

Statistical and dynamical behaviour in the unimolecular reaction dynamics of polyatomic molecules¹

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Abstract

The dominant theories of unimolecular reaction are statistical. A fundamental assumption is that the timescale on which energy moves about a reactant molecule is much shorter than the timescale for reaction. It is assumed that intramolecular vibrational energy redistribution (IVR) is globally rapid throughout the molecular phase space.

It has been widely thought that the assumption of rapid IVR referred to above is valid for sufficiently large polyatomics. Much of the supporting evidence for this view comes from indirect experimental studies of IVR and comparisons of statistical and dynamical calculations.

However, the presence of a fast IVR rate, as derived from some experiments, does not automatically ensure the reaction dynamics will be statistical. In fact, in recent studies, we have shown that even in the presence of fast IVR rates between some modes the reaction dynamics can be extremely non-statistical. Secondly, most comparisons of statistical and dynamical calculations have made simplifying assumptions which render the comparisons ambiguous.

In the present paper, we investigate results of recent statistical and dynamical calculations performed on identical potential energy surfaces for a range of polyatomic molecules. Our ultimate goal is to determine how the extent and timescale of IVR plays a role in determining the statistical or non-statistical behaviour in the subsequent unimolecular reaction dynamics of locally and microcanonically excited polyatomic molecules.

Keywords: Unimolecular reactions; Polyatomic molecule; Intramolecular vibrational energy redistribution

1. Introduction

Unimolecular reactions are commonly treated using some form of statistical theory – RRKM [1] or variational transition state theory (TST) [2]. These theories assume that prior to reaction the

molecular energy is microcanonically distributed amongst the reactant molecules internal modes. The energetically accessible phase space of the reactant molecule is assumed to have been fully explored on the timescale of chemical reaction (see Fig. 1).

It has generally been assumed [3] that a total intramolecular vibrational energy redistribution (IVR) rate that is fast relative to the unimolecular reaction rate is a sufficient condition to ensure statistical behaviour and an absence of mode-specific chemical effects.

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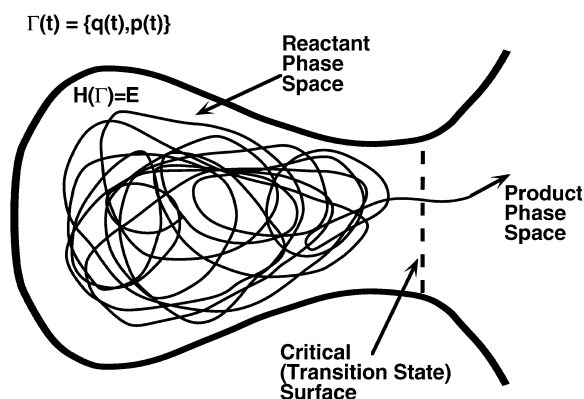


Fig. 1. Evolution of a statistical trajectory through reactant phase space.

Reliable experimental tests of this assumption have to some extent been limited by inadequate knowledge of the potential energy surface.

One approach which more directly tests the foundations of statistical unimolecular rate theories is by comparison with trajectory calculations. However, most previous comparisons of statistical predictions and dynamical calculations of unimolecular reaction rates have made simplifying assumptions which render the comparisons ambiguous. Frequently, the potential energy surface used for the dynamical calculations is approximated by a normal mode analysis for the statistical calculations. In addition, commonly used initial state selection procedures used for the dynamical calculations often cause artefacts such as short time transients which need to be deconvoluted from the true dynamical behaviour.

In order to clearly identify the presence or absence of statistical behaviour in a chemical reaction it is necessary to compare statistical predictions and dynamical calculations performed for exactly the same model (potential energy surface) under the same (initial) conditions. In the present paper we describe a series of recent studies of polyatomic systems for which we have made such comparisons [4–7]. The systems studied are disilane (Si_2H_6), 1,2-difluoroethane ($1,2\text{-C}_2\text{H}_4\text{F}_2$), the 2-chloroethyl radical ($2\text{-C}_2\text{H}_4\text{Cl}$) and methyl isocyanide (CH_3NC). In the Section 2 section we briefly describe the computational methods that were employed. Results of the calculations are given in Section 3 and conclusions are summarized in Section 4.

