

## REACTION RATE FOR ISOMERIZATION IN A MOLECULAR BEAM

Bruce J. BERNE \*

*Department of Chemistry, Columbia University, New York, New York 10027, USA*

Received 19 March 1984

It is shown that in an ideal gas (molecular beam), at temperature  $T$ , consisting of molecules that can isomerize and whose molecular dynamics can be non-ergodic, the observed decay rate of the concentration can be greater than that,  $k_{\text{TST}}$ , predicted by transition state theory. The "observed" rate constant is then given by  $(Q/Q_{\neq}^{(1)})k_{\text{TST}}$  where  $Q_{\neq}^{(1)}$  is the contribution to the canonical partition function  $Q$  arising from only activated and irregular states. It is also shown that in the presence of strong collisions the long-time decay rate of the concentration provides no information about the intramolecular rate process, but at low collision rates it is sensitive to the non-ergodic dynamics.

In this short note we consider the reaction dynamics of an ideal gas of polyatomic molecules in equilibrium at temperature  $T$ , where the molecules are capable of undergoing an isomerization reaction between two isomeric states labelled A and B. The reaction can be described by the motion of a reaction coordinate  $q$  in a double well with barrier height  $E^{\ddagger}$ . We wish to consider the case where the molecules cannot interact at all. One method for preparing such a system is to let a real gas come to equilibrium at temperature  $T$  and then use this real gas as a source for the production of a molecular beam \*\*. In the absence of energy transfer between molecules, the energy of each molecule is a constant of the motion. We assume that a molecule of energy  $E$  has a kinetic rate constant  $k(E)$  for barrier crossing. If the modes within the molecule are strongly coupled so that for energy  $E$  the motion is strongly chaotic (mixing) and if further-

more the time required for equipartitioning is rapid compared to the barrier traversal time, then the molecule will have a kinetic rate constant  $k(E)$  for barrier crossing given by RRKM theory [1,2]:

$$k_{\text{RRKM}}(E) \equiv \frac{\int d\Gamma \delta(E - H(\Gamma)) \dot{q} \delta(q) \theta(\dot{q})}{\int d\Gamma \delta(E - H(\Gamma))}. \quad (1)$$

If equipartitioning is not rapid compared to barrier crossing there will be dynamic corrections to the RRKM rate constant such that the true rate constant  $k(E) \leq k_{\text{RRKM}}(E)$ .

This rate constant will be an upper bound on the real rate constant if the molecular dynamics of the molecule is fully chaotic. The presence of  $\delta(q)$  in the numerator ensures that only those microscopic states contribute to the numerator for which  $H(\Gamma) \geq E^{\ddagger}$ . Thus  $k_{\text{RRKM}}(E) = 0$  for  $H(\Gamma) \leq E^{\ddagger}$ . Moreover  $k_{\text{RRKM}}(E)$  increases with  $E$ .

If the intramolecular mode coupling is not strong the molecular dynamics can be non-ergodic [2]. Phase space can then be decomposed into regular and irregular regions of measure  $\Omega_{\text{R}}(E)$  and  $\Omega_{\text{I}}(E)$  respectively. The set of all trajectories that cross the barrier consist of a subset of regular (or quasiperiodic) crossing trajectories and a subset of irregular (or chaotic) crossing trajectories. Only the chaotic crossing trajectories can give rise to an exponential decay of the popula-

\* This work was supported by a grant from the National Science Foundation.

