Quasi-classical trajectory study of the effect of reactant rotation in H(D) + HBr → H_2(HD) + Br reactions

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Received 27 March 1990

Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

The influence of the rotational state of reactants on the reaction cross-section of the two reactions: H + HBr → H_2 + Br and D + HBr → HD + + Br was studied by the method of quasi-classical trajectories. The results obtained are compared with the values calculated according to Sathyamurthy's relation for the rotational quantum number $J_{\min}$. We find good agreement between his predictions and the QCT calculations.

The QCT results were the basis for the analysis of the rotational and vibrational states of products and their dependence on J. The validity of the vibrational adiabaticity was confirmed for all cases followed and the effect of the rotational excitation of reactants on the rotational excitation of the products was revealed.

The current experimental and theoretical study of the influence of the rotational quantum number J of reactants on the rate of the chemical reaction and the properties of its products brought several new interesting facts [1]. Attention has mainly been focused on a change in the reaction cross-sections σ as a function of the rotational excitation of the molecule BC (J) in reactions of the type A + BC (J) → AB + C. Two effects, known as orientation and energy effects, are seemingly responsible for the changes of σ with J. The essence of the orientation effect consists in deviation from the optimum transition state as a result of an increased rotation of the molecule BC; then σ decreases with increasing J. On the other hand, the energy effect leads to an increase in σ with increasing J because coupling of the rotational and vibrational motions raises the component of the rotational energy which transforms into translational energy in the direction of the reaction coordinate supporting transition through the reaction barrier. Competition between the contradictory effects leads usually to two situations. In the first case, at lower values of J, the orientation effect predominates. At higher J values, the energy effect prevails and the curve of $\sigma = f(J)$ passes, after the initial decrease, through minimum and then raises. The position of the minimum can approximately be determined according to eqn (*3*)

[2]. In the second situation which is common at higher translational energies of reactants, the energy effect prevails and the curve $\sigma = f(J)$ monotonously increases. The character of the potential energy surface plays here an important role; where, *e.g.* high barrier, strong angle dependence of the barrier height and the shape of the entry channel which orientates molecules into the optimum transition state, lead to remarkable orientation effect [3].

Less attention has so far been paid to other effects and properties of the product molecules in connection with the rotational excitation of the BC molecules. The influence of simultaneous rotational and vibrational excitation was examined in reactions O + HCl, Cl + HCl [4]; no qualitative changes in the course of the function $\sigma(J)$ with the changing vibrational quantum number v were observed. The distribution of the vibrational and rotational energy in the molecules of the products was evaluated for various J for the reaction D + H_2 ($v = 1$) [5]. At higher values of J, vibrational adiabaticity of the reaction was perturbed in the direction to higher values of the vibrational quantum numbers of the products. Similarly rotational distribution was at high values of J shifted to higher rotational quantum numbers of products.

On the basis of QCT calculations we follow in this paper the influence of the rotational excitation in two reactions.

$$\mathrm{H} + \mathrm{HBr}\ (v = 0, 2;\ J) \rightarrow \mathrm{H_2} + \mathrm{Br} \qquad (A)$$

$$\mathrm{D} + \mathrm{HBr}\ (v = 0, 2;\ J) \rightarrow \mathrm{HD} + \mathrm{Br} \qquad (B)$$

We direct our attention mainly towards the course of the function $\sigma(J)$ at various collisional energies and vibrational quantum numbers. Rotational and vibrational distributions in H_2 and HD molecules and their dependence on rotational excitations of HBr are also discussed.

Trajectory calculations

Trajectory calculations were carried out on the LEPS surface for H + HBr system determined by *Sudhakaran* and *Raff* [6]. We used the surface denoted there as the surface III. For QCT calculations the QCPE trajectory code CTAMYM [7] was used. Batches of 1000 trajectories were run for two values of translational energy as well as for selected rotational and vibrational states of HBr molecule. In each of these batches of trajectories the maximum value of the impact parameter, b_{max}, was determined. Its values ranged between $(1.9\text{—}3.2) \times 10^{-10}$ m for various cases. Other variables necessary for the calculation of the reaction probability for collision were generated by the standard Monte Carlo method. Trajectories were initiated at an atom—diatomic molecule separation 7×10^{-10} m. Twelve Hamilton's equations were integrated with an integration step size of 0.5×10^{-16} s. The precision of the integration was controlled by conservation of the total energy and total angular momentum.

