Termolecular Collisions: Comparison between Analytical Expression and Trajectory Calculations[†]

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The fraction of the rates of termolecular collisions/bimolecular collisions is calculated by an analytical and semianalytical expression. The results are compared with results obtained by classical trajectory calculations on benzene and Ar, which are used to find directly the number of bimolecular and termolecular collisions as a function of pressure for a given set of initial conditions. The comparison indicates very good agreement for the semianalytical model and very reasonable agreement for the analytical model, both in the range 20−150 atm. Equation 15 in the text is a reliable and convenient "hard sphere" formula for calculating the fraction of termolecular collisions rate as a function of pressure.

Introduction

Termolecular collisions play a major role in chemical reactions at high pressures such as combustion and atmospheric reactions. In such collisions, the role of the third body is to remove energy from a collision complex, stabilize it, and enable a binary reaction to take place. Schematically, the process can be described by a two-step mechanism: $A + B \rightarrow AB^*$; $AB^* + M \rightarrow AB + M$ where A and B are the reactants, AB* is the collision complex, M is the third body, and AB is the product of the binary reaction. We have done an extensive study of three-body collisions in the system benzene, B, in argon bath at high pressures[1] by classical trajectory calculations (paper I). The work indicated that there are several mechanisms for three body collisions: chaperon mechanism, where there is an exchange of partners during the collision of the third body with the collision complex and the chaperon leaves with the excess energy (1) $B + Ar \rightarrow BAr^*$ and (2) $BAr^* + Ar' \rightarrow BAr' + Ar$ where the prime indicates the second argon atom; energy transfer mechanism, where M hits the collision complex and departs with excess energy (1) $B + Ar \rightarrow BAr^*$ and (2) $BAr^* + Ar' \rightarrow BAr + Ar'$; concerted mechanism where all the three bodies separate almost instantaneously (1) $B + Ar \rightarrow BAr^*$ and (2) $BAr^* + Ar' \rightarrow B + Ar + Ar'$. Paper I goes into the details of the mechanisms and gives, in addition, parameters such as the average energy transferred per collision, collision lifetimes, and the effects of temperature and pressure on these quantities. In addition to the nonreactive system described above, there are some computational examples of three body reactive collisions: (a) the formation of ozone by the energy transfer mechanism[2−4] (1) $O_2 + O \rightarrow O_3^*$ and (2) $O_3^* + Ar \rightarrow O_3 + Ar$, for which energy transfer mechanism was assumed, and the reactions[5−8] (b) $H + O_2 + Ar \rightarrow HO_2 + Ar$ and (c) $H + CN + Ar \rightarrow HCN + Ar$, for which the chaperon mechanism was assumed, and (d) the reaction[9,10] $2Ne + H \rightarrow Ne_2 + H$, where the direct three body mechanism dominates over the ET or chaperon mechanisms. As indicated above, in the B/Ar case described in paper 1, all three mechanisms operate, and it is, therefore, incorrect to single out one mechanism as the dominating one.

One quantity of great interest is the fraction of three-body collisions as a function of the pressure for a given system, and to obtain it, one must perform extensive computations. Unlike a binary collision, where the hard sphere collision is the reference model to which actual collisions are compared, termolecular collisions do not have a universal analytical collision model that can serve as a basis for comparison and as a tool for "back of the envelope" calculations. The work described below tests analytical models against exact results of classical trajectory calculations and suggests it as reference model.

Theory

The ability to obtain the number of bimolecular and the number of termolecular collisions from trajectory calculations provided us with an excellent tool, not available before, with which to compare the rates of bimolecular and termolecular collisions obtained from analytical and semianalytical expressions. In the following, we give two such models and compare the results with trajectory calculations.