\*\* Another case occurs, when a molecule dissolved in a very-low-viscosity solvent is excited to an electronic state with a double-well potential. If there is rapid intramolecular equipartitioning, then the subsequent barrier crossing dynamics can be described in a manner similar to the above case except that there will be a different energy distribution function.

tion and thereby to the existence of a reaction rate. If the irregular crossing trajectories are highly unstable, and furthermore give rise to rapid energy exchange on the time scale of barrier crossing then it is possible to derive a RRKM-like statistical theory for barrier crossing in such non-ergodic systems [2]. The rate constant is then

$$k(E) = k_{\text{NEST}}(E) = \frac{\int d\Gamma I(\Gamma) \delta(E - H(\Gamma)) \dot{q} \delta(q) \theta(\dot{q})}{\int d\Gamma I(\Gamma) \delta(E - H(\Gamma))} \quad (2)$$

where NEST stands for non-ergodic statistical theory, and where  $I(\Gamma)$  is a characteristic function which is unity on the irregular region of phase space and zero on the regular region. As in RRKM theory, if energy exchange is slow compared to barrier crossing dynamical corrections will be required. Furthermore if all crossing trajectories are chaotic the numerators of eqs. (1) and (2) become identical and [2]

$$k_{\text{NEST}}(E) = [\Omega(E)/\Omega_1(E)] k_{\text{RRKM}}(E) \quad (3)$$

since  $\Omega = \Omega_R + \Omega_I \geq \Omega_1$ , it follows that  $k_{\text{NEST}}(E) \geq k_{\text{RRKM}}(E)$ . Thus in non-ergodic systems, rate constants can be larger than given by RRKM theory. This has recently been observed in model systems [3]. In the following we assume that (a) the rate constant is given by  $k_{\text{NEST}}(E)$  and (b) all crossing trajectories are assumed to be chaotic for simplicity.

Let us first consider an ideal gas (or collisionless gas) consisting of these molecules, all at the same energy  $E > E^\ddagger$ . Suppose that this gas is produced with a small excess  $\delta \bar{N}_B(0)$  of molecules in the isomeric state B over the number found at equilibrium,  $\bar{N}_B(E)$ , in the  $(N, V, E)$  ensemble. The time decay of the initial population excess is then

$$\begin{aligned} C_B^{(0)}(t; E) &\equiv \delta \bar{N}_B(t; E) / \delta \bar{N}_B(0; E) \\ &= \Omega_R(E) / \Omega(E) + [\Omega_I(E) / \Omega(E)] e^{-k(E)t}, \quad E > E^\ddagger, \\ &= 1, \quad E \leq E^\ddagger, \end{aligned} \quad (4)$$

where  $\Omega_R/\Omega$  and  $\Omega_I/\Omega$  are the fractions of molecules moving on "regular" and irregular trajectories respectively. Because the regular molecules cannot cross the barrier (by assumption) their initial numbers are frozen. The irregular molecules, on the other hand, can cross the barrier with kinetic rate constant  $k(E)$  given by eq. (3) (or with dynamic corrections). We note in passing that if the regular trajectories could

cross the barrier, then  $\Omega_R/\Omega$  would be multiplied by a quasiperiodic function. Moreover dynamical corrections might require that the exponential be replaced by a non-monotonic function.

In a constant temperature ensemble the relaxation function becomes

$$C_B^{(0)}(t) = \int_0^\infty dE p(E) C_B^{(0)}(t; E), \quad (5)$$

where  $p(E)$  is the canonical energy distribution function,  $p(E) = \Omega(E) e^{-\beta E} / Q$ ,  $\Omega(E)$  is the density of states (given by the denominator of eq. (1)), and  $Q$  is the canonical partition function  $Q = \int_0^\infty dE \Omega(E) e^{-\beta E}$ . The quantity  $C_B^{(0)}(t)$  is identical to the normalized autocorrelation function of the spontaneous fluctuation of the concentration of molecules in the B state discussed in several previous papers [4]. The superscript 0 indicates that the system is an ideal gas. Because  $k(E) = 0$  for  $E \leq E^\ddagger$ , it follows that

$$\begin{aligned} C_B^{(0)}(t) &= \int_0^{E^\ddagger} dE p(E) C_B^{(0)}(t; E) \\ &+ \int_{E^\ddagger}^\infty dE p(E) C_B^{(0)}(t; E). \end{aligned} \quad (6)$$

