State-to-State Dynamics of H + O₂ Reaction, Evidence for Nonstatistical Behavior

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The reaction between H(^{2}S) and O$_2$($^3\Sigma$) to form HO($^2\Pi$) and O(^{3}P) is a prototype complex-forming reaction dominated by a HO$_2$(X^2A'') potential well ~2.4 eV below the H + O$_2$ asymptote. It has attracted intense interest over the years as "the single most important combustion reaction" because of its role in chain branching ignition.[1] The reverse reaction is also of considerable interest in atmospheric and interstellar chemistry. One of the long-standing controversies[2,3] concerning this reaction is to what extent its dynamics can be described by a statistical model,[4] in which the reaction intermediate is so long-lived that it decays evenly into all open channels, rendering dynamics unimportant. Resolving this controversy will help us to gain a deeper understanding of other complex-forming reactions.

A complete characterization of the title reaction has not been achieved experimentally, mainly because of the small cross section resulting from its large endothermicity (~0.7 eV). Although the rate constant and total cross section are known,[5,6] only a few experimental studies have reported state resolved scattering attributes.[7−12] In particular, information on the product angular distribution is mostly inferred and incomplete.

The experimental difficulties underscore the need to characterize the reaction dynamics theoretically. However, such efforts have also been fraught with complications, despite the simple appearance of the reaction. In addition to difficulties in constructing an accurate global potential energy surface (PES) suitable for scattering calculations,[13,14] the treatment of the reaction dynamics is nontrivial. For instance, the traditional quasi-classical trajectory (QCT) method is quite arbitrary in determining the fate of reactive trajectories emerging in the product channel with internal energies less than the OH zero-point energy (ZPE ~0.23 eV).[2,15] On the other hand, a quantum mechanical (QM) solution of the scattering problem requires a huge basis due to the deep well, heavy masses, and the long-range interaction potential in the product channel.[16−22] Converging the reactive cross section also involves a large number of partial waves, thanks to the barrierless nature of the reaction path.[16,23−26] So far, the only converged QM state-to-state cross sections for the H + O$_2$ reaction have been reported using a time-independent method at energies just above the threshold.[24] Due to steep scaling laws, the extension of the time-independent QM calculations to higher energies is extremely expensive, if not impossible.

Here, we report converged state-to-state differential and integral cross sections (DCSs and ICSs) for the H + O$_2$($v = 0$, $j = 1$) → OH($v' = 0$, j') + O reaction up to 1.1 eV of collision energy. These calculations were made possible by using an efficient wave packet method, which has much more favorable scaling laws than the time-independent approach. The fully state-resolved DCSs reported here represent, to our best knowledge, the most extensive QM dynamics calculations by far for any triatomic system, and they allow a detailed characterization of the reaction dynamics, including the statistical nature of the reaction.

The scattering calculations were performed on an improved version of the original Xu−Xie−Zhang−Lin−Guo (XXZLG) PES for the ground (X^2A'') state of HO$_2$,[27] which correlates adiabatically to both the reactants and products of the title reaction. Although the earlier XXZLG PES allowed the convergence of ICSs,[26] it had trouble converging the DCSs, due to small artifacts related to the anisotropy in the OH + O asymptotic region. We have hence recalculated the potential energies in this region using a denser angular grid which generated better initial guesses for the *ab initio* calculations. The new PES is much smoother in the OH + O channel and yields converged DCSs. The *ab initio* calculations were performed at the multireference configuration interaction (MRCI) level with a large correlation-consistent basis set, as discussed in our earlier work.[27]

The time-dependent wave packet propagation for extracting S-matrix elements was carried out in reactant Jacobi coordinates to take advantage of the permutation symmetry of the O$_2$ reactant. The method is based on our earlier work,[28] but new improvements detailed in ref 29 reduced the computational effort to ~$^1/_5$. The technical details of the calculations are given in the Supporting Information (SI). Briefly, 51 partial waves were included to converge the cross sections to 1.1 eV of collision energy.
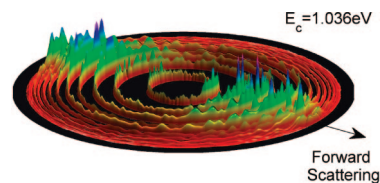
Figure 1. Polar plot of the differential cross section for the H + O$_2$($v = 0$, $j = 1$) reaction at 1.036 eV of collision energy.