2. Computational methods

2.1. Potential energy surfaces

So as to provide the basis for an unambiguous comparison, it is necessary that a global potential energy surface be obtained for each polyatomic system and used directly for both the dynamical and statistical calculations.

We either employed existing global potential energy surfaces, as in the case of disilane [4] and 1,2-difluoroethane [5], or we constructed new global potential energy surfaces, as in the case of the 2-chloroethyl radical [6] and methyl isocyanide [7]. These potential energy surfaces employ many-body parameterized potential terms with functional forms based on physical and chemical considerations. The potential parameters were chosen so that the surface accurately reproduces many of the experimental or theoretical observables (e.g. equilibrium geometries, normal modes and dissociation energies) of the system. Details of the potential energy surfaces employed are available elsewhere [4–7].

2.2. Classical trajectory calculations

The dynamical calculations were performed using standard classical trajectory methods [4–7] with various local [4–7] and microcanonical (EMS, EJZ) initial state selection procedures [8]. The local initial state selection procedures [4–7] were designed to insert the bulk of the internal energy into specific vibrational (local or normal) modes. This local preparation served as a test of whether or not IVR was sufficiently rapid to redistribute the energy in a global fashion over reactant phase space so that the rate of reaction could be described by simple statistical considerations [1,2]. The EMS and EJZ initial state selection procedures [8] were designed to prepare microcanonical ensembles of initial states to test whether the dynamics would maintain (or perturb) the initial microcanonical distribution so that a statistical (or non-statistical) rate of reaction would result.

For each ensemble of initial states, classical trajectories were performed by integrating the equations of motion until unimolecular reaction (e.g. bond fission, isomerization) was achieved (reactive trajectories) or an upper time limit was reached (unreactive

trajectories). For each reactive trajectory, the lifetime to unimolecular decay was recorded. Each ensemble of trajectory lifetimes could be converted into a time-dependent decay probability $P(t)$ of reactant molecules remaining at time t . The dynamical microcanonical rate constants $k(E)$ were then estimated from the decay probability $P(t)$ by making the usual assumption of exponential decay [4–7]:

$$P(t) = \exp[-k(E)t] \quad (1)$$

The above procedure assumes that the recrossing of the transition state may be neglected on the timescale of reaction. This is likely to be true in the case of dissociation reactions if the criterion for dissociation (e.g. a critical bond length separation) is reasonable (e.g. large enough). In the case of isomerization, the products may recross back to reactants, so the above procedure would lead to an overestimation of the trajectory-derived rate constant. However, in the present case of CH_3NC isomerization, the trajectory-derived rate constant is much lower than the statistical TST prediction so that our conclusions will be unaffected.

2.3. Statistical calculations

Microcanonical rate constants were calculated for the same potential energy surfaces as used in the dynamical calculations by use of classical microcanonical variational TST [2]. The statistical microcanonical rate constants $k(E)$ and $k(E, J=0)$ were evaluated using the EMS-TST and EJZ-TST methods [4–8] which employ efficient microcanonical sampling (EMS) algorithms [8] to calculate the equilibrium flux through the critical (transition state) surface as

$$k(E) = \frac{1}{2} \langle \delta(q_{\text{RC}} - q_{\text{C}}) | \dot{q}_{\text{RC}} | \rangle_{\text{MC}, E} \quad (2)$$

and

$$k(E, J) = \frac{1}{2} \langle \delta(q_{\text{RC}} - q_{\text{C}}) | \dot{q}_{\text{RC}} | \rangle_{\text{MC}, E, J} \quad (3)$$

respectively.