Defining

$$Q_\neq^{(1)} \equiv \int_{E^\ddagger}^\infty dE \Omega_I(E) e^{-\beta E} \quad (7a)$$

and

$$C_\neq^{(0)}(t) \equiv \frac{\int_{E^\ddagger}^\infty dE \Omega_I(E) e^{-\beta E} e^{-k(E)t}}{Q_\neq^{(1)}} \quad (7b)$$

eq. (6) can be expressed as,

$$C_B^{(0)}(t) = \frac{Q - Q_\neq^{(1)}}{Q} + \frac{Q_\neq^{(1)}}{Q} C_\neq^{(0)}(t). \quad (8)$$

Thus we see that in an ideal gas the population does not decay to equilibrium; that is,  $C_B^{(0)}(t)$  decays to the constant  $(Q - Q_\neq^{(1)})/Q$ . This is because those molecules with either  $E < E^\ddagger$  or which are moving in the regular region of phase space cannot cross the barrier.

The normalized correlation function  $C_\neq^{(0)}(t)$ , can be expressed in terms of the cumulant expansion

$$C_{\neq}^{(0)}(t) = \langle e^{-k(E)t} \rangle_{\neq} = \exp\left(\sum_{n=1}^{\infty} k_n t^n / n!\right), \quad (9)$$

where  $\langle (\ ) \rangle_{\neq}$  denotes an average

$$\langle (\ ) \rangle_{\neq} \equiv \frac{\int_{E^{\neq}}^{\infty} dE \Omega_1(E) e^{-\beta E} (\ )}{Q_{\neq}^{(0)}}. \quad (10)$$

Truncation after the first cumulant gives an exponential decay

$$C_{\neq}^{(0)}(t) = e^{-k_{\neq} t}, \quad (11)$$

where

$$k_{\neq} = \langle k(E) \rangle_{\neq} = \frac{\int_0^{\infty} dE \Omega_1(E) e^{-\beta E} k(E)}{Q_{\neq}^{(1)}} \quad (12)$$

and  $k(E)$  is given by eq. (3).

This should be compared with the transition state theory (TST) rate constant

$$k_{\text{TST}} = \frac{\int_0^{\infty} dE \Omega(E) e^{-\beta E} k_{\text{RRKM}}(E)}{Q}. \quad (13)$$

Thus the decay rate of  $C_{\neq}^{(0)}(t)$  (ignoring higher cumulants and assuming all crossing trajectories are irregular) is

$$k_{\neq} = \frac{Q}{Q_{\neq}^{(1)}} k_{\text{TST}} = \frac{Q}{Q_{\neq}} \frac{Q_{\neq}}{Q_{\neq}^{(0)}} k_{\text{TST}} \quad (14)$$

and not  $k_{\text{TST}}$ . Since  $Q \geq Q_{\neq} \geq Q_{\neq}^{(0)}$  it follows that

$$k_{\neq} \geq k_{\text{TST}}, \quad (15)$$

so that  $k_{\neq}$  and not  $k_{\text{TST}}$  is the upper bound on the decay rate of  $C_{\neq}^{(0)}(t)$  in an ideal gas. It is not difficult to show that when  $\beta E^{\neq} \gg 1$ ,

$$\frac{Q_{\neq}}{Q} = \sum_{n=1}^{s-1} [(\beta E^{\neq})^n / n!] e^{-\beta E^{\neq}}, \quad (16a)$$

$$k_{\text{TST}} = (\omega_0 / \pi) e^{-\beta E^{\neq}}, \quad (16b)$$

$$k_{\neq} = (\omega_0 / \pi) \left( \sum_{n=1}^{s-1} (\beta E^{\neq})^n / n! \right)^{-1} Q_{\neq} / Q_{\neq}^{(0)} \quad (16c)$$

