArH)			*ortho*-Xylene (A)/toluene (B) (Ar'H/Ar"H)		
	$\frac{k_\lambda^A}{k_\lambda^B}$	$\frac{k^A}{k^B} = \frac{k_\lambda^A(1+\alpha^A\lambda)}{k_\lambda^B(1+\alpha^B\lambda)}$	$\frac{k_\lambda^A}{k_\lambda^B}$	$\frac{k_\lambda^A}{k_\lambda^B}$	$\frac{k^A}{k^B} = \frac{k_\lambda^A(1+\alpha^A\lambda)}{k_\lambda^B(1+\alpha^B\lambda)}$	$\frac{k_\lambda^A}{k_\lambda^B}$
	experiment	calculated by equation (7)	calculated by equation (14)	experiment	calculated by equation (7)	calculated by equation (14)
0.65	1.93	71	1.93	1.25	1.19	1.25
1.20	1.70	103	1.71			
2.31	1.46	138	1.48	1.51	1.34	1.52
5.61	1.22	182	1.24	1.77	1.45	1.77
12.20	1.10	209	1.10	1.95	1.51	1.97
21.00	1.04	220	1.04	2.07	1.53	2.07
	$C_1 = 1.69,\ C_2 = 238,\ C_3 = 12.1$			$C_1 = 1.61,\ C_2 = 1.57,\ C_3 = 1.68$		
	$k_g^A/k_g^B = 0.95 \quad k_l^B/k_g^B\alpha^X = 0.44$			$k_l^A/k_l^B = 1.04 \quad k_g^A/k_g^B = 2.26$		
				$k_l^A/k_g^A\alpha^X = 0.19 \quad k_l^B/k_g^B\alpha^X = 0.42$		

Table 2. Relative gas-phase rate constants ($k_g^{RH}/k_g^{n\text{-}C_5H_{12}}$) for the oxidation of alkanes with the system ($NaNO_2$–H_2O_2)/acetate buffer solution (pH 4.27) and with $^•OH$ radicals at 25°C

Hydrocarbon	α	$NaNO_2$–H_2O_2 calculated		$^•OH$ [5, 33, 34]
		by equation (15)	by equation (20)	
1. Propane	29	0.32	0.30	0.33
2. *n*-Butane	37	0.65	0.62	0.66
3. *n*-Pentane	49	1.00	1.00	1.00
4. *n*-Hexane	65	1.33	1.48	1.58
5. *n*-Heptane	86	1.68	1.71	1.95
6. *n*-Octane	110	2.20	2.10	2.33
7. Isobutane	48	0.58	0.61	0.64
8. Cyclopentane	7.7	1.23	1.21	1.26
9. Cyclohexane	8.0	1.63	1.62	1.80
10. Cyclohexane-d_{12}	8.0	0.62	0.62	0.78

of these reactions, as is illustrated by the following data:

	HOONO	$^•OH$ [5]
$k_g^{cyclo\text{-}C_6H_{12}}/k_g^{cyclo\text{-}C_5H_{10}}$	1.32	1.42
$(KIE)_g$	2.65	2.50

Proceeding from similarity in the relative rate constants for the gas-phase reaction of alkanes with HOONO and for the gas-phase reaction of the same substrates with $^•OH$ radicals, we conclude that the nature of active species in the reactions studied is close. It is likely that peroxynitrous acid distributed between the phases during the reaction rapidly attains equilibrium and then interacts with hydrocarbons either as a radical pair $HO^• \cdots NO_2$ or as a free radical. In the case of alkanes, the abstraction of H atom takes place in the slow step of the reaction:

