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A comparative study of the kinetics and dynamics of the reaction of H atoms with ground-state and excited O₂

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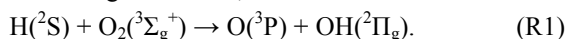
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Abstract

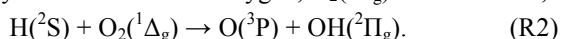
The kinetics and dynamics of the H + O₂ → OH + O reaction have been studied in quasiclassical trajectory (QCT) calculations on both the ground and the excited-state potential energy surface. The excitation function for the reaction starting from excited-state O₂ was found to rise above zero at about 0.3 eV in good agreement with the exact quantum mechanical calculations by Guo *et al.* This reflects much larger reactivity than that of the ground state where the threshold energy is 0.6 eV and the cross sections remain much smaller than in the excited-state. Similarly to the reaction of ground-state O₂ with H atoms, the basic assumptions of statistical rate theories are not fulfilled. In the H + O₂(¹Δ_g) reaction i) 80 of the trajectories cross the barrier region twice and are nonreactive, b) The energy is not equilibrated in the HO₂ potential well. The rate coefficient is given by $k_2 = 5.81 \times 10^{-16} T^{1.45} \exp(-18870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction of O₂(¹Δ_g). It is 4 or 5 orders of magnitude higher than for that of the triplet one at low, and by a factor of about 10 at high temperatures. The consequence is that if 10 % of oxygen is present in the form of O₂(¹Δ_g) in a flame, then the rate of the chain-branching step is doubled. We estimate that above 1500 K about 70% of the H + O₂(¹Δ_g) collisions results in electronic quenching and 30% in chemical reaction.

Introduction

The reaction of H atom with O₂ has been considered “the single most important” elementary reaction in combustion [1], because it is a chain-branching step present in every combustion system. The HO₂ intermediate can be collisionally stabilized at high pressures, under such condition the reaction is a chain-termination step. The reaction has been thoroughly studied both experimentally and theoretically [2-27], when O₂ is in its electronic ground state,



Much less is known about the reaction of the electronically excited molecular oxygen, O₂(¹Δ_g) with H atoms,



This reaction seems also to be feasible in the higher stratosphere and in high-temperature flames. Application of excitation of molecular oxygen to the singlet state has been proposed as a way to accelerate combustion [28]. Electronically excited oxygen will not necessarily be present in high concentrations in flames even at high temperatures, but it is produced in almost all oxygen-containing plasmas, because the singlet-triplet energy gap of O₂ is relatively low (94.5 kJ/mol) [29]. The radiative lifetime of O₂(¹Δ_g) is relatively long (>3800 s) [30], so that it can live long enough in flames to perturb the kinetics of combustion if it proves to be reactive enough. Both the experiments in which the reaction mixture was directed to pass through an electric discharge and the related combustion modeling studies [31-36] demonstrated that the concept works: the flame velocity was found to increase in the presence of electronically excited oxygen.

Several experimental studies [37-42] have been reported about the kinetics of the reaction of O₂(¹Δ_g) and hydro-

gen atoms. Early work [37,38] resulted in estimates of the rate coefficient. Schmidt and Schiff [39] followed the O₂(¹Δ_g) concentration to get the rate of loss due to collisions with H atoms at room temperature and obtained a rate coefficient of $2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Table 1 Experimental thermal rate coefficients for reaction R2 with or without nonreactive quenching (Q) in Arrhenius form (units: $10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$, kJ/mol)

Reaction	A	E _a	T / K	Ref.
R2+Q	1.46	16.75	300-423	[40]
R2 + Q	18.2	26.30	520-933	[41]
R2 + Q	6.55	21.03	300-933	[32]
R2	0.0183	13.00	299-423	[42]

The technique they used does not allow distinction between chemical reaction and physical quenching. Cupitt *et al.* [40] measured the rate at several temperatures between 300 and 430 K and argued that chemical reaction dominates in the process. The Arrhenius parameters they derived are shown in Table 1. Basevich and Vedenev [41] did similar experiments at higher temperatures (500-800 K). The corresponding Arrhenius parameters differ from those of Cupitt *et al.*, [40] the activation energy being more than 50 % higher. Several years later, Popov [31] combined the rate coefficients measured in both studies, and fitted an Arrhenius expression to the points to lying in fact along essentially the same line. The Arrhenius parameters he derived (Table 1) have been widely used in flame simulations. The latest reported experiments were performed by Hack and Kurzke [42] who showed that the rate of reac-