for a molecule containing  $s - 1$  harmonic degrees of freedom and one reactive degree of freedom involving motion in a symmetric piecewise harmonic bistable potential, where  $\omega_0$  is the harmonic frequency in the well. Clearly  $k_{\neq}$  can be much larger than  $k_{\text{TST}}$ , also †

$$\lim_{s \rightarrow \infty} k_{\neq} = k_{\text{TST}} \quad (17)$$

It is important to note that as the number of degrees of freedom, of the ideal gas molecule is increased,  $Q_{\neq} \rightarrow Q$  and  $k_{\neq} \rightarrow k_{\text{TST}}$ . It is also worth noting that the initial rate of change of  $C_{\text{B}}^{(0)}(t)$  is

$$\begin{aligned} \lim_{t \rightarrow 0^+} -dC_{\text{B}}^{(0)}(t)/dt &= \lim_{t \rightarrow 0^+} (Q_{\neq}^{(0)} / Q) (-dC_{\neq}^{(0)}(t)/dt) \\ &= (Q_{\neq}^{(1)} / Q) k_{\neq} = k_{\text{TST}}. \end{aligned} \quad (18)$$

This follows from eqs. (7) and (10). The important lesson learned from this is that the initial value of the reactive flux [4] gives  $k_{\text{TST}}$ , but the reactive flux itself decays exponentially with decay rate  $k_{\neq}$ .

A question that immediately arises is what happens if the molecules can exchange energy? In this case regular molecules can become irregular, and molecules initially with  $E \leq E^{\neq}$  can gain sufficient energy by collision so that  $E > E^{\neq}$  and can thereby cross the barrier. The correlation function  $C_{\text{B}}(t)$  will then decay to zero instead of to  $(Q - Q_{\neq}^{(0)})/Q$ . To gain some insight into this process we devise a very simple strong collisional model ‡. A molecule initially with energy  $E_1$  undergoes intramolecular dynamics with rate constant  $k(E_1)$ . It suffers a collision at time  $t_1$ , after which it has energy  $E_2$  and rate constant  $k(E_2)$ . It then suffers a collision at  $t_2$ , after which its energy and rate constant become  $E_3$  and  $k(E_3)$ , etc. The collisions are assumed to be independent binary collisions of zero duration occurring at collision rate  $\alpha$ . The collisions are assumed to thermalize the energy, that is, the energies before and after any collision are assumed to be uncorrelated and distributed according to  $p(E)$ . Because this model belongs to a class of models (extended diffusion models) that has been treated many times in many different contexts [6], it suffices to give the result. The Laplace transform of  $C_{\text{B}}(t)$  is then given by

$$\tilde{C}_{\text{B}}(s) = \tilde{C}_{\text{B}}^{(0)}(s + \alpha) / [1 - \alpha \tilde{C}_{\text{B}}^{(0)}(s + \alpha)], \quad (19)$$

where  $s$  is the Laplace variable, and  $\tilde{C}_{\text{B}}^{(0)}(s)$  is the Laplace transform of eq. (8), that is

$$\tilde{C}_{\text{B}}^{(0)}(s + \alpha) = \frac{Q - Q_{\neq}^{(0)}}{Q} \frac{1}{s + \alpha} + (Q_{\neq}^{(1)} / Q)_{\neq} \tilde{C}^{(0)}(s + \alpha). \quad (20)$$

† It is assumed here that if  $s \rightarrow \infty$  the system will become completely chaotic. If this is not the case  $k_{\text{TST}}$  should be multiplied by  $Q_{\neq}^{(1)} / Q_{\neq} = X_1^{\neq}$  in eq. (17).

‡ This collisional model is similar in spirit to a model considered in ref. [5].

where

$$\tilde{C}_{\neq}^{(0)}(s + \alpha) = \langle [s + \alpha + k(E)]^{-1} \rangle_{\neq} \approx (s + \alpha + k_{\neq})^{-1} \quad (21)$$

In the last equality we have used the approximation obtained by keeping only the first cumulant (cf. eq. (11)).