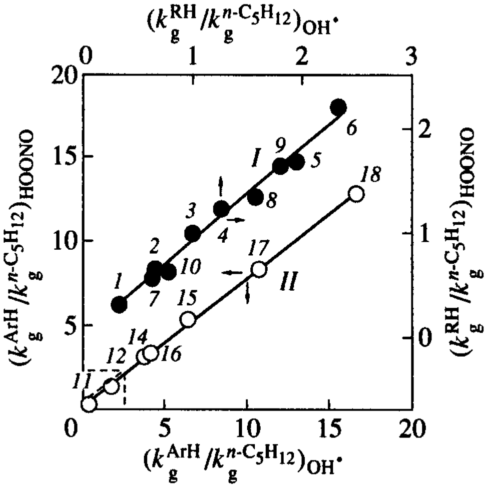


Fig. 2. Correlation between relative rate constants for the gas-phase oxidation of (I) alkanes and (II) alkylbenzenes with the system $NaNO_2–H_2O_2$ and with $^\bullet OH$ radicals. In the square on the lower left, the position of the alkane line in the line of arenes is shown by a dotted line. Numbering of points is the same as in Tables 2 and 3.

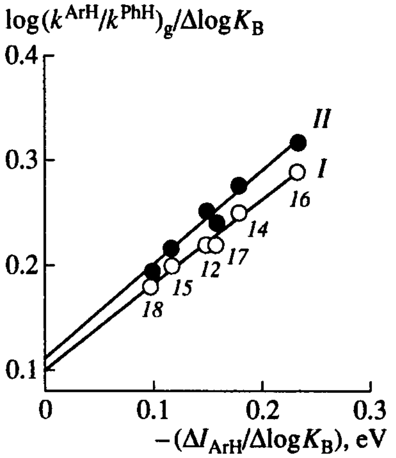


Fig. 3. Fit of equation (19) for the gas-phase oxidation of arenes with the system (*I*) $NaNO_2–H_2O_2$ and with (*II*) $^\bullet OH$ radicals. Conditions and numbering of points are the same as in Table 3. Here, $\Delta\log K_B$ and ΔI_{ArH} correspond to expressions $\log(K_B^{ArH}/K_B^{PhH})$ and $(\Delta I_{ArH} - \Delta I_{PhH})$ in equation (19).

$$RH + [^\bullet OH\cdots NO_2] \longrightarrow \{\dot{R}\cdots\dot{H}\cdots\dot{O}H\cdots NO_2\} \longrightarrow R^\bullet + H_2O + NO_2. \quad \text{(IV)}$$

Reactions of alkylbenzenes in the gas phase. As in the case of alkanes, for all arenes under study, the linear correlation exists between the relative rate constants for the gas-phase reactions with HOONO and $^\bullet OH$ radicals with the slope c equal to 0.8 (Fig. 2, line *II*). However, in the case of alkylbenzenes, stronger correlation is expressed by a curve whose slope changes from 0.9 for less active substrates (benzene, toluene) to 0.7 for more active substrates (pseudocumene, mesitylene). It is important that the points for alkanes ($c \sim 1$) fall on the initial portion of the line for arenes; that is, the same correlation (16) is valid for all hydrocarbons.

We obtained KIE = 1 for the pair toluene/toluene-d_8 (Table 3). Because KIEs observed in the reactions of alkanes were noticeable, it may be concluded that active species in the $H_2O_2–HNO_2$ system, similarly to $^\bullet OH$ radicals [37], attack arenes at aromatic rings.

$^\bullet OH$ radicals act as electrophiles in reactions with arenes [37]. According to [38], relative rate constants for aromatic electrophilic substitution reactions of a wide series of alkylbenzenes may be controlled by the basicity of arenes (K_B):

$$\log(k^{ArH}/k^{PhH}) = a\log(K_B^{ArH}/K_B^{PhH}), \quad (17)$$

or by their ionization potentials (I):

$$\log(k^{ArH}/k^{PhH}) = b(I_{ArH} - I_{PhH}), \quad (18)$$

or by both parameters simultaneously:

$$\log(k^{ArH}/k^{PhH}) = a'\log(K_B^{ArH}/K_B^{PhH}) + b'(I_{ArH} - I_{PhH}). \quad (19)$$

Equations (17)–(19) point to the occurrence of the process via the slow step of the formation of the σ-complex, the charge-transfer complex, or a transition state intermediate between the σ-complex and the charge-transfer complex [38]. For reagents OH^- and CF_3COOH [38], $HMnO_4$ [39], and MnO_3^+ [40], two-parameter relationship (19) is much better suited than relationships (17) and (18).

