Contribution of the Tail of a Biexponential Energy-Transfer Probability Distribution to Thermal Unimolecular Rate Coefficients

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Experiments and quasiclassical trajectory calculations of intermolecular energy transfer indicate that the energy-transfer probability distribution function, $P(E',E)$ has a significant contribution from high-energy collisions, sometimes denoted as supercollisions. One functional form of $P(E',E)$ which is used to fit the data is a biexponential function with a low-energy exponential and a high-energy exponential which provides the high-energy tail. To assess the importance of the high-energy collisions, the present work evaluates the contribution of the high-energy tail to the value of the unimolecular rate coefficient by assuming model biexponential probability functions and solving the appropriate master equations. Since the strong collision part of the biexponential function contributes to small values of the energy exchanged, ΔE, as well, a distinction is made between the high-energy exponential and the tail of the probability function that represents supercollisions. Solving a master equation with the tail only, shows that supercollisions, in spite of their small numbers, contribute, under certain conditions, significantly to the values of the low pressure unimolecular rate coefficient.

Introduction

Collisional energy transfer provides the mechanism for accumulation and dissipation of energy in thermal unimolecular reactions. The competition between the chemical reaction and the energy transfer is determined by the energy-dependent rate coefficients, $k(E)$, for chemical reactions and the pseudo first-order energy transfer rate coefficients, $R(E',E)$ of getting from level E to level E'.[1−6] Little is known experimentally about the energy-transfer rate coefficients, their dependence on the initial energy, E, and on the energy gap, $E' - E$. Experiments in reactive systems[7−9] showed first in 1988 that these rate coefficients are not negligible even at large energy gaps, and more recent physical experiments are aimed at mapping the entire energy-transfer rate coefficient matrix.[10−13] This same goal can be achieved by modeling using classical trajectory calculations.[14−18] The technology of such calculations has been established, and it seems that they can be trustfully applied to gain energy-transfer details that are not available experimentally. These calculations support the observation that $R(E',E)$, as a function of the energy gap, has a long tail,[19−24] and cannot be represented by a single exponential. An indirect comparison between classical calculations and quantum scattering calculations for benzene−rare gas atoms[25a,b] and a direct comparison for CS_2−He[25c] indicate that classical calculations can be used to study intermolecular energy transfer.

Collisions transferring an unexpectedly large amount of energy (in terms of the traditional picture of energy transfer in unimolecular systems which assumes an exponential or a stepladder form of $P(E',E)$) are termed *supercollisions*. A quantitative definition of them is that they are collisions that transfer more energy than some multiple of the average energy transferred per collision in the given system.[24−27] The fraction of collisions belonging to this class of collisions is generally very small, but their effect on energy transfer is much larger than expected from their relative weight. Detailed model studies were performed in order to quantitatively determine the influence of the high-energy collisions on the pressure dependent rate coefficients.[27,28] In these calculations, the matrix of $R(E',E)$ was built up in a way which enabled a separation of "weak" from "strong" collisions. They are represented by the first and second terms respectively of the right-hand side of eq 1. Then, the matrixes were changed systematically by changing the amount or size of the strong collision part of $R(E',E)$ such that the effect of supercollisions could be evident. In these calculations, the energy gap dependence of the energy-transfer rate coefficient was constructed from a double-exponential probability function which for down transition is given by

$$P(E',E) = [a_1 \exp(-\Delta E/\alpha_1) + a_2 \exp(-\Delta E/\alpha_2)]/C(E) \quad (1)$$

multiplied by the hard-sphere collision rate Z. $C(E)$ is the normalization coefficient and the sum of a_1 and a_2 equal unity. One of the exponential contributions, α_1, describes the bulk of the collisions and has a much larger weight, a_1, than the part containing α_2. However, it decreases much faster with the energy gap in agreement with the fact that most collisions are weak. The second exponential describes the long tail of the distribution. Some of the collisions that are represented by this part are also "weak", i.e., this distribution is also skewed toward small gaps. Clearly, another functional form for $P(E',E)$ could be used. However, in the absence of information on the actual shape of the function, the biexponential function provides a facile expression to handle and insight into the strong and weak collisions contributions to the values of the rate coefficients and average quantities.

