Dissociation Rate Coefficient of Oxygen for $O_2 + O$ Reaction*

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Key Words: Molecular Dissociation, Physical-Chemical Kinetics, High-Enthalpy Flows, Oxygen

1. Introduction

Thermal-chemical nonequilibrium processes in gases appear in the flowfield around hypersonic vehicles, so it is necessary to predict the processes when designing such vehicles. In the theoretical approach, microscopic physical-chemical kinetics using state-to-state rate coefficients is believed to be the most reliable method.^{1,2)}

The $O_2 + O \rightarrow 3O$ dissociation reaction is one of the processes, and is composed of multiple state-to-state processes. When rotational equilibrium is assumed, the microscopic processes are described as $O_2(n, v) + O(n') \rightarrow 3O$, where n and v are the quantum numbers for the electronic and vibrational states, respectively. Thus, all the state-to-state rate coefficients for the processes are essentially needed to calculate the dissociation reaction using microscopic kinetics.

Meanwhile, the O_3 collision system has multiple electronic states and corresponding potential energy surfaces (PESs). There are nine electronic states of the system that degenerate to the $O_2(^3\Sigma_g^-, v) + O(^3P)$ asymptote as the distance between the O_2 molecule and the O atom increases: $1^{\mu}A'$, $2^{\mu}A'$ and ${}^{\mu}A''$ ($\mu = 1, 3, 5$), where μ is the spin multiplicity of the system. Thus, the $O_2(^3\Sigma_g^-, v) + O(^3P)$ collision, which plays an important role in the $O_2 + O$ collision, involves these multiple electronic states; and hence, these electronic states must also be known to calculate the collision process.

In view of these needs, the author³⁾ has constructed a model for the nine PESs on the basis of *ab initio* molecular orbital computation. Then, the vibrational transition rate coefficients for the $O_2 + O$ collision were calculated using quasi-classical trajectory (QCT) method and this potential model.

As for the $O_2 + O \rightarrow 3O$ dissociation reaction, the dissociation rate coefficient in a temperature range up to 10,000 K was calculated by Esposito and Capitelli⁴⁾ using QCT method. In their calculation, only a single PES for the ground electronic state of the O_3 collision system, the $1^1A'$ state, was considered.

This note presents the dissociation rate coefficient calculated on the basis of the potential model for the multiple PESs constructed in the author's previous study.

2. Methods

The potential model used in this study was constructed in the previous study as follows.³⁾ The PESs were computed using the GAMESS *ab initio* molecular orbital method package⁵⁾ on the basis of the cc-pVTZ basis set: the CASSCF method was used to compute electronic wave functions including static electron correlation, and the MCQDPT method was used to include dynamic electron correlation. An analytic model for the PESs was constructed to fit PES values computed to an analytical function proposed by Aguado and Paniagua.⁶⁾

In molecular collision, electronic transition among the electronic states of the collision system may occur during the collision process. This results in electronic excitation of the colliding molecules. Thereby, for the $O_2 + O$ collision, electronically excited O_2 molecules are produced, and dissociation from the excited electronic states proceeds in addition to that from the ground electronic state. In this study, the $O_2 + O$ dissociation rate coefficient was calculated as follows, taking into account the contribution of electronic transition by Nikitin's correction.⁷⁾

First, a dissociation rate coefficient in the electronically adiabatic collision on each of the nine PESs was calculated using the QCT code applied in the previous study. Since rotational equilibrium is assumed for the QCT code, the dissociation rate coefficients calculated are vibrational-state-dependent. The dissociation rate coefficients thus obtained are described as $k_v^{[m]}(T)$, where T is temperature and the superscript indicates that this dissociation rate coefficient is obtained on the m -th PES. The temperature ranged from 2,000 K to 10,000 K at intervals of 1,000 K. For each of the PESs, a batch of 50,000 trajectories was computed at each temperature with a maximum impact parameter of 5 Å. These parameters were chosen on the basis of preliminary computations for the ground PES where the number of trajectories varied as 10,000, 50,000, 100,000, and 150,000, and the impact parameter varied as 3, 5, and 7 Å. The computation of a trajectory was terminated when two of the three internuclear distances in the O_3 collision system exceeded 5.1 Å. The O_2 molecule was considered to be dissociated when the internal energy after collision was above the dissociation energy of 5.21 eV. This means that the O_2 molecule in the quasi-bound states (QBSs) after collision was considered to be dissociated. More details on the QCT method are described in the previous paper.³⁾

