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Predictive Unimolecular Kinetics for the Decomposition of Small Hydrocarbons and Hydrocarbon Radicals in Several Baths

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Ensembles of classical trajectories are used to study collisional energy transfer in highly vibrationally excited methane, ethane, propane, vinyl radical, ethyl radical, and propyl radical for several bath gases. The accuracy of using a simplifying "separable pairwise" assumption in the trajectory calculations to describe the target–bath interaction potential is validated against full dimensional direct dynamics trajectory calculations for the CH_4 and C_2H_5 targets. The validated approach allows for the efficient and accurate calculation of energy transfer averages for larger hydrocarbons and hydrocarbon radicals. Trends in the calculated relative collisional energy transfer efficiencies with respect to both the target and bath gas are discussed. The relative efficiencies for the different baths are found to be a function of temperature, with room temperature relative efficiencies differing significantly from combustion temperature ones. The average energy transferred in deactivating collisions $\langle \Delta E_d \rangle$ is shown to increase with the number of carbon atoms in the target and to be relatively insensitive to the number of hydrogen atoms. Calculated values of $\langle \Delta E_d \rangle$ can be used to parameterize a single-exponential-down model for collisional energy transfer for use in master equation calculations. The resulting theoretical decomposition rate coefficients are free from empirical parameters and agree fairly well with available experimental rate coefficients.

1. Introduction

Collisions with bath gas molecules play an important role in controlling the rates of unimolecular and chemically activated reactions [1]. Pressure dependent kinetics may be characterized using the master equation (ME) [2,3,4], which, in general, describes the time dependence of the microcanonical state populations of the reactants, products, and intermediates. ME calculations require knowledge of the intramolecular potential energy surface (dissociation energies, isomerization barriers, vibrational frequencies, etc.), which may be obtained with known uncertainties from electronic structure calculations. Likewise, the required intramolecular isomerization and capture rate coefficients may be calculated using transition state theory [5], with well-validated, predictive strategies for treating barrierless reactions, tunneling, etc. In contrast, the models used in ME calculations for describing collisional energy transfer remain highly empirical.

In recent work [6,7], we have used ensembles of classical trajectories combined with ab initio or semiempirical potential energy surfaces to parameterize the single exponential down energy transfer model for use in ME calculations of the decomposition of methane in eight baths. The resulting parameter-free rate coefficients were shown to be in good agreement with low pressure and falloff measurements from the literature.

Here we extend these previous studies to a variety of larger molecular (ethane and propane) and radical (vinyl, ethyl, and propyl) targets. These systematic studies allow us to identify trends in collisional energy transfer dynamics due to properties of the bath gas and of the target molecule.

2. Calculations

A scheme for preparing ensembles of target–bath gas collisions appropriate for calculating energy transfer parameters for ME calculations has been described previously [6,7]. Our methods are similar to the methods developed by Lim and Gilbert [8]. Briefly, ensembles of classical trajectories were prepared with thermal distributions of the initial relative collision energy and of the initial rotational state of the target, J'. The initial vibrational energy of the target was (in general) chosen to be a function of J' and close to but less than the rotationally adiabatic dissociation threshold, with the initial geometries and vibrational momenta distributed microcanonically. Using this prescription, the ensembles are defined by a single parameter T, which is the temperature of the bath gas.

The final target–bath gas separation used as the criterion for terminating each trajectory was chosen to be suitably large so that the final total energy (and therefore the change in the total energy of the target due to the collision, ΔE) could be calculated unambiguously. The ensemble-averaged energy transferred in deactivating collisions $<\Delta E_d>$ is used as an input parameter for the "single exponential down" model [1] for energy transfer in ME calculations; $<\Delta E_d>$ was calculated from the trajectory ensembles as

$$<\Delta E_{\mathrm{d}}> = -\frac{Z_{\mathrm{HS}}}{Z_{\mathrm{LJ}}}\sum_{i=1}^{N} w_i^b \min(\Delta E_i, 0)/N_{\mathrm{d}}, \tag{1}$$

where i labels trajectories, Z_{HS} and Z_{LJ} are the hard sphere and Lennard-Jones collision frequencies (calculated using typical tabulated parameters and the usual combining rules), respectively, N is the size of the ensemble, and N_d is the number of deactivating collisions. The weights w_i^b correct for importance sampling of the impact parameter [7]. We also consider the first-order average energy transfer rate coefficient (i.e., a per-time average, whereas eq 1 defines a per-collision average), defined as

$$<r_{\mathrm{d}}> \equiv Z_{\mathrm{LJ}} <\Delta E_{\mathrm{d}}> n_{\mathrm{M}} \tag{2}$$

where n_M = 1 Torr/k_B T; $<r_d>$ has units of energy transferred per unit time (cm^{-1}/s).