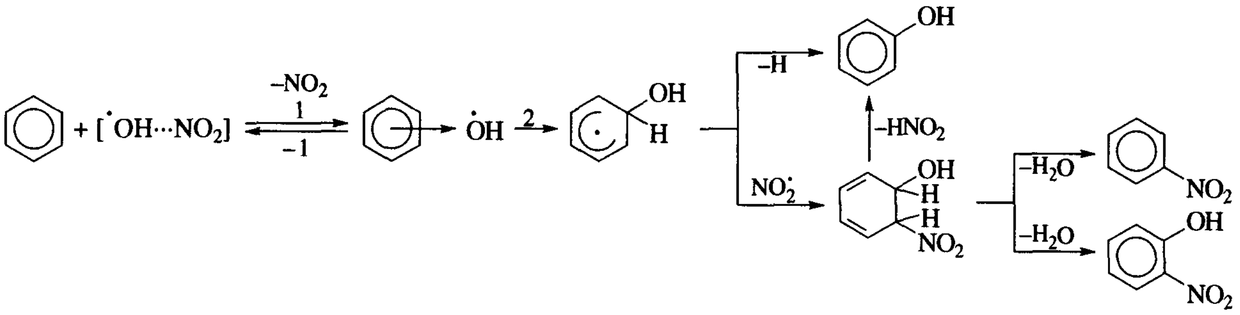
We found that relative gas-phase rate constants for the studied reactions of alkylbenzenes with peroxynitrous acid, as well as with $^\bullet OH$ radicals, poorly correlate with both the basicity (correlation coefficients r are 0.960 and 0.961, respectively) and the ionization potentials of arenes (r = 0.947 and 0.949), but they are well described by equation (19) (r = 0.992 and 0.990, respectively) (Fig. 3). Within the experimental error, the values of parameters $a' = 0.10 \pm 0.01$ and $-b' = 0.81 \pm 0.05$ for the reaction with HOONO are equal to the corresponding values for the reaction with $^\bullet OH$ radicals ($a' = 0.11 \pm 0.01$ and $-b' = 0.90 \pm 0.05$).

Proceeding from the closeness of the substrate selectivity in gas-phase reactions of methylbenzenes with peroxynitrous acid and with $^\bullet OH$ radicals and proceeding from the satisfiability of linear correlation (16) for all of the substrates under study, we conclude that a free $^\bullet OH$ radical or more likely a radical pair $OH^\bullet\cdots NO_2$ is the active species for both arenes and

Table 3. Relative rate constants for the oxidation of arenes in the system ($NaNO_2$–H_2O_2)/acetate buffer solution (pH 4.27) and with $^{\bullet}OH$ radicals in gas ($k_g^{ArH}/k_g^{n\text{-}C_5H_{12}}$) and solution ($k_l^{ArH}/k_l^{PhH}$) at 25°C

Arene	α	$NaNO_2$–H_2O_2			$^{\bullet}OH$ [35–37]	
		$\frac{k_g^{ArH}}{k_g^{n\text{-}C_5H_{12}}}$	$\frac{k_l^{ArH}}{k_l^{PhH}}$	$\frac{k_l^{ArH}}{k_g^{ArH}\alpha^X}$	$\frac{k_g^{ArH}}{k_g^{n\text{-}C_5H_{12}}}$	$\frac{k_l^{ArH}}{k_l^{PhH}}$
11. Benzene	0.23	0.33	1.00	1.20	0.32	1.0
12. Toluene	0.26	1.43	1.10	0.40	1.71	1.0
13. Toluene-d_8	0.26	1.43	1.10	0.40	–	–
14. *ortho*-Xylene	0.18	3.23	1.10	0.20	3.82	(1)
15. *meta*-Xylene	0.29	5.36	0.95	0.13	6.41	(1)
16. *para*-Xylene	0.26	3.40	1.30	0.25	4.09	(1)
17. Pseudocumene	0.21	8.40	0.92	0.07	10.70	(1)
18. Mesitylene	0.36	12.9	0.71	0.05	16.60	(1)

alkanes in the HNO_2–H_2O_2 system. The dependence of relative rate constants on both the basicity and ionization potentials of arenes suggests that the active species reacts with ArH by the mechanism of aromatic electrophilic substitution (V), where step 1 is rapid and equilibrium, and the transition state of step 2 has a structure which is intermediate between the charge-transfer complex and the σ-complex (cyclohexadienyl radical):



(V)

All products presented in scheme (V) are formed in the H_2O_2–HNO_2–ArH system [3].