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*Received 15 May 2015; final revision received 14 April 2016; accepted for publication 20 July 2016.

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Next, the dissociation rate coefficient for dissociation from the electronic ground state was calculated using

$$k_v(T) = \sum_{m=1}^9 w_m k_v^{[m]}(T), \quad (1)$$

where w_m is the statistical weight corresponding to the degeneracy of the electronic state of each PES. The statistical weight for the ground electronic state w_1 is 1/27, for example. More details on Eq. (1) are described in the previous paper.³⁾

Then, using the vibrational-state-dependent dissociation rate coefficient of Eq. (1), the dissociation rate coefficient in vibrational equilibrium (namely, the thermal dissociation rate coefficient) for dissociation from the electronic ground state was calculated using

$$k(T) = \sum_v \rho_v(T) k_v(T), \quad (2)$$

where ρ_v is the vibrational Boltzmann distribution function. Substituting Eq. (1) into Eq. (2) gives

$$k(T) = \sum_{m=1}^9 w_m k^{[m]}(T), \quad (3)$$

where

$$k^{[m]}(T) = \sum_v \rho_v(T) k_v^{[m]}(T) \quad (4)$$

Finally, the contribution of electronic transition was taken into account applying the approximate correction proposed by Nikitin.⁷⁾ In this correction, the dissociation rate coefficient for dissociation from the ground electronic state (Eq. (3)) is multiplied by a factor based on the degeneracies of the electronic states. For the $O_2 + O$ dissociation, the factor is determined to be 16/3.⁷⁾ Thus, the corrected dissociation rate coefficient was obtained using

$$k^{corr}(T) = \frac{16}{3} k(T). \quad (5)$$

When a gas containing O_2 is heated, O_2 molecules in the ground electronic state are vibrationally excited, and subsequently dissociate into O atoms. The dissociation comes mainly from highly excited vibrational states near the dissociation limit. The dissociation limit of the O_2 molecule is 5.21 eV above the ground electronic level, whereas the first excited state is 0.98 eV above the ground state. In addition, the O_2 molecule has five excited electronic states that have the same dissociation limit as that of the ground states.^{7,8)} The electronic levels of these excited states are below the dissociation limit. These excited electronic states are populated by transition with small energy transfer between higher vibrational states in the ground electronic state and lower ones in the excited electronic states. Therefore, dissociation from these excited electronic states proceeds in addition to that from the ground state. As a result, dissociation proceeds, producing O atoms in the ground electronic state with O_2 molecules vibrationally and electronically excited.

For the dissociation process of O_2 molecules mentioned above, Nikitin assumed that the ground and excited elec-

tronic states of the O_2 molecule are in equilibrium during the dissociation process. On the basis of this assumption, the dissociation rate coefficient is calculated as in Eq. (2) using the electronic Boltzmann distribution function and the dissociation rate coefficients from each electronic state. Nikitin estimated the dissociation rate coefficients from the excited electronic states, and thus obtained Eq. (5) as the result. More details on Nikitin's correction are described in Nikitin.⁷⁾