Results and discussion

A very simple model for determining the dependence of the reaction cross-section on J was proposed by *Sathyamurthy* [2]. A relation was derived for calculation of the value of J at which σ is minimum

$$J_{\min} = 4\pi(2\,E_{\mathrm{tr}}/\mu_{\mathrm{A,BC}})^{1/2}\ \mu_{\mathrm{BC}}/h\ (r^2_{\mathrm{BC}}/b_{\max}) \qquad (1)$$

$\mu_{\mathrm{A,BC}}$ is the reduced mass of reactants

$$\mu_{\mathrm{A,BC}} = \frac{m_{\mathrm{A}}(m_{\mathrm{B}} + m_{\mathrm{C}})}{m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}}}$$

and μ_{BC} is the reduced mass of BC molecule. Other symbols have their usual meaning. $J_{\min}$ depends on $b_{\max}$ and E_{tr}. Its value is for various collision systems determined by reduced mass of reactants. For instance in the system $\mathrm{H} + \mathrm{H}_2$ $J_{\min} \approx 5$ [2]; for the reaction (*A*) $J_{\min}$ is 16.5 (for $v = 0$ and $E_{\mathrm{tr}} = 8.4\,\mathrm{kJ\,mol^{-1}}$) and 10.1 (for $v = 2$ and $E_{\mathrm{tr}} = 8.4\,\mathrm{kJ\,mol^{-1}}$). We use these predictions (and similarly for reaction (*B*), where $J_{\min}$ is 9.6 for $v = 0$ and $E_{\mathrm{tr}} = 8.4\,\mathrm{kJ\,mol^{-1}}$) for selection of the interval of J values in the study of dependence of σ on J; $J \in \langle 4, 20 \rangle$. Calculation of the reaction cross-section was done for the energy of $8.4\,\mathrm{kJ\,mol^{-1}}$ This energy was assumed to be close enough to the barrier of the abstraction reaction ($0.8\,\mathrm{kJ\,mol^{-1}}$) [6] so that both J effects would appear in the results: orientation and energy effect. At high collision energies, the orientation effect does not occur and as follows from the analysis in the introduction, σ should in this case increase with the increasing J. To verify this effect, calculation at $E_{\mathrm{tr}} = 41.8\,\mathrm{kJ\,mol^{-1}}$ was done.

We have also been interested how σ depends on vibrational excitation of the reactants and how the functional dependence of the reaction cross-section on J will be influenced at the variation of the vibrational state of the molecules of reactants. The calculation for this purpose was done also for $v = 2$ in addition to that for the ground vibrational state of reactants ($v = 0$).

Fig. 1*a* clearly shows how the orientation effect operates. In all four cases of the reactions (*A*) and (*B*) calculated, σ at first decreases with increasing J. This trend is the same for both vibrational states of reactants. The minimum of σ is shallow for the reaction (*A*) at $v = 0$ and $E_{tr} = 8.4\,\mathrm{kJ\,mol^{-1}}$. In all other cases, it is however clearly visible. A comparison of J values for σ_{min} from the relation (*1*) with the results of QCT calculation (Fig. 1) shows that in spite of the simplicity of the model used [2], the results are in good qualitative agreement. In reaction (*A*) the curve from collision calculation for $v = 0$ and $E_{tr} = 8.4\,\mathrm{kJ\,mol^{-1}}$ does not have well defined minimum; J_{min} is 16.5 according to the formula (*1*). At $v = 2$, where the formula (*1*) assumes $J_{min} = 10.1$, the lowest value of σ is around $J = 10$. In reaction (*B*) at $E_{tr} = 8.4\,\mathrm{kJ\,mol^{-1}}$, both curves ($v = 0$ and $v = 2$) from collision calculations have σ_{min} about $J = 10$. Sathyamurthy's expression gives $J_{min} = 9.6$ for $v = 0$ and 6.1 for $v = 2$. As seen from Fig. 1*Ba* the last value ($J_{min} = 6.1$) differs from QCT results.

Fig. 1*a* shows that in the reactions studied, the orientation effect occurs, which determines the shape of curves as a function of J up to the value of J_{min}. The next dependence of the reaction cross-section on J is a consequence of the

