

Vibrational Nonequilibrium and Electronical Excitation in the Hydrogen-Oxygen Reaction

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1 Introduction

A hydrogen - oxygen reaction, being important from the practical standpoint, remains over decades a central model containing all the key features of the kinetics of gas-phase ignition, combustion, and detonation. After works of N.N. Semenov and C.N. Hinshelwood, over the past seventy years, this reaction was carefully investigated, and presently its mechanism is considered as the most studied one (in contrast, for example, to hydrocarbon oxidation). However, all the kinetic calculations executed for interpretation of experiments was based on use of the assumption about an availability of equilibrium on internal and external degrees of freedom of molecules and radicals. Comparative (from the practical standpoint) successes of kinetic descriptions in terms of the equilibrium approach have been achieved owing to considerable variations of the rate coefficients of important processes. Thus, the rate coefficients of the most important chain branching reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ obtained by different authors (see [1]) considerably differ depending on experimental conditions, about half obtained values are over the theoretical upper bound estimate (see [2]). Frequently, an agreement of theory with experiments is achieved owing to an infringement of the correlation between rate coefficients of direct and reverse reactions, or by introducing non-existent reactions and/or unreal rate coefficients. The assigned and recommended (for numerical simulation of experiments) rate constant values for dissociation of the most important principal and intermediate species [1] (see, also, for example, [3, 4] and references therein) exceed the highest possible ones (collision frequency multiplied by Arrhenius factor) in several times (H_2 , O_2) or orders of magnitude (OH , HO_2 , H_2O_2 , H_2O) that takes out theirs beyond bounds of a physical sense converting into formal adjusting parameters.

An impossibility to explain in this terms the formation (already during the most early steps of combustion process) of the electronically excited radical $\text{OH}^* \equiv \text{OH}(^2\Sigma^+)$ is another significant example of insufficiency and inconsistency of this (traditional) equilibrium kinetic concept. At the same time, the emission $\text{OH}^* \rightarrow \text{OH} + h\nu$ has long been used in research practice to determine the induction time of ignition.

These and other facts (for more details, see [2]) suggest a necessity of not only making the kinetic scheme more precise and detail but also a revision of itself kinetic concept which is based on the assumption about availability of equilibrium on the internal (vibrational) degrees of freedom. In accordance with conclusions of the work [2], it relates first of all to the reactions with participation of vibrationally excited radical $\text{HO}_2(\text{v})$ which forms in result of bimolecular recombination $\text{H} + \text{O}_2 \rightarrow \text{HO}_2(\text{v})$ and the following (fast for high vibrational excitations) redistribution of $\text{H}\cdots\text{O}_2$ bond energy

between vibrational degrees of freedom (modes) of HO_2 . These are the following main (in conventional chain branching mechanism of hydrogen oxidation) reactions: the above reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ and the inhibiting reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. (In terms of existing kinetic concept, these and other overall reactions interpret as the elementary ones depending only on the gas temperature, T .) The process of forming OH^* during the most early steps of combustion process¹ we suppose proceeds by two following steps: $\text{H} + \text{O}_2 \rightarrow \text{HO}_2(\text{v})$ and $\text{HO}_2(\text{v}) + \text{H}_2 \rightarrow \text{OH}^* + \text{H}_2\text{O}$, i.e., via forming the vibrationally excited $\text{HO}_2(\text{v})$ radical, and in accordance with the only quantitatively acceptable overall reaction $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{OH}^*$ suggested as far back as in [5].

The subject of this research is the creation and approbation of theoretical model based on consistent account of the vibrational nonequilibrium of HO_2 radical that is assumed to act as a key intermediate in the process of chain branching and in a generation of electronically excited species [2]. In terms of the proposed model, the chain branching $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ and inhibiting $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ reactions are considered as a general multi-channel process of forming, intramolecular energy redistribution between modes, relaxation, and monomolecular decay of the comparatively long-lived (see [2, 6, 7]) vibrationally excited $\text{HO}_2(\text{v})$ radical which is capable moreover to react and exchange of energy with another components of the mixture.