Trajectory calculations were carried out for several systems using several choices for describing the combined target–bath potential energy surfaces. For CH_4 + He, CH_4 + H_2, CH_4 + CH_4, and C_2H_5 + He collisions, direct dynamics trajectory calculations were carried out [1] using full-dimensional MP2/aug'-cc-pVDZ potential energy surfaces. These results were used to test the accuracy of representing the full-dimensional, fully-coupled potential energy surface as

$$V = V_{\mathrm{T}} + V_{\mathrm{M}} + V_{\mathrm{T-M}}, \tag{3}$$

where V_T is the intramolecular potential energy surface of the target and is a function of the internal coordinates of the target, V_M is the internal potential energy for the bath gas (V_M = 0 for atomic baths) and is a function of the internal coordinates, if any, of the bath, and $V_{T–M}$ is the intermolecular potential and is rigorously a function of all of the internal

coordinates of the target–bath gas system. The intermolecular potential V_{T-M} was further approximated as a sum of pairwise atom-atom interactions, i.e.,

$$V_{T-M} \approx \sum_j V_2(R_j), \tag{4}$$

where j labels pairs of intermolecular atoms, and R_j is their separation. Equation 4 neglects higher order terms (e.g., $V_3(R_j,R_{j'},R_{j''})$, etc.) in the interaction potential that are responsible for screening effects, etc. Two forms for V_2 were considered: the Lennard-Jones (LJ) form and a modified Buckingham (exp/6) form.

The LJ and exp/6 expressions for V_2 contain two and four parameters, respectively, for each type of interacting atom pair; these parameters were determined for CH_4 + M [7,9] by fitting V_{T-M} to high-level ab initio (counterpoise corrected QCISD(T)/CBS or CCSD(T)/CBS) energies. Here we consider the accuracy of using the parameters developed with CH_4 as the target molecule as "universal" hydrocarbon–bath gas interaction parameters for other targets.

We refer to eqs 3 and 4 as the "separable pairwise" approximation to the interaction potential. This approximation (along with either the LJ or exp/6 functional forms for V_2) is almost always employed in trajectory studies of energy transfer.

Within the separable pairwise approach, one has a choice for how to describe the intramolecular target potential energy surface, V_T, and we consider using either the MP2 method or the semiempirical tight binding (TB) approach [10]. The TB approach is orders of magnitude less computationally demanding than the MP2 method.

3. Results and Discussion

Accuracy of the separable pairwise approximation. The accuracy of eqs 3 and 4 was tested by comparing calculated values of $\langle\Delta E_d\rangle$ using nonseparable direct dynamics (MP2) with several separable pairwise potential energy surfaces. The separable pairwise calculations are labeled A+B, where A = MP2 or TB and describes the method used to calculate the intramolecular forces and B = LJ or exp/6 and describes the method used to describe the interaction potential. These test are shown in Fig. 1 for the CH_4 + He [6,7], CH_4 + H_2 [7], and C_2H_5 + He systems.

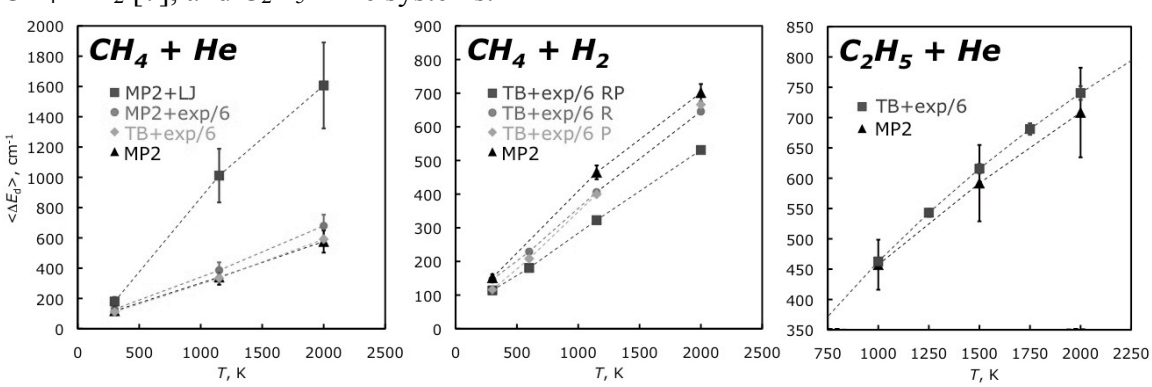

Figure 1: Average energy transferred in deactivating collisions for (a) CH_4 + He, (b) CH_4 + H_2, and (c) C_2H_5 + He.