When the $R(E',E) = ZP(E',E)$ matrix was introduced into the master equation and the latter was solved, the very important role of supercollisions became evident. The omission of the latter lead to rate coefficients of up to 10 times less than obtained in their presence even if their relative weight was very small. In the following we refer to the first part of the probability function as the "weak collision" (WC) part and to the second

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as the "strong collision" (SC) part. Comparison of the weight and exponential parameters obtained by fitting a double-exponential function to experimental results obtained from deconvolution of shape functions[29] with those obtained by fitting a biexponential function to trajectory calculations results[21,24,26] showed that for the latter the relative weight of the "strong" contribution was too large (a_2 being 1 order of magnitude smaller than a_1 in contrast to 2 or 3 orders of magnitude obtained in fitting experimental results), and the rate of decrease with the energy gap was too small (α_2 too small compared with α_1). Model calculations using experimentally based values[27] and using trajectory-based energy-transfer rate coefficient matrixes[26] also emphasized the importance of the "strong" contribution (involving supercollisions) both in the relaxation of ensembles of excited molecules in the absence of reactions[21] and in reactive systems.[27] If α_2 is systematically increased when all other parameters are fixed, the ratio of the unimolecular rate coefficient with the "strong" contribution to that without it increases monotonously up to 10−50 depending on the ratio of the weighting factors a_2 and a_1.

It is not clear from model calculations performed so far as to how the high-energy collisions affect the rate coefficient since they were not clearly separated from the "weak" collisions which emanate from the strong and weak parts of the biexponential function. This is so because the "strong" contributor to the distribution introduces also collisions with values of ΔE smaller than the threshold value assigned to the high-energy collisions, and therefore only a fraction of the class of strong collisions belongs to the class of supercollisions. To evaluate the pure effect of the high-energy tail, we performed another set of model calculations in which only the contribution of collisions in the supercollision tail of the distribution was considered.

Methods

In the model calculations reported here, the maximum contribution of the high-energy collisions to the value of the unimolecular rate coefficient was studied at the low-pressure region,[27] where the supercollision effect is expected to be the largest. At pressures in the falloff the effect is smaller, and at the high-pressure limit the value of the unimolecular rate coefficient is independent of collisional effects, and therefore high-energy collisions are not expected to affect its value. To evaluate the supercollision contribution, an assumed double exponential transition probability function is used (eq 1). Equation 1 describes the down collisions part of $P(E',E)$ which is kept constant. The up-collision part has a temperature dependence via microscopic reversibility. Figure 1 indicates the contributions of WC and SC to the value of $P(E',E)$ as a function of the amount of energy transferred, ΔE. In our systematic study we have "taken $P(E',E)$ apart" and solved the master equation, ME, for cyclobutene isomerization (and cyclobutane fission not reported here). The double-exponential probability function was normalized, and detailed balance was strictly observed. From this $P(E',E)$ we have calculated the value of the unimolecular rate coefficient k_{uni}. When we studied the effect of various parts of $P(E',E)$ on the kinetics of the reaction, we omitted parts of the distribution without changing the remaining elements of the energy-transfer probability function matrix. This enabled us to evaluate the relative contribution of the various parts of the distribution to the low-pressure rate coefficient. Our results, therefore, are presented as k_{uni}/P, where P is the pressure. Throughout the calculations of the low-pressure rate coefficient the value of α_1 was kept constant at 300 cm^{-1} and the value of α_2 was varied systematically between 300 and 10 000 cm^{-1} and the temperature changed between 500 and 1500 K. The details of the calculations, threshold energies, vibrational frequencies, and the rest of the RRKM theory parameters, are given in refs 28 and 30.

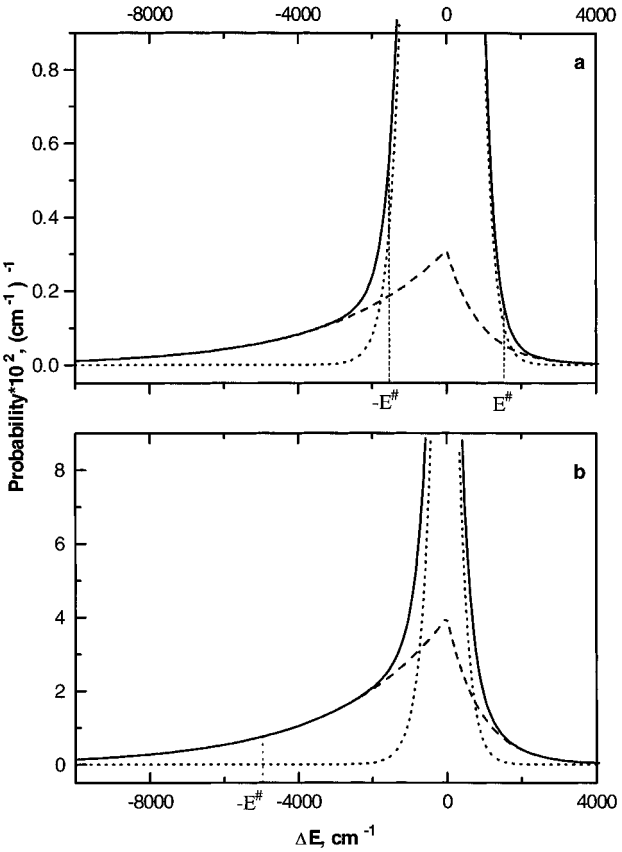

Figure 1. Biexponential transition probability function (—) as function of the ΔE showing the weak (···) and strong (- - -) collisions parts and the cutoff value $\Delta E^{\#}$ (vertical line) for $\alpha_1 = 300$ cm^{-1}, $\alpha_2 = 3000$ cm^{-1}, and T = 1000 K. (a) Probability function for $a_1 = 0.995$ and $a_2 = 0.005$. (b) $a_1 = 0.9$ and $a_2 = 0.1$.

