

Kinetics and Mechanism of the Oxidation of Alkanes and Alkenes with Peroxynitrous Acid in Aqueous Solution–Gas Phase Systems

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Abstract—The reactions of alkane and alkene oxidation with peroxynitrous acid (HOONO) in aqueous solution–gas phase systems were studied using a modified kinetic distribution method. The rate constants of oxidation of hydrocarbons (RH) were found to be unusual bell-shaped functions of the volume ratio between liquid and gas phases in a reactor. This result, as well as the previously found proportionality of the rate constants of the gas-phase RH + HOONO and RH + OH[·] reactions for alkanes, alkenes, and alkylbenzenes, was quantitatively interpreted assuming the rapid equilibrium distribution of HOONO and RH between a gas and a solution, the formation of OH[·] radicals in the two phases, and the interaction of these radicals with RH. The rate constant of peroxynitrous acid decomposition in the gas phase and the distribution coefficient of this acid between the gas phase and solution $\alpha = (0.4–2) \times 10^{-6}$ were estimated. The capacity of HOONO for partition between different phases and for generation of OH[·] radicals in either of these phases can be of paramount importance for understanding the mechanism of lipid membrane oxidation initiated by peroxynitrous acid.

INTRODUCTION

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

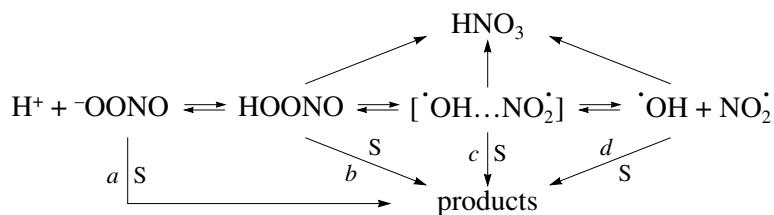


The stable ONOO[−] peroxynitrite anion is formed *in vivo* in the rapid recombination ($k = (4–19) \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$) of nitrogen monoxide and the O₂^{·−} superoxide anion [2–4].¹ Under physiological conditions, it is protonated to peroxynitrous acid ($\text{p}K_a = 6.8$), which rapidly ($\tau_{1/2} \sim 1 \text{ s}$) isomerizes to nitrate [5–7]. The isomerization of peroxynitrous acid is accompanied by the homolysis of the HO–ONO bond with the formation of

OH[·] and NO₂[·] free radicals, whose yields were estimated at 0–40% [8–12]. Peroxynitrite decomposition is catalyzed by carbon dioxide [13–15] because of the formation of highly reactive nitrosyl peroxy carbonate (ONOOCO₂[−]).

Being strong one-electron and two-electron oxidizing agents ($E^0 = 1.4$ [5] and 1.67 V [16], respectively), peroxynitrous acid and peroxynitrite oxidize substrates (S)—strong reducing agents such as sulfides [17], sulfhydryls [18], complexes of metals in lower oxidation states [19], I[−] ions [19], Br[−] ions [20], and biomolecules [7]. The oxidation occurs by a direct attack (Scheme 1, reaction paths *a* and *b*). The reaction path including the intermediate formation of active radical species of unknown nature is considered to be a more general mechanism [7–12, 17, 19]. A hydroxyl radical-like intermediate was named as a direct reagent [5, 21]. There is experimental evidence [8, 9] that the free hydroxyl radical serves as this reagent (reaction path *d*), whereas, according to quantum-chemical calculations [22], the [OH[·]...NO₂[·]] radical pair plays this role (reaction path *c*).

¹ Interest in the chemistry of peroxynitrous acid has quickened because it was found that this compound plays a most important role in physiological processes. In the past 12 years, more than 700 publications on the chemistry of peroxynitrite have been released. In 1997, 1999, and 2001, the First, Second, and Third International Conferences on the Chemistry and Biology of Peroxynitrite were held in Geneva, Cyprus, and Philadelphia, respectively.



Scheme 1.

Previously, only reactions of peroxynitrous acid with strong reducing agents were studied. Data on the oxidation of hydrocarbons are scanty [20, 22–25]. Only two experimental studies, devoted to the oxidation products of cyclohexane and cyclohexene [24], as well as arenes [20] in the H_2O_2 – HNO_2 system, were known. We pioneered in systematically studying the kinetics of peroxynitrous acid reactions with hydrocarbons as reducing agents. We found [26–29] that alkanes, alkenes, and alkylbenzenes are oxidized by aqueous peroxynitrous acid solutions at pH 7.0–7.5, as well as by the H_2O_2 – HNO_2 model system (pH 4.3), which generates HOONO *in situ*. Cyclohexanone, cyclohexanol, dicyclohexyl, and traces of nitrocyclohexane (<1%) are simultaneously formed in the case of cyclohexane [26, 28]. Under these conditions, alkylbenzenes give a mixture of phenols, nitrophenols, and nitroarenes [20]. The oxidation of cyclohexane with peroxynitrous acid in a phosphate buffer solution (pH ≈ 7) and the model system results in a wide variety of products. Cyclopentanecarboxyaldehyde, cyclohexyl epoxide, cyclohexanone, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 2-hydroxy-cyclohexanone, cyclohexene-1-nitrocarboxylic acid, and 2-cyclopentene-1-carboxylic acid were identified by chromatography–mass spectrometry [29].

The reaction kinetics of alkanes, alkenes, and alkylbenzenes with various oxidizing agents and radicals in aqueous solutions has been much studied [30–33]. Therefore, hydrocarbons are convenient substrates for the identification of the nature of active species. However, conventional kinetic methods cannot be used because of the extremely low water solubility and high volatility of hydrocarbons. This problem can be solved by the kinetic distribution method (KDM) [30, 31]. We applied this method to find the relative rate constants of oxidation of a wide range of alkanes, alkenes, and alkylbenzenes in H_2O_2 – HNO_2 /acetate buffer solutions at pH 4.3. The results were unexpected: we found that the rate constants thus found depended on the volume ratio between liquid and gas phases in a reactor [26–29]. This fact, which has no analogies with other hydrocarbon oxidation reactions [30, 31], was quantitatively explained [26–29] based on the assumption that the oxidation of hydrocarbons by the HOONO acid simultaneously occurs in both aqueous and gas phases. Based on this idea, we developed an extended KDM model [26, 27]. This model implies an equilibrium distribution of the substrate and the reagent between a gas and a solution and the simultaneous occurrence of the

reaction in two phases. We calculated the relative rate constants (substrate selectivities) of hydrocarbon reactions. We found a surprising similarity between the substrate selectivities of the $\text{RH} + \text{HOONO}$ and $\text{RH} + \text{OH}^\cdot$ reactions (published data [32, 33]) in solution and in a gas. However, the individual (nonrelative) rate constants were not determined previously [26–29] because of the rapid degradation of peroxynitrous acid at pH ≤ 7 .