The principal results of these tests, along with other tests described elsewhere [7], are:

1. The separable pairwise approximation fails badly when the LJ form is used. As seen in Fig. 1(a), the MP2+LJ method overpredicts $\langle\Delta E_d\rangle$ for CH_4 + He by almost a factor of

three. The poor performance of the LJ approximation can be attributed to the r^{12} repulsive wall, which is significantly "harder" than realistic repulsive walls.

2. The separable pairwise approach can be very accurate when the exp/6 interaction potential is used and when the exp/6 parameters are determined via fits to ab initio energies throughout the van der Waals well. For CH_4 + He (Fig. 1(a)), the MP2+exp/6 and TB+exp/6 methods have errors of only ~10% relative to the MP2 results.
3. For some systems, however, the interaction potential cannot be well described when nonpairwise interactions are neglected. We found this to be the case for CH_4 interacting with diatomic baths [7], which led us to develop three exp/6 parameterizations for CH_4 + H_2 by fitting to three sets of ab initio data. In the R data set H_2 was oriented radially (i.e., along the axis of approach) to CH_4, in the P data set H_2 was oriented perpendicularly to CH_4, and in the RP parameterization both sets of data were fit. As shown in Fig. 1(b), the parameterization fit to all of the ab initio data (RP) is the least accurate relative to the MP2 results, with an error of ~30%. If either the radially-oriented or perpendicularly-oriented data were used exclusively, the accuracy of the exp/6 parameterization improved, even though these parameterizations fit the excluded data very poorly. We interpret this improvement in accuracy as accidental, and we conclude that energy transfer averages calculated using the separable pairwise method for systems where the nonpairwise terms are important can have additional uncertainties of up to 50% [7].
4. The use of "universal" hydrocarbon–bath gas exp/6 parameters for targets other than CH_4 can be very accurate. In Fig. 1(c), the values of $<\Delta E_d>$ calculated for C_2H_5 + He using TB+exp/6 parameters taken from CH_4 + He are shown to agree well with MP2 results. In another test not shown here, the Kr exp/6 parameters from CH_4 + Kr were tested against a parameterization obtained from fits to propyl + Kr interaction energies; the predicted values of $<\Delta E_d>$ for propyl + Kr differed for the two TB+exp/6 parameterizations by less than 10%.
5. The calculated energy transfer averages are relatively insensitive to the choice of the method used to describe the intramolecular potential. Using the MP2+exp/6 and TB+exp/6 methods gives very similar results in all of our tests.

These results suggest that the TB+exp/6 method along with "universal" exp/6 parameters taken from CH_4 + M can be used to efficiently study energy transfer in hydrocarbons. The accuracy of this approach is likely to be limited by the complexity of the interaction potential. The CH_4 + He system may be particularly well described by the separable pairwise approximation due to its nearly spherical interaction potential. For less isotropic interaction potentials (and for diatomic baths in particular), one can likely expect additional uncertainties in the TB+exp/6 approach, although the good accuracy for C_2H_5 + He in Fig. 1(c) is encouraging.

Trends with respect to the target. Energy transfer averages and average rate coefficients for several targets in Ar are shown in Fig. 2. In principle, $<r_d>$ may be more readily interpreted than $<\Delta E_d>$ due to the somewhat arbitrary scaling to the Lennard-Jones collision rate employed in eq 1 [7,8]. Nevertheless, both averages show clear trends with respect to the number of carbon atoms in the target. At 2000 K, $<\Delta E_d>$ for the C_2 species is ~300 cm^{-1} larger than $<\Delta E_d>$ for methane, and likewise $<\Delta E_d>$ for the C_3 species is ~300 cm^{-1} larger than $<\Delta E_d>$ for the C_2 species. A similar trend appears in $<r_d>$, where the C_1, C_2, and C_3 species have high temperature energy transfer rate coefficients of 1.1,

2.0, and 3.0 x 10^{-9} cm^{-1}/s, respectively. In contrast, there is relatively little difference in $<\Delta E_d>$ (or $<r_d>$) due to the number of hydrogen atoms in the target.

