Reaction kinetics of H_2 with O_2 in highly excited electronic states

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The reactions of electronically excited oxygen in the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states (excitation energy values T_e are 0.98 and 1.63 eV, respectively) with molecular hydrogen are assumed to be the critical chain initiation channels under the conditions of laser-induced and plasma-assisted combustion of H_2-containing mixtures [1]. Reactions with higher (Herzberg) electronic states of O_2, such as $c^1\Sigma_u^-$ (T_e =4.05 eV) and $A'^3\Delta_u$ (T_e =4.20 eV), can also be potentially important in the latter case [1, 2]. However, the available kinetic data on these processes are rather scarce. In the past, relatively much attention was paid only to the kinetics of H_2+O_2($a^1\Delta_g$) reaction [3–6]. The rate constant for the H_2+O_2($b^1\Sigma_g^+$) process was estimated in the past, to our best knowledge, based on semiempirical schemes only [6], whereas the reactions of higher electronic states of O_2 with H_2 were considered neither theoretically nor experimentally until recently.

Comprehensive quantum chemical analysis with the usage of multireference state-averaged complete active space self-consistent field approach was carried out to study the reactions of H_2 with O_2 in $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, and $A'^3\Delta_u$ electronically excited states. The energetically favorable reaction pathways and possible intersystem crossings were revealed. The energy barriers were refined employing the extended multi-configuration quasi-degenerate second-order perturbation theory [7]. It was shown that the interaction of O_2($a^1\Delta_g$) and O_2($A'^3\Delta_u$) with H_2 occurs through the H-abstraction with relatively low activation barriers that resulted in the formation of the HO_2 molecule in A'' and A' electronic states, respectively. Meanwhile, O_2 in singlet sigma states ($b^1\Sigma_g^+$ and $c^1\Sigma_u^-$) was proved to be nonreactive with respect to H_2.

Appropriate rate constants for revealed reaction and quenching channels were estimated using variational transition-state theory including the corrections for tunneling, possible nonadiabatic transitions, and anharmonicity of vibrations for transition states and reactants. It was demonstrated that the calculated reaction rate constant for the H_2+O_2($a^1\Delta_g$) process is in reasonable agreement with known experimental data [3, 8].

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