The aim of this work was to obtain kinetic data on the oxidation of hydrocarbons and the decomposition of peroxynitrous acid in two phases and to determine individual rate constants and the distribution coefficient of peroxynitrous acid between a gas and a solution. For this purpose, it was necessary to develop approaches to the determination of individual constants with consideration for the distribution of reactants between phases and a rapid change in the reagent concentration in the course of the reaction. The problem was significantly simplified by choosing special reaction conditions and

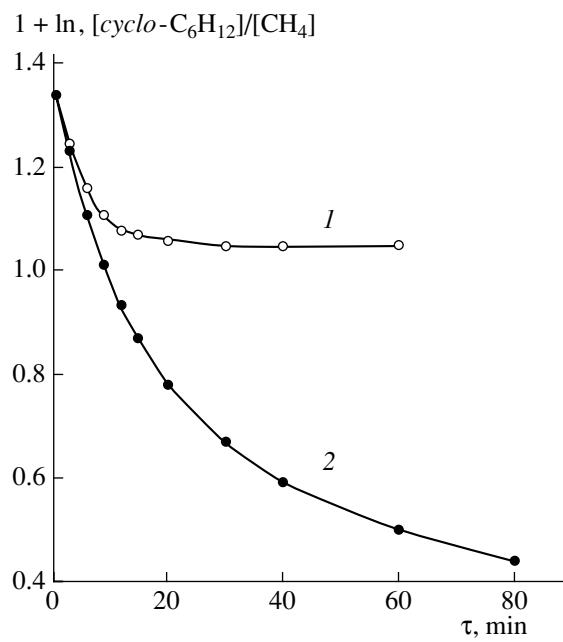


Fig. 1. Kinetics of cyclohexane decay at (1) $[\text{H}_2\text{O}_2] = 0.1 \text{ mol/l}$ and $[\text{NaNO}_2] = 0.01 \text{ mol/l}$ or (2) $[\text{H}_2\text{O}_2] = [\text{NaNO}_2] = 0.042 \text{ mol/l}$; pH 4.27; 25°C; and $\lambda = 2.31$. Lines correspond to data calculated from Eqs. (10) and (14), respectively, and points correspond to experimental data.

by using normal alkanes, cycloalkanes, and alkenes as substrates (according to previously published data [27–29], they are oxidized primarily in the gas phase).

EXPERIMENTAL

Reagents. All chemicals (reagent grade) were used without additional purification.

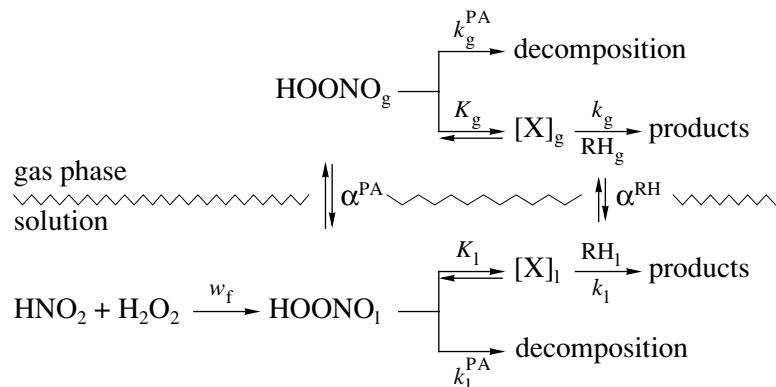
Kinetic measurements. The reactions of hydrocarbons with peroxy nitrous acid in an acetate buffer solution (pH 4.27; $[NaOAc] = 0.1$ mol/l; $[HOAc] = 0.25$ mol/l) at $25^\circ C$ were studied by measuring the consumption of a substrate from the gas phase using the KDM. The working solutions were prepared by reaction (I) immediately before experiments. A mixture of hydrocarbon vapor and methane (internal standard), which is stable under reaction conditions, was injected into the gas space of a thermostated shaken reactor ($V = 66.24$ cm³) containing sodium nitrite (0.04–0.1 mol/l) in an acetate buffer solution. After the establishment of an equilibrium distribution of RH between the gas phase and the solution, the required amount of a 30% H_2O_2 solution was injected into the reactor. In all cases, the concentrations of H_2O_2 and $NaNO_2$ were much higher than the concentration of the hydrocarbon. The gas phase was sampled (a sample volume of 0.1 cm³) at regular intervals through a Teflon septum in the reactor stopper using a glass syringe and analyzed by gas–liq-

uid chromatography (an LKhM-80 chromatograph with a flame-ionization detector; SE-30 stationary phase on Chromaton N-AW). A high reactor shaking frequency (500 min⁻¹) ruled out the diffusion control of the reaction [34]. The coefficients of substrate distribution between the gas and the solution $\alpha^{RH} = [RH]_g/[RH]_l$, which are required for the calculation of rate constants, were determined in accordance with a published procedure [30]. The sum of squared deviations of experimental data from calculated data was minimized using the Origin 5.0 program.

RESULTS AND DISCUSSION

Kinetics. The oxidation of hydrocarbons in H_2O_2 – $NaNO_2$ /acetate buffer solutions does not obey first-order kinetics with respect to the substrate even under conditions of a great excess of reactants (Fig. 1). This suggests a change in the concentration of the direct reagent X in the course of the reaction due to the rapid decomposition of peroxy nitrous acid. We found that the degrees of conversion of all of the test substrates and the shapes of the decay curves remained unchanged on going from air to an atmosphere of argon.

Kinetic model. Because the oxidation of hydrocarbons with peroxy nitrous acid simultaneously occurs in solution and in the gas phase of a reactor [26–29], let us consider the following model.



Scheme 2.

