Quasiclassical calculation of the chemical reaction Ba+C_3H_7Br→BaBr+C_3H_7*

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The quasi-classical trajectory (QCT) method based on the extended London–Eyring–Polanyi–Sato potential energy surface is used to investigate the product vibrational distribution, angular distribution and angle-resolved kinetic distribution of the reaction Ba+C_3H_7Br→BaBr+C_3H_7 at 2.58 kcal/mol. The calculated results show that the product BaBr vibrational distribution is quite hot, the vibrational population peaks are located at $\upsilon = 12$, and the angular product distribution tends to backward scattering. The calculated angle-resolved kinetic distribution shows that the kinetic distribution is obviously related to angle. The QCT results are always qualitatively acceptable and sometimes even quantitatively.

Keywords: quasi-classical trajectory, vibrational distribution, potential energy surface

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1. Introduction

Over the past dozen years, laser induced fluorescence (LIF) has made possible the detailed study of the reaction of alkaline earth metal atoms M with hydrocarbon halide

$$\mathrm{M} + \mathrm{RX} \rightarrow \mathrm{MX} + \mathrm{R}. \quad (1)$$

The analogous reaction was extensively studied.[1−6] Sigel and Schultz[1] studied reaction Ba+$CH_{4-n}H_n$ (n = 1, 2, 3, 4). They found that the product BaBr has a mainly reverse distribution of vibrational state. Recently, Han *et al.*[2,3,7−9] have done much experimental work, in which crossed molecular beams, laser induced fluorescence (LIF), are used, and they also performed some theoretical simulations for investigating the very high detailed dynamical features of the reaction like expression (1). In 1990, Han[2] used the LIF technique to study the reaction of Ca($^1S_0$) and Ca(^3P) with CH_2Cl_2 and $CHCl_3$, afterwards the similar instruments to probe the internal energy state of the nascent BaBr product formed in the reaction of barium atom with alkyl bromides. Recently, Han *et al.*[7] obtained the vibrational state distribution of the product for the title reaction by LIF, and found that product is mainly vibrationally hot, the vibration and rotation of BaBr account for over 36.2% and 16% of the overall available energy, respectively.

A great deal of experimental work has been done, however, only a little theoretical study has been conducted. To shed more light on the kinds of the reactions, the quasi-classical trajectory method is used to study the reaction of Ba with C_3H_7Br on the extended London–Eyring–Polanyi–Sato (LEPS) potential energy surface. To start with, a brief description of the theoretical method and the potential energy surface are presented, and then the results and discussion of the calculations are given.

2. Potential energy surface

The extended LEPS potential energy surface is employed in this calculation, and expressed as[7−10]

$$\begin{aligned} &V(r_1, r_2, r_3) \\ &= Q_1 + Q_2 + Q_3 \\ &\quad - (J_1^2 + J_2^2 + J_3^2 - J_1J_2 - J_1J_3 - J_2J_3)^{1/2}, \end{aligned} \quad (2)$$

where

$$Q_i = ({}^1E_i + {}^3E_i)/2, \quad (3)$$

$$J_i = ({}^1E_i - {}^3E_i)/2. \quad (4)$$

Here, ${}^1E_i$ is defined as the diatomic Morse potential function, and ${}^3E_i$ denotes the anti-Morse function. And they are expressed, respectively, as

$${}^1E_i = D_i(\{1 - \exp[-\beta_i(r - r_0)]\}^2 - 1), \quad (5)$$

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$$^3E_i = {}^3D_i(\{1-\exp[-\beta_i(r-r_0)]\}^2 - 1), \quad (6)$$

where

$$^3D_i = D_i(1-S_i)/2(1+S_i), \quad (7)$$

and S_i is an adjustable parameter (the so-called Sato parameter), D_i, β_i, and r_i represent the Morse parameters of the diatom. Subscript i = 1, 2, 3 indicates BaBr, BrR, and BaR, (R=C_3H_7) respectively. The parameters of D_i, r_0, and β_i for potential energy surface are cited from Ref. [7] for the title reaction, and the potential energy surface is constructed by adjusting S_i (i = 1, 2, 3). All the parameters are presented in Table 1.

Table 1. Parameters used in the LEPS potential energy surface of the Ba + C_3H_7Br reaction.