Figure 1 displays in polar coordinates the QM DCS for the title reaction at 1.036 eV. It is clear that the product angular distribution is dominated by scattering in both the forward and backward angles,

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consistent with the complex-forming mechanism. Thanks to the relatively large rotational constant of the OH product, these plots show clear rotational state resolution which might be detectable experimentally. Interestingly, the DCSs are not entirely symmetrical with respect to the forward and backward directions, and the asymmetry varies with the collision energy (see SI). These observations are in qualitative agreement with the earlier experimental data based on Doppler profiles of OH laser-induced fluorescence studies.[12]

The rotational state distribution of the $OH(v' = 0)$ product is shown in Figure 2. (Higher product vibrational channels are closed at these energies.) It is apparent from these figures that the OH product is highly excited in the rotational degree of freedom. In particular, the rotational state distribution increases monotonically with the rotational quantum number (j') and peaks near the highest allowed rotational state. Such behavior is consistent with the complex-forming mechanism and with earlier experimental observations.[7−9] As shown in the figure, the agreement with the only experiment in our energy range[8] is reasonably good.
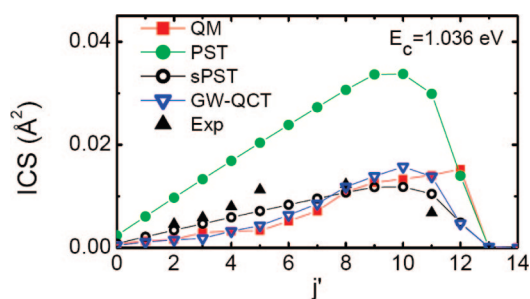
Figure 2. Comparison of the QM rotational state distribution of OH (■) with the PST results (●), GW-QCT results (▼), and available experimental data (▲). The PST result normalized to the QM distribution (sPST) is also presented (○).

In Figure 2, the QM rotational state distribution is also compared with that obtained from the Gaussian weighted QCT (GW-QCT) method.[30] Unlike the traditional QCT in which a square window was used to bin the trajectories, a Gaussian weighting function with a width of 0.05 was used here to determine the final state distributions. The result is in surprisingly good agreement with the QM distribution (except for $j' = 12$), as shown in Figure 2. An equally impressive agreement for both ICS and DCS was found at all energies. These results highlight the importance of the proper treatment of the ZPE in QCT studies of reaction dynamics.

To examine the statistical nature of the title reaction, we compare the QM rotational state distribution with the statistical limit represented by the phase space theory (PST),[4,25] which assumes that the formation and decay of the reaction intermediate are separate events and the decay probability is proportional to the number of open channels. The details of the PST model used here are given in the SI. As shown in Figure 2, the shape of the PST distribution is similar to that of the QM counterpart; namely it increases with j' until the highest accessible rotational state. However, the statistical model severely overestimates the QM distribution, as observed before.[25] Even when comparing with the normalized PST distribution, as shown in the same figure, the QM distribution typically overpopulates at large j' values and under-populates at small j' values. As shown in the SI, similar differences exist in other collision energies. Interestingly, this trend has previously been observed experimentally at even higher collision energies[7−9] and was taken as an indication that the reaction is not entirely statistical.

The deviation of the QM rotational state distribution from the statistical limit is a convincing piece of evidence in support of the argument that the title reaction has a significant nonstatistical component despite its complex-forming nature. In other words, the dynamics plays a non-negligible role in the reaction. This conclusion is consistent with the slight forward−backward asymmetry of the calculated DCSs reported here and the nonstatistical decay of the HO_2 complex observed in QCT studies.[31−33] The origin of the nonstatistical behavior can presumably be attributed to the relatively short lifetime of the HO_2 intermediate. Indeed, our QM results showed that the reaction flux maximizes near 400 fs, and 95% of the flux has exited the interaction region within a picosecond. Apparently, the lifetime is too short for the HO_2 complex to completely lose its memory and behave statistically. To summarize, the title reaction could be considered as an intermediate case between the fast direct reaction regime and the statistical limit. It is our hope that the theoretical predictions reported here will stimulate further experimental studies of this important reaction.