This model includes the formation of peroxy nitrous acid in solution at the rate $w_f = d[PA]/d\tau$, the equilibrium distribution of a hydrocarbon (α^{RH}) and peroxy nitrous acid ($\alpha^{PA} = [PA]_g/[PA]_l$) between gas and liquid phases, the decomposition of $HOONO$ (k_g^{PA} , k_1^{PA}), the preactivation of the reagent (K_g , K_1) with the formation of active species X (the $[OH^\cdot \dots NO_2^\cdot]$ radical pair or the OH^\cdot radical [27–29]), and the interaction of this species with the substrate RH (k_g , k_1) in both of the phases. The $[OH^\cdot \dots NO_2^\cdot]$ radical pair or the OH^\cdot free radical chosen as a direct reagent has no effect on the

results of calculations in accordance with Scheme 2. The nature of the active species is discussed below.

Under the test conditions (pH 4.27; $25^\circ C$), the rate of formation of peroxy nitrous acid is much lower than the rate of its subsequent transformations [5–7, 16, 35]. From a steady-state condition, we obtain

$$\begin{aligned}
 w_f V_l &= k_g^{PA} [PA]_g V_g + k_1^{PA} [PA]_l V_l + k_g [RH]_g [X]_g V_g \\
 &+ k_1 [RH]_l [X]_l V_l = [PA]_l V_l \{ (k_1^{PA} + k_g^{PA} \alpha^{PA} \lambda) \\
 &+ [RH]_l (k_1^{RH} + k_g^{RH} \alpha^{RH} \alpha^{PA} \lambda) \}, \quad (1)
 \end{aligned}$$

where $k_g^{\text{RH}} = K_g k_g$ and $k_l^{\text{RH}} = K_l k_l$ are the apparent rate constants of the reaction of peroxy nitrous acid with a hydrocarbon in the gas and liquid phases, respectively; V_g and V_l are the volumes of the liquid and gas phases, respectively, in the reactor; and $\lambda = V_g/V_l$. Let us introduce the following designations: n_g^{PA} and $[\text{PA}]_g = n_g^{\text{PA}}/V_g$ are the amount and concentration of peroxy nitrous acid in the gas phase, respectively, and n_l^{PA} and $[\text{PA}]_l$ are the analogous values for the solution. Because the rate of decomposition of peroxy nitrous acid is much higher than the rate of its reaction with a substrate even in the case of strong reducing agents [7, 17–20], it is believed that $k_l^{\text{PA}} + k_g^{\text{PA}} \alpha^{\text{PA}} \lambda \gg [\text{RH}]_l (k_l^{\text{RH}} + k_g^{\text{RH}} \alpha^{\text{RH}} \alpha^{\text{PA}} \lambda)$. In this case, Eq. (1) takes the form

$$w_f V_l = [\text{PA}]_l V_l (k_l^{\text{PA}} + k_g^{\text{PA}} \alpha^{\text{PA}} \lambda). \quad (2)$$

The total amount of peroxy nitrous acid is

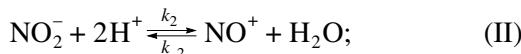
$$\begin{aligned} N^{\text{PA}} &= n_g^{\text{PA}} + n_l^{\text{PA}} \\ &= [\text{PA}]_g V_g + [\text{PA}]_l V_l = [\text{PA}]_l V_l (1 + \alpha^{\text{PA}} \lambda). \end{aligned} \quad (3)$$

Substituting Eq. (3) into Eq. (2), we find the current reagent concentration

$$[\text{PA}] = [\text{PA}]_l (1 + \alpha^{\text{PA}} \lambda) = \frac{w_f (1 + \alpha^{\text{PA}} \lambda)}{(k_l^{\text{PA}} + k_g^{\text{PA}} \alpha^{\text{PA}} \lambda)}, \quad (4)$$

where $[\text{PA}] = (N^{\text{PA}}/V_l)$ is the reagent concentration in solution without consideration for the reagent distribution between phases.

According to Anbar and Taube [35], peroxy nitrous acid is formed in acidic media by the following mechanism:



Therefore, we can find the value of w_f .

The calculation of Scheme 2 is simplified at $[\text{H}^+] = \text{const}$ (buffer solutions) in the following two cases: at $[\text{H}_2\text{O}_2]_0 \gg [\text{NO}_2^-]_0 \gg [\text{RH}]$ (system I) and at $[\text{H}_2\text{O}_2]_0 = [\text{NO}_2^-]_0 \gg [\text{RH}]$ (system II). Let us consider these systems.

System I. In this case, the concentration of peroxy nitrous acid depends only on the current concentration $[\text{NO}_2^-]$, which is related to the initial concentration $[\text{NO}_2^-]_0$ by the equation

$$[\text{NO}_2^-] = [\text{NO}_2^-]_0 \exp(-k_f^{\text{I}} \tau), \quad (5)$$

where k_f^{I} is the apparent first-order rate constant of peroxy nitrous acid formation. According to Anbar and Taube [35], this rate constant is equal to

$$\begin{aligned} k_f^{\text{I}} &= w_f / [\text{NO}_2^-] \\ &= k_2 k_3 [\text{H}^+]^2 [\text{H}_2\text{O}_2] / (k_{-2} [\text{H}_2\text{O}] + k_3 [\text{H}_2\text{O}_2]). \end{aligned} \quad (6)$$

Substituting $k_f^{\text{I}} = w_f / [\text{NO}_2^-]$ and expression (5) for $[\text{NO}_2^-]$ into Eq. (4), we obtain

$$[\text{PA}] = \frac{k_f^{\text{I}}}{k_{\lambda}^{\text{PA}}} [\text{NO}_2^-]_0 \exp(-k_f^{\text{I}} \tau), \quad (7)$$

where

$$k_{\lambda}^{\text{PA}} = (k_l^{\text{PA}} + k_g^{\text{PA}} \alpha^{\text{PA}} \lambda) / (1 + \alpha^{\text{PA}} \lambda) \quad (8)$$

is the apparent rate constant of peroxy nitrous acid decomposition at a given value of λ . According to [26, 27], the kinetics of substrate decay on the simultaneous occurrence of the reaction in the gas phase and in the solution obeys the equation

$$-d[\text{RH}]_g/d\tau = k_{\lambda}^{\text{RH}} [\text{RH}]_g [\text{PA}]. \quad (9)$$