Equation (3) was calculated using the potential model for the electronic states of the O_3 collision system that correlates with the $O_2(^3\Sigma_g^-) + O(^3P)$ asymptote. Therefore, the dissociation rate coefficient calculated in this study is for dissociation by collision with O atoms in the ground electronic state. Meanwhile, the ground electronic state of the O_2 molecule correlates with that of the O atom. Therefore, in the calculation of Eq. (3), O_2 molecules dissociate into O atoms in the ground electronic state. On the other hand, electronically excited O atoms are populated by the O + O collision.^{9,10)} The O_2 molecule has an excited electronic state whose electronic level is 0.96 eV above the dissociation limit of the ground state.⁸⁾ O_2 molecules in this excited state are formed by non-adiabatic transition, where a repulsive electronic state of the colliding O atoms changes to a binding one. Subsequently, O_2 molecules in this excited electronic state dissociate, producing O atoms in the first excited state. However, since the excitation energy (0.96 eV in one collision) in this process is much larger than those for the vibrational excitation and dissociation (it is noted that the dissociation energy of 5.21 eV is not an energy transferred in one collision), the rate coefficient for the excitation of O atoms is much smaller than those for the vibrational excitation and dissociation. This results in small population for the first excited state of the O atom. Therefore, the contribution of O atom excited states to the dissociation rate coefficient was assumed to be negligible compared to that of the ground state.

3. Results and Discussion

Figure 1 shows dissociation rate coefficients calculated using Eq. (4) for the singlet PESs ($1^1A'$, $2^1A'$ and $1^1A''$) of the nine PESs. The error bars show 2σ errors arising from Monte Carlo integration in the QCT computation. We can see that there is little difference among the three PESs. Just like the singlet PESs, there was also little difference among all nine PESs. It is known that only the $1^1A'$ PES has a different characteristic from the other PESs: the $1^1A'$ PES has a potential well of about 1 eV and the other PESs are globally repulsive.^{3,11)} However, in a region where the intermolecular distance is short, all the PES are simply repulsive including the $1^1A'$ PES. These results indicate that the dissociation is dominated by the repulsive region of the PESs, and hence all the dissociation rate coefficients take almost the same value. It should be noted here that Eq. (3) approximately reduces to

$$k(T) \approx k^{[1]}(T) \quad (6)$$

in this case because the summation of w_n equals unity.

Fig. 1. Thermal dissociation rate coefficient calculated using Eq. (4) for singlet PESs.

Fig. 2. Comparison of the thermal dissociation rate coefficients.

Figure 2 shows dissociation rate coefficients calculated using Eq. (3) and Eq. (5). In this figure, a prediction using the Park model¹²⁾ and a calculation by Esposito and Capitelli⁴⁾ are also shown for comparison. The Park model is semi-empirical and based on shock tube experiments. Esposito and Capitelli calculated the dissociation rate coefficient on the basis of Eq. (6) using a potential model¹³⁾ for the $1^1A'$ ground electronic state. A similar correction to Eq. (5) was also applied in their calculation. It can be seen that the present calculation using Eq. (3) is smaller than the prediction using the Park model throughout the temperature range: deviations are about 10, 4.5 and 2.8 times at 2,000 K, 5,000 K and 10,000 K, respectively. Therefore, the deviation increases as the temperature decreases. This is because QCT method tends to underestimate rate coefficients at low temperatures where quantum effects such as tunneling become dominant for dissociation.¹⁴⁾ On the other hand, the present calculation with the correction agrees well with the prediction using the Park model and the calculation by Esposito and Capitelli. This result indicates that it is quantitatively important to take into account the contribution of electronically excited O_2 molecules to the $O_2 + O$ dissociation. In contrast, since both of these calculations are based on the contribution of electronically ground O atoms, that

of electronically excited O atoms is negligible over the present temperature range.

4. Conclusion

This study presented the dissociation rate coefficient for the $O_2 + O \rightarrow 3O$ reaction calculated on the basis of the multiple PESs involved in this reaction.

There was little difference among the contributions of each of the PESs to the dissociation rate coefficient for dissociation from the ground electronic state. Taking into account the contribution of electronically excited O_2 molecules to $O_2 + O$ dissociation was quantitatively important, whereas that of electronically excited O atoms was negligible over the present temperature range.

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Associate Editor