2 Theoretical model

Equations of chemical and vibrational kinetics for general case of reacting multi-component gas mixture in the frames of macroscopic (or hydrodynamic) description (i.e., in the form of equations for average energies of vibrational modes, ε_k , and concentrations of mixture components, n_i) were first published in [8]. According to the model [8] (see also [9]), chemical and vibrational kinetics of HO_2 radical and another molecules is described by the equations for n_i and ε_k for given gas temperature, T , and pressure, p (for more details, see [10]).

The vibrational nonequilibrium manifests itself via the dependence of corresponding rate constants on the vibrational temperatures T_k (or averaged energies, ε_k) of modes:

$$k_r(T, T_k) = \kappa_r(T, T_k) k_r^0(T), \quad \kappa_r(T, T_k) = \exp \left[E_r \left(\frac{1}{T} - \frac{\sum_i \beta_{ri}^2}{\sum_i \beta_{ri}^2 T_i} \right) \right], \quad T_k = \frac{\theta_k}{\ln[(1 + \varepsilon_k) / \varepsilon_k]}.$$

Here, k_r^0 is the rate constant of r th reaction provided the thermodynamic equilibrium; E_r is the portion of the activation energy of r th reaction belonging to the vibrational degrees of freedom (for more details, see [10]); θ_k is the characteristic temperature of k th vibration; $\sum_i \beta_{ri}^2 = 1$, $\beta_{r1} = \beta_{r2} = \dots$.

The effect of the chemical reactions on the process of vibrational relaxation is expressed through the terms in the right parts of vibrational kinetics equations for ε_k :

$$\left(\frac{d\varepsilon_k}{dt} \right)_{chem} = (\rho n_j)^{-1} \sum_r (v'_{jr} - v_{jr}) [(\chi_{rk} - \varepsilon_k)(R_r - R'_r)].$$

Here, χ_{rk} is the average numbers of vibrational quanta obtained by k th mode in one act of formation of the j -type molecule in r th reaction. The total set of χ_{rk} values characterizes an energy distribution between modes of the r th reaction products.

¹ During later stages of combustion process and while forming the maximum OH^* concentration, other reactions (see [2]) play an important role also.

For description of the initiation and chain reactions in the $\text{H}_2 + \text{O}_2 + \text{Ar}$ system for temperatures $1000 < T < 1200$ K and pressures $0.9 < p < 2.0$ atm, we have used the kinetic scheme, which takes into account chemical reactions with participation H_2 , O_2 , H_2O , HO_2 , H , O , OH , H_2O_2 , O_3 in the ground electronic state as well as $\text{O}_2(^1\Delta)$, $\text{O}(^1\text{D})$, $\text{OH}(^2\Sigma^+)$, and relaxation channels of the vibrational modes H_2 , O_2 , $\text{O}_2(^1\Delta)$, $\text{HO}_2(\nu_1) \equiv \text{HO}_2(100)$, $\text{HO}_2(\nu_2) \equiv \text{HO}_2(010)$, and $\text{HO}_2(\nu_3) \equiv \text{HO}_2(001)$; in all the details, see [10].

The behaviour of intermediate HO_2 radicals are described by the following elementary processes:

- (1) $\text{H} + \text{O}_2 \rightarrow \text{HO}_2(100)$ (formation as a result of bimolecular recombination);
- (2) $\text{HO}_2(3E\ 0\ 0) \rightarrow \text{HO}_2(EEE)$, $3E \approx D_{\text{H-O}_2}$, (intramolecular redistribution of $\text{H}\cdots\text{O}_2$ bond energy);
- (3) $\text{HO}_2 + (\text{M}) \rightarrow \text{H} + \text{O}_2 + (\text{M})$ (dissociation along $\text{H}\cdots\text{O}_2$ bond);
- (4) $\text{HO}_2 + (\text{M}) \rightarrow \text{O} + \text{OH} + (\text{M})$ (dissociation along $\text{O}\cdots\text{OH}$ bond, i.e. chain branching);
- (5) $\text{HO}_2(100) + \text{X}(0) \leftrightarrow \text{HO}_2(000) + \text{X}(1)$, $\text{X} = \text{H}_2, \text{O}_2$ (VV'-exchange);
- (6) $\text{HO}_2(010) + \text{X}(0) \leftrightarrow \text{HO}_2(000) + \text{X}(1)$, $\text{X} = \text{H}_2, \text{O}_2$ (VV'-exchange);
- (7) $\text{HO}_2(001) + \text{M} \leftrightarrow \text{HO}_2(000) + \text{M}$, $\text{M} = \text{H}_2, \text{O}_2, \text{H}_2\text{O}, \text{Ar}$ (VT-exchange);
- (8) $\text{HO}_2 + \text{Y}_i \leftrightarrow \text{Y}_j + \text{Y}_k$, $i, j, k = 1, 2, \dots, N$ (chemical reactions).