Substituting Eq. (7) into Eq. (9) and integrating the latter, we obtain the rate equation

$$\ln \frac{[\text{RH}]_g^0}{[\text{RH}]_g} = \frac{k_{\lambda}^{\text{RH}}}{k_{\lambda}^{\text{PA}}} [\text{NO}_2^-]_0 [1 - \exp(-k_f^{\text{I}} \tau)], \quad (10)$$

where $[\text{RH}]_g^0$ and $[\text{RH}]_g$ are the initial and current concentrations of RH in the gas phase, respectively. According to [26, 27], the apparent rate constant of substrate decay (k_{λ}^{RH}) at a given λ is

$$k_{\lambda}^{\text{RH}} = (k_l^{\text{RH}} + k_g^{\text{RH}} \alpha^{\text{RH}} \alpha^{\text{PA}} \lambda) / \{(1 + \alpha^{\text{RH}} \lambda) (1 + \alpha^{\text{PA}} \lambda)\}. \quad (11)$$

The applicability of the kinetic model to the reactions of alkanes in system I at pH 4.27 and a constant value of λ was tested using cyclohexane. Equation (10) is valid throughout the substrate decay region (Fig. 1). This fact allowed us to calculate k_f^{I} and $k_{\lambda}^{\text{RH}}/k_{\lambda}^{\text{PA}}$. As expected, the values of $k_{\lambda}^{\text{RH}}/k_{\lambda}^{\text{PA}}$ are independent of the initial concentrations of H_2O_2 and NaNO_2 and the value of k_f^{I} at a given pH depends only on $[\text{H}_2\text{O}_2]$ (Table 1). In view of Eq. (6), the following linear relationship (Fig. 2) is true:

$$\frac{1}{k_f^{\text{I}}} = \frac{1}{k_2 [\text{H}^+]^2} + \frac{k_{-2} [\text{H}_2\text{O}]}{k_2 k_3 [\text{H}^+]^2 [\text{H}_2\text{O}_2]}. \quad (12)$$

The values of k_2 and $k_3/k_{-2}[\text{H}_2\text{O}]$ thus calculated are close to the values estimated by Anbar and Taube [35] using a fundamentally different procedure, from kinet-

Table 1. Effect of the concentrations of H_2O_2 and NO_2^- on the parameters of Eq. (10) in the oxidation of cyclohexane in system I

$[\text{H}_2\text{O}_2]_0$, mol/l	$[\text{NO}_2^-]_0$, mol/l	$k_f^I \times 10^3$, s ⁻¹	$k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$, l/mol
0.1	0.014	3.1	30
0.1	0.010	3.2	35
0.1	0.007	3.3	38
0.1	0.005	3.0	36
0.15	0.01	4.0	34
0.2	0.01	5.2	37
0.3	0.01	6.4	33

Note: pH 4.27; 25°C; $\lambda = 2.31$.

ics of peroxy nitrous acid formation, as illustrated below.

Parameter	This work	Earlier data [35]
$k_2 \times 10^{-6}$, l ² mol ⁻² s ⁻¹	3.4 ± 0.6	5.8
$k_3/k_{-2}[\text{H}_2\text{O}]$, l/mol	3.6 ± 1.0	2.4

At $[\text{NO}_2^-]_0 \ll [\text{H}_2\text{O}_2]_0 = \text{const}$, variation of the concentration of NO_2^- has no effect on k_f^I and $k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$ (Table 1). This suggests the first order of cyclohexane reaction in the $\text{H}_2\text{O}_2\text{-NaNO}_2$ /acetate buffer system

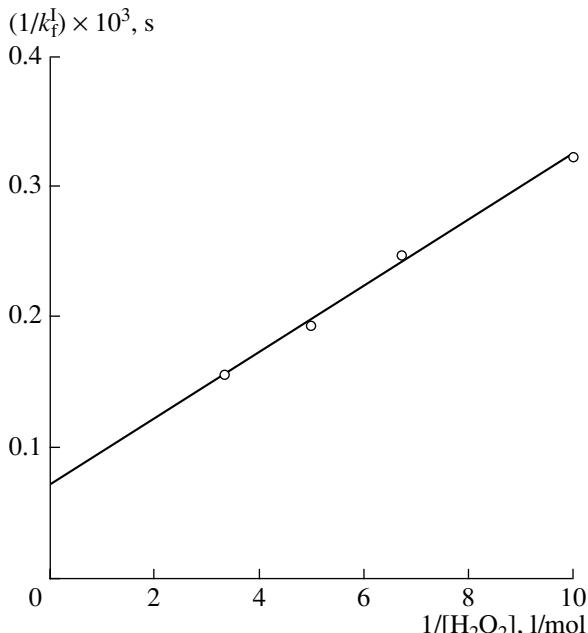


Fig. 2. The fulfillment of Eq. (12) for cyclohexane oxidation in the $\text{H}_2\text{O}_2\text{-NaNO}_2$ /acetate buffer system (pH 4.27; 25°C; $\lambda = 2.31$).

with respect to the nitrite anion and, consequently, the first order of reaction with respect to peroxy nitrous acid, in accordance with Scheme 2.

System II. In this case, the quasi-steady-state concentration of peroxy nitrous acid is related to the initial reactant concentrations $[\text{H}_2\text{O}_2]_0 = [\text{NO}_2^-]_0$ by the equation

$$[\text{PA}] = \frac{k_f^{\text{II}} [\text{NO}_2^-]_0^2}{k_\lambda^{\text{PA}} (1 + [\text{NO}_2^-]_0 k_f^{\text{II}} \tau)^2} \quad (13)$$

and the consumption of the substrate from the gas phase follows the equation

$$\ln \frac{[\text{RH}]_g^0}{[\text{RH}]_g} = \frac{k_f^{\text{II}} k_\lambda^{\text{RH}} [\text{NO}_2^-]_0^2 \tau}{k_\lambda^{\text{PA}} (1 + [\text{NO}_2^-]_0 k_f^{\text{II}} \tau)}. \quad (14)$$

Here, k_f^{II} is the apparent second-order rate constant of peroxy nitrous acid formation at a given pH.

Because the initial nitrite concentration in system I is low, the consumption of hydrocarbons in the course of the reaction is no higher than 30%; therefore, k_f^I and $k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$ cannot be reliably determined. In system II, hydrocarbon conversion is as high as 60–80%, which considerably improves the accuracy of kinetic measurements. Equation (14) adequately describes the apparent kinetics of decay of hydrocarbons (*n*-hexane, cyclopentane, cyclohexane, and propene) in system II (Fig. 1) and provides an opportunity to determine the values of k_f^{II} and $k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$. As expected, the values of k_f^{II} are independent of λ and the hydrocarbon chosen (Table 2) because the formation of HOONO occurs only in solution without the participation of RH. The average value of $k_f = (2.5 \pm 0.5) \times 10^{-2}$ l mol⁻¹ s⁻¹ is close to 3.3×10^{-2} l mol⁻¹ s⁻¹, which was calculated from published data [35] for pH 4.27 and 25°C.