tion R2, with or without physical quenching, cannot be determined if only the concentration of the reactants is monitored. They derived the rate coefficients of the pure chemical step, R2 by following the concentration of H and O atoms as well as OH radicals and fitting a complex model including about 20 reactions to the measured data. The values they obtained in the temperature range of 299-423 K are smaller by about an order of magnitude than those measured by Cupitt *et al.* **Error! Bookmark not defined.** [40], indicating that the reactive rate is below 10% of the total rate of $O_2(^1\Delta_g)$ removal. Note that under the conditions of the Hack and Kurzke experiment, the possible loss of $O_2(^1\Delta_g)$ is negligible because of the small initial H atom concentration so that physical quenching, if occurs, does not influence of the radical concentration profiles.

Early theoretical studies assumed that the activation energy of the reaction of singlet molecular oxygen can be derived from that of the reaction of ground-state oxygen from a simple curve-crossing model [43]. This view seems to be oversimplified in the light of the recent calculations of the potential energy surface (PES) of the reaction by high-level electronic structure methods by Li *et al.* [44], indicating the presence of a barrier in the entrance channel. The most important properties of the PES of reaction R2 together with those of reaction R1 are summarized in Fig. 1.

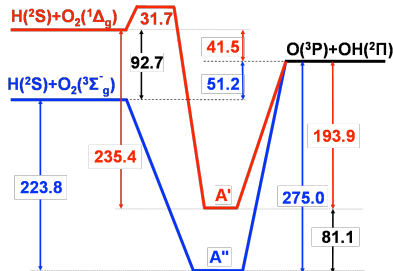


Fig. 1. The energies (in kJ/mol) of the stationary points of the potential energy surfaces of reactions (R1) (blue) and R2 (red).

The two potential surfaces are degenerate on the product $O + OH$ side. A deep potential well corresponds to HO_2 on both PES. However, while the reaction of $O_2(^3\Sigma_g^-)$ is endothermic and displays no barrier either in the entrance or the exit channel, the excited-state reaction is exothermic but there is a barrier in the entrance valley. This indicates that the dynamics and accordingly, the kinetics of the two reactions can be expected to show significant differences. An analytical potential energy surface (PES) for reaction R2 has been developed by Li *et al.* [44] (based on potential energies at some 17,000 points, made continuous with spline fit). Sections of the PES are shown in Fig. 2, plotted as a function of the location of the H atom in the triatomic plane with respect to the center of mass of the O_2 molecule. The O–O distance is set to: 1.1 Å, the inner turning point of the ground vibrational state of $O_2(^1\Delta_g)$, 1.2 Å, the equilibrium bond length of O_2 , 1.4 Å, the equilibrium O–O dis

tance in electronically excited HO_2 , and 1.8 Å which corresponds to an almost separate OH radical and an O

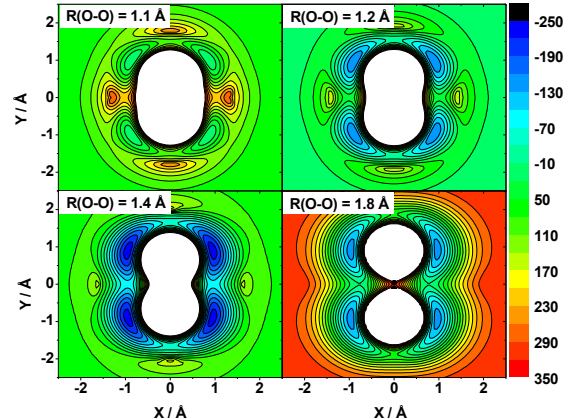


Fig. 2. The section of the potential energy surface for reaction R2 in the H-O-O plane as a function of the location of the H atom with respect to the center of mass of O_2 . O_2 is aligned along the y axis, its bond length is as specified on each plot. The unit of energy is kJ/mol.

atom. Note that the PES is cylindrically symmetric around the O–O axis.

Due to the presence of both a well (making possible the formation of long-lived complexes) and a barrier on the PES, the most reliable way of estimating the rate coefficient of the reaction is through reaction dynamics calculations. Using their PES Guo and coworkers performed accurate quantum mechanical calculations [45] to derive the basic dynamical properties of reaction R2 but only the ground vibrational and rotational state of $O_2(^1\Delta_g)$ was considered, so a reliable calculation of the thermal rate coefficient was not possible.