Species	D_e/eV	β/Å^{-1}	r_0/Å	S_i
Ba–Br[a]	3.72	0.947409	2.82	0.16
C_3H_7–Br[a]	2.458	1.6810	1.94	−0.269
C_3H_7–Ba[b]	1.71	3.5016[c]	2.71	0.49

3. Quasi-classical trajectory calculation (QCT)

The method of calculating quasi-classical trajectory is a standard method,[11,12] and this method is developed by Han *et al.* This method has also been adopted by other researchers.[13−15] The classical Hamilton's equations are integrated numerically for motion in three dimensions. In our calculations, 10^5 trajectories are sampled and the trajectory is initiated with the BrR molecule in the $\upsilon = 0$ and $j = 0$ levels. The integration step size in the trajectories is chosen to be 0.1 fs.

4. Results and discussion

The calculated and measured vibrational population distributions of the BaBr ground state are plotted each as a function of vibrational quantum number for the title reaction in Fig. 1. As can be seen from the comparison between the experimental vibrational state distribution[8] and theoretical one, it is clear that the vibrational population distribution is reasonably in agreement with the experimental one. However, there is a small discrepancy between the experimental result and the theoretical result. The calculated vibration population of the nascent product BaBr peak is located at $\upsilon = 12$, while the experimental vibrational population peak is located at $\upsilon = 11$. This slight difference between experiment and theory is ascribed to the technique of the code, in which the vibrational number is enlarged to the near neighbouring integer. It is also clear that the product BaBr is mostly reverse, similar to the precious results of the reaction Ba+ $CH_{4-n}H_n$ (n = 1, 2, 3, 4). The calculations of vibration and rotation of BaBr account for over 31% and 17% of the overall available energy, respectively, which qualitatively accord with the experimental results.

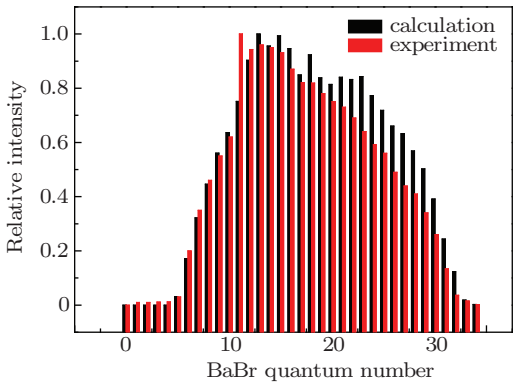


Fig. 1. (color online) Vibrational population distributions of the BaBr ground state.

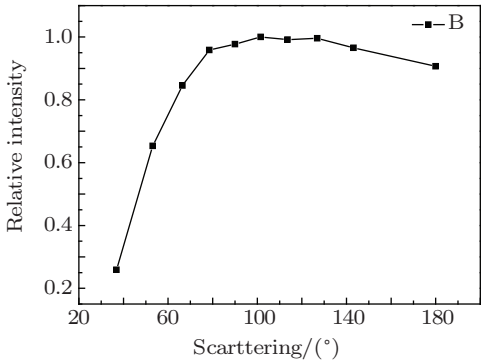


Fig. 2. Product angular distribution.

Figure 2 shows the product angular distribution. It is quite clear that the BaBr product in the title reaction is mainly backward scattered with respect to the Ba atom beam direction. From the angular distribution, it is obvious that the BaBr formation process proceeds primarily via a direct abstraction mechanism similar to the reaction Ca+CF3I in the present study. In order to validate our calculation, the polarization-dependent generalized differential cross section (PDDCS) $((2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t))$, which is proportional to the differential cross section (DCS) and

can predict the angular distributions of the molecular product, is calculated too. It is presented in Fig. 3. It is calculated using the improved code but the same potential energy surface, and the trend of the $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ is well consistent with the angular distribution in Fig. 2.

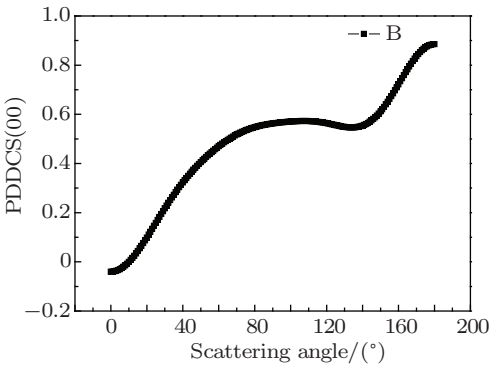


Fig. 3. The PDDCS.