The EMS-TST and EJZ-TST methods evaluate the required reactive flux by performing a Markov walk (Fig. 2) with the appropriate (EMS or EJZ) weight function $W(\mathbf{q})$ through the accessible configuration space \mathbf{q} of the reactant molecule [4–9]. Variational

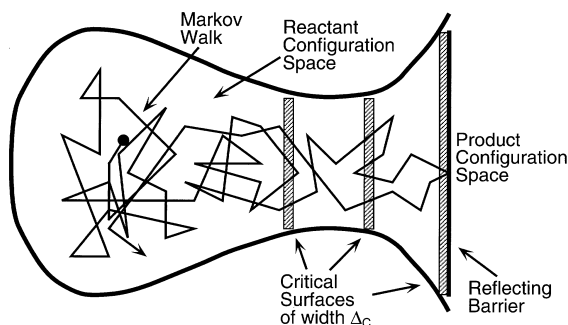


Fig. 2. Schematic view of a Markov walk used to sample reactant configuration space for EMS-TST and EJZ-TST calculations.

minimization of the reactive flux is achieved by varying the location of the critical surface.

3. Statistical and dynamical comparisons

3.1. Disilane

The simple bond fission channels of highly excited disilane were investigated by classical trajectory calculation [4] for energies ranging from 5.31 to 9.31 eV for a variety of different initial energization patterns: microcanonical, random, and Si–Si and Si–H normal mode excitations. The comparison of these results with the statistical EMS-TST predictions is shown for the Si–H fission channel in Fig. 3 and for the Si–Si fission channel in Fig. 4. Clearly, in both

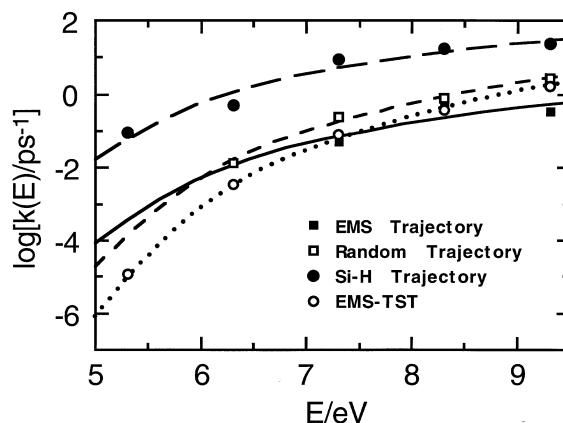


Fig. 3. Statistical and dynamical calculations of the rate of Si–H fission of Si_2H_6 : ■, EMS trajectory; □, random trajectory; ●, Si–H trajectory; ○, EMS-TST.

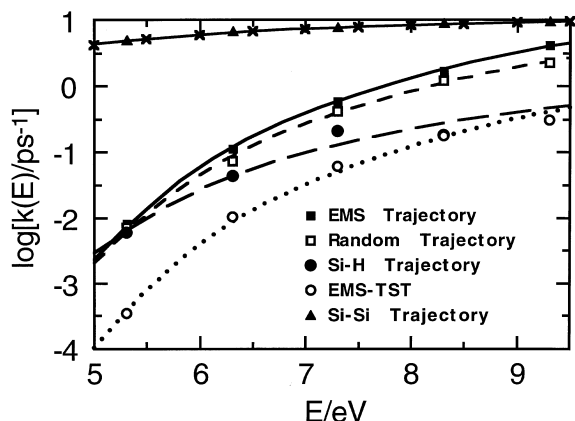


Fig. 4. Statistical and dynamical calculations of the rate of Si-Si fission of Si_2H_6 : ■, EMS trajectory; □, random trajectory; ●, Si-H trajectory; ○, EMS-TST; ▲, Si-Si trajectory.

cases the trajectory calculations differ markedly (by orders of magnitude in some cases) from the statistical predictions. At the lower energies, the statistical calculations predict much slower rates of reaction than those calculated from trajectories.