The purpose of the present work is to derive ab initio the thermal rate coefficient for reaction (1). To this end we extend the range of the initial conditions, in particular, the number of initial rotational states considered as compared with the earlier dynamics calculations to allow a reliable basis to thermal averaging at flame temperatures. We use the quasiclassical trajectory (QCT) methodology, which – after “calibration” against the existing quantum dynamical data – allows us not only to get the excitation functions needed for rate coefficient calculations, but also provides some insight into the dynamics of reactions on potential surfaces involving a deep potential well with an entrance but no exit barrier. To refine the calculated rate coefficients, we introduce a tunneling correction using the exact quantum mechanical excitation functions.

In the following, we first summarize the methodology together with the validation of the QCT method, and then focus on the dynamics and kinetics of reaction R2. This will be followed by a comparison of the microscopic dynamics of reactions R1 and R2.

Methods

The quasiclassical trajectory calculations were performed using an extensively modified version of the VENUS code. 2×10^5 trajectories were calculated at each collision energy. For the integration of Hamilton's equation of motion in Cartesian coordinates, the sixth-order Adams-Moulton predictor-corrector algorithm initiated by a fourth-order Runge-Kutta integrator was used. The step size of 0.1 fs was employed for integration. The conservation of the total energy was better than 0.05 kJ/mol. The initial H–O₂ separation was fixed at 9 Å. In the evaluation of trajectories we tested several commonly used techniques, including: 1. QCT: all reactive trajectories included in the calculation, 2. QCT-ZP: trajectories producing OH with smaller than 0 vibrational quantum number are discarded without replacement, 3. GW-QCT: trajectories are considered with a Gaussian weight depending on the distance of the final classical action variable of the product molecule from the nearest quantum state. We use the standard value of 0.05 for the width of the Gaussian “window.”

Results

Validation of QCT calculations.

Ma *et al.* [45] performed exact quantum scattering (EQ) calculations on the A' PES for O₂(¹Δ_g, $v=0, j=0$) at collision energies from 20 to 90 kJ/mol. We performed QCT calculations for the same conditions to evaluate the performance of the three ways of handling final vibrational states. The results are shown in Fig. 3. The QCT-ZP method considerably underestimates the EQ cross sections. The simple QCT and the GW-QCT methods provide very similar cross sections that match excellently those obtained in the exact quantum scattering calculation (except the sudden rise in the threshold region). We consider this a validation of the simple QCT and the GW-QCT methods and assume that it can be reliably used to predict the dynamical details of the reaction outside the region covered by the exact quantum mechanical method. Hereinafter only the results obtained with the GW-QCT method are presented.

Integral cross sections

The GW-QCT excitation functions for various vibrational states of O₂(¹Δ_g) are presented in Fig. 4. The integral cross sections are monotonic functions of the collision energy. The threshold energy is 28.9 kJ/mol at $v=0$ and $j=0$. The sum of this collision energy and the zero-point energy of the oxygen molecule is 38.1 kJ/mol, 6.4 kJ/mol higher than the entrance channel barrier (31.7 kJ/mol). This indicates that probably only a small fraction of trajectories pass the barrier at the price of zero-point violation, which is in agreement with the early position of the barrier. Investigation of the effect of vibrational excitation on the cross sections further supports the lack of vibrational nonadiabaticity of classical trajectories near the potential barrier. Vibrational excitation of O₂ to $v=1$ and $v=2$ reduces the threshold energy by only 3 and 4 kJ/mol, respectively. Furthermore, surprisingly, above the $v=0$ threshold up to E_{coll}

= 110 kJ/mol the reaction cross sections are smaller if O₂ is vibrationally excited. Rotational excitation of the singlet oxygen molecule up to $j=20$ does not change the cross sections except at collision energies very close

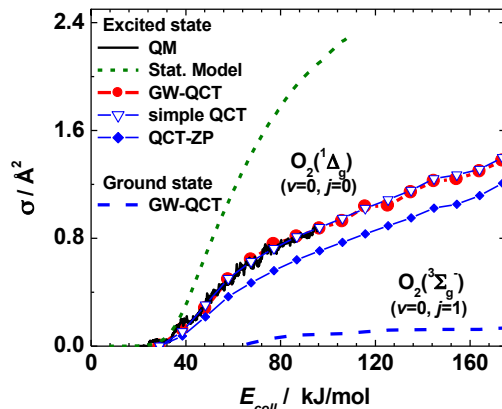


Fig. 3. Excitation functions for reactions R1 and R2 calculated with exact and statistical quantum mechanical as well as three versions of the quasiclassical trajectory method.

