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Dependence of Collision Lifetimes on Translational Energy

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Clusters and collision complexes are stabilized by three-body collisions that are two-step bimolecular collisions $A + B \rightarrow AB^*$ and $AB^* + M \rightarrow AB + M$, where M is a bath molecule that removes the excess energy from AB. The lifetime of AB* determines the probability of a third-body collision; therefore, we have calculated binary collision lifetimes as a function of translational energy and temperature by quasiclassical trajectory calculations and compared the results with the analytical expressions of Bunker (*J. Chem. Phys.* **1960**, *32*, 1001). We find that the analytical expressions, which were developed for centrosymmetric potentials, are in poor agreement with the trajectory results of benzene/Ar for low values and in good agreement for high values of translational energies and temperatures.

Introduction

Three-body collisions play an important role in chemical reactions at high and low temperatures and pressures. From cluster formation and reactive scattering in molecular beams to addition reactions at very high pressures, long-lived collision complexes are the intermediates that are stabilized by a collision with inert bath-gas atoms and molecules. The mechanism is a two-stage process where the reactants A and B form a collision complex that is stabilized by a third body, M:

$$A + B \rightarrow AB^*$$

$$AB^* + M \rightarrow AB + M$$

This mechanism was used to explain the formation of mixed, weakly interacting, binary clusters in molecular beams. The first step is the formation of a binary complex followed by stabilization by a collision with a monatomic carrier gas, which carries away the excess energy. Larger clusters can be stabilized by a dissociating monomer that carries with it the excess energy.[1] In some cases chemical reactions in molecular beams are enhanced when a reactant reacts with a binary complex rather than with the monomer alone.[2,3] Thus, the reaction of atomic oxygen with $HCl{\cdot}M$ [M = HCl or Ar] is enhanced by 3 orders of magnitude over reaction with HCl monomer. Third-body collisions are also involved in near-resonance vibrational energy transfer in the gas phase.[4] The third body stabilizes the collision complex and reduces the probability for energy transfer by increasing the frequency mismatch between the collision partners in the neat gas. Very-high-pressure addition reactions of OH to NO and to NO_2 entail third-body stabilization of the products.[5] Another example of third-body stabilization is the high-pressure addition reaction of O to NO in the presence of N_2.[6] At these high pressures it is possible to obtain the limiting high-pressure value of the rate coefficient. The mechanism of formation of excited Na_2 molecules is a three-body collision among an excited sodium atom, a sodium atom, and a buffer gas atom.[7] The formation of the diatomic molecules is facilitated by removal of the excess energy by the bath gas. The examples above involve a true collision complex, albeit, of a very short lifetime. This is different from the three-body collision that occurs during the formation of a diatomic molecule.[8] Here, a simultaneous collision of three atoms leads to the formation of a diatomic molecule, with the third atom carrying the excess energy. The collision complex lifetime, or collision duration, which depends on the vibrational, rotational, and translational temperatures, is therefore a key to estimating the contribution of third-body collisions to the mechanism of chemical reactions and cluster formation.

The first attempt to give an analytical expression for the collision lifetime (τ) of a binary collision was given by Bunker,[9] who used it to calculate the lifetimes of collision complexes. He used a plane polar center-of-mass (CM) coordinate system and a CM spherical (Lennard-Jones) potential to give an expression for the dependence of τ on the relative translational energy (E_t):

$$\tau(E_t) = 1.50\sigma\mu^{1/2}\epsilon_0^{\,1/6}E_t^{\,-2/3} \tag{1}$$

σ and ϵ_0 are the collision radius and well depth of the Lennard-Jones (LJ) potential, respectively, and μ is the reduced mass. If one is interested in the average lifetime of a collision complex as a function of the temperature, then the relative translational energy can be replaced by the average quantity[10] $2k_BT$ to give

$$\langle\tau(T)\rangle = 1.50\sigma\mu^{1/2}\epsilon_0^{\,1/6}(2k_BT)^{-2/3} \tag{2}$$

For stochastically independent collisions, the probability that a collision complex will not undergo a collision in time τ is $\exp(-\tau Z_{eff})$,[11] where Z_{eff} is the *effective* number of collisions, Z, of the bath gas with the collision complex.[1] The probability that a collision complex has undergone a collision during time τ is[1]

$$P(\tau) = 1 - \exp(-\tau Z_{eff}) \tag{3}$$

The value of Z_{eff} can be calculated by multiplying Z for collisions of the bath gas with the collision complex by the