The main difference from traditional schemes is an absence of $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ reaction as the elementary one. The process of the $\text{HO}_2(\nu)$ radical formation has been presented by the fast bimolecular recombination reaction (1). The reactivity of $\text{HO}_2(\nu)$ and its subsequent evolution are determined by the processes of energy redistribution between modes (2) up to the uniform energy distribution, relaxation (5)-(7), and monomolecular (or bimolecular) decay (3), (4), as well as the reactions with its participation (8).

3 Some results

Results of the calculations are called to illustrate the efficiency of suggested approach from standpoint of both elucidating a physically adequate mechanism of the high-temperature hydrogen oxidation and quantitative interpreting experimental data. In calculations, the coordinate system was attached to the flow behind the shock wave (the gas rests, $T = \text{const}$, $p = \text{const}$, $t = 0$ when the shock front is passing).

The results [11, 12] was chosen for comparison with our kinetic (isothermal) calculations. Comparison of the results of simulative kinetic calculations in terms of single kinetic scheme with the corresponding experimental results is illustrated by Table 1. Describing the results of the comparison on the whole, we establish a qualitative and quantitative agreement of calculated results with experimental ones (at the worst case, No. 4, the difference is 24%).

Table 1: Experimentally measured [11 ^{a)}, 12 ^{b)}] and calculated (within one kinetic scheme ^{c)}) values t_{50} ^{d)} and t^* ^{e)}

No	T, K	p, atm	Experiment		Calculation	
			t^* , μs [12]	t_{50} , μs [11]	t^* , μs	t_{50} , μs
1	1050	1.9	945÷1120	–	1102	
2	1225	1.5	600	–	603	
3	1052	2.2	–	618		525
4	1074	0.935	–	1005		1241
5	1086	0.94	–	985		1130
6	1102	1.2	–	836		911
7	1115	2.248	–	393		404

^{a)} reflected shock wave, reach mixture (4% H_2 +1% O_2 +95% Ar), measurement of absorption by OH; ^{b)} incident shock wave, stoichiometric mixture (0.93% H_2 +0.46% O_2 +98.61% Ar), measurement of emission from OH*; ^{c)} see [10]; ^{d)} time interval between the passage of the shock front and the moment at which light absorption by the OH radical reaches its half-maximum (in the calculations, the moment at which the OH concentration reaches its

half-maximum); ^{e)} time interval between the passage of the shock front and the moment of maximum emission at ≈ 306 nm (in calculations, the maximum OH* concentration moment).

Especially nonequilibrium character of the hydrogen oxidation process is illustrated by Figure 1 in which the typical time dependences for vibrational temperatures, T_k , are given. One can see that the account for vibrational nonequilibrium results in most important effects running throughout all the process. The reaction rate constants, $k_r(T, \{T_k\})$, depend on vibrational temperatures of the reactants, and these dependencies are described by factors as large as several orders of magnitude (see Figure 2). This is particularly true for reactions involving the HO₂ radical.