Binary and Termolecular Collision: Semianalytical Expression. We have tried to calculate the ratio of the rate of termlecular to the rate of bimolecular collision from basic principles by using the expressions for binary collision[11]

$$Z_2 = \left(\frac{\mu_2}{k_B T}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} c_1 c_2 I_i \tag{1}$$

where I_i is the collision integral, μ is the reduced mass, and c is the concentration

$$I_i = \int_0^\infty \exp\left(-\frac{\mu_i {v_{rel}}^2}{2k_B T}\right) S_i(v_{rel}) {v_{rel}}^3 \, dv_{rel} \tag{2}$$

S_i is the energy dependent collision cross section and the subscript i is 2 for binary collisions and 3 for termolecular collisions. μ_2 is calculated by the conventional expression and μ_3 is given by

$$\mu_3 = \frac{m_3(m_1 + m_2)}{m_1 + m_2 + m_3} \tag{3}$$

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If we assume, as in paper I, that the termolecular collision is a two step mechanism where the third body collides in the second step with a collision complex, we can write an expression for a binary collision between the third body and the collision complex

$$Z_3 = \left(\frac{\mu_3}{k_B T}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} c_{1\ldots2} c_3 I_3 \tag{4}$$

where $c_{1\ldots2}$ is the concentration of the binary collision complex. Assuming equilibrium between the colliders and the collision complex,[11] the concentration of the collision complex is

$$c_{1\ldots2} = c_1 c_2 4\pi \int_{r_{\mathrm{eq}(12)}}^{r_{(1\ldots2)}} \exp\{-U_2(r)/k_B T\} r^2 \, \mathrm{d}r \tag{5}$$

where U_2 is the global bimolecular potential and the integration limits are between the equilibrium distance of the diatomic molecule at the bottom of the potential well, r_{12}, and the distance between 1 and 2 at the top of the centrifugal barrier, $r_{1\ldots2}$. We have calculated numerically U_2 and U_3, the global termolecular potential, of a thermal equilibrium system at 500 K and found that they are very similar. Therefore, the subscript is omitted and U is calculated as a binary global potential. Using eqs 1−5, one obtains the final expression for the ratio of Z_3/Z_2 is

$$\frac{Z_3}{Z_2} = \frac{4\pi P}{k_B T}\frac{I_3}{I_2}\left(\frac{\mu_3}{\mu_2}\right)^{3/2} \int_{r_{123}}^{r_{12\ldots3}} \exp[-U(r)/k_B T] r^2 \, \mathrm{d}r \tag{6}$$

To obtain numerical values, one has to know I_2 and I_3, that is to say, the energy dependent cross sections.

Binary and Termolecular Collisions: Analytical Expression. The total rate of binary collisions between molecules (or atoms) of type1 and type 2 is given by the expression

$$Z_2 = \sigma_2 v_2 c_1 c_2 \tag{7}$$

σ is the cross section, which for hard spheres is $\pi[(r_1 + r_2)/2]^2$; r_1 and r_2 are the hard sphere radii of species 1 and 2; v is the average velocity

$$v_2 = (8k_B T/\pi\mu_2)^{1/2} \tag{8}$$

The subscript 2 on σ, v, and Z indicates a binary collision, whereas the subscript 3 below indicates a termolecular collision.

The expression for the rate of termolecular collisions is

$$Z_3 = \sigma_3 v_3 c_1 c_2 c_3 \tag{9}$$

In both bimolecular and termolecular expressions, the assumption is that σ is independent of energy. Even with this assumption, the quantities σ_3 and v_3 are not easily found. We follow the treatment by Smith,[12] which has a degree of empiricism in it, and use our computational results for the benzene−Ar system to check how good the assumptions in the expressions by Smith are.

σ_3 is defined in terms of an average length r_0 by using the formula for the volume of a 5-sphere which is the cross section of a 6-dimensional hypersphere

$$\sigma_3 = (8\pi^2/15) r_0^{\,5} \tag{10}$$

In binary collision the average length is defined by a clear-cut expression $r_1 + r_2$, in termolecular collisions, the definition of a single radius is more complicated and is defined as a geometric mean

$$r_0 = (p_{12} p_{23} p_{31})^{1/3} \tag{11}$$

where p_{ij} was obtained by Smith[12] from general kinematic considerations using normalized interparticle distances

$$p_{ij} = (r_i + r_j)\left[\frac{m_i m_j (m_i + m_j + m_k)}{m_k (m_i + m_j)^2}\right]^{1/4} \tag{12}$$

r_i is the collision radius of molecule i and m_i is the mass of molecule i.