As we attempt to explore the role supercollisions play in the collisional effects in the kinetics of unimolecular reactions, a quantitative definition is needed. The collisions that transfer "extremely large" amounts of energy are represented by the long tail of the energy-transfer probability distribution that was not assumed in the traditional model probability distributions. The single-exponential function used previously to fit experimental data had a tail much smaller than the tail of the function used in the present study. The value of the energy transferred in a supercollision is certainly not a universal one and, to some extent, must be system dependent. It was recommended in the past that those high-energy collisions should transfer more than 5 times the average energy transferred in a down collision.[25] This applies to microscopic systems, and it takes in consideration only the properties of the energy-transfer probability matrix, i.e., the energy transferred from an excited molecule in a single collision. In the bulk, the interplay between energy transfer and chemical reaction must be taken into account.

To have an indication of the intrinsic average size of the energy transferred under the actual conditions for reaction, we have to take into consideration the steady-state population which is involved in the energy-transfer process. We do so by calculating the ensemble average energy transferred per down collision in the system defined as

$$\langle\langle \Delta E \rangle\rangle_d = \int_0^\infty \langle \Delta E \rangle_d f(E)\, dE \qquad (2)$$

where $f(E)$ is the steady-state population which for weak collider

at low pressures is different from the Boltzmann population distribution. Supercollisions can be considered as those collisions that transfer much larger values of energy than this average. As an approximate measure, one could say the threshold value for such high-energy collisions should be larger than some multiple of $\langle\langle\Delta E\rangle\rangle_d$ (or for that matter of $\langle\langle\Delta E\rangle\rangle_{up}$). As a rough estimate, we chose a factor of 5, as was done in previous studies[25] of a microscopic system where $\langle\Delta E\rangle_d$ applies, as the limit above which one would consider a "supercollision". Therefore, we have calculated $\langle\langle\Delta E\rangle\rangle_d$, at predetermined temperature and pressure, for a given reaction with a biexponential probability distribution, and considered the effect of the "tail of the distribution" by omitting all collisions which transfer (up or down) $|\Delta E|$ values which are smaller than $5\langle\langle\Delta E\rangle\rangle_d$. The factor of 5 used may be too small or can shift the limit of "high-energy collisions tail" to too large energies, but it will certainly give an indication on the role of the tail in thermal unimolecular reactions. The effect will definitely be the largest at the low-pressure limit and will decrease with increasing pressure. Using ensemble average instead of average energy transferred in a down collision is justified also because the latter is independent of the temperature while $f(E)$, and therefore $\langle\langle\Delta E\rangle\rangle_d$, is temperature dependent. This reflects the interaction between energy-transfer and chemical reaction which affects the energy transfer process. In any event, the value of $\langle\Delta E\rangle_{all}$ cannot be used as a criterion for isolating the effect of the tail since it averages up and down collisions. Each of the two can have a large value, but the sum will be small. Thus, it will give no indication of the actual average energy-transfer step size.

The following configurations of the probability function were used in the solution of the master equation: (a) The whole double-exponential expression was used. (b) The contribution of the WC part of the biexponential function was removed. (c) Only collisions that transfer large quantities of energy are considered. Their probability is kept as in the full biexponential function. The calculations are done by using the tail of the double exponential distribution above a threshold value $\Delta E^{\#} = 5\langle\langle\Delta E\rangle\rangle_d$. (d) The WC part of the biexponential function was removed, as in (b), but only the tail above $\Delta E^{\#}$ was considered. This isolates the contribution of the strong collider to the tail of the distribution. Comparison of the results obtained in the above configurations enable us to draw conclusions that are reported in the next section.