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probability P_{coll} that a collision is a deactivating collision that removes energy from the collision complex such that the complex is below the dissociating limit E_d:

$$P_{\mathrm{coll}} = \int_{E_d}^{\infty} P(E',E)\, dE' \tag{4}$$

$P(E',E)$ is the normalized energy-transfer collision probability density function[12] that can be calculated from trajectory calculations.[14a] The integration is performed over all down collisions larger than E_d. As an example, eq 3 can be used to calculate the probability of dimer formation in a molecular beam as a function of the distance from the nuzzle.[1]

Previous applications of eqs 1−3 involve simple spherical potentials such as a LJ potential.[1,9] However, many molecules, such as cyclic and polycyclic molecules, have a nonspherical intermolecular potential, and in addition, their vibrational/rotational energies affect the collision complex lifetime. Therefore, we have undertaken to study the dependence of τ on E_t for a molecular system with inter- and intramolecular potentials derived from ab initio calculations and to compare our calculations with the predictions of eqs 1 and 2.

Theory

The numerical methods used in the present work were discussed in detail previously,[15,16] and only a general outline will be presented here. The equations of motion were integrated by using a modified public domain program, Venus.[17] For an intermolecular potential we have used a potential calculated by Bludsky, Spirko, Herouda, and Hobza[18] (BSHH), who reported ab initio calculations of an Ar−benzene cluster and fitted the results to a potential function which is based on pairwise atom−atom interactions. This is called the BSHH potential:

$$V_{ij} = \frac{A_{ij}}{r_{ij}^{\alpha}} - B_{ij}\left(\frac{1}{r_{ij}^{6}} - \frac{C_{ij}}{r_{ij}^{7}}\right) \qquad i, j = 1-6 \tag{5}$$

A, B, and C are constants, r is the CM relative distance, i indicates a carbon or a hydrogen atom, and j indicates an argon atom. For the benzene−Ar system[19] $\alpha = 13.30$,

$A_{\mathrm{H-Ar}} = 77.211 \times 10^{-7.305}$ cm^{-1} nm$^{13.305}$, $B_{\mathrm{H-Ar}} = 120.279 \times 10^{-3}$ cm^{-1} nm^6, $C_{\mathrm{H-Ar}} = 0.271\,49$ nm,

$A_{\mathrm{C-Ar}} = 287.901 \times 10^{-6.305}$ cm^{-1} nm$^{13.305}$, $B_{\mathrm{C-Ar}} = 343.979 \times 10^{-3}$ cm^{-1} nm^6, and

$C_{\mathrm{C-Ar}} = 0$ nm.

The intramolecular potential includes all the normal mode contributions, stretching, bending, and wagging. The values of the parameters of this potential were obtained from the modified valence force field calculations by Draeger[20] and are also given in refs 15 and 16. The initial translational energy was chosen at fixed energy intervals. Rotational energies were chosen from the appropriate thermal energy distributions, and the initial vibrational energies were the average thermal energies at the temperatures of the calculations. The energy was distributed statistically among all the normal modes of the molecule. The initial impact parameter (b) was chosen randomly from values between 0 and its maximum value b_m. The maximum value of the impact parameter b_m was determined separately.[15,16] A value of 0.9 nm was used in the present calculations. To obtain good statistical sampling in the binning process, 5000−15000 trajectories were used for each temperature.

In addition, we have calculated[14,21] an average, or global, dynamic potential by averaging many single-trajectory potentials. It represents a quantity that is based on averaging tens of thousands of trajectories with all possible orientations and impact parameters chosen by Monte Carlo sampling of impact parameters and Euler's angles. It is obtained by binning the potential energy as a function of the CM distance for all the trajectories and dividing the sum in each bin by the number of times the atom traverses a given CM distance that is represented by a particular bin. Global potentials are especially useful for nonspherical molecules with an anisotropic potential such as benzene.[14] The parameters of the global potential at 300 K are $\epsilon_{\mathrm{eff}} = 228$ cm^{-1} and $\sigma_{\mathrm{eff}} = 0.335$ nm. For comparison we have also used a LJ intermolecular potential for which the literature values are well depth $\epsilon = 148$ cm^{-1} and collision radius $\sigma = 0.447$ nm.[21]