Reactions of arenes in solution. All arenes studied are oxidized with peroxynitrous acid at almost the same rate (k_l^{ArH}/k_l^{PhH} = 1.0 ± 0.1, Table 3). According to [36, 37], all methylbenzenes (from benzene to hexamethylbenzene) react with an equal rate with $^{\bullet}OH$ radicals as well. Thus, the data obtained support the assumption that, in this case too, either an $^{\bullet}OH$ radical or an $HO^{\bullet}\cdots NO$ radical pair serves as a reacatant. The fact that no substrate selectivity was observed in the liquid-phase oxidation of arenes may be attributed to the high reactivity of the reagent due to which the reaction rate of step 1 is diffusion-controlled (Scheme (V)), as in the case of the reaction with $^{\bullet}OH$ radicals [37].

The contribution ratio of alkane reactions proceeding in the gas phase and in the solution. A limit of the cyclohexane concentration decrease measured by the syringe-reactor method [5] in the absence of the gas phase ($\lambda = 0$) at $[H_2O_2] = [NaNO_2] = 4.1 \times 10^{-2}$ mol/l was at most 14% with respect to the initial substrate. As the gas phase appeared in the reactor ($\lambda \neq 0$), the consumption of cyclohexane at the same concentrations of reagents sharply increased, which is illustrated by the following data:

$\lambda = V_g/V_l$	0	0.65	2.31	5.61	12.2	21.0
Consumption of cyclo-C_6H_{12}, %	14	67	70	76	77	76

According to equation (13), in the presence of the gas phase, the rate of RH consumption drastically increased. Because of the high values of α in aqueous solutions (8–110, Table 2), at $\lambda > 1$, alkanes occur and react with HOONO predominantly in the gas phase. Even at the lowest experimental values of $\lambda (\approx 0.6)$, the liquid-phase reaction contributes from 5 to 15% to the overall rate of the substrate consumption for different alkanes; therefore, the overall reaction rate no longer depends on the rate of the liquid-phase reaction. Thus, for all pairs of substrates studied, where A is alkane and B is arene, one can neglect the term k_g^A/k_g^B involving the liquid-phase rate constant $(1/\lambda)C_3$ in the calculation of k_l^A values by equation (15). This leads to the linear dependence

$$L = C_2 - C_1(L/\lambda), \qquad (20)$$

which is accurate to $r = 0.997$–0.999. The values of relative gas-phase rate constants obtained by equations (15) and (20) virtually coincide (Table 2).

Thus, several arguments favor the fact that hydrocarbons react with peroxynitrous acid simultaneously in two phases:

(1) The kinetic distribution method that implies the occurrence of the reaction only in solution does not work in this case.

(2) The extended model of the kinetic distribution method accounting for the simultaneous occurrence of reactions in the solution and in the gas phase allows the quantitative description of the rate constants as functions of λ.

(3) Reactions of hydrocarbons with HOONO are slow in solutions, but their rates significantly increase with the appearance of the gas phase.

(4) Substrate selectivities, including KIEs, of the gas-phase reactions of alkanes and arenes with both HOONO (calculations were performed by the extended model of the kinetic distribution method) and $^{\bullet}$O H radicals were equal.

The low sensitivity of the used method with regard to the rates of the liquid-phase oxidation of alkanes fails to obtain data on this group of reactions. A purely liquid-phase reaction calls for further investigation; it is now clear that it can be studied only when the gas-phase route of the reaction is totally excluded.

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