Substitution of eqs. (20) and (21) into eq. (19) gives after some manipulation

$$\tilde{C}_{\text{B}}(s) = \frac{s + \alpha + k_{\neq} - k_{\text{TST}}}{(s + \alpha)(s + k_{\neq}) - \alpha(k_{\neq} - k_{\text{TST}})} \quad (22)$$

This can be easily Laplace inverted. It suffices to exhibit the solution in two limits. When  $\alpha \gg k_{\neq}$

$$C_{\text{B}}(t) = \exp(-k_{\text{TST}}t) \quad (23)$$

and when  $\alpha \ll k_{\neq}$

$$C_{\text{B}}(t) = \frac{Q - Q_{\neq}^{(0)}}{Q} \exp\left(-\frac{Q_{\neq}^{(0)}}{Q} \alpha t\right) + \frac{Q_{\neq}^{(0)}}{Q} \exp\left[-\left(k_{\neq} + \frac{Q_{\neq}^{(0)} - Q}{Q} \alpha\right) t\right]. \quad (24)$$

These two limits are very instructive. When  $\alpha \gg k_{\neq}$ , activation takes place sufficiently rapidly that all molecules can pass back and forth over the barrier. The decay rate is then the TST rate constant  $k_{\text{TST}}$ . When  $\alpha \ll k_{\neq}$ , there is a rapid decay (with decay constant  $\approx k_{\neq}$ ) of the product deviation from 1 to  $(Q - Q_{\neq}^{(0)})/Q$  for those molecules initially having  $E > E_{\neq}^{\ddagger}$ , but a very slow decay (with decay constant  $\sim \alpha$ ) for those molecules starting in irregular states or with  $E \leq E_{\neq}^{\ddagger}$  because these latter molecules must either first be transferred to an irregular state or be activated. This agrees with our intuitive expectations. The long-time exponential decay is given by rate constant,  $(Q_{\neq}^{(0)}/Q)\alpha$ , a quantity proportional to the slow collision rate  $\alpha$ , and thus the interesting rate constant  $k_{\neq}$  which is related to the intramolecular dynamics does not contribute to this kinetic rate constant.

The correlation time  $\tau_{\text{C}} (\equiv \lim_{s \rightarrow 0} \tilde{C}_{\text{B}}(s))$  of the correlation function  $C_{\text{B}}(t)$ , found directly from eq. (9), is

$$1/\tau_{\text{C}} = \alpha k_{\text{TST}} / [\alpha + (k_{\neq} - k_{\text{TST}})]. \quad (25)$$

This is similar to what would be obtained from the Lindemann mechanism. For  $\alpha \rightarrow 0$ ,  $\tau_{\text{C}}^{-1} \rightarrow 0$  and  $\tau_{\text{C}} \rightarrow \infty$ , because part of the population — the unactivated or regular part — does not decay. Thus at low  $\alpha$ ,  $\tau_{\text{C}}$  does not give any information about inherent rate processes of interest; this is  $k_{\neq}$ . In the opposite

limit,  $\alpha \rightarrow \infty$ , energy transfer is so rapid that each molecule is frequently activated, and  $\tau_{\text{C}}^{-1} = k_{\text{TST}}$ . In this extreme  $\tau_{\text{C}}^{-1}$  and the kinetic rate constant are identical.