Results and Discussion

Before exploring the effect of the high-energy tail on the unimolecular rate coefficient it is worthwhile to study the relative contribution of the tail above the threshold to the probability integral. This is given by the value of the integral

$$A = \int_{-E}^{-\Delta E^{\#}} P(\Delta E)\, d\Delta E + \int_{\Delta E^{\#}}^{\infty} P(\Delta E)\, d\Delta E \qquad (3)$$

where $\Delta E = E' - E$ and A is the cumulative probability of supercollisions which includes the area of the tail above $\Delta E^{\#}$ and below $-\Delta E^{\#}$. A is energy dependent through the dependence of $P(E',E)$ and $C(E)$ on E. In the present work, the calculations were made at 35 088 cm^{-1} (103 kcal/mol) at 500 K and 42 100 cm^{-1} (120 kcal/mol) at 1000 and 1500 K. Table 1 shows the contribution of the strong collision part of $P(E',E)$ (eq 1) to the total probability of energy transfer and the values of cumulative probabilities A for various values of α_2 and of the temperature for cyclobutene/Ar at 10^{-3} Torr. Integration of the strong collision term of the probability function, eq 1 (column 4 of Table 1) yields the contribution coming from this part only. For $a_2 = 0.005$ we obtain values of the integral which vary from ~0.005 to ~0.09 depending on the value of α_2. This shows that the coefficients a_1 and a_2 do not represent the true contributions of the WC and the SC parts of the probability distribution function to the WC and SC collisions. That is to say, the fraction of collisions described by the SC part only is always larger than the value of a_2. Thus $a_2 = 0.005$ does not mean that there are 0.5% SC (of which supercollisions are only a part). Evaluation of the tail only, e.g., the value of A, calculated with the SC part only (column 5 of Table 1) indicates that the tail of the SC part contributes up to 85% of the **total** value of A. This shows that in this case supercollisions are a major part of the SC contribution. As the fraction of SC that meets the criterion of high-energy collisions depends on α_2, the value of a_2 never gives the supercollision fraction of the total probability. At low values of α_2 and low values of a_2 the SC part contributes **less** than the WC part. It is the interplay between all the coefficients in the probability function that eventually determine the relative contribution of the WC and SC parts.

For the case of $a_2 = 0.1$ the situation is more complicated. Table 1 gives the values of the SC part and of A for various values of α_2 and the temperature. Here the contribution of the SC part can reach up to 70% of the total probability. The value of A, however, can be as large as 77% of the SC part at low

TABLE 1: Values of the Energy-Transfer Probability Integral

α_2	$-\langle\langle\Delta E\rangle\rangle_d$	$\Delta E^{\#}$	0/0.005[a]	tail only[b] 0/0.005	tail only[c] 0.995/0
			$T = 500$ K		
300	213	1064	5.00*E*−03	8.77*E*−05	1.75*E*−02
1500	218	1089	1.89*E*−02	7.62*E*−03	1.72*E*−02
3000	221	1105	3.39*E*−02	2.11*E*−02	1.69*E*−02
5000	224	1120	5.17*E*−02	3.83*E*−02	1.66*E*−02
10000	226	1130	8.25*E*−02	6.82*E*−02	1.26*E*−02
			$T = 1000$ K		
300	264	1320	5.00*E*−03	4.69*E*−05	9.34*E*−03
1500	284	1420	1.97*E*−02	5.93*E*−03	5.63*E*−03
3000	318	1590	3.45*E*−02	1.70*E*−02	3.40*E*−03
5000	354	1770	5.17*E*−02	3.13*E*−02	1.61*E*−03
10000	401	2003	8.33*E*−02	6.02*E*−02	7.54*E*−04
			$T = 1500$ K		
300	262	1308	5.00*E*−03	4.74*E*−05	9.44*E*−03
1500	285	1427	2.08*E*−02	6.63*E*−03	7.03*E*−03
3000	340	1700	3.64*E*−02	1.70*E*−02	2.27*E*−03
5000	405	2025	5.44*E*−02	3.08*E*−02	7.37*E*−04
10000	507	2534	9.00*E*−02	6.22*E*−02	1.36*E*−04
			0/0.1[a]	0/0.1[b]	0.9/0[c]
			$T = 500$ K		
300	213	1064	1.00 *E*−01	1.75*E*−03	1.58*E*−02
1500	306	1530	3.00 *E*−01	9.03*E*−02	2.96*E*−03
3000	358	1790	4.40 *E*−01	2.20*E*−01	9.23*E*−04
5000	385	1935	5.60 *E*−01	3.50*E*−01	4.58*E*−04
10000	413	2065	7.00 *E*−01	5.40*E*−01	1.93*E*−04
			$T = 1000$ K		
300	264	1320	1.00*E*−01	8.98*E*−04	8.08*E*−03
1500	579	2895	3.03*E*−01	3.20*E*−02	2.53*E*−05
3000	1002	5010	4.40*E*−01	6.66*E*−02	1.81*E*−08
5000	1356	6780	5.47*E*−01	1.22*E*−01	4.24*E*−11
10000	1749	8745	6.88*E*−01	2.54*E*−01	4.24*E*−14
			$T = 1500$ K		
300	257	1285	1.00*E*−01	1.00*E*−03	9.05*E*−03
1500	625	3125	3.10*E*−01	2.79*E*−02	1.30*E*−05
3000	1266	6330	4.39*E*−01	4.01*E*−02	2.03*E*−10
5000	1922	9610	5.59*E*−01	6.41*E*−02	2.78*E*−15
10000	2771	13855	6.89*E*−01	1.38 *E*−01	1.61*E*−21