Unusual extremal dependence of rate constants on λ . For all of the known reactions of hydrocarbon oxidation in aqueous solutions [30], the apparent rate constants k_λ^{RH} decrease with increasing λ in accordance with the equation

$$\begin{aligned} -d[\text{RH}]/d\tau &= k_\lambda^{\text{RH}} [\text{RH}]_g [\text{X}] \\ &= k_1 [\text{RH}]_1 [\text{X}] / (1 + \alpha^{\text{RH}} \lambda). \end{aligned} \quad (15)$$

However, in the case of peroxy nitrous acid, we found that the $k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$ – λ plot is an unusual bell-shaped curve (Fig. 3). This can be explained only in the framework of the extended KDM model [26, 27] (Scheme 2).

Table 2. Dependence of the parameters of Eq. (14) on the values of λ in system **II**

λ	<i>n</i> -Hexane ($\alpha^{RH} = 65$)		Cyclopentane ($\alpha^{RH} = 7.7$)		Cyclohexane ($\alpha^{RH} = 8.0$)		Propene ($\alpha^{RH} = 11$)	
	$k_\lambda^{RH}/k_\lambda^{PA}$, l/mol	$k_f^{II} \times 10^2$, 1 mol ⁻¹ s ⁻¹	$k_\lambda^{RH}/k_\lambda^{PA}$, l/mol	$k_f^{II} \times 10^2$, 1 mol ⁻¹ s ⁻¹	$k_\lambda^{RH}/k_\lambda^{PA}$, l/mol	$k_f^{II} \times 10^2$, 1 mol ⁻¹ s ⁻¹	$k_\lambda^{RH}/k_\lambda^{PA}$, l/mol	$k_f^{II} \times 10^2$, 1 mol ⁻¹ s ⁻¹
0.32	24.5	2.3	—	—	—	—	—	—
0.66	25.0	2.5	18.0	2.3	26.0	2.4	98.6	2.6
1.20	24.8	2.4	21.0	2.5	27.4	2.4	108	2.3
2.31	23.6	2.6	20.8	2.2	28.0	2.6	107	2.8
5.61	21.0	2.5	18.2	2.4	26.0	2.5	91.9	2.7
8.46	—	—	16.5	2.4	24.0	2.8	81.7	2.5
12.2	17.6	2.6	14.8	2.0	21.0	2.6	72.5	2.6
21.0	15.0	2.4	—	—	—	—	—	—
	$(k_f^{II})_{av} = (2.5 \pm 0.1) \times 10^{-2}$ 1 mol ⁻¹ s ⁻¹ ,	$(k_f^{II})_{av} = (2.3 \pm 0.1) \times 10^{-2}$ 1 mol ⁻¹ s ⁻¹ ,	$(k_f^{II})_{av} = (2.6 \pm 0.1) \times 10^{-2}$ 1 mol ⁻¹ s ⁻¹ ,	$(k_f^{II})_{av} = (2.6 \pm 0.1) \times 10^{-2}$ 1 mol ⁻¹ s ⁻¹ ,	$(k_g^{PA}/k_g^{RH}) = (1.4 \pm 0.2) \times 10^{-3}$ mol/l,	$(k_g^{PA}/k_g^{RH}) = (1.7 \pm 0.2) \times 10^{-3}$ mol/l,	$(k_g^{PA}/k_g^{RH}) = (1.2 \pm 0.2) \times 10^{-3}$ mol/l,	$(k_g^{PA}/k_g^{RH}) = (3.3 \pm 0.5) \times 10^{-4}$ mol/l,
	$(k_1^{PA}/k_g^{PA} \alpha^{PA}) = 27 \pm 4$	$(k_1^{PA}/k_g^{PA} \alpha^{PA}) = 27 \pm 3$	$(k_1^{PA}/k_g^{PA} \alpha^{PA}) = 26 \pm 2$	$(k_1^{PA}/k_g^{PA} \alpha^{PA}) = 26 \pm 5$				

Note: pH 4.27; 25°C; $[H_2O_2]_0 = [NO_2^-]_0 = 0.042$ mol/l.

According to Eqs. (8) and (11), the $k_\lambda^{RH}/k_\lambda^{PA}$ ratio as a function of λ ,

$$\frac{k_\lambda^{RH}}{k_\lambda^{PA}} = \frac{(k_g^{RH} \alpha^{RH} \alpha^{PA} \lambda + k_1^{RH})}{(k_g^{PA} \alpha^{PA} \lambda + k_1^{PA})(1 + \alpha^{RH} \lambda)}, \quad (16)$$

includes terms with λ in the numerator and with λ and λ^2 in the denominator. At certain values of k_1^{RH} , k_g^{RH} , k_1^{PA} , k_g^{PA} , α^{RH} , and α^{PA} , this results in $k_\lambda^{RH}/k_\lambda^{PA}$ being an extremal function of λ . Previously [27–29], we found that alkanes and alkenes mainly occur and interact with peroxy nitrous acid in the gas phase because of a low solubility (high values of α^{RH}). Even at the lowest experimental values of $\lambda = 0.32$, the contribution of a liquid-phase reaction path to the overall rate of substrate decay was 5–15% for these hydrocarbons. Consequently, $k_1^{RH} \ll k_g^{RH} \alpha^{RH} \alpha^{PA} \lambda$. On this condition, Eq. (16) can be represented in the linear form

$$\frac{k_\lambda^{PA}}{k_\lambda^{RH}(1 + \alpha^{RH} \lambda)} = \frac{k_g^{PA}}{k_g^{RH} \alpha^{RH}} + \frac{k_1^{PA}}{k_g^{RH} \alpha^{RH} \alpha^{PA} \lambda} \quad (17)$$

This relationship adequately describes the experimental data for *n*-hexane, cyclopentane, cyclohexane,

and propene over the entire range of λ (Fig. 4). Note that, as expected, the values of $k_1^{PA}/k_g^{PA} \alpha^{PA}$ derived from the slope and intercept of function (17) are equal for various hydrocarbons (Table 2). Moreover, the ratios between the rate constants of gas-phase oxidation of *n*-hexane, cyclopentane, cyclohexane, and propene k_g^A/k_g^B are consistent with the results of competitive measurements [27–29], as illustrated by the data given below.