It is important to note that for high activation barriers ( $E_{\neq}^{\ddagger} \gg kT$ ) and small collision rates ( $\alpha \ll k_{\neq}$ ),  $1/\tau_{\text{C}}$  increases linearly with  $\alpha$  as,

$$1/\tau_{\text{C}} \xrightarrow{\alpha \rightarrow 0} X_{\text{I}}^{\neq} (Q_{\neq}/Q) [1 - X_{\text{I}} Q_{\neq}/Q]^{-1} \alpha, \quad (26)$$

where  $X_{\text{I}}^{\neq} (= Q_{\neq}^{(0)}/Q_{\neq})$  is the fraction of activated states that are irregular. Substitution of eq. (16a) into eq. (26) gives an estimate for the slope, and shows that it increases very rapidly with the number of degrees of freedom. For example for  $\beta E_{\neq}^{\ddagger} = 10$ , and  $X_{\text{I}}^{\neq} = 1$  the slopes for  $s = 2, 10$  and  $50$  are  $4.5 \times 10^{-2}, 84.5$  and  $2.2 \times 10^4$  respectively. Thus if  $E_{\neq}^{\ddagger}$  can be determined independently it may be possible to determine  $X_{\text{I}}^{\neq}$  from the slope and to see if the dynamical consequence of ergodicity is observable.

All of the foregoing is based on eqs. (1), (2) and (11). In real isolated molecules, as in simple model systems [2,6], the correlation function  $C_{\neq}^{(0)}(t)$  will often exhibit a damped oscillatory decay. This occurs because the intramolecular energy coupling is not strong enough to produce rapid equipartitioning among the modes. The observed rate constant and the effects of collisions on the rate will then be quite different from the preceding — a subject presently under consideration.

The lessons learned from this study are:

(a) The statistical theory of isomerization dynamics in ideal gases gives the rate constant

$$k_{\neq} = (Q/Q_{\neq}^{(0)}) k_{\text{TST}} \geq k_{\text{TST}}, \quad (27)$$

which can be larger than the usual transition state rate constant.

(b) When energy transfer is allowed and the rate of energy transfer between molecules is much larger than  $k_{\neq}$ , the statistical rate constant is  $k_{\text{TST}}$ .

(c) As the number of degrees of freedom in the polyatomic increases,  $Q_{\neq}^{(0)}/Q \rightarrow 1$  and  $k_{\neq} \rightarrow k_{\text{TST}}$ .

(d) For small energy transfer rates, the decay of an excess of product molecules is characterized by two widely different time scales. A fast decay with rate approximately given by the dynamically interesting  $k_{\neq}$ , and a slow decay with rate proportional to the collision rate. The long-time decay tells us nothing about the intramolecular dynamics. One must study

the short-time decay to learn something about this former constant.

(e) The correlation time  $\tau_C$  and  $\tau_C^{-1}$  is not related to the intramolecular dynamics except at high energy exchange rate.

(f) At low energy exchange rates the observed rate constant  $1/\tau_c$  will increase linearly with  $\alpha$ , with a slope given by the term in brackets in eq. (26). This term depends on three parameters,  $s$ , the number of degrees of freedom,  $E^\ddagger$ , the activation energy, and  $X_1^\ddagger$ , the fraction of activated states which are irregular. In complex molecules ( $s$  large) it will be difficult to observe any dependence of the rate constant on pressure.

Except for (f) all of the comments are valid even when the isolated molecular dynamics is completely chaotic.

The author is indebted to his colleagues, Professors Philip Pechukas and James Skinner, for numerous discussions about chemical kinetics.

### References

- [1] W. Forst, Theory of ultramolecular reactions (Academic Press, New York, 1982).
- [2] N. De Leon and B.J. Berne, *J. Chem. Phys.* 75 (1981) 3495;  
B.J. Berne, N. De Leon and R. Rosenberg, *J. Phys. Chem.* 86 (1982) 2166.
- [3] N. De Leon and B.J. Berne, *Chem. Phys. Letters* 93 (1982) 162, 169.
- [4] D. Chandler, *J. Chem. Phys.* 68 (1978) 2994.
- [5] J. Skinner and P.G. Wolynes, *J. Chem. Phys.* 69 (1978) 2143.
- [6] B.J. Berne and R. Pecora, *Dynamics light scattering* (Wiley, New York, 1976), and references therein.