[a] Strong collision part of $P(E',E)$ $a_1 = 0$, $a_2 = 0.005$, or $a_2 = 0.1$. [b] Same as in *a*, but the integration is taken from the cutoff value $\Delta E^{\#}$. [c] Weak collision part of $P(E',E)$ $a_1 = 0.995$ and or $a_1 = 0.9$ and $a_2 = 0$. The integration is performed from the cutoff value $\Delta E^{\#}$.

TABLE 2: Average Energies, Cutoff Limits (cm^{-1}), and Rate Coefficients (s^{-1} $Torr^{-1}$) as a Function of Temperature and the Strong Collision Part of a Biexponential Probability Function (Eq 1, $\alpha_1 = 300$ cm^{-1} and $P = 10^{-3}$ Torr, $a_1 = 0.995$, $a_2 = 0.005$ for All Calculations

α_2	$-\langle\Delta E\rangle_d$[a]	$-\langle\langle\Delta E\rangle\rangle_d$	$\Delta E^{\#}$	0.995/0.005[b]	tail only[c]	0/0.005	tail only	0.995/0	tail only
$T = 500$ K						$k_{uni}/P\cdot10^3$			
300	297	213	1064	64.0	5.35	1.20	0.00	63.0	5.10
1500	327	218	1089	72.0	7.60	6.90	5.50	64.0	6.80
3000	426	221	1105	85.0	17.0	11.0	3.60	63.0	3.30
5000	657	224	1120	100.0	24.0	18.0	17.0	60.0	8.40
10000	1510	226	1130	110.0	31.0	29.0	26.0	59.0	6.30
$T = 1000$ K						$k_{uni}/P\cdot10^{-2}$			
300	297	264	1320	49.9	6.50	0.25	.003	49.7	6.43
1500	327	284	1420	61.7	12.8	11.0	8.20	48.9	4.40
3000	426	318	1590	91.3	32.8	34.8	29.4	48.2	2.98
5000	657	354	1770	128	58.4	64.9	56.4	47.5	1.64
10000	1510	401	2003	183	102	113	101.	46.7	0.88
$T = 1000$ K						$k_{uni}/P\cdot10^{-3}$			
300	297	262	1308	29.5	4.84	0.148	.024	29.4	4.81
1500	327	285	1427	43.0	14.5	12.0	10.2	28.8	3.93
3000	426	340	1700	89.1	45.7	49.1	43.2	28.2	1.76
5000	657	405	2025	152	90.9	102	89.7	27.6	0.752
10000	1510	507	2534	252	164	188	164	26.8	0.193

[a] Asymptotic value obtained numerically as in ref 27. [b] The first number indicates the value of a_1 and the second indicates the value of a_2 at which calculations were made. [c] The values of k_{uni}/P obtained when only values of $P(E',E)$ above $\Delta E^{\#}$ were considered.

TABLE 3: Average Energies, Cutoff Limits (cm^{-1}), and Rate Coefficients (s^{-1} $Torr^{-1}$) as a Function of Temperature and the Strong Collision Part of a Biexponential Probability Function (Eq 1, $\alpha_1 = 300$ cm^{-1} and $P = 10^{-3}$ Torr, $a_1 = 0.90$, $a_2 = 0.10$ for All Calculations

α_2	$-\langle\Delta E\rangle_d$[a]	$-\langle\langle\Delta E\rangle\rangle_d$	$\Delta E^{\#}$	0.9/0.1[b]	tail only[c]	0/0.1	tail only	0.9/0	tail only
$T = 500$ K						$k_{uni}/P\cdot10^3$			
300	297	213	1064	64.0	5.35	6.50	0.80	57.0	4.86
1500	725	306	1530	127.	55.6	78.0	48.0	46.5	1.51
3000	1716	358	1790	196.	97.2	147.	95.0	36.1	2.22
5000	3327	385	1935	240.	157.	200.	155.	28.9	*d*
10000	7094	413	2065	285.	201.	254.	200.	28.7	*d*
$T = 1000$ K						$k_{uni}/P\cdot10^{-3}$			
300	297	264	1320	4.99	0.65	0.50	.065	4.50	0.579
1500	725	579	2895	21.3	6.18	17.0	6.18	3.41	0.004
3000	1716	1002	5010	49.1	13.2	44.3	13.3	2.77	*d*
5000	3327	1356	6780	75.0	9.30	70.1	9.30	2.36	*d*
10000	7094	1749	8745	105.	1.50	99.8	1.50	1.96	*d*
$T = 1500$ K						$k_{uni}/P\cdot10^{-4}$			
300	297	257	1285	2.95	0.50	0.30	0.05	2.66	0.435
1500	725	625	3125	20.7	7.93	18.0	7.66	1.89	0.002
3000	1716	1266	6330	62.1	10.9	58.5	10.8	1.41	*d*
5000	3327	1922	9610	105.	3.20	101.	3.28	1.10	*d*
10000	7094	2771	13855	154.	0.55	150.	0.57	8.37	*d*