Furthermore, the rates of reaction depend markedly on the nature of the initial excitation, with microcanonical or random excitation yielding slower rates of reaction than excitation into modes directly related to the reaction coordinate. Thus, considerable enhancement is seen for Si-H excitation in Fig. 3 and Si-Si excitation in Fig. 4. Further investigations [4] reveal that the IVR out of the Si-H and Si-Si vibrational modes is rapid on the timescale of reaction. However,

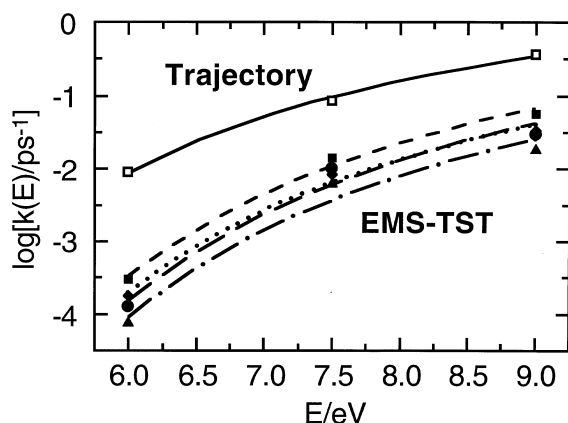


Fig. 5. Statistical and dynamical calculations of the rate of C-C fission of $1,2\text{-C}_2\text{H}_4\text{F}_2$: □, EMS trajectory; ■, ◆, ●, ▲, EMS-TST.

the rates of bond fission are non-statistical because many of the mode-mode IVR rate coefficients are much slower than the rate of reaction, implying the presence of IVR bottlenecks.

3.2. 1,2-Difluoroethane

Similar behaviour is found in a study of the C-C, C-F and C-H bond fission channels of 1,2-difluoroethane [5]. For example, the rate of C-C bond fission predicted by microcanonically initialized trajectory calculation is orders of magnitude in excess of the statistical EMS-TST predictions as shown in Fig. 5. This is despite the fact that IVR out of the C-H and C-C vibrational modes is rapid on the timescale of reaction [5].

3.3. 2-Chloroethyl radical

Despite the non-statistical behaviour found above for the unimolecular reaction dynamics of disilane [4] and 1,2-difluoroethane [5], a recent trajectory study of the C-H and C-Cl bond fission reactions of the 2-chloroethyl radical [6] yield reaction rates well described by statistical EMS-TST and EJZ-TST predictions. The comparisons are shown in Figs 6 and 7. The statistical predictions form an upper bound to the trajectory rates and the latter are relatively insensitive to the nature of the initial energization pattern. More detailed analysis [6] revealed that the statistical

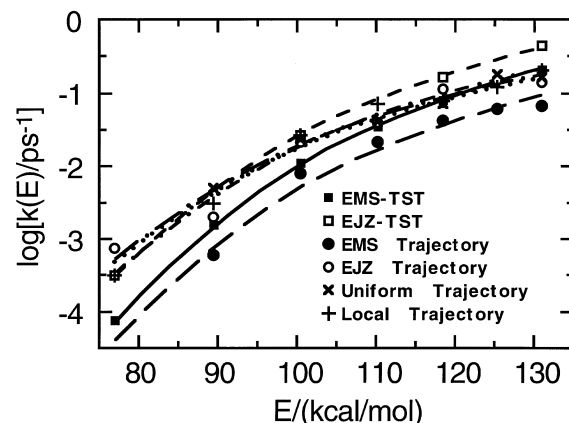


Fig. 6. Statistical and dynamical calculations of the rate of C-H fission of $2\text{-C}_2\text{H}_4\text{Cl}$: ■, EMS-TST; □, EJZ-TST; ●, EMS trajectory; ○, EJZ trajectory; ×, uniform trajectory; +, local trajectory.

