

Vibrational Nonequilibrium of the HO₂ Radical in the Hydrogen-Oxygen Reaction. Comparison with Experiment

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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 an assumption about 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 $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ 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. Meanwhile, in [2] was suggested “the dependence of the apparent rate constant of the process $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ on the concentration of the third body $\text{M} = \text{H}_2$ ”, and it was stated the need to consider this reaction as the “ $\text{H} + \text{O}_2 \rightarrow \text{HO}_2(\nu) \rightarrow \text{O} + \text{OH}$ with consideration for intramolecular energy redistribution in the $\text{HO}_2(\nu)$ radical and its vibrational relaxation in collisions”. Such a consideration was performed in [10], where it was shown that “the nonequilibrium character of the process with respect to vibrational degrees of freedom is responsible for the observed dependence of the effective rate constant of the overall reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ on experimental conditions”.

These and other facts suggest a necessity a revision of the 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 HO₂(v) which forms in result of bimolecular recombination H+O₂ → HO₂(v) and the following redistribution of H··O₂ bond energy between vibrational degrees of freedom (modes) of HO₂. These are the following main reactions: the above reaction H+O₂ → O+OH and the inhibiting reaction H+O₂+M → HO₂+M.

The process of forming OH* during the most early steps of combustion process we suppose proceeds by two following steps: H+O₂ → HO₂(v) and HO₂(v)+H₂ → OH*+H₂O, i.e., via forming the vibrationally excited HO₂(v) radical, and in accordance with the only quantitatively acceptable overall reaction H+O₂+H₂ → H₂O+OH* suggested as far back as in [5].

The subject of this research is a presentation and comparison with experiments 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]. The paper is the continuation of the works [2] and [10]. In terms of the proposed model, the chain branching H+O₂ → O+OH and inhibiting H+O₂+M → HO₂+M formal 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 HO₂(v) radical which moreover is capable to react and to exchange of energy with other components of the mixture. This significantly changes the physical understanding of the chemical mechanism in the reacting hydrogen-oxygen system.

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 HO₂ 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, 11]). 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:

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

Here, k_r^0 (or equilibrium value) is the rate constant of the r th reaction in which all degrees of freedom are at 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, 11]); θ_k is the characteristic temperature of k th vibration; $\sum_i \delta_{ri} = 1$, $\delta_{r1} = \delta_{r2} = \dots$.

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 :

$$\left(\frac{d\varepsilon_k}{dt} \right)_{chem} = (\rho n_j)^{-1} \sum_r (v'_{jr} - v_{jr}) [(\chi_{rk} - \varepsilon_k)(R_r - R'_r)]. \quad (2)$$

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.

For description of the initiation and chain reactions in the H₂ + O₂ + Ar system for temperatures 1000 < T < 2500 K and pressures 0.5 < p < 4 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* \equiv O₂(¹ Δ), O* \equiv O(¹D), OH* \equiv OH(² Σ^+), and relaxation channels of the vibrational modes H₂, HO₂(ν_1) \equiv HO₂(100), OH, O₂, O₂*, HO₂(ν_2) \equiv HO₂(010), HO₂(ν_3) \equiv HO₂(001), H₂O(ν_1) \equiv H₂O(100), H₂O(ν_2) \equiv H₂O(010), and H₂O(ν_3) \equiv H₂O(001). Here, in contrast to [10], we take into account the vibrational nonequilibrium of the important intermediate OH and main reaction product H₂O.

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

- (1) H+O₂ \rightarrow HO₂(ν) (formation as a result of bimolecular recombination and the fast intramolecular redistribution of H...O₂ bond energy (or energy randomization) which is simulated by setting up $\delta_{1,2} = \delta_{1,6} = \delta_{1,7}$);
- (2) HO₂ + (M) \rightarrow H+O₂ + (M) (dissociation along H...O₂ bond);
- (3) HO₂ + (M) \rightarrow O+OH + (M) (dissociation along O...OH bond, i.e. chain branching);
- (4) HO₂(100)+X(0) \leftrightarrow HO₂(000)+X(1), X = H₂, O₂, H₂O(ν_1), ... (VV'-exchange);
- (5) HO₂(010)+X(0) \leftrightarrow HO₂(000)+X(1), X = H₂, O₂, ... (VV'-exchange);
- (6) HO₂(001)+M \leftrightarrow HO₂(000)+M, M = H₂, O₂, H₂O, Ar (VT-exchange);
- (7) HO₂(3E 0 0) \rightarrow HO₂(EEE), 3E \approx D_{H-O₂}, (intramolecular redistribution of H...O₂ bond energy or energy randomization);
- (8) HO₂+Y _{i} \leftrightarrow Y _{j} + Y _{k} , $i, j, k = 1, 2, \dots, N$ (chemical reactions).