[a] Asymptotic value as obtained numerically.[27] [b] The first number indicates the value of a_1 and the second indicates the value of a_2 at which calculations were made. [c] The values of k_{uni}/P obtained when only values of $P(E',E)$ above $\Delta E^{\#}$ were considered. [d] Values below numerical accuracy of the calculations.

temperatures and only 20% at high temperatures. This comes about because the value of $\Delta E^{\#}$ increases with temperature to such an extent that the area encompassed by A decreases. This behavior will have a profound effect on the values of the rate coefficients as reported in the next section. The contribution of the tail, the value of A, considered over the whole α_2 and temperature range is also not represented by a_2. It varies over a wide range of values depending on the initial conditions of α_2 and temperature. In those cases where the value of A is very high, the values of a_2 and α_2 are unrealistically high and probably do not represent physical reality.

We have evaluated the low-pressure thermal unimolecular rate coefficients by solving the master equation with the four configurations of $P(E',E)$ listed in the method section. The results of our calculations of the values of the rate coefficient are given in Table 2 for $a_1 = 0.995$ and $a_2 = 0.005$ and in Table 3 for $a_1 = 0.9$ and $a_2 = 0.1$. We analyze the results section by section as listed in the methods section.

(a) Unimolecular Rate Coefficient from a Double-Exponential Transition Probability. The effects of the weight coefficients a_i and the SC exponent α_2 were explored. There is a systematic increase in the value of k_{uni} as a function of the increase in the value of α_2. It is worth noting the large effect the SC term has on the value of the unimolecular rate coefficient. In some cases the rate coefficient can be up to an order of magnitude larger than the value obtained with the WC alone. This happens when the values of α_2 and the temperature are very high. Actually, these facts were reported before,[27] and the only reason these values appear in the Tables 2 and 3 is that they serve as reference values with which all other numbers in the tables will be compared.

(b) Net Contribution of the Strong Collision Part to the Overall Rate Coefficient. In this part of our study, the contribution of the SC part, the second term on the right-hand side of eq 1, was evaluated by totally removing the WC contribution. The values of the unimolecular rate coefficients evaluated by using this form of the probability function in the ME were compared with values of the reference rate coefficients obtained by using the full double-exponential expression (eq 1) and reported in part (a). The contribution of the SC part in

TABLE 4: Cutoff Limits (cm^{-1}) and Rate Coefficients (s^{-1} $Torr^{-1}$) Based on the Tail Only of the Distribution and on $\langle\langle\Delta E\rangle\rangle_d$ and on $\langle\langle\Delta E\rangle\rangle_{up}$

	$a_1 = 0.995$, $a_2 = 0.005$				$a_1 = 0.9$, $a_2 = 0.1$			
α_2	$\Delta E^{\#}{}_{up}$	$\Delta E^{\#}{}_{d}$	up	down	$\Delta E^{\#}{}_{up}$	$\Delta E^{\#}{}_{d}$	up	down
$T = 500$ K			$k_{uni}/P\cdot10^{3}$				$k_{uni}/P\cdot10^{3}$	
300	1064	1064	5.35	5.35	1064	1064	5.35	5.35
1500	1089	1089	7.60	7.60	1530	1530	55.6	55.6
3000	1105	1105	17.0	17.0	1790	1790	97.2	97.2
5000	1120	1120	24.0	24.0	1935	1935	157.	157.
10000	1130	1130	31.0	31.0	2065	2065	201.	201.
$T = 1000$ K			$k_{uni}/P\cdot10^{-3}$				$k_{uni}/P\cdot10^{-3}$	
300	1345	1320	0.54	0.65	1345	1320	0.54	0.65
1500	1455	1420	1.28	1.28	3030	2895	5.70	6.18
3000	1655	1590	3.18	3.28	5350	5010	11.6	13.2
5000	1855	1770	5.74	5.84	7310	6780	4.45	9.30
10000	2155	2003	9.97	10.2	9490	8745	0.56	1.50
$T = 1500$ K			$k_{uni}/P\cdot10^{-3}$				$k_{uni}/P\cdot10^{-3}$	
300	1435	1308	4.84	4.84	1435	1285	5.00	5.00
1500	1645	1427	12.0	14.5	4300	3125	40.3	79.3
3000	2285	1700	39.7	45.7	10000	6330	6.00	109.
5000	3180	2025	75.0	90.9	15750	9610	0.50	32.0
10000	4670	2534	113.	164.	22480	13855	0.00	5.50