Parameter	<i>n</i> -Hexane (A) cyclopentane (B)	Cyclohexane (A) cyclopentane (B)	Propene (A) cyclopentane (B)
k_g^A/k_g^B from Eq. (17)	1.2 ± 0.3	1.4 ± 0.4	5.1 ± 1.5
k_g^A/k_g^B from competitive measure- ments	1.1	1.3	5.0

OH[·] radicals as a direct reagent: arguments and consequences. Various substrates can interact with HOONO via the four reaction paths shown in Scheme 1. Reaction paths *a* and *b*, which are of first order with respect to the substrate and peroxy nitrite, were found for sulfides [17], sulphydryls [18], nickel(II) complexes of 1,4,8,11-tetraazocyclotetradecane [18], Br[−] anions [20], and I[−] anions [19], as well as for the nucleophilic

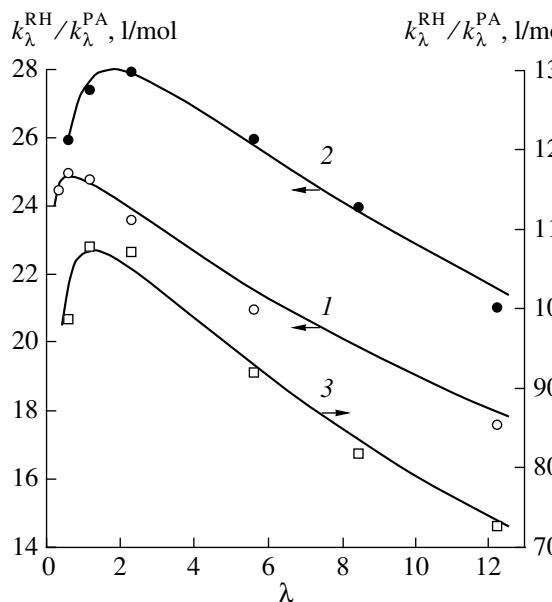


Fig. 3. $k_\lambda^{\text{RH}}/k_\lambda^{\text{PA}}$ versus λ for the oxidation of (1) cyclohexane, (2) *n*-hexane, and (3) propene in the $\text{H}_2\text{O}_2\text{--NaNO}_2$ /acetate buffer system (pH 4.27; 25°C). The lines represent data calculated from Eq. (16) for $k_g^{\text{PA}}/k_g^{\text{RH}}$ and $k_l^{\text{PA}}/k_g^{\text{PA}} \alpha^{\text{PA}}$ values from Table 2.

addition of OONO^\cdot to CO_2 with the formation of nitrosyl peroxy carbonate (ONOOCO_2^\cdot) [13–15].

Paths *c* and *d* were found for reactions with $\text{Fe}(\text{CN})_6^{4-}$ [19] and typical traps of free radicals: dimethyl sulfoxide [8, 21] and 2,2'-azinobis(3-ethylbenzothiazole-6-sulfonate) [8]. Reactions of this type are first-order with respect to peroxy nitrous acid and zero-order with respect to the substrate. In this case, it is believed that, in addition to the free OH^\cdot radical [8, 9] and the $[\text{OH}^\cdot \dots \text{NO}_2^\cdot]$ radical pair [22], the excited *trans*-HOONO species, which is close to the radical pair because the O–O bond is weak [5, 19], can also be an active species. The oxidation of methionine, 2-keto-4-thiomethylbutanoic acid, and the ascorbate anion occurs via reaction path *b* at a high substrate concentration, whereas it occurs via paths *b* and *d* at a low substrate concentration [36, 37].

As noted above, data on the kinetics and selectivity of hydrocarbon reactions with HOONO were unavailable before our publications [26–29]. According to quantum-chemical calculations, the oxidation of alkanes via reaction path *b* is improbable [23], while the oxidation of alkenes occurs with the participation of the *cis* form of HOONO [25].

We found [26–29] a surprising similarity between the substrate selectivities of the oxidation of a wide

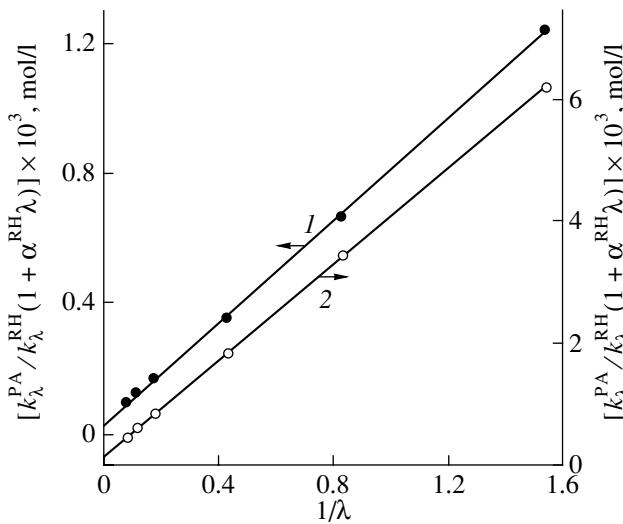


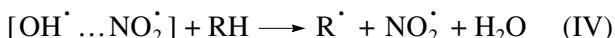
Fig. 4. The fulfillment of relationship (17) for (1) propene and (2) cyclohexane oxidation at pH 4.27 and 25°C.

range of hydrocarbons with peroxy nitrous acid and OH^\cdot radicals. Figure 5 summarizes the results of these studies. Previously, we interpreted the general correlation

$$\Delta \log k_{g(\text{HOONO})} = (0.98 \pm 0.01) \Delta \log k_{g(\text{OH}^\cdot)} \quad (18)$$

for gas-phase oxidation in the entire range of substrates (alkanes, alkenes, and alkylbenzenes) as evidence for the fact that either the free hydroxyl radical or the $[\text{OH}^\cdot \dots \text{NO}_2^\cdot]$ radical pair is a common active species in the reactions of hydrocarbons with peroxy nitrous acid.