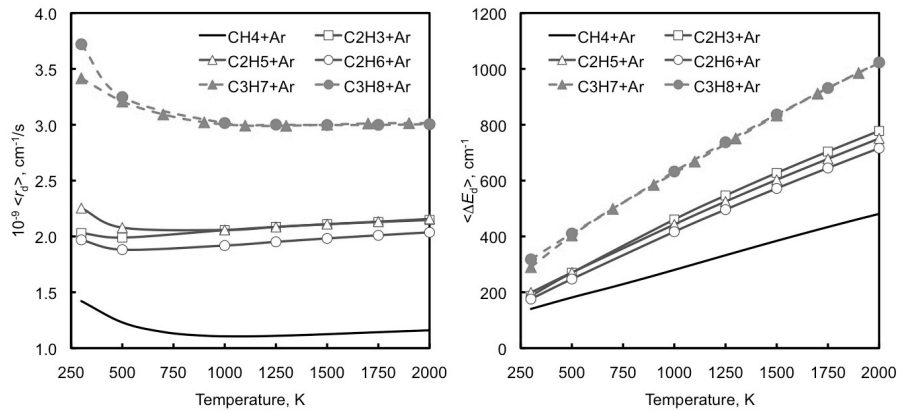

Figure 2: (a) Average deactivating energy transfer rate coefficient and (b) average energy transferred in deactivating collisions for several targets in Ar.

Trends with respect to the bath gas. Trends in the calculated energy transfer averages with respect to the bath gas have also been studied for CH_4 in eight baths [7] and for several targets in four atomic baths. For CH_4 at room temperature, the relative values of $<r_d>$ are 1.0:0.70:0.97:1.0:1.9:1.1:1.0:3.3 for the He, Ne, Ar, Kr, H_2, N_2, CO, and CH_4 colliders, i.e., the efficiencies are similar for all the baths except for Ne which is relatively weaker and H_2 and CH_4 which are relatively stronger colliders. At 2000 K, the relative efficiencies of the lighter baths increase, with ratios of 1.0:0.50:0.55:0.52:1.6:0.82:0.71:1.9. These results may be rationalized by noting that at lower temperatures there is some influence on $<\Delta E_d>$ due to the strength of the target–bath interaction energy, whereas at higher temperatures the relative efficiencies are more directly determined by the collision frequency and therefore the mass of the bath. Similar trends with respect to the bath gas were obtained for other targets.

Fully predictive pressure dependent kinetics calculations. The values of $<\Delta E_d>$ calculated as discussed above using classical trajectories may be used along with quantum chemistry and transition state theory calculations to make parameter-free ME calculations of pressure dependent kinetics. This is in contrast to the usual situation, where, due to a lack of knowledge of the relevant energy transfer parameters, these parameters are often adjusted empirically to match some experimental data or are simply estimated. We have tested our parameter-free kinetics calculations against experimental data for CH_4 in several baths [6,7] and for C_2H_5 and C_3H_7 in Ar. For CH_4 in He, Ar, and CH_4, the agreement between the predicted and experimental rate coefficients is excellent and is within the experimental uncertainty or scatter. For C_2H_5 and C_3H_7, however, the predicted values of $<\Delta E_d>$ appear to be somewhat too large. The source of this discrepancy is under investigation.

One major source of error in the ME calculations is in the determination of the rovibrational density of states, ρ, of the target. Typically, the rigid rotor–harmonic oscillator approximation is used to calculate ρ, and this approximation can lead to errors of a factor of ~2 in the low pressure rate coefficients [7,11]. This error (and others in the quantum chemistry and transition state theory parts of the calculation) make it difficult to judge the accuracy of the present predictions for $<\Delta E_d>$ and of the energy transfer models

by comparing experimental and theoretical rate coefficients. It is likely that in many calculations of low pressure rate coefficients, the error due to the use of harmonic values of ρ is larger than the error due to $<\Delta E_d>$ calculated using the methods described here.

Finally, we note that it may be desirable to extend the single-exponential-down model for energy transfer used here to include dependence on the initial energy and/or rotational state of the target and to better describe the "long-tail" of the energy transfer distribution. This additional information may be readily obtained from trajectory studies.

4. Conclusions

Energy transfer in highly vibrationally excited methane, ethane, propane, vinyl radical, ethyl radical, and propyl radical has been studied using classical trajectories for several bath gases. The quality of the resulting energy transfer averages was shown to depend on the accuracy of the potential energy surface, and the magnitude of the error due to this source was quantified to be as much as 50%. A separable pairwise strategy combined with universal interaction potential parameters for hydrocarbons and a semiempirical method for describing the intramolecular potential was described and validated. This scheme was used to study trends in energy transfer averages for several baths and for several targets. The relative efficiencies of several baths were shown to be a function of temperature, which cautions against the use of room temperature values to inform energy transfer models for combustion applications. A clear trend in $<\Delta E_d>$ was observed with respect to the number of carbon atoms in the target. Work is underway to study larger species and to understand the effect of rings and carbon chain branching, etc, on energy transfer properties. Finally, the accuracy of the resulting parameter-free pressure dependent rate coefficients was discussed, along with other possible sources of error in the ME calculations.

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