eq 1 depends on the values of the coefficient a_2 and the value of the exponent, α_2, and on the temperature. For cyclobutene at 500 K with $a_2 = 0.005$, the SC part with $\alpha_2 = 1500$ cm^{-1} contributes only ~7% to the rate coefficient but, with $\alpha_2 =$ 10 000 cm^{-1} it contributes ~30%. The higher the temperature the larger the contribution of the SC part. At 1500 K and $\alpha_2 =$ 10 000 cm^{-1} it contributes more than 74%. Such a high value of α_2 at $a_1 = 0.005$ may not represent a physical reality.

As the contribution of the SC is increased[25] to $a_2 = 0.1$, the proportional contribution of this part to the overall rate coefficient increases as well. It can reach ~90−100% depending on the value of α_2 and temperature. Exactly the same trends are observed for cyclobutane fission (not shown), and the conclusions are identical. It should be recalled that the SC part contributes also to the transfer of small values of ΔE. Thus we next proceed to remove all contributions to the rate coefficient from values of $P(E',E)$ below the threshold value of $\Delta E^{\#}$.

(c) Contribution of the Tail of Whole Transition Probability Function to the Value of the Rate Coefficient. This part deals with the pure contribution of the tail of the biexponential distribution above the threshold energy $\Delta E^{\#}$ to the value of the unimolecular rate coefficient In this part we use the whole $P(E',E)$ expression which contains WC and SC parts. In the next section we use only the SC part of the probability distribution.

As can be seen from Tables 2 and 3, there is a difference in the magnitude of the contribution to the rate coefficient and in the trend between the $a_2 = 0.005$ case and the $a_2 = 0.1$ case. In the former, the tail of the biexponential function with $a_2 = 0.005$ contributes between ~15% and ~65% to the overall rate coefficient, depending on the temperature and the value of α_2. The larger the value of α_2 and the higher the temperature the larger the contribution of the tail. It should be pointed out that the value of $\Delta E^{\#}$ increases with an increase in the value of α_2. Thus, a 65% contribution at 1500 K and $\alpha_2 =$ 10 000 cm^{-1} takes place at a larger value of the cutoff limit than at lower values of α_2. Even at the extremely high values of $\Delta E^{\#}$, the contribution of the tail is very significant.

For the case of $a_2 = 0.1$ the situation is more complicated. The value of $\Delta E^{\#}$ is so high that the contribution of the tail starts to decline. At 1000 K $\Delta E^{\#}$ ranges from ~3000 to ~9000 cm^{-1} and at 1500 K it ranges from ~3000 to ~14 000 cm^{-1}. For example, at 1500 K and $\alpha_2 = 1500$ cm^{-1}, realistic numbers obtained from fitting trajectory results to a continuous probability function,[21,24,26] the contribution of the tail to the unimolecular rate coefficient is ~40%. At $\alpha_2 = 10\,000$ cm^{-1} the contribution of the tail is only ~0.4% simply because the value of $\Delta E^{\#}$ jumps to a whopping ~14 000 cm^{-1}. The collisions in the high ΔE range, albeit of low probability, do most of the energy-transfer work. The ever increasing value of the onset of $\Delta E^{\#}$ causes, despite an increase in $P(E',E)$ due to an increase in α_2, a decline in the value of the tail. At high values of $\Delta E^{\#}$ the tail is so low that it overcompensates for the increase in $P(E',E)$ and there is an overall decline in the contribution of the tail to the rate coefficient. This indicates that, in this case, the combination of values of a_2 and α_2 are unrealistically too high. This limitation on the values of a_2 and α_2 is an important outcome of the present work in as much as it provides constraints on the shape of $P(E',E)$.

(d) Contribution of the Tail of the Strong Collision Part of the Transition Probability Function to the Value of the Rate Coefficient. In this part we examine the contribution of the tail of the SC part of the probability function. For the case of 0.005 SC the tail contributes ~90% of the value of k_{uni} obtained from using the whole SC part. Its contribution to the overall rate coefficient obtained from a biexponential function, is, as mentioned before, between 15% and 65%. As the value of α_2 increases so does the value of $\Delta E^{\#}$ and the value of k_{uni}. However, the value of the cutoff $\Delta E^{\#}$ does not vary by much, and therefore the contribution of the tail is very significant.