Supporting Information Available: Details about the methods used in this work and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Miller, J. A.; Kee, R. J.; Westbrook, C. K. *Annu. Rev. Phys. Chem.* **1990**, *41*, 345.
(2) Miller, J. A. *J. Chem. Phys.* **1986**, *84*, 6170.
(3) Harding, L. B.; Maergoiz, A. I.; Troe, J.; Ushakov, V. G. *J. Chem. Phys.* **2000**, *113*, 11019.
(4) Pechukas, P.; Light, J. C. *J. Chem. Phys.* **1965**, *42*, 3281.
(5) Shin, K. S.; Michael, J. V. *J. Chem. Phys.* **1991**, *95*, 262.
(6) Abu Bajeh, M.; Goldfield, E. M.; Hanf, A.; Kappel, C.; Meijer, A. J. H. M.; Volpp, H.-R.; Wolfrum, J. *J. Phys. Chem. A* **2001**, *105*, 3359.
(7) Kleinermanns, K.; Linnebach, E. *J. Chem. Phys.* **1985**, *82*, 5012.
(8) Kleinermanns, K.; Linnebach, E.; Pohl, M. *J. Chem. Phys.* **1989**, *91*, 2181.
(9) Bronikowski, M. J.; Zhang, R.; Rakestraw, D. J.; Zare, R. N. *Chem. Phys. Lett.* **1989**, *156*, 7.
(10) Rubahn, H.-G.; van der Zande, W. J.; Zhang, R.; Bronikowski, M. J.; Zare, R. N. *Chem. Phys. Lett.* **1991**, *186*, 154.
(11) Kim, H. L.; Wickramaaratchi, M. A.; Zheng, X.; Hall, G. E. *J. Chem. Phys.* **1994**, *101*, 2033.
(12) Fei, R.; Zheng, X. S.; Hall, G. E. *J. Phys. Chem. A* **1997**, *101*, 2541.
(13) Pastrana, M. R.; Quintales, L. A. M.; Brandão, J.; Varandas, A. J. C. *J. Phys. Chem.* **1990**, *94*, 8073.
(14) Kendrick, B.; Pack, R. T. *J. Chem. Phys.* **1995**, *102*, 1994.
(15) Varandas, A. J. C. *J. Chem. Phys.* **1993**, *99*, 1076.
(16) Zhang, D. H.; Zhang, J. Z. H. *J. Chem. Phys.* **1994**, *101*, 3671.
(17) Pack, R. T.; Butcher, E. A.; Parker, G. A. *J. Chem. Phys.* **1995**, *102*, 5998.
(18) Dai, J.; Zhang, J. Z. H. *J. Phys. Chem.* **1996**, *100*, 6898.
(19) Meijer, A. J. H. M.; Goldfield, E. M. *J. Chem. Phys.* **1998**, *108*, 5404.
(20) Meijer, A. J. H. M.; Goldfield, E. M. *J. Chem. Phys.* **1999**, *110*, 870.
(21) Lin, S. Y.; Guo, H.; Honvault, P.; Xie, D. *J. Phys. Chem. B* **2006**, *110*, 23641.
(22) Hankel, M.; Smith, S. C.; Meijer, A. J. H. M. *J. Chem. Phys.* **2007**, *127*, 064316.
(23) Goldfield, E. M.; Meijer, A. J. H. M. *J. Chem. Phys.* **2000**, *113*, 11055.
(24) Honvault, P.; Lin, S. Y.; Xie, D.; Guo, H. *J. Phys. Chem. A* **2007**, *111*, 5349.
(25) Bargueño, P.; González-Lezana, T.; Larrégaray, P.; Bonnet, L.; Rayez, J.-C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1127.
(26) Lin, S. Y.; Sun, Z.; Guo, H.; Zhang, D. H.; Honvault, P.; Xie, D.; Lee, S.-Y. *J. Phys. Chem. A* **2008**, *112*, 602.
(27) Xu, C.; Xie, D.; Zhang, D. H.; Lin, S. Y.; Guo, H. *J. Chem. Phys.* **2005**, *122*, 244305.
(28) Yuan, K.; Cheng, Y.; Liu, X.; Harich, S.; Yang, X.; Zhang, D. H. *Phys. Rev. Lett.* **2006**, *96*, 103202.
(29) Sun, Z.; Lin, X.; Lee, S.-Y.; Zhang, D. H. *J. Chem. Phys.*, submitted.
(30) Bonnet, L.; Rayez, J.-C. *Chem. Phys. Lett.* **1997**, *277*, 183.
(31) Miller, J. A.; Garrett, B. C. *Int. J. Chem. Kinet.* **1997**, *29*, 275.
(32) Miller, J. A.; Klippenstein, S. J. *Int. J. Chem. Kinet.* **1999**, *31*, 753.
(33) Lendvay, G.; Xie, D.; Guo, H. *Chem. Phys.* **2008**, *349*, 181.

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