

Vibrational Nonequilibrium of HO₂ Radical in a Model of Chain Branching in Hydrogen-Oxygen Reaction

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1 Introduction

The mechanism of the reaction of hydrogen with oxygen is considered now 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 the 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]). Experimental facts and results of quantitative comparison of theory with experiment (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 an 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 HO₂(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 H...O₂ bond energy between vibrational degrees of freedom (modes) of HO₂. 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 less important for considered conditions) overall reactions interpret as the elementary ones depending only on the gas temperature, T .

The subject of this research is the creation and approbation of theoretical model based on consistent account of the vibrational nonequilibrium of HO₂ 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 multichannel process of forming, intramolecular energy redistribution between modes, relaxation, and unimolecular decay of the long-lived (see [2]) intermediate or vibrationally excited HO₂(v) radical which is capable moreover to react with another components of a mixture.

2 Vibrationally nonequilibrium model of hydrogen oxidation

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 [3]. According to the model [3] (see also [4]), chemical and vibrational kinetics of HO₂ radical and another molecules is described by the equations for n_i as well as ε_k for given gas temperature, T , and pressure, p .

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; 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; $\sum_i \beta_{ri}^2 = 1$, $\beta_{r1} = \beta_{r2} = \dots$. The total set of χ_{rk} values characterizes an energy distribution between modes of the r th reaction products.

For description of the initiation and chain reaction in the H₂ + O₂ + 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 H₂, O₂, H₂O, HO₂, H, O, OH, H₂O₂, O₃ in the ground electronic state as well as O₂(¹Δ), O(¹D), OH(²Σ⁺), and relaxation channels of the vibrational modes H₂, O₂, O₂(¹Δ), HO₂(ν_1) ≡ HO₂(100), HO₂(ν_2) ≡ HO₂(010), and HO₂(ν_3) ≡ HO₂(001); in all the details, see [5].

The behaviour of intermediate HO₂ radicals are described by the following elementary processes:

- (1) H+O₂ → HO₂(100) (formation as a result of bimolecular recombination);
- (2) HO₂(3E 0 0) → HO₂(EEE), 3E ≈ D_{H-O_2} , (intramolecular redistribution of H...O₂ bond energy);
- (3) HO₂ + (M) → H+O₂ + (M) (dissociation along H...O₂ bond);
- (4) HO₂ + (M) → O+OH + (M) (dissociation along O...OH bond, i.e. chain branching);
- (5) HO₂(100)+X(0) ↔ HO₂(000)+X(1), X = H₂, O₂ (VV'-exchange);
- (6) HO₂(010)+X(0) ↔ HO₂(000)+X(1), X = H₂, O₂ (VV'-exchange);
- (7) HO₂(001)+M ↔ HO₂(000)+M, M = H₂, O₂, H₂O, Ar (VT- exchange);
- (8) HO₂+Y_i ↔ Y_j+Y_k, $i, j, k = 1, 2, \dots, N$ (chemical reactions).

The main difference from traditional schemes is an absence of H+O₂ → O+OH reaction as the elementary one. The process of the HO₂(ν) radical formation has been presented by the fast bimolecular recombination reaction (1). The reactivity of HO₂(ν) 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 unimolecular decay (3), (4), as well as the reactions with its participation (8).

3 Main results and conclusions

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, $T=const$, $p=const$, $t=0$ when the shock front is passing).

The results [6, 7] 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: Measured [6 ^{a)}, 7 ^{b)}] and calculated in terms of the single kinetic scheme ^{c)} the values t_{50} ^{d)} and t^* ^{e)}

No	T, K	p, atm	Experiment		Calculation	
			t^* , μs [7]	t_{50} , μs [6]	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% H₂+1% O₂+95% Ar), monitoring absorption of OH; ^{b)} incident shock wave, stoichiometric mixture (0.93% H₂+0.46% O₂+98.61% Ar), monitoring emission of OH*; ^{c)} see [5]; ^{d)} the time between a front and the point in time at which the light absorption OH→OH* reached a half of its maximum value (in the calculations, the point in time at which a half-maximum concentration of OH radicals was reached); ^{e)} the time between a front and the point in time at which the emission at $\lambda \approx 306$ nm reached a maximum (at the calculations, it was identified with the point in time at which a maximum concentration of OH* was reached).

Being extracted from calculation, the apparent **rate constant of the H+O₂ → O+OH overall process** is $k_{H+O_2 \rightarrow O+OH}^{eff} = R_3/[H][O_2]$; it **depends on experimental conditions**. The values of $k_{H+O_2 \rightarrow O+OH}^{eff}$ as functions of t are obtained in the calculations corresponding the cases for practically the same temperatures $T \cong 1050$ K (No. 1 and No. 3 of Table 1). The pronounced dependence, on pressure and time, of the apparent rate constant of the most important overall reaction determining the rate of full process on the whole is a consequence of its nonequilibrium character and a change of the role of different elementary reactions and vibrational relaxation channels during different stages.

Especially nonequilibrium character of the hydrogen oxidation process is illustrated by Figure 1 in which the typical time profiles 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 reagents, and these dependencies are described by multipliers $\kappa_r(T, \{T_k\})$ of several orders of magnitude. So considerable difference of nonequilibrium factors, κ_r , from 1 means that **the nature of hydrogen-oxygen reaction is especially nonequilibrium, and the vibrational nonequilibrium of HO₂ radical is the essence of hydrogen oxidation process**.

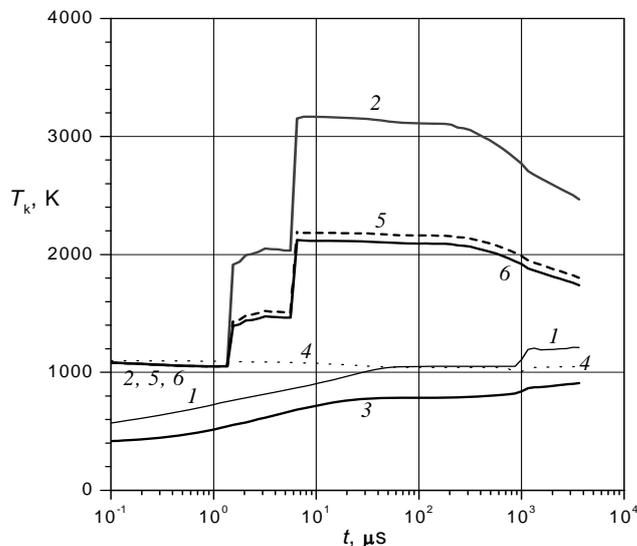


Figure 1: Typical, for considered conditions, the time profiles of vibrational temperatures, T_k . The curves are numbered by order of decreasing characteristic temperatures of vibrational modes, θ_k , namely: 1 is H_2 , 2 is $HO_2(\nu_1)$, 3 is O_2 , 4 is O_2^* , 5 is $HO_2(\nu_2)$, and 6 is $HO_2(\nu_3)$. Here, the calculated variant No. 1 of Table 1 is illustrated.

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