Reaction Dynamics of $Ba+CH_3Br/HBr \rightarrow BaBr+CH_3/H$

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QCT calculations for reactions $Ba+CH_3Br$ and Ba+HBr on LEPS surfaces within $0.01 \leq E_{rel} \leq 3.0$ eV by comparison with available experimental data within $0.075 \leq E_{rel} \leq 2.31$ eV have been done. The reaction dynamics of both chemical reactions have been obtained and their mechanisms have been deduced. The difference of the reaction dynamics via stripping and migration have been graphically described. The H atom of HBr shows enormous contribution of migration in the reaction of Ba+HBr, though the volume of H is comparably much smaller.

The QCT (quasi-classical-trajectory) calculations,[1,2] in which the newtonian mechanics and quantized energy levels are applied, have been extensively used to study chemical reaction dynamics.[3] Dynamics of both reactions have been calculated on the respective potential energy surfaces (PESs),[4-6] which are constructed by parametricalized formula known as LEPS (London-Eyring-Polanyi-Sato).[7,8] The integral cross sections (σ_{BaBr}), mean scattering angles (ω_{BaBr}), fractions (F_t, F_v, and F_r) of the relative translational (E_{rel}), vibrational (E_v), and rotational (E_r) energies as functions of collisional energies have been obtained. The obtained PES is more reliable, if not only σ but also F_v and F_r are compared with experimental values. Part of the calculated results, especially F_v and F_r is clearly in good agreement with the experimental data (Table). The discrepancies of ca. 5-20% are still well acceptable under the consideration of the experimental uncertainties, especially at low $E_{rel} \leq 0.5$ eV. The PESs are attractive and possess well at (2.88, 2.08) and barrier at (3.50, 1.375) in Å for $Ba+CH_3Br$ and Ba+HBr respectively. The depth of the well is -1.4886 and -0.8897 eV, the height of the barrier is 0.0569 and 0.1049 eV relative to the reactants and products of both reactions respectively. They have no translational threshold (E_{th}) down to E_{rel} = 0.01 eV. Interactions as well as reaction dynamics of Ba with CH_3Br and HBr have been investigated.

Quite a lot of experiments for reactions of alkaline earth atoms with alkyl[4,5,9-14] or hydrogen bromides[15-17] by use of beam-gas or crossed beams have been done in recent years. But the experimental data for the product molecule BaBr as functions of E_{rel} should be as sufficient as possible and the range of E_{rel} should be as broad as possible, in order to make the comparison between the calculated and experimental results significant.

For $Ba+CH_3Br$: There are experimental values for σ_{BaBr} within $0.075 \leq E_{rel} \leq 0.2$ eV by Xu,[4] F_v and F_r within $0.13 \leq E_{rel} \leq 0.21$ eV by Munakata et al.[9,10] available. For Ba+HBr: There are σ_{BaBr} and F_v within $0.13 \leq E_{rel} \leq 0.5$ eV by Siegel and Schultz,[16] σ_{BaBr} within $0.13 \leq E_{rel} \leq 2.31$ eV by Wu[17] also available. Because different kinds of these experimental data cover rather broad range, the obtained QCT results as well as PESs under the full considerations of them can be rather reasonable. Our interest to see the influences of CH_3 and H of the molecular reactants during the interactions can be well answered.

Table The calculated and experimental values of F_v, F_r of $Ba+CH_3Br$ and Ba+HBr. In our calculations the internal energies of the reactants are chosen as v''=0 and j''=0, distances before the reactions $Ba+CH_3Br$ and Ba+HBr are 12 and 10 Å respectively, and total tried trajectories at each E_{rel} are 2000.