Both the opacity function and the angular resolved kinetic distribution are calculated, and they are predictive, because no experimental data have been reported. It is clear that the relative reaction ability decreases as collision parameter increases. The max collision parameter is 4.53 Å and shown in Fig. 4.

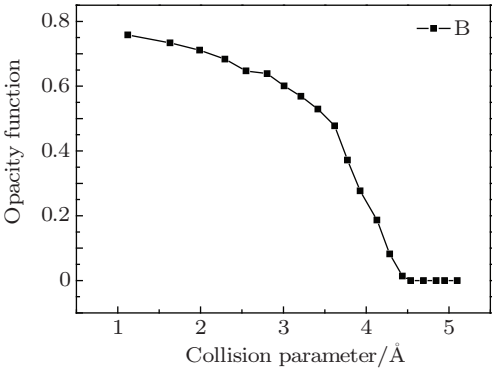


Fig. 4. Curve of the opacity function versus collision parameter (1 Å=0.1 nm).

It is very interesting to compare the angle resolved kinetic distributions in Fig. 5. From the kinetic distributions obtained theoretically, the kinetic distribution changes notably as angle varies, and the backward scattering products are noticeably different from the forward and sideways products. There is somewhat a trend that the probability peak increases as angle decreases. The maximal probabilities of the three different angles are 13.2 kcal/mol, 18.2 kcal/mol, 22.7 kcal/mol respectively, and their corresponding probabilities are 17%, 19%, and 31%.

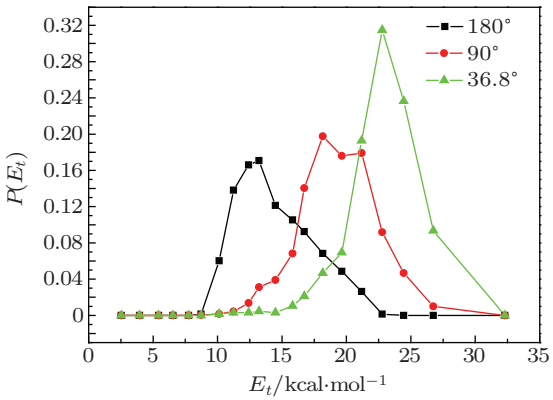


Fig. 5. (color online) Kinetic distribution changes under different angles.

5. Conclusion

In this paper, it is shown that the QCT calculations accord well with the experimental data for the reaction of Ba+C_3H_7Br. The calculation shows that the BaBr vibrational distribution is hot. The products of the title reaction are mostly of backward scattering, the BaBr formation process proceeds primarily via a direct abstraction mechanism. The opacity function and angular resolved kinetic distribution are also calculated for the prediction of the title reaction.

References

[1] Sigel A and Schultz A1980 *J. Chem. Phys.* **72** 6227
[2] Han K L, He G Z and Lou N Q 1991 *Chem. Phys. Lett.* **178** 528
[3] Han K L, He G Z and Lou N Q 1993 *Chem. Phys. Lett.* **203** 509
[4] Zhang X, Xie T X, Zhao M Y and Han K L 2002 *Chin. J. Chem. Phys.* **15** 169
[5] Wang M L, Han K L, Zhan J P, Wu V, He G Z and Lou N Q 1997 *J. Chem. Phys.* **278** 307
[6] Cai M Q, Zhang L, Tang B Y, Chen M D, Yang G W and Han K L 2000 *Chem. Phys.* **255** 283
[7] Han K L, Mo Y X, He G Z and Lou N Q 1990 *Acta Physico-Chemica Sinica* **6** 376
[8] Han K L, Zheng X G, Sun B F and He G Z 1991 *Chem. Phys. Lett.* **181** 474
[9] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699
[10] Wang M L, Han K L and He G Z 1998 *J. Chem. Phys.* **109** 5446
[11] Porter R N and Raff M L 1976 *Dynamics of Molecule Collision* ed. W. H. Miller (New York: Plenum Press) Part B
[12] Truhlar D G and Muckerman J T 1976 *Atom–Molecule Collision Theory* ed. R. B. Bernstein (New York: Plenum Press) p. 505
[13] Yue X F 2012 *Chin. Phys.* B **21** 073401
[14] Ge M H and Zheng Y J 2011 C*hin. Phys.* B **20** 083401
[15] Li H, Zheng B, Yin J Q and Meng Q T 2011 C*hin. Phys.* B **20** 123401