However, summarizing the results of this and other works, we obtained arguments that hydroxyl radicals ($\text{X} = \text{OH}^\cdot$ in Scheme 2) serve as a direct reagent in the gas and liquid phases, whereas the radical pair does not play a detectable role in the test reactions. The main argument is the following: According to Houk *et al.* [22], the $[\text{OH}^\cdot \dots \text{NO}_2^\cdot]$ radical pair is more stable than the free radicals $\text{OH}^\cdot + \text{NO}_2^\cdot$ by only 2 kcal/mol because of hydrogen bond formation. Consequently, the rate constant of the reaction

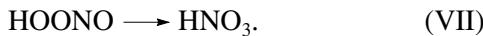
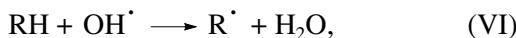
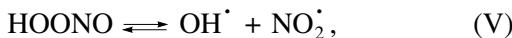


cannot be higher than that of the reaction of RH with free hydroxyl radicals ($10^9\text{--}10^{10} \text{ mol}^{-1} \text{ s}^{-1}$ [30, 32]). Because $[\text{RH}] < 10^{-4} \text{ mol/l}$ in our kinetic measurements, $k_4[\text{RH}] \leq 10^5\text{--}10^6 \text{ s}^{-1}$. At the same time, the rate constant of decomposition of the radical pair into $\text{OH}^\cdot + \text{NO}_2^\cdot$ was estimated to be $k = 10^{10}\text{--}10^{12} \text{ s}^{-1}$ (we assumed that the activation energy is equal to 2 kcal/mol and the preexponential factor is $A =$

10^{12} – 10^{14}). Taking into account that the value of $k_4[\text{RH}]$ is lower than k by four to seven orders of magnitude, we concluded that the main reaction path of the conversion of the radical pair is degradation with the formation of free hydroxyl radicals, which are active species in the oxidation of hydrocarbons.

The following facts also argue for this mechanism: (1) equal substrate selectivities of hydrocarbon reactions with HOONO and OH^\cdot expressed in the unit slope of relation (18); (2) similar sets of products in the two reactions [26, 29, 38, 39]; (3) a ratio between the yields of products ($[\text{cyclohexanol}]/[\text{cyclohexanone}] \approx 2$) that is characteristic of reactions with OH^\cdot radicals [38] found in the reaction of cyclohexane with peroxy-nitrous acid [26–28]; and (4) experimental evidence for a high yield of OH radicals in the decomposition of HOONO [8–12].

Let us consider the reactions that occur in the two phases in more detail:



According to the estimated free energies of homolysis ($\Delta G_{\text{hom}}^0 = -RT \ln K_5$) of peroxy-nitrous acid in solution and in the gas phase (16.0 ± 2.4 [40] and 7.2 – 9.0 kcal/mol [22, 40], respectively), equilibrium (V) is almost completely shifted to the right in both phases: $-K_{5(\text{l})} = (0.01\text{--}1) \times 10^{-12}$ and $K_{5(\text{g})} = (0.3\text{--}6) \times 10^{-6}$ mol/l. With consideration for this fact, the overall rate constant of HOONO decomposition in a gas phase or solution in accordance with Eqs. (V) and (VII) is equal to

$$k^{\text{PA}} = k_5 + k_7 \quad (19)$$

and the apparent second-order rate constant of RH oxidation in accordance with Eq. (VI) is

$$k^{\text{RH}} = k_5 k_6 / (k_5 + k_7) \quad (20)$$

From Eqs. (19) and (20), we find the $k_g^{\text{PA}}/k_g^{\text{RH}}$ and $k_1^{\text{PA}}/k_1^{\text{PA}} \alpha^{\text{PA}}$ ratios:

$$k_g^{\text{PA}}/k_g^{\text{RH}} = (k_5 + k_7)^2 / k_5 k_6, \quad (21)$$

$$k_1^{\text{PA}}/k_g^{\text{PA}} \alpha^{\text{PA}} = k_1^{\text{PA}} / (k_5 + k_7) \alpha^{\text{PA}}. \quad (22)$$

Note that the interaction of OH^\cdot radicals with acetate ions [30] can occur in parallel with reaction (VI) in a buffer solution:



This reaction has no effect on the values of k_1^{PA} , k_g^{PA} , and k_g^{PH} because equilibrium (V) is almost completely

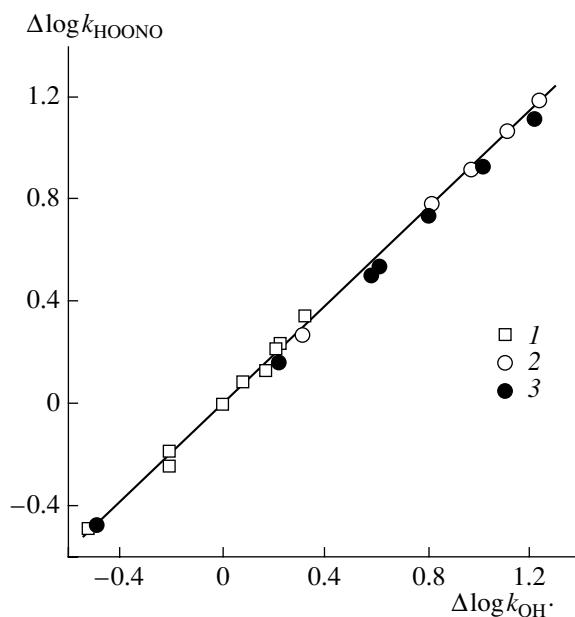


Fig. 5. Generalized correlation between the relative reaction rate constants of the gas-phase oxidation of (1) alkanes, (2) alkenes, and (3) alkylbenzenes by the $\text{H}_2\text{O}_2\text{--HNO}_2$ system [27–29] and by OH^\cdot radicals [30, 32, 33].

shifted to the right; however, it decreases the rate of RH oxidation in solution because $k_1^{\text{RH}} = k_5 k_6 / (k_5 + k_{6a} + k_7)$.

The rate constants of HOONO decomposition in aqueous solutions at 25°C are well known: $k_1^{\text{PA}} = (k_5 + k_7)_{(\text{l})} = 1.2 \text{ s}^{-1}$ [5, 16] and $k_{5(\text{l})} = (0.34 \pm 0.08) \text{ s}^{-1}$ [16]. Thus, we find that the yield of OH^\cdot radicals $k_{5(\text{l})}/k_1^{\text{PA}}$ in the decomposition of peroxy-nitrous acid in aqueous solutions is 28%.