	$Ba+CH_3Br$				Ba+HBr		
	calculation		experiment		calculation		experiment
E_{rel}/eV	F_v/-	F_r/-	F_v/-	F_r/-	F_v/-	F_r/-	F_v/-
0.507	0.221	0.355	-	-	0.329	0.406	0.254^c
0.4	0.307	0.311	-	-	0.322	0.378	0.275^c
0.306	0.341	0.280	-	-	0.332	0.355	0.283^c
0.256	0.347	0.276	0.304^a	0.235^a	0.318	0.346	-
0.212	-	-	0.249^b	0.159^b	-	-	-
0.204	0.377	0.287	0.330^a	0.231^a	0.324	0.327	-
0.185	0.379	0.290	-	-	0.324	0.325	0.316^c
0.178	0.402	0.253	0.279^b	0.153^b	0.319	0.324	-
0.160	0.394	0.269	0.290^b	0.162^b	0.316	0.311	-
0.127	0.454	0.252	0.356^a	0.195^a	0.325	0.280	-
0.126	-	-	0.318^b	0.157^b	-	-	-
0.125	-	-	-	-	-	-	0.352^c
0.1	0.490	0.218	-	-	0.333	0.248	-
0.0956	0.493	0.220			0.333	0.242	0.364^c
0.0927	-	-	-	-	-	-	0.36^d
0.075	0.525	0.187	0.391^a	0.199^a	0.346	0.213	-

[a] Values are taken from ref. 4. [b] Values are taken from ref. 9 and 10. [c] Values are taken from ref. 16. [d] Value is taken from ref. 15.

There are in general 3 kinds of reaction dynamics: stripping, migration and rebound. In general the product molecules are scattered within $0° \approx \omega_{min} \leq \omega \leq 40°$ for stripping, $60° \approx \omega_{min} \leq \omega \leq 90°$ or $90° \leq \omega \leq \omega_{max} \approx 120°$ for migration, $120° \leq \omega \leq 180°$ for rebound. Coulomb interaction via electron jump (Harpoon mechanism) from a metallic atom to molecular reactant can also happen and be mixed with stripping and migration or rebound and migration during the reaction. For our cases is the mixture of stripping and migration.

Migration here means metallic atom Ba will come closer and interact with methyl or hydrogen atom of the reactant molecule first. Ba will then migrate to Br, before BaBr will be scattered as product. This phenomenon can be explained with the participation of charge transfer or electron jump: Because the electronegativity of H (2.2) or C (2.5) is not very different from that of Br (2.7), and that of Ba (1.0) is much smaller, the Ba can be easily positively charged after loosing one electron to H or C of CH_3Br or of HBr during the approach. Then positively charged Ba picks negatively charged Br up, after the negative charge has been transferred from CH_3 or H to Br. Such a phenomenon of electron jump during $Ba+CH_3Br$ is much more significant than during Ba+HBr. The highly vibrational excitation of BaBr can be induced more efficiently during the interaction after the electron jump from Ba to CH_3 or H than during the impulsive attraction between Ba and Br after the charge transfer from CH_3 or H to Br and migration.

The proportions of migration and stripping in both reactions

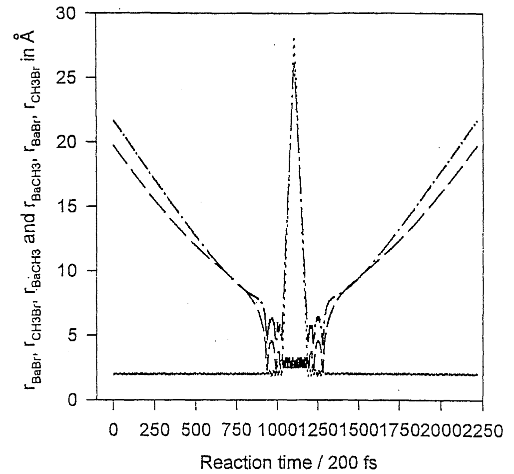

Figure 1. r_{BaBr} (— — —), r_{CH3Br} (- - - -), r_{BaCH3} (— - —) and r_{BaCH3} (— — —), r_{BaBr} (- - - -), r_{CH3Br} (— - —) in Å are the distances of the interaction pairs before and after the reaction of Ba+CH$_3$Br at E_{rel} = 0.01 eV respectively. They are plotted as the functions of the interaction time in fs. The first three are represented as the time of approach of the reactants Ba and CH$_3$Br. The reactants are transformed predominantly via stripping into the products BaBr and CH$_3$ at the time, where the maximum appears.