The average three-body velocity is

$$v_3 = \frac{15\pi}{32}\left(\frac{8k_B T}{\pi\mu_3'}\right)^{1/2} \tag{13}$$

μ_3' is given by the expression[12]

$$\mu_3' = \left(\frac{m_1 m_2 m_3}{m_1 + m_2 + m_3}\right)^{1/2} \tag{14}$$

Note that μ_3' is defined differently than μ in eq 3. The ratio of the rates of termolecular collision to bimolecular collisions in a vessel at a give set of initial conditions for the system benzene + 2Ar is given by the expression

$$Z_3/Z_2 = \pi^2 (2M')^{5/3} r_2^{5/3} (r_1 + r_2)^{4/3} (\mu_2/\mu_3')^{1/2} P/(4000 k_B T) \tag{15}$$

where the factor 4000 comes from adjustments of units and factors that appear in the various equations leading to eq 15. In obtaining eq 15, we let $r_2 = r_3$ and $m_2 = m_3$ and M' is given by

$$M' = [m_1(m_1 + 2m_2)^3/(4(m_1 + m_2)^4)]^{1/4} \tag{16}$$

The ratio Z_3/Z_2 in eq 15 will be compared to trajectory results in the next section.

Trajectory Calculations. The details of the calculation are reported in detail in paper I and only a brief summary will be given here. The mechanism of a termolecular collision is a sequence of two binary collisions. In the first, a single Ar atom collides with a benzene, B, molecule. The beginning and the end of the binary collision are defined by the FOBS[13,14] method. In the pressure dependent termolecular trajectory calculations, the starting distance, R_{in}, between the centers of mass of the binary collision complex between benzene and Ar, BAr, and the third-body, Ar′, of the second collision is chosen randomly from the combined distance-volume probability density distribution function which has the general form

$$P(R_{\mathrm{in}}) = R_{\mathrm{in}}^{\;2} \exp(-R_{\mathrm{in}}/\lambda)/C \tag{17}$$

where λ is the mean free path and C is a normalization factor. This type of a distribution ensures that the termolecular trajectories that are initiated at large distances will not have an undue effect on energy transfer quantities. It should be noted that R_{in} includes the excluded volume of the binary collision complex. Taking just the center-of-mass distances will bias the results, especially at high pressure where the mean free path is short.

The inter- and intramolecular potentials, which were used in the calculations, as well as the methodology, are given in great detail in paper I and will not be repeated here. The numbers of binary and of ternary collisions, in a given time interval, were

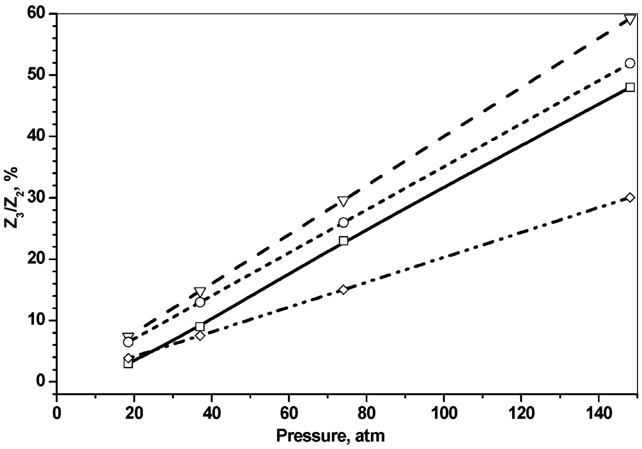

Figure 1. 1. Ratio of termolecular to bimolecular collision rates as a function of pressure at 500 K. □, Trajectory results; ◇, semianalytical model with termolecular global potential; ○, semianalytical model with bimolecular global potential; ▽, analytical model.

counted directly using the FOBS criterion. The ratio of the two gives directly the ratio Z_3/Z_2. The number of binary collisions includes all of the binary collisions that occur up to the maximum impact parameter, b_m, whether they lead to termolecular collision or not.