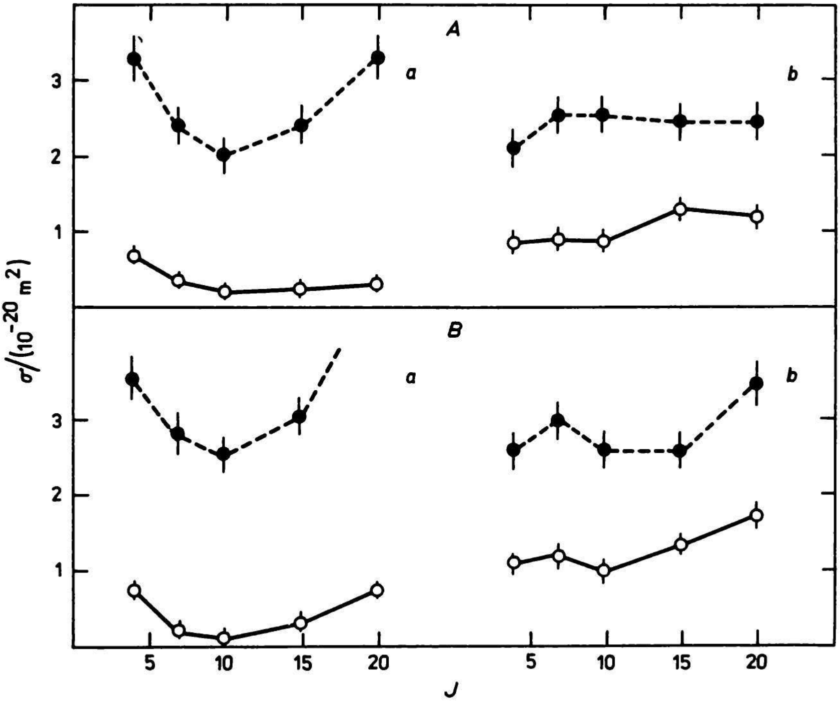

Fig. 1. Dependence of the reaction cross-section on J for $E_{tr} = 8.4\,\mathrm{kJ\,mol^{-1}}$ (*a*) and $E_{tr} = 41.8\,\mathrm{kJ\,mol^{-1}}$ (*b*) for the reactions (*A*) and (*B*), respectively. ○ $v = 0$; ● $v = 2$.

energy effect. A similar result was obtained in the reaction H + DBr → HD + + Br [8].

Fig. 1*b* demonstrates the assumption already discussed, *i.e.* that at high energies, the orientation effect does not operate. In all cases σ raises with increasing J (oscillations are within the error of the method).

The QCT method allows analysis of the vibrational and rotational structure of the reaction products. Fig. 2 presents the dependence of the vibrational states of the products upon the rotational states of reactants for $v = 0$ and $v = 2$ and $E_{\mathrm{tr}} = 8.4\ \mathrm{kJ\ mol^{-1}}$ The character of the curves is similar as in Fig. 1. Moreover, they show how the vibrational states correspond to the particular conditions. In the first place, it follows from all four cases (except for $J = 10$; Fig. 2*Ba*) that the most populated vibrational state of products corresponds with the particular vibrational state of reactants ($\Delta v \approx \Delta v'$ in the case of vibrational adiabaticity). Moreover, at higher values of J, higher vibrational states of products are populated (Fig. 2*Ba*, *Bb*) or new higher vibrational states of the products occur (Fig. 2*Ba*, *Ab*).

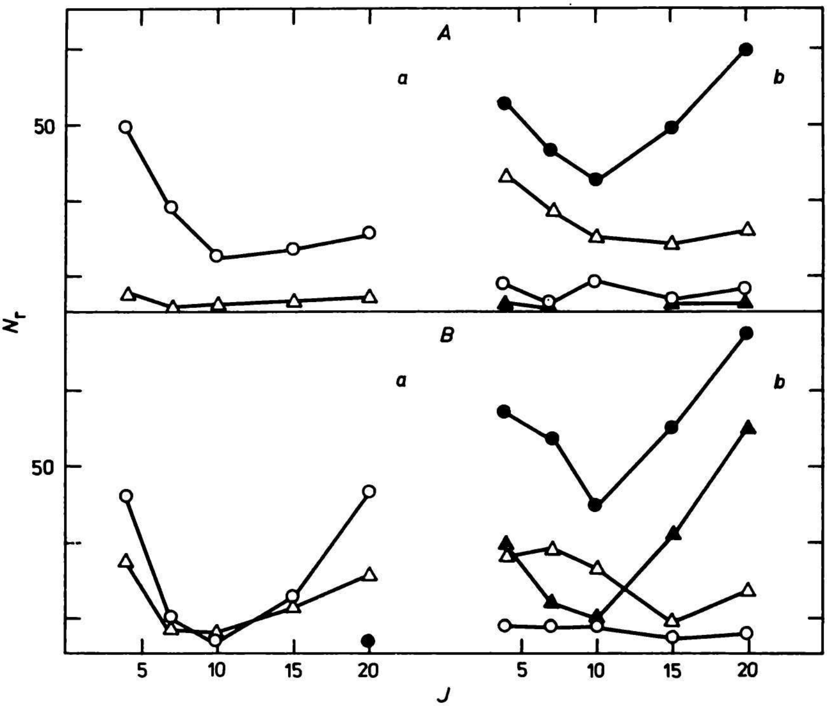

Fig. 2. Vibrational distribution of product molecules at $E_{\mathrm{tr}} = 8.4\ \mathrm{kJ\ mol^{-1}}$ for $v = 0$ (*a*) and $v = 2$ (*b*) of the HBr molecule for the reactions (*A*) and (*B*), respectively. ○ $v' = 0$; △ $v' = 1$; ● $v' = 2$; ▲ $v' = 3$.