The process of the HO₂(ν) radical formation has been presented by the fast bimolecular recombination (1). The reactivity of HO₂(ν) and its subsequent evolution are determined by the processes of decay (2) and (3), relaxation and energy redistribution between modes up to the uniform energy distribution (4) - (7), , as well as the reactions with its participation (8). The recent results on dynamics in the HO₂ system (see [12] and references therein) showed the existence of significant regularity embedded in the chaotic phase space. I.e., the HO₂ system was found to be (in dynamic sense) an intermediate case between regular and chaotic behavior. Here, that latter is simulated (on the kinetic level) by the processes (1) - (3). To take into account the regular dynamic behavior on the kinetic level, we introduce in the kinetic scheme the one-stage (via a direct mechanism on the doublet potential energy surface [2, 10]) process H+O₂ \rightarrow O+OH in addition to the processes (1) - (3).

3 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). All the calculations was performed within one (fixed) kinetic scheme The calculated (isothermal kinetics) results are compared with the shock tube experimental data [13-15] for strongly diluted H₂-O₂ mixtures at 1000 < T < 2500 K, 0.5 < p < 4 atm. Comparison of the results of simulative kinetic calculations in terms of single kinetic scheme with the corresponding experimental results is illustrated by Table 1 for compositions I – VI.

As a general result of this comparison, one can state qualitative and quantitative agreement between calculated and experimental data. It should be noted here (more detailed see [2]) that the traditional equilibrium kinetic models (see for example [3, 4, 14] and references therein) are unable to provide the

quantitative interpretation of these experiments by means of one kinetic scheme without variations of rate constants of many elementary processes.

Table 1. Experimentally measured [13-15] and calculated (within one kinetic scheme) values of τ^* ^a and τ_{50} ^b for different composition at two equivalence ratios $\Phi = 1$ and $\Phi = 2$

No	Composition, experimental conditions, measured value, Refs	<i>T</i> , K	<i>p</i> , atm	Experiment	Calculation
1		1050	1.90	945-1120	950
2	$\Phi = 1$	1052	2.025	1135	1140
3	I: 0.93% H ₂ +0.46% O ₂ +98.61% Ar,	1060	1.666	907	903
4	incident shock wave, τ^* , Ref. (14)	1178	1.675	684	684
5		1225	1.50	600	604
6		1260	1.407	524	551
1		1060	0.64	1475	1452
2		1095	0.67	1160	1190
3	$\Phi = 1$	1108	0.68	997	1008
4	II: 2.0% H ₂ +1.0% O ₂ +97.0% Ar,	1183	0.74	680	680
5	incident shock wave, τ^* , Ref. (15)	1220	0.77	573	552
6		1313	0.84	355	389
7		1472	0.97	366	249
8		1596	1.1	152	173
1		1142	0.71	820	820
2	$\Phi = 2$	1212	0.77	467	469
3	III: 4.0% H ₂ +1.0% O ₂ +95.0% Ar,	1362	0.90	209	210
4	incident shock wave, τ^* , Ref. (15)	1692	1.17	100	90
5		1968	1.40	99	51
6		2390	1.75	40	24
1		1155	0.957	1274	1277
2	$\Phi = 2$	1274	0.781	814	813
3	IV: 2.0% H ₂ +0.5% O ₂ +97.5% Ar,	1387	0.778	537	541
4	reflected shock wave, τ_{50} , Ref. (13)	1472	0.859	384	356
5		1596	0.852	269	289
6		1809	0.846	161	185
7		2136	0.851	92	106
1		1525	2.005	703	732
2	$\Phi = 2$	1639	2.049	550	577
3	V: 0.4% H ₂ +0.1% O ₂ +99.5% Ar,	1934	1.922	293	334
4	reflected shock wave, τ_{50} , Ref. (13)	2132	2.094	185	202
5		2409	2.095	127	126
1		1527	3.77	647	623
2	$\Phi = 2$	1658	3.654	476	489
3	VI: 0.2% H ₂ +0.05% O ₂ +99.75% Ar,	1763	3.843	356	272
4	reflected shock wave, τ_{50} , Ref. (13)	2001	4.088	203	185
5		2211	3.715	158	160

^a Time interval between the passage of the shock front and the moment of maximum emission at ~ 306 nm (in calculation, the maximum OH* concentration moment).