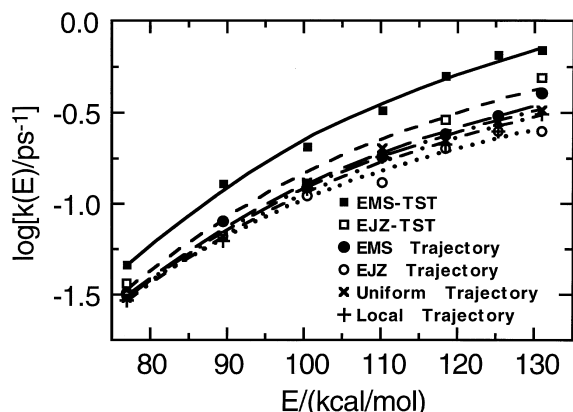


Fig. 7. Statistical and dynamical calculations of the rate of C–Cl fission of 2-C₂H₅Cl: ■, EMS-TST; □, EJZ-TST; ●, EMS trajectory; ○, EJZ trajectory; ×, uniform trajectory; +, local trajectory.

behaviour can be largely ascribed to an increase in potential coupling on conversion of the C–C single bond into a C=C double bond as the bond fission takes place.

3.4. Methyl isocyanide

A classic prototype reaction in the study of unimolecular reactions is the isomerization of methyl isocyanide. While experimental studies [10–12] yield agreement with fitted RRKM calculations, theoretical studies [13–16] show indications of non-statistical behaviour. A recent study [7] was performed to determine whether CH₃NC undergoes unimolecular

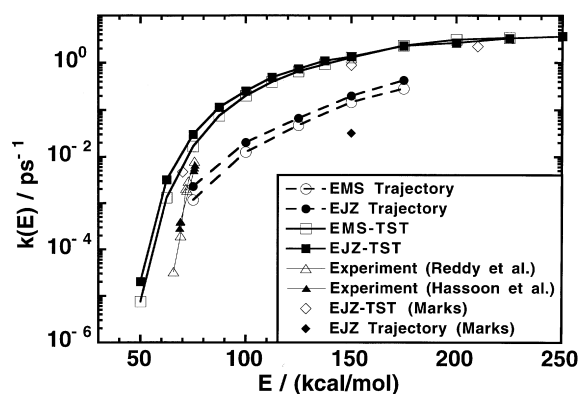


Fig. 8. Statistical and dynamical calculations and experimental estimates of the rate of isomerization of CH₃NC: ○, EMS trajectory; ●, EJZ trajectory; □, EMS-TST; ■, EJZ-TST; △, experiment ([11]); ▲, experiment ([12]); ◇, EJZ-TST ([16]); ◆, EJZ trajectory ([16]).

reaction in a statistical manner or whether mode-specific effects are possible.

Comparison of the results of microcanonically excited trajectories and statistical calculations reveals that the statistical TST predictions form an upper bound. The dynamical calculations yield isomerization rates much slower than statistical predictions (Fig. 8). This is despite the highly coupled nature of the potential energy surface. Apparently, the isomerization coordinate is somewhat decoupled from the other vibrational modes on the timescale of reaction.

Thus, the extent of coupling of the reaction coordinate with the remaining modes appears to be a major factor in determining the nature of the isomerization dynamics. In further work in progress [7], we find that trajectory rates calculated on the basis of very short time trajectories agree markedly better with the statistical predictions. This implies that states near the transition state can react normally, but that states much further away (in phase space terms) are impeded by an IVR bottleneck of some kind. The root cause of the bottleneck would seem to be the insufficient coupling between the reaction coordinate (essentially the isomerization angle for the CN fragment) and the other modes in the molecule. This explanation is consistent with results of a recent calculation by Marks [16] using a much simpler potential energy surface without any coupling which showed a much greater deviation between the statistical and dynamical rate constants (Fig. 8) than our more sophisticated model.