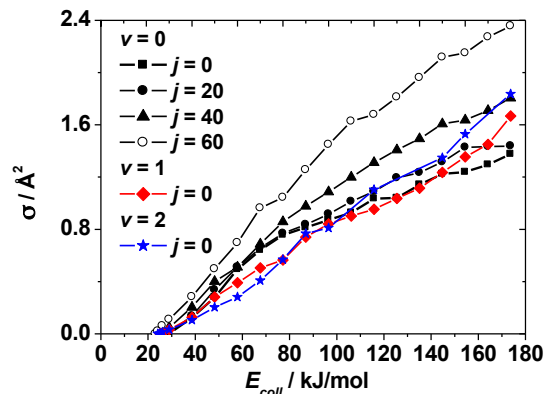


Fig. 4. Influence of vibrational and rotational excitation of the reactant O₂(¹Δ_g) on the excitation function of reaction R2.

to threshold, reducing the latter by about 1 kJ/mol. At higher excitation the threshold energy is further reduced with increasing j , by about 5 kJ/mol (wrt. the ground rotational state) at $j=40$ and 8 kJ/mol at $j=60$, and the cross sections are also larger at individual collision energies. The reduction of threshold is about 10 times smaller than the rotational energy indicating that the rotation of O₂ only marginally facilitates the system when crossing the barrier.

The threshold energy from exact quantum scattering calculations is 21.2 kJ/mol for the reaction of the vibrational ground state of O₂(¹Δ_g), above which the cross sections remain very small until the classical threshold energy where it starts to increase so that the EQ and QCT excitation functions in fact overlap. Considering this and the lack of zero-point energy violation, one can conclude that the reaction proceeds through tunneling at collision energies between 21 and 31

kJ/mol. Comparison with the excitation function calculated quantum mechanically for the reaction of O_2 in electronic ground state with H shows significant enhancement of the reactivity of O_2 towards H atoms by

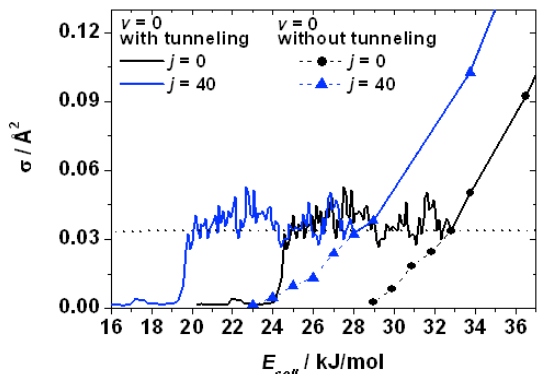


Fig. 5. Combined (QM + QCT) excitation functions used for tunneling correction at different rotational states of $O_2(^1\Delta_g)$ in the threshold region obtained by merging the classical and QM curves at cross section $\sigma = 0.0335 \text{ \AA}^2$ (indicated by a dotted straight line)

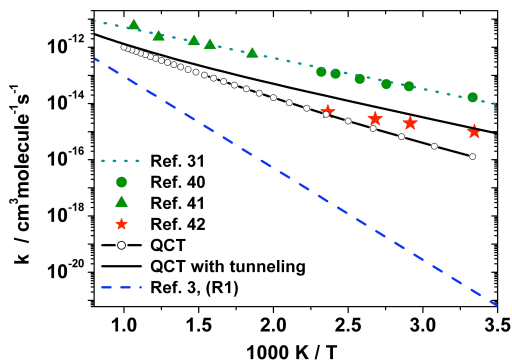


Fig. 6. Comparison of the experimental and calculated thermal rate coefficients reaction R2. The blue dashed line shows the data recommended by Baulch et al. [3] for reaction R1.

electronic excitation. The threshold energy for the reaction of triplet O_2 is 57.9 kJ/mol, much larger than in the excited state. In addition, the magnitude of the ground-state cross sections is smaller by about an order of magnitude at identical collision energies than the excited-state ones. Both these factors indicate that the reactivity of electronically excited O_2 towards H is much larger than that of triplet molecular oxygen and one can expect this will be reflected in the rate constants.

Thermal Rate Coefficients

The rotational and vibrational state-resolved reaction rates were calculated from the excitation functions at $v = 0, 1$, and for all even- j rotational states of O_2 from $j = 0$ to $j = 60$. (Note that $O_2(^1\Delta_g)$ has only even quantum states due to nuclear symmetry.) These very large rotational quantum numbers are needed when thermal averages of j -specific rate coefficients are calculated: Due to the large moment of inertia of O_2 , the Boltzmann weight

of the highly excited rotational states is not negligible at flame temperatures. For example, above 1000 K the population of rotational levels is significant up to $j = 60$.