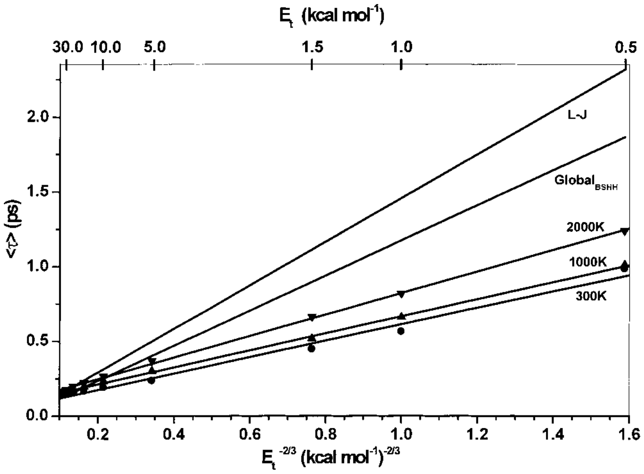

Figure 1. Collision lifetimes as a function of the relative translational energy in benzene−Ar collisions. Runs are based on 5000−15000 trajectories. The vibrational−rotational temperatures were 300 K (●), 1000 K (▲), and 2000 K (▼). The lines marked by BSHH and LJ are based on eq 1 with the parameters of the BSHH dynamic global potential, $\sigma_{\mathrm{eff}} = 0.335$ nm, $\epsilon_{\mathrm{eff}} = 228$ cm^{-1}, and the parameters of the Lennard-Jones potential, $\sigma = 0.447$ nm, $\epsilon = 148$ cm^{-1}.

The average lifetime of a collision $\langle\tau\rangle$ is given by

$$\langle\tau\rangle = \frac{\sum_{i=1}^{N} \tau_i}{N} \tag{6}$$

τ_i is the lifetime of a cluster in trajectory i, and N is the total number of trajectories.

The beginning and the end of a collision were determined by the forward- and backward-sensing (FOBS) method.[15,22] In this method, each trajectory is scanned forward and the moment is noted that, for the first time, a change ϵ in the internal energy of the hot molecule in a time period Δt occurred. Then, the trajectory is scanned backward, and again, when a change ϵ is detected in a time period Δt, the time is noted again. These two points in the trajectory time bracket the collisional event. The value of the gradient $\Delta\epsilon/\Delta t$ was 0.35 cm^{-1} fs^{-1}. This value was obtained after a careful study in which ϵ was changed systematically, and it was verified that a small variation in ϵ did not change the initial time or duration of the collision.[15,22]

Results and Discussion

The dependence of the average lifetime of a binary collision between benzene and argon as a function of $E_t^{-2/3}$ is shown in Figure 1 for three temperatures, 300, 1000, and 2000 K, together with a linear best fit to the data. The straight lines, as predicted by eq 1, are a surprise. Because of the complexity of the system, we have expected a complex dependence of $\langle\tau\rangle$ on E_t, one that

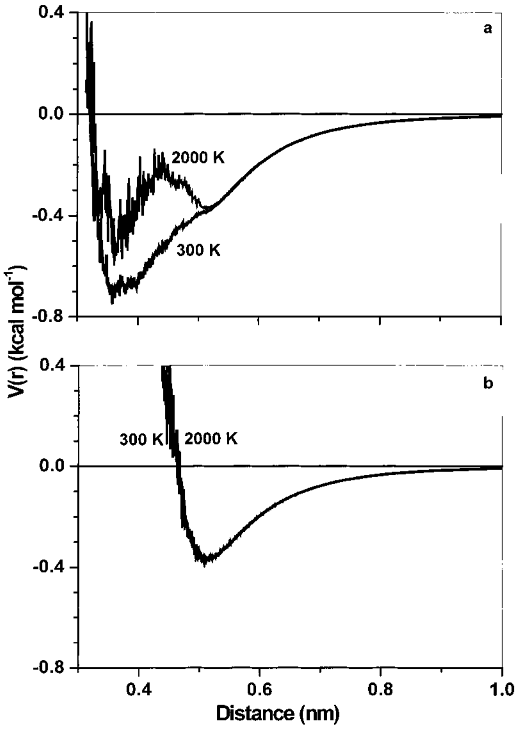

Figure 2. Global dynamic potentials vs center-of-mass distance obtained by averaging 5000−15000 trajectories at 300 and 2000 K. The translational energy, E_t, is (a) 0.5 kcal/mol and (b) 30 kcal/mol.