Results and Discussion

The fraction of termolecular collisions out of all binary collisions that take place as a function of the pressure for benzene + 2 Ar which was obtained from trajectory calculations is given in Figure 1. The plot is linear at high pressures but curves at low pressures where the value of Z_3 approaches zero. It should be pointed out that nothing in the calculations (an equation of motion, potentials, or any other parameter) has embedded in it this linearity. This by itself encourages exploring analytical models since both models presented above yield linear dependence of the ratio Z_3/Z_2 on pressure.

The results of the calculation of the semianalytical model are also presented in Figure 1. In obtaining these results, we have used, in eq 2, hard-sphere cross sections,[11] obtained from FOBS, instead of energy dependent cross sections. The distance where the particles first interact by FOBS is averaged over hundreds of thousands of trajectories and this distance is taken as the hard sphere radius. The bimolecular collision radius is 0.606 nm and the termolecular one is 0.649 nm. The agreement between the trajectory results and the model is very pleasing and one could not hope for better results. Two lines are given in the figure. One represents eq 6 with U_2 and one with U_3. The deviation of the U_3 results at 150 atm is 23% and of the U_2 it is 8%. One could not hope for better results. Both lines extrapolate to zero, as expected from a linear model. However, there are uncertainties and difficulties in the calculations. The energy dependent cross sections are not known and even if one assumes hard-sphere cross-sections, as we have done, there is the problem of the limits in eq 6. To evaluate $r_{12...3}$ and r_{123}, one has to calculate the global potential which is not trivial and against the philosophy of this work to have a simple, analytical expression for termolecular collisions for reasonably accurate back of the envelope calculations. Therefore, although we have spent a great deal of effort in numerical calculations of eq 6 and although the results are excellent, we judge the model to be of limited interest to the general public. Thus, our conclusion is that eq 6 can provide excellent results for those who are ready to invest a great deal of effort to obtain them.

Also given in Figure 1 is a plot of eq 15. As can be seen, the analytical expression yields very good agreement with the trajectory results, which are the basis for comparison. The results deviate by 0−60% in the pressure range 0−150 atm. Since the trajectory results were obtained for a Lennard-Jones intermolecular potential, we have used the same Lennard-Jones parameters[15] in eq 15. The collision radius of benzene−Ar was 0.447 nm and $\epsilon/k_B = 213$ K. Correcting for the collision integral at 500 K, $\sigma^* = \sigma\,(\Omega^{2,2})$,$^{1/2}$ we obtain $\sigma^* = 0.473$ nm. From σ^*, we obtain the value of the "hard sphere" equilibrium distance $r_0 = 2^{1/6}\sigma^* = 0.531$ nm. The hard sphere radii of Ar and benzene where calculated in the same way as above. For Ar, it is 0.189 nm and for benzene 0.365 nm. The values of the various r's are the great unknowns and slight changes in their values can improve the agreement markedly. This is a known problem also in calculating the number of bimolecular collisions and in this respect the old problem of unknown cross sections is with us as always.

In summary, using classical trajectory calculations with a Lennard-Jones intermolecular potential, we have calculated and reported the ratio of the rates termolecular collisions to bimolecular collisions for given sets of initial conditions. We have compared the results with a semianalytical and an analytical expression. We obtain very good agreement between the analytical results and the direct count of trajectories from our classical calculations. The importance of this work is in having a totally independent reference point, the trajectory calculations, to which analytical models can be compared. We recommend using the analytical expression, eq 15, for back of the envelope calculations of the rate of termolecular collisions.

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