3.5. Effective number of vibrational degrees of freedom

An analysis of the microcanonical rate constants $k(E)$ can be made in terms of the classical RRK theory of unimolecular reaction [1] yielding an effective parameter denoted as the “ s -value”. Within the framework of RRK theory, which assumes a separable harmonic oscillator model of a reactant molecule, the s -value is equal to the number of vibrational degrees of freedom. However, this model, while retaining the spirit of the phenomenon, may be quantitatively inaccurate due to the influences of anharmonicity and the non-separable nature of the true potential energy surface. Even so, given due care, the s -value parameter can still be qualitatively interpreted as the effective

Table 1
Effective number of vibrational degrees of freedom

Reaction	Method	s_{eff}
$\text{Si}_2\text{H}_6 \rightarrow \text{SiH}_3 + \text{SiH}_3$ $s_{\text{RRK}} = 18$	EMS trajectory	12.7
	Si–H trajectory	9.0
	Si–Si trajectory	2.2
	EMS-TST	14.0
$\text{Si}_2\text{H}_6 \rightarrow \text{Si}_2\text{H}_5 + \text{H}$ $s_{\text{RRK}} = 18$	EMS trajectory	10.4
	Si–H trajectory	9.0
	EMS-TST	16.7
$\text{C}_2\text{H}_4\text{F}_2 \rightarrow \text{CH}_2\text{F} + \text{CH}_2\text{F}$ $s_{\text{RRK}} = 18$	EMS trajectory	8.5
	EMS-TST	12.5
$\text{C}_2\text{H}_4\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{Cl}$ $s_{\text{RRK}} = 15$	EMS trajectory	15.7
	EJZ trajectory	14.0
	Local trajectory	15.3
	EMS-TST	17.7
	EJZ-TST	16.5
$\text{C}_2\text{H}_4\text{Cl} \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{H}$ $s_{\text{RRK}} = 15$	EMS trajectory	17.1
	EJZ trajectory	13.1
	Local trajectory	14.4
	EMS-TST	17.6
	EJZ-TST	15.9
$\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ $s_{\text{RRK}} = 12$	EMS trajectory	15.9
	EJZ trajectory	17.2
	EMS-TST	10.3
	EJZ-TST	9.0

number of vibrational degrees of freedom that are explored on the timescale of chemical reaction.

Typical s -values are given in Table 1 for the above unimolecular reactions. In the case of disilane and 1,2-difluoroethane, the trajectory calculations yield effective s -values much smaller than the statistical predictions, the actual value being highly sensitive to the nature of the initial energization. This behaviour reflects the smaller volume of phase space seen by the trajectories. In the case of the 2-chloroethyl radical, the effective s -values for the trajectory calculations are quite close to the corresponding statistical predictions, reflecting the statistical nature of the fission channels. On the other hand, the trajectory calculations of the isomerization of methyl isocyanide yield effective s -values much larger than the statistical predictions. This discrepancy is a result of the relative isolation of the isomerization channel on the timescale of reaction – the larger effective s -value for the

trajectory calculations merely indicating the slower rate of isomerization (not that the reactant molecule has more vibrational modes than actually exist).

4. Conclusions

In studies [4,5] of the unimolecular dissociation of Si_2H_6 and 1,2- $\text{C}_2\text{H}_4\text{F}_2$ we have shown that, even in the presence of fast IVR rates between some modes, the reaction dynamics can be extremely non-statistical, implying the presence of substantial IVR bottlenecks.

In contrast, in the unimolecular dissociation of 2- $\text{C}_2\text{H}_4\text{Cl}$ [6] there was good agreement between the statistical predictions and the dynamical calculations of the reaction rate for C–H or C–Cl fission. This is in large part due to enhanced potential coupling associated with the formation of a C=C double bond upon fission.

The existence of a considerable bottleneck to IVR for the isomerization channel of CH_3NC [7] is rather surprising considering the highly coupled nature of the current potential energy surface. Further calculations are necessary to reconcile the deviations seen in the present study [7] with the experimental results [10–12].

In summary, it is clear that one of the important conditions for statistical behaviour is that IVR must be globally fast on the timescale of chemical reaction [6]. A typical trajectory must explore all of the energetically accessible reactant phase space.

Acknowledgements

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