The case of $a_2 = 0.1$ at high temperatures provides a different story, not unlike that in section (c). The SC part is the main contributor to the value of the rate coefficient. However, when one examines the contribution of the tail above $\Delta E^{\#}$ there is the bell-shape behavior seen in section (c). The rate coefficient increases and then decreases again. The value of $\Delta E^{\#}$ increases to such values that even though $P(E',E)$ increases at high values of ΔE the tail decreases even faster, causing a decline in the value of the rate coefficient. This shows that some combinations of high values of a_2 and α_2 are physically unrealistic. There are some indications that experimental results yield low values of a_2 and high values of α_2 while trajectory calculations generally yield high values of a_2 but low values of α_2. The combination of high values of a_2 and α_2 is unphysical and is probably the cause for the decline in the values of the rate coefficient under such conditions.

As discussed above, the definition of $\Delta E^{\#}$ is arbitrary and it leads, in some cases, to unreasonably large threshold values. This causes in turn an artificial reduction of the contributions

of the tail to the values of the rate coefficients. In addition to the choice of a_i and α_i, an element of arbitrariness is the value of the factor multiplying the value of $\langle\langle\Delta E\rangle\rangle_d$. Another is the choice of $\langle\langle\Delta E\rangle\rangle_d$ instead of $\langle\langle\Delta E\rangle\rangle_{up}$, which, in the low-pressure region, might be more appropriate. Table 4 shows a summary of the calculations with $\Delta E^{\#}$ based on 5 $\langle\langle\Delta E\rangle\rangle_{up}$ and a comparison with calculations obtained by using the previous definition of $\Delta E^{\#}$. As can be seen from the Table at 500 and 1000 K the values of $\langle\langle\Delta E\rangle\rangle_{up}$ do not differ significantly from the values of $\langle\langle\Delta E\rangle\rangle_d$. Thus, every conclusion obtained from calculations using $\langle\langle\Delta E\rangle\rangle_d$ applies also to $\langle\langle\Delta E\rangle\rangle_{up}$. At high temperature, 1500 K, the values of $\langle\langle\Delta E\rangle\rangle_{up}$ are so high that they cannot form a basis for the definition of $\Delta E^{\#}$. For example at $\alpha_2 = 5000$ and 10 000 cm^{-1} the values of $\Delta E^{\#}$ emanating from $\langle\langle\Delta E\rangle\rangle_{up}$ are 15 750 and 22 480 cm^{-1}, respectively. These values are way over any reasonable estimate of a supercollision limit. They clearly indicate that the values of α_2 are on the high side.

Conclusion

The contribution of the tail of a biexponential energy-transfer probability to the value of the low-pressure thermal unimolecular rate coefficient was evaluated for a variety of experimental conditions by using master equation calculations. An arbitrary threshold value for high-energy transferring collisions was defined and the fraction of supercollisions was evaluated. It was shown that (1) the fraction of strong collisions, a_2, and their energy gap exponent, α_2, do **not** represent the contribution of the high-energy tail, e.g., supercollisions. (2) Not every combination of the two parameters is allowed. High values of both are unphysical and yield unacceptable values for the high-energy threshold. (3) The fraction of supercollisions is a function of the parameters that define the probability function as well as of the temperature.

The contribution of the tail to the thermal unimolecular rate coefficient for the isomerization of cyclobutene to butadiene was evaluated for four cases:

(a) The whole probability function was considered. In this case, adding a second exponential can increase the value of the rate coefficient by ~2−8-fold depending on the values of the fraction of the high-energy exponential, a_2, and energy gap constant α_2.

(b) Only the strong collision part of the probability function was considered. At low values of a_2 the contribution of this part varies between 9% and 75% depending on the value of α_2. At high values of a_2 it can vary between 60% and almost 100% again depending on the value of α_2.

(c) Only the tail of part (a) was considered. The tail contributes 12−20% at low values of the high-energy exponential, a_2, and energy gap constant α_2. It contributes up to 65% at high values of α_2. At high values of a_2, the contribution of the tail increases as α_2 increases and can be as high as 50%, and then it declines due to high values of the high-energy threshold.

(d) Only the tail of (b) was considered. At low values of a_2 and α_2 the contribution of the tail is only ~7% while for high values of α_2 it can reach as much as 65%. For high values of a_2 the contribution of the tail varies with α_2 from 38% at low values of α_2, and it declines rapidly due to unrealistically high threshold values.

In many of the cases considered, the tail contributes significantly to the value of the unimolecular rate coefficient. In other cases, high temperatures and large values of a_2 and α_2, the contribution declines due to a decrease in the tail at the very high energies which define the supercollisions threshold. In these cases, the parameters defining the biexponential probability functions are clearly unrealistically high.

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