At room temperature, rotational excitation of the oxygen molecule to $j = 40$ increases the rate coefficient by a factor of 5.6 which drops to 1.6 at 1000 K. The j -averaged rate coefficients are close the value of the rate of $j = 10$ at all temperatures, and are larger than the $j = 0$ values by a factor of 1.6 at 300 K and 1.2 at 1000 K.

Vibrational excitation of O_2 slightly reduces the reaction cross-section and, accordingly, slows down the reaction. This minor hindrance is only observable around 1000 K where the $v = 1$ state of O_2 has appreciable Boltzmann-weight.

To obtain more reliable thermal rate coefficients, we introduce a tunneling correction of the vibrationally and rotationally resolved excitation functions as follows: For the reaction of the vib-rotational ground state of $O_2(^1\Delta_g)$, the EQ excitation function was used between $E_{\text{coll}} = 22$ kJ/mol (the EQ threshold) and 32.8 kJ/mol where it crossed first the QCT one (at $\sigma = 0.0335 \text{ \AA}^2$). Above that energy the QCT cross sections were used in the rate coefficient calculation. For the description of tunneling at higher j and v , the same fragment of the quantum scattering excitation function was applied in a similar way to modify the classical excitation function (Fig. 5). Below that energy the QCT cross sections were replaced by the EQ ones.

The tunneling corrected thermal reaction rate coefficient averaged over the Boltzmann distribution of initial rotational and vibrational states is shown in Fig. 6 together with the experimental data. The rate coefficient including the tunneling correction as described above is (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) 1.34×10^{-15} at 300 K, 1.31×10^{-12} at 1000 K and 1.18×10^{-11} at 2000 K. The enhancement of the thermally averaged rate coefficients due to tunneling is a factor of 9.3 at 300K and 1.3 at 1000K. The calculated values are closer to the measured data of Hack and Kurzke [42] than to those of the experiments where reaction and electronic quenching was not separated. The deviation from the Hack and Kurzke rate coefficients is only a factor of 1.2 at the lowest and 3 at the highest measured temperature. The average Arrhenius activation energy (Table 1) for the rate constants thermally averaged over the initial states is 24.4 kJ/mol, larger than that proposed by Hack and Kurzke but is close to that derived by Popov [31] from the measurements including quenching and chemical reaction.

Comparison of the rate coefficients for reactions of R1 and R2 shows that electronic excitation enhances the reactivity of O_2 towards H. At low flame temperatures the rate coefficient for reaction of excited $O_2(^1\Delta_g)$ is 4 or 5 orders of magnitude higher than for $O_2(^3\Sigma_g^+)$, while at 1000 and 2000 K the difference is a factor of about 13 and 3, respectively. This is in good agreement with the observation that the presence of $O_2(^1\Delta_g)$ speeds up flame propagation. If one accepts that the rate coefficients measured by Cupitt *et al.* [40] and by Basevich and Vedenev [41] include both reactive and nonreactive quenching, then from the ratio of these experimental

rate constants (interpolated using the formula derived by Popov) to those derived from the QCT calculations one can estimate that nonreactive quenching is 3 to 12 times faster than the chemical reaction.

It is interesting to note that as long as the conditions in flames ensure thermal equilibrium between ground-state and singlet molecular oxygen, the population of the latter is about 0.1%, 0.6% and 1.9% at 1500, 2000 and 2500 K, respectively. As long as these equilibrium populations hold in shock tubes where the experimental rate coefficients for R1 were obtained, the measured data contain respectively a 0.5%, 1.9% and 4.7% contribution from R2. This is much smaller than the experimental error bar, so there is no need to make a correction. It can also be noted that, although at high temperatures the contribution of R2 to the thermal average rate of R1 and R2 increases quickly (it would achieve 30% at 5000 K), it will never be larger than that of R1 because at high temperatures the latter is also very fast.