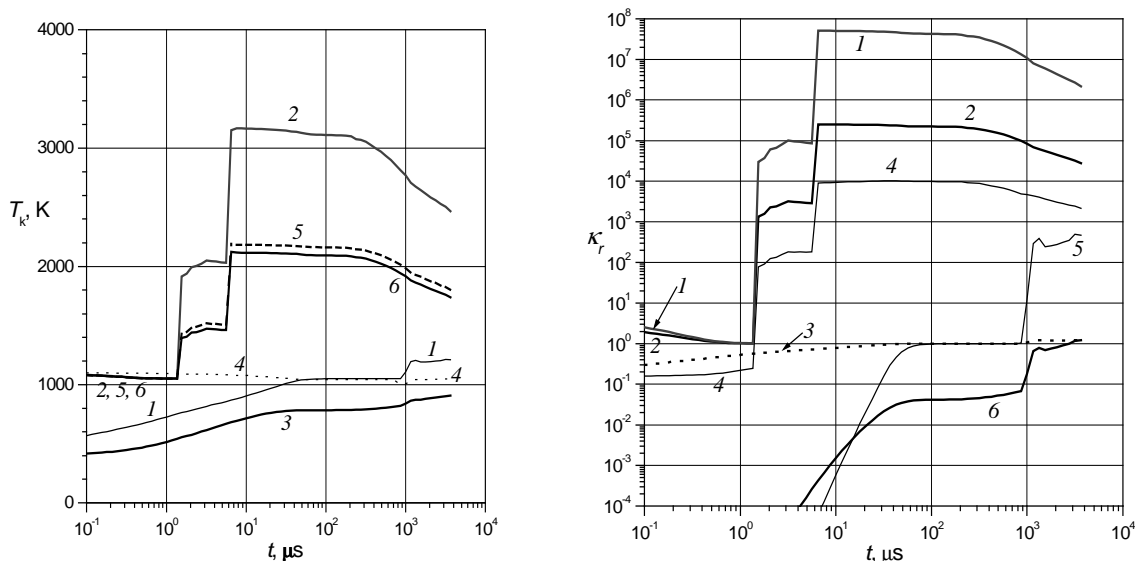


Figure 1 (left): Typical time dependences of the vibrational temperatures T_k . The curves are numbered in the order of decreasing characteristic temperatures of vibrational modes (θ_k): (1) H₂, (2) HO₂(ν_1), (3) O₂, (4) O₂*, (5) HO₂(ν_2), and (6) HO₂(ν_3). This figure and the figures presented below illustrate calculation variant 1 in Table 1.

Figure 2 (right): Time dependences of the nonequilibrium factor $\kappa_r(T, \{T_k\}) = k_r(T, \{T_k\})/k_r^0(T)$ for various reactions at the vibrational temperatures T_k examined in figure 1: (1) HO₂ → O+OH, (2) HO₂ → H+O₂, (3) H₂+O → OH+H, (4) HO₂+H₂ → OH*+H₂O, (5) H₂+ Ar → 2H+Ar, (6) H₂+O₂ → H+HO₂.

Figures 3 and 4 illustrate the typical behavior of component concentrations under the conditions examined.

The duration of the induction period, being estimated as the beginning of the fall of H₂ and O₂ concentrations (about 800 μs in given calculation, No 1 of Table 1) varies depending strongly on conditions (composition, temperature, pressure). However, in all the cases, the beginning and the end of the intensive reaction stage corresponds to the time at which the HO₂ radical concentration is near its maximum value.

Note that considerable amounts of singlet molecular oxygen O₂* appear at the earliest stages of the process. As the reaction proceeds, the O₂* concentration reaches a level indicating that singlet molecular oxygen is among the major intermediates along with HO₂, H, O, or OH.

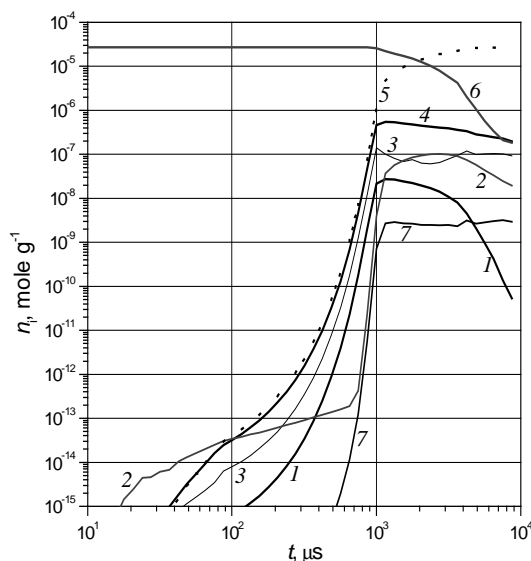


Figure 3 (left): Time dependences of the concentrations (n_i) of (1) HO_2 , (2) O_2^* , (3) OH , (4) H , (5) H_2O , (6) H_2 , and (7) H_2O_2 .