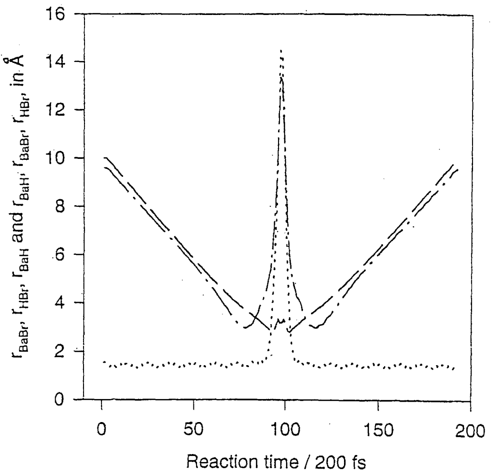

Figure 2. r_{BaBr} (— — —), r_{HBr} (- - - -), r_{BaH} (— - —) and r_{BaH} (— — —), r_{BaBr} (- - - -), r_{HBr} (— - —) in Å are the distances of the interaction pairs before and after the reaction of Ba+HBr at E_{rel} = 3.0 eV respectively. They are plotted as the functions of the interaction time in fs. The first three are represented as the time of approach of the reactants Ba and HBr. The reactants are transformed predominantly via migration into the products BaBr and H at the time, where the maximum appears.

are also different and dependent upon E_{rel}. For Ba+CH$_3$Br; Most of BaBr are scattered via stripping at 25° ≤ ω_{BaBr} ≤ 60° within 0.5 ≤ E_{rel} ≤ 2.0 eV, via stripping mixed with migration, i.e. partly also scattered at 70° ≤ ω_{BaBr} ≤ 90° within 0.01 ≤ E_{rel} ≤ 1.0 eV and 2.0 ≤ E_{rel} ≤ 3.0 eV. The fraction of BaBr via stripping to migration at E_{rel} = 0.01 eV is ca. 3/1. For Ba+HBr: Most of BaBr are scattered via migration at 70° ≤ ω_{BaBr} ≤ 90° within 0.05 ≤ E_{rel} ≤ 0.1 eV. The fraction of BaBr within 2.0 ≤ E_{rel} ≤ 3.0 eV via migration to those via stripping is ca. 1/1. The products within 0.01 ≤ E_{rel} ≤ 0.02 eV are scattered almost only via migration.

In order to see the significant difference in the reaction dynamics of the reactants via migration and stripping we have plotted two diagrams (Figure 1 and 2) with the diatomic distances as a function of the interaction time. We have chosen E_{rel} = 0.01 eV and 3.0 eV for Ba+CH$_3$Br and Ba+HBr respectively, because there are almost pure stripping as well as migration for Ba+CH$_3$Br and Ba+HBr at these E_{rel}. We can see Ba comes closer to CH$_3$ or H first, then migrates to Br and scattered as products during the interaction with the time around 205.6-237.4 (Figure 1) or 18.2-20.8 ps (Figure 2) for Ba+CH$_3$Br or Ba+HBr at E_{rel} = 0.01 or 3.0 eV respectively. The approach of Ba to CH$_3$ in Ba+CH$_3$Br via migration is not as significant as Ba to H in Ba+HBr. BaBr will be scattered before three atomic corpuscle rotates for one rotational period.

Both reactions run rather different: Only 20-30% of Ba+CH$_3$Br run via migration, on the contrary ca. 10-30% of Ba+HBr via stripping and only within 0.05 ≤ E_{rel} ≤ 1.0 eV. Although H is much smaller than Br or CH$_3$, the migration mechanism in Ba+HBr also contributes to the reaction dynamics and more predominantly than stripping within E_{th} ≤ 0.01 ≤ E_{rel} ≤ 0.5 eV. The very strong migration effect during Ba+HBr though only a little bit of exothermicity (= 0.032 eV comparing 0.717 eV for Ba+CH$_3$Br) causes also abnormally high vibrational levels (v' ≈ 4 comparing v' ≈ 30 for Ba+CH$_3$Br at E_{rel} = 0.01 eV) and vibrational distribution of products. BaBr from Ba+CH$_3$Br are reactively scattered into very high vibrational levels within 0.01 ≤ E_{rel} ≤ 0.5 eV, even the reactants interact together at an very large impact parameter, e.g. 12 Å (Figure 1) and very small E_{rel}. The potential well can be the reason to explain this phenomenon.

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