cannot be expressed in the simple form of eq 1. Counterintuitive is the fact that $\langle\tau\rangle$, at a given E_t, is longer the higher the temperature. To understand the reasons for that, we need to remember that a collision is defined by FOBS, that is to say, the first and last instance in a trajectory that there is a change ϵ in the internal energy of the benzene molecule. These points are determined, on the average, by the dynamic global potential that is shown in Figure 2. At low translational energy, $E_t = 0.5$ kcal/mol, and at low temperature, 300 K, the potential well is deeper than at 2000 K, more potential energy is converted into translational energy, and the Ar atom approaches the repulsive wall faster than at 2000 K. Therefore, the time it takes the Ar to get in and out of the collision region is shorter at 300 K than at 2000 K. In addition, at 2000 K the fast rotations and excited vibrations "inflate" the molecule, and there is a repulsive part at $\sim$5.3 nm, which is the distance from the center of mass to the Ar atom along the CM−C−H line. Therefore, the Ar travels a longer path than at low temperatures. At 300 K, on the other hand, the molecule is rotating and vibrating very slowly, and the moving atom is able to reach the repulsive wall without being slowed. At the high velocity of 30 kcal/mol the dynamic global potentials at 300 and 2000 K, shown in Figure 2b, look almost identical. The atom is moving so fast that the details of the potential are unimportant and the values of $\langle\tau\rangle$ are almost identical, as can be seen from Figure 1.

There are two additional lines in Figure 1. One is calculated from eq 1 with the parameters of the global dynamic potential of a thermal system at 300 K,[21] which is shown in Figure 2a. It should be compared with the 300 K trajectory line, which yields shorter $\langle\tau\rangle$ values. There is an additional line that is calculated by using the parameters of a LJ potential of the benzene−Ar system. The values of $\langle\tau\rangle$ are larger by a factor of $\sim$3−4 at low velocities. It is clear that eq 1 is not satisfactory for low translational energies.

Unlike eq 1, which predicts linear plots of $\langle\tau\rangle$ vs $E_t^{-2/3}$, plotting $\langle\tau\rangle$ vs $T^{-2/3}$ does not yield the linear dependence expected from eq 2. The curved plot is shown in Figure 3. As can be seen, the low-temperature data are not linear with $T^{-2/3}$. Moreover, over the temperature range of 300−2000 K the values of $\langle\tau\rangle$ vary very little, from 500 fs at 300 K to 360 fs at 2000 K. When the values of $\langle\tau\rangle$ are calculated by eq 2, using the LJ parameters, the variations in the values of $\langle\tau\rangle$ can be more than a factor of 3. This is also shown in Figure 3, where the trajectory results are compared with results that were obtained by the use of eq 2. The reasons for the nonlinearity of the trajectory data are that at low temperature the average E_t is low and the molecules hardly rotates and vibrates while at high temperatures the average E_t is high and the molecule is "inflated" by the highly excited vibrations/rotations. Therefore, the dynamic global potential, which is shown in Figure 2, changes as the temperature increases. At 300 K and low translational energy the potential well is deeper and the repulsive wall occurs at closer CM distance than at 2000 K, which has a higher average E_t and a shallower potential well. These facts affect the value of $\langle\tau\rangle$ and cause the nonlinearity that appears in Figure 3. The nonlinearity also means that at very low temperatures the values of $\langle\tau\rangle$ can exceed those that are predicted by eq 2 with LJ parameters.

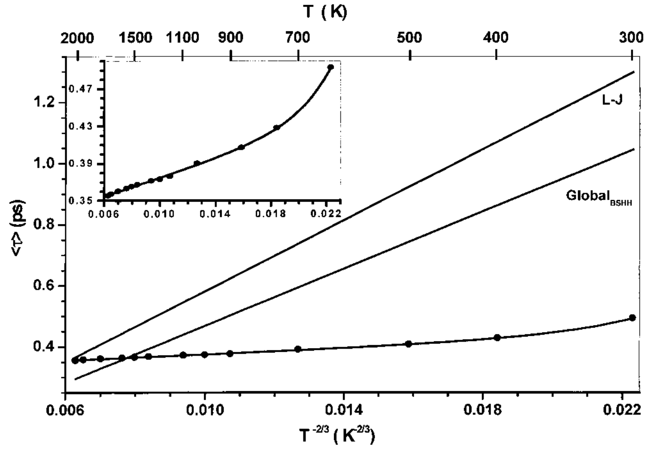

Figure 3. Collision lifetimes of benzene−Ar as a function of temperature. Runs are based on 5000−15000 trajectories. The plots are of eq 2 with parameters of Lennard-Jones and BSHH potentials (as in Figure 1) and of trajectory calculation results (●). Inset: expansion of the trajectory plot.

In conclusion, the collision lifetime of benzene with Ar increases as the relative kinetic energy of the colliding partners decreases. The long lifetimes of the collision complex at low kinetic energies enable stabilizing termolecular collisions to occur, and this fact explains the formation of clusters in low-temperature molecular beams. The values of collision lifetimes from eqs 1 and 2 do not agree with trajectory results, and care should be exercised when the former are used to predict three-body collisions. At high temperatures and high kinetic energies the collision lifetimes are very short and can be calculated from eqs 1 and 2.

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