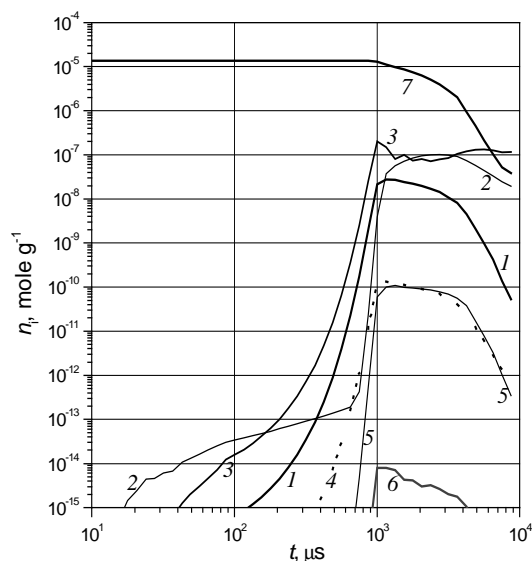


Figure 4 (right): Time dependences of the concentrations (n_i) of (1) HO_2 , (2) O_2^* , (3) O , (4) O_3 , (5) O^* , (6) OH^* , and (7) O_2 .

The rate of chain branching is determined by the rate of the monomolecular decomposition of the vibrationally excited radical $\text{HO}_2(v)$: $\text{HO}_2 \rightarrow \text{O} + \text{OH}$. Being extracted from calculation, the apparent rate constant of the $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ overall process is $k_{\text{H}+\text{O}_2 \rightarrow \text{O}+\text{OH}}^{\text{eff}} = R_3/[\text{H}][\text{O}_2]$; it depends on experimental conditions. The values of $k_{\text{H}+\text{O}_2 \rightarrow \text{O}+\text{OH}}^{\text{eff}}$ as functions of t are obtained in the calculations for the cases at practically the same temperatures ($T \cong 1050 \text{ K}$) and close pressures (No. 1 and No. 3 of Table 1). Besides that it varies in time, the apparent rate constant of this most important overall reaction strongly depends on the mixture composition differing for these cases in 2.5 - 3 times for the induction period and intensive reaction stage ($t > 10 \mu\text{s}$). This is a consequence of the nonequilibrium character of the process and a change of the role of different elementary reactions and vibrational relaxation channels during different stages of process.

4 Conclusions

A theoretical model based on consistent account of the vibrational nonequilibrium of HO_2 radical has been elaborated and experienced. It is shown that the hydrogen-oxygen reaction proceeds in absence of vibrational equilibrium. Vibrationally excited $\text{HO}_2(v)$ radical acts as a key intermediate in the principally important chain branching process and in generation of electronically excited species. The nature of hydrogen-oxygen reaction is especially nonequilibrium, moreover, the vibrational nonequilibrium of HO_2 radical is the essence of this process.

The overall process $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$, being conventional in current literature as the most important chain branching reaction, proceeds via forming the vibrationally excited $\text{HO}_2 \equiv \text{HO}_2(v)$ radical. It is the nonequilibrium character of the process that causes the obvious dependence of observed rate

constant on experimental conditions via vibrational relaxation processes and reactions with participation of $\text{HO}_2(\text{v})$.

Such approach elucidates physical mechanism of hydrogen oxidation what is principal to the search for effective means of affecting ignition and combustion processes. This approach is also capable to solve the problem of agreement between theoretical predictions and experimental results obtained by different authors in different conditions and for various compositions.

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