Data on the rates of decomposition of peroxy-nitrous acid in the gas phase are unavailable. However, from the equilibrium constant $K_{5(\text{g})} = (0.3\text{--}6.0) \times 10^{-6}$ mol/l and the rate constant of the reverse reaction at atmospheric pressure $k_{-5(\text{g})} = 4 \times 10^8 1 \text{ mol}^{-1} \text{ s}^{-1}$ [41], we can evaluate the rate constant of homolysis $k_{5(\text{g})} = K_{5(\text{g})} k_{-5(\text{g})} = (0.1\text{--}2.4) \times 10^3 \text{ s}^{-1}$, which is much higher than that for aqueous solutions.

At $\text{X}=\text{OH}^\cdot$ in Scheme 2, $k = k_6 = k_{\text{OH}}$. For the gas-phase oxidation reactions of *n*-hexane, cyclopentane, cyclohexane, and propene, $k_{\text{OH}(\text{g})} = 3.6 \times 10^9, 2.8 \times 10^9, 4.0 \times 10^9$, and $16 \times 10^9 1 \text{ mol}^{-1} \text{ s}^{-1}$, respectively [30, 32]. With the use of these values of k_{OH} , the experimental ratios $k_g^{\text{PA}}/k_g^{\text{RH}}$ (Table 2), and estimated $k_{5(\text{g})} = (0.1\text{--}2.4) \times 10^3 \text{ s}^{-1}$, we derived $k_g^{\text{PA}} = (0.2\text{--}1) \times 10^5 \text{ s}^{-1}$ from Eq. (21). A comparison of the values of k_g^{PA} and $k_{5(\text{g})}$ suggests that the yield of OH^\cdot radicals in the gas-phase decom-

position of peroxy nitrous acid can vary from 0.1 to 10%.

Evaluation of the gas/water distribution coefficient of peroxy nitrous acid. The absence of deviations from Eq. (15) in the oxidation of alkanes with OH[·] radicals in the Fenton system [30] allowed us to conclude that hydroxyl radicals cannot independently pass from the solution to the gas phase. With the use of the found values of $k_1^{\text{PA}}/k_g^{\text{PA}} \alpha^{\text{PA}} = 27$ (Table 2) and $k_g^{\text{PA}} = (0.2-1) \times 10^5 \text{ s}^{-1}$ for Eq. (22) at $k_1^{\text{PA}} = 1.2 \text{ s}^{-1}$ [5], we evaluated the coefficient of peroxy nitrous acid distribution between the gas and the aqueous phase $\alpha^{\text{PA}} = (0.4-2) \times 10^{-6}$. As would be expected, the resulting value of α^{PA} lies between the values of α for H₂O₂ and HOONO₂ (calculated from published data [42, 43] on Henry's coefficients in aqueous solutions at 25°C, $\alpha = 0.041/K_H$):

Compound	HOONO	H ₂ O ₂	HOONO ₂	CH ₃ COOOH	CH ₃ OOH
$\alpha \times 10^6$	0.4-2	0.5	3	50	130

This value of α^{PA} corresponds to the solvation energy of peroxy nitrous acid in water $\Delta G_{\text{solv}}^0 = -RT \ln \alpha^{\text{PA}} = 7.8-8.7 \text{ kcal/mol}$. It lies in the region of $\Delta G_{\text{solv}}^0 = 6 \pm 3 \text{ kcal/mol}$ roughly estimated from the free energies of formation of peroxy nitrous acid in a gas ($\Delta G_{\text{f(g)}}^0 = 13 \pm 3 \text{ kcal/mol}$) [40] and in an aqueous solution ($\Delta G_{\text{f(l)}}^0 = 7.1 \pm 0.2 \text{ kcal/mol}$) [16].

CONCLUSIONS

We found that the plots of the rate constants of alkane and alkene oxidation with peroxy nitrous acid against the volume ratio between the liquid and gas phases in a reactor are unusual bell-shaped curves. We also found a linear correlation with the unit slope between the values of $\log k$ for the reactions of alkanes, alkenes, and alkylbenzenes with HOONO and OH[·] radicals. These findings can be quantitatively described by Scheme 2, which includes rapid equilibrium distributions of peroxy nitrous acid and RH between the gas and the solution, parallel reactions of HOONO isomerization into HNO₃ and HOONO homolysis with the formation of OH[·] radicals in the two phases, and the subsequent interaction of the free hydroxyl radicals with RH. Evidence for the assumption that OH[·] radicals serve as a direct reagent was obtained. The rate constants of isomerization and homolysis of peroxy nitrous acid in the gas phase and the coefficient of HOONO distribution between the gas phase and the

solution were evaluated (the results of this work are marked with asterisks):

Conditions	$k^{\text{PA}}, \text{ s}^{-1}$	$k_5, \text{ s}^{-1}$	Yield of OH [·] radicals, %	α^{PA}
Solution	1.2	0.34	28	
Gas phase	$(0.2-1) \times 10^5^*$	$(0.1-2.4) \times 10^3^*$	0.1-10*	$(0.4-2) \times 10^{-6}^*$

It is believed [44-46] that peroxy nitrous acid, which is a strong oxidizing agent, permeates through lipid membranes via anionic channels or by passive diffusion and initiates the oxidation of lipids. The capacity of peroxy nitrous acid for distribution between different phases and for the generation of OH[·] radicals in either of these phases is of importance for understanding the mechanisms of lipid membrane oxidation. Previously [44, 46], the following two reaction paths were proposed for peroxy nitrous acid with various lipophilic substrates: (1) radicals are formed in aqueous solutions; next, they react with the substrate on the membrane surface; and (2) peroxy nitrous acid penetrates into a lipid membrane and undergoes homolysis in a lipophilic medium. Previously, there was no direct experimental evidence for the possibility of the second reaction path. The value of α^{PA} estimated in this work is low and close to the values of α for peroxy nitric acid and H₂O₂. Because the distribution coefficient of hydrogen peroxide in the benzene/water system $\alpha = 0.013$ [47] is higher than that in the gas/water system by approximately four orders of magnitude, it is believed that the equilibrium concentration of peroxy nitrous acid in a hydrocarbon (lipophilic) medium is much higher than that in the gas phase. The results of this work and previous data [26-29] allow us to conclude that peroxy nitrous acid can diffuse from an aqueous medium to a gas atmosphere and, especially, to a lipophilic phase and decompose with the formation of OH radicals. Next, these OH radicals attack the alkyl and alkene fragments of cell membranes.

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