Microscopic mechanism

To understand the details of the dynamics, we monitored trajectories that enter the deep part of the potential well, i.e. in which H and O₂ form a complex. To this end we recorded the trajectories that access the region of the configuration space where the potential energy is one half of the dissociation energy of the complex to O + OH (138 kJ/mol below the reactant level). The number of collisions getting into this region will provide a very conservative estimate on the rate of complex formation. By following the trajectories after capture one can tell apart reactive and nonreactive captured trajectories. The cross section of complex formation is plotted against the collision energy in Fig. 7. The threshold for entering the potential well is the same for reactive and nonreactive collisions and the ratio of reactive to complex-forming nonreactive cross sections remains constant when the collision energy increases. About four times more trajectories leave the complex in the reactant direction towards products. This means that about 80% of trajectories cross the barrier at least twice, once from the reactant side and once in the opposite direction (the chance of passing it more than twice is negligible). This holds not only at high collision energies but also in the threshold region. Based on this one can conclude that one of the basic assumptions of transition state theory, the existence of a “point of no return” is not fulfilled for this reaction: One can not find, even microcanonically, a dividing surface in the barrier region that satisfies the condition that no trajectory crosses it more than once.

For comparison, we also investigated the role of complex formation and the ratio of reaction to re-dissociation for the ground-state reaction. What is common in both the ground- and excited state is that, for reaction to occur it is necessary that the system enters the potential well. One of the major differences is that in the ground state the exit channel is 51.2 kJ/mol above the entrance well, which means that below that energy all collisions entering the well will be nonreactive. As Fig. 9 shows, the fraction of collisions in which

the system gets out of the well in the product direction depends significantly on the energy in excess to the

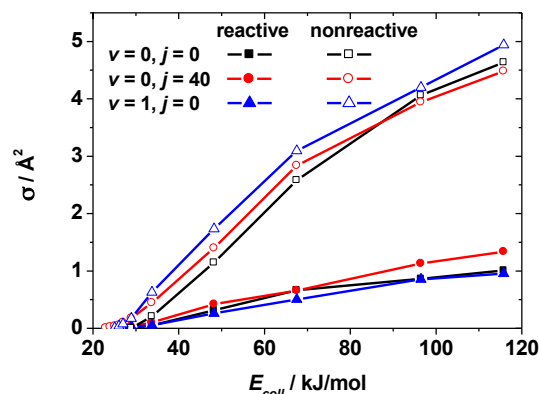


Fig. 7. Cross sections characterizing complex formation by H and O₂(¹Δ_g). See text for details.

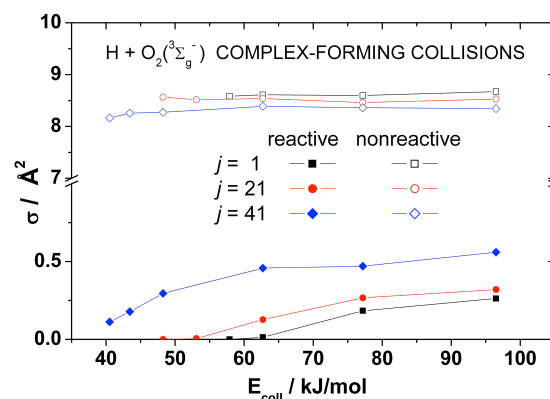


Fig. 8. Cross sections characterizing complex formation by H and O₂(³Σ_g⁻). Note the axis break and the scale change.

reaction energy. Close to threshold the reactive fraction is negligible, which qualitatively conforms the expectations based on a statistical model. At large excess energies about 5% of all complexes is reactive, which seems not to increase further. Several differences between reactions R1 and R2 are observable. First, in reaction R1 much more collisions are nonreactive than in R2. This can be understood taking into account that the reaction of triplet O₂ is endothermic, that of the singlet is exothermic. Second, in reaction R1 the rotational excitation significantly reduces the threshold energy not only for reaction (see also Refs. 46 and 47) but also for complex formation, while in R2 the reduction is very small. The reason for the difference is that in reaction R1 the conversion of rotational energy to the O–O stretch is more efficient than in R2. Third, in reaction R1 the cross section the contribution of the reaction increases at the price of the reduction of the nonreactive fraction of complex-forming collisions, because of the lack of a barrier for complex formation. In reaction R2, on the other hand, rotational excitation tends to increase the magnitude of both the reactive and nonreactive complex formation cross sections.

Summary

The reaction of H atoms with e $O_2(^1\Delta_g)$ is significantly faster than with ground-state $O_2(^3\Sigma_g^+)$. The reaction still seems to be slower than nonreactive quenching of $O_2(^1\Delta_g)$ by H atoms. The rate coefficient of reaction R2 can be described by the modified Arrhenius expression $k_2 = 5.81 \times 10^{-16} T^{1.45} \exp(-18870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The complex formed in the reaction was shown not to behave statistically.

Acknowledgements

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