^b 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 calculation, the moment at which the OH concentration reaches its half-maximum).

This approach is promising from the standpoint of reconciling the predictions of the theoretical model with experimental data obtained by different authors for various compositions and conditions using different methods. It is demonstrated that the vibrational nonequilibrium (and consequently its influence on the rate constants and the process on the whole) decreases with increasing the gas

temperature T and pressure p remaining determinant up to temperatures $T = 1500$ K. At $T < 1500$ K, the nature of hydrogen-oxygen reaction is especially nonequilibrium, and the vibrational nonequilibrium of HO₂ radical is the essence of this process.

In the fitting of the calculated values τ^* and τ_{50} to experimental ones, the main point was variation and fitting essentially unknown kinetic constants, which characterize the collisional vibration-translational, vibration-vibrational, and intramolecular processes of energy transfers involving vibrational modes of HO₂. The performed calculations have showed that the unknown kinetic constants $\tau_6^{(M)}$ (V-RT energy transfer of the HO₂ radical vibrational modes), $k_{H_2,HO_2}^{(4)}$ (VV'-exchange HO₂(100)+H₂(0) \leftrightarrow HO₂(000)+ H₂ (1)), and $k_{HO_2=O+OH}^0$, $k_{H+O_2=O+OH}^0$ (see Equ. (1)) are the most important from the standpoint of an influence on the calculated values τ^* and τ_{50} . In one's turn, the process of vibrational - to-rotation-translational (V-RT) energy transfer of the HO₂ radical vibrational modes in its collisions with H₂ molecules was found as the most important one under the compositions and conditions examined at $T < 1500$ K (in accordance with conclusions [10] about key role of the HO₂ radical in the hydrogen oxidation reaction). The value, $\tau_6^{(H_2)}$, i.e., the characteristic time of the V-RT energy transfer united for all three modes of the HO₂ radical in its collisions with H₂ molecules, was the only adjustable parameter in performing the calculations illustrated by the Table 1. The limits of variation are characterized by the following relation:

$$2.25 \cdot 10^{-11} \cdot \exp(70.23 \cdot T^{-1/3}) \leq \tau_{HO_2}^{(H_2)} \leq 1.41 \cdot 10^{-12} \cdot \exp(107.9 \cdot T^{-1/3}), \quad (3)$$

which is illustrated by Fig. 1.

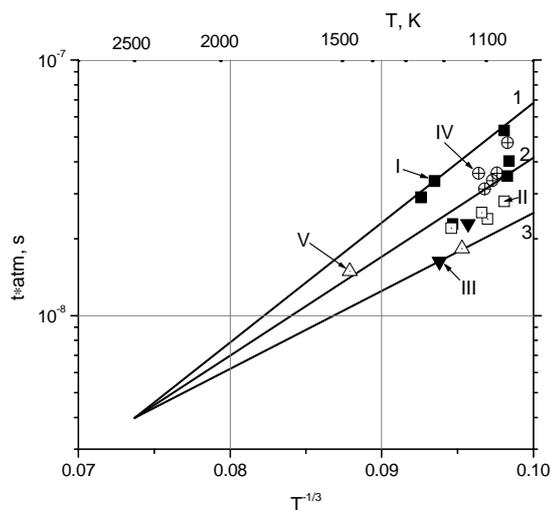


Fig. 1. Characteristic time of the V-RT energy transfer of the HO₂ radical in its collisions with H₂ molecules at different temperatures. 1 – the superior limit; 2 – the mean value, $5.62 \cdot 10^{-12} \cdot \exp(89.08 \cdot T^{1/3})$ (used in calculations for all the systems at $T > 1500$ K); 3 – the inferior limit. Different markers correspond to the values of $\tau_{HO_2}^{(H_2)}$ used in the calculations (the results are added in the Table 1) for the different (I ÷ V) systems at $T < 1500$ K.

This relation should be considered as the quantitative estimation of the unknown at present value of $\tau_{HO_2}^{(H_2)}$ at $2500 > T > 1000$ K with the maximum error equal $(1.5)^{\pm 1}$ at T about 1000 K. This uncertainty characterizes the extent of our ignorance of the elementary reaction dynamic details described on kinetic level by the values E_r , δ_{rk} , χ_{rk} ; see eqs. (1), (2). In future, as the range of compositions and conditions on temperature and pressure will be extended, the kinetic constants will be corrected. For optimization of the kinetic scheme, the results of *ab initio* analysis of Potential Energy Surfaces for

corresponding molecular systems as well as the results of corresponding dynamical calculations must be the most important independent non-empirical source of kinetic information.

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