Rotational structure of the products was studied so that the reactive trajectories were classified into bins containing five values of J' and their values were plotted for individual J. We can see (Fig. 3) that in addition to the dependence of the number of reactive trajectories N_r on J, rotational distribution of the products also depends on the vibrational state of reactants (it is also evident from Fig. 1). At higher rotational states of reactants and $v = 2$, new products occur in higher rotational states. It is particularly evident in the reation (*B*) for $v = 2$ (Fig. 3*Bb*), where at higher J values the products are in the rotational states with $J' \in \langle 16, 20 \rangle$. Fig. 3*b* shows that under the same reaction conditions higher rotational states are more populated in reaction (*B*) (Fig. 3*Ab* and *Bb*). The main reason is the fact that in the reactions (*A*) and (*B*) H_2 and HD molecules are formed respectively. The values of the spectroscopic constants B_e of these molecules are in the ratio $B_e(H_2)/B_e(HD) = 1.3$ and that is why also at the same value of the rotational energy of these two molecules the energy levels with higher value of J' will be occupied in HD.

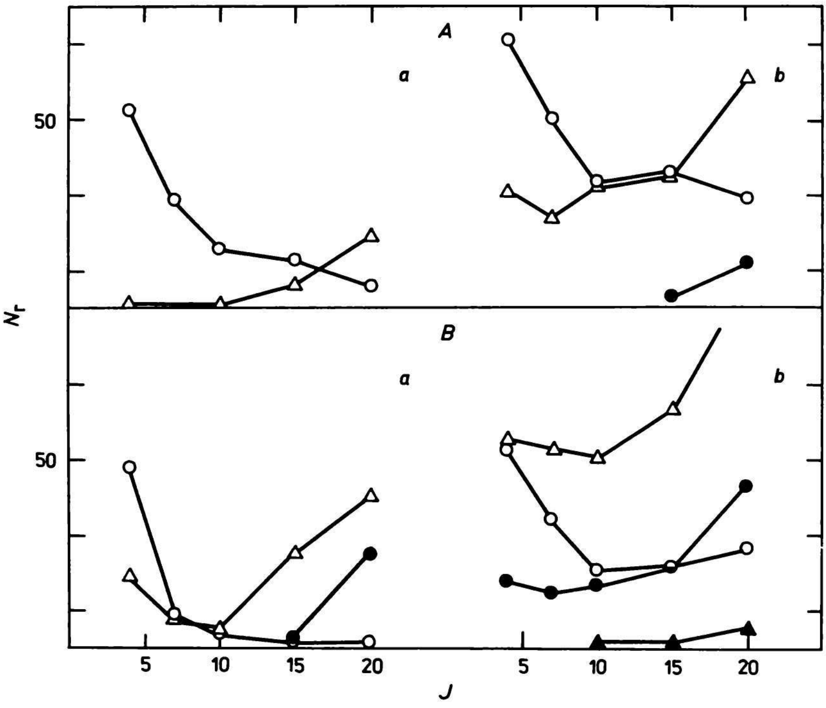

Fig. 3. Rotational distribution of product molecules at $E_{tr} = 8.4\,\text{kJ mol}^{-1}$ for $v = 0$ (*a*) and $v = 2$ (*b*) of the HBr molecule for the reactions (*A*) and (*B*). ○ $J' \in \langle 0, 5 \rangle$; △ $J' \in \langle 6, 10 \rangle$; ● $J' \in \langle 11, 15 \rangle$; ▲ $J' \in \langle 16, 20 \rangle$.

Conclusion

The QCT method was used for studying the dependence of the reaction cross-section of the reactions (*A*) and (*B*) on the rotational excitation of reactants. It was found that both the orientation effect and the energy effect manifest themselves in the reaction at the energy of 8.4 kJ mol^{-1} and that there was perfect agreement between the values of J_{min} predicted by Sathyamurthy's equation and the QCT calculations ($J_{\text{min}} \approx 10$).

The analysis of the vibrational structure shows that in both reactions the rule of vibrational adiabaticity ($\Delta v \approx \Delta v'$) is obeyed. Rotational structure of the products strongly depends on the rotational as well as vibrational states of reactants. Under the same conditions, rotational states of the products are higher in reaction (*B*) than in reaction (*A*).

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Translated by A. Rebrová