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DYNAMICAL ASPECTS OF PRECURSOR STATE KINETICS

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An examination of precursor adsorbed states from a dynamical viewpoint reveals that two commonly used models of precursor kinetics are not generally applicable. For the case of molecular chemisorption, simple, linear rate laws may not be valid unless the adsorbate–solid system meets certain dynamical criteria. On the other hand, for dissociatively chemisorbed species, a serious error can be made in estimating the effect of temperature on the adsorbate dissociation rate if one ignores, as is usually done, the temperature dependence of the initial sticking probability of the molecule.

1. Introduction

Although the existence of precursor adsorbed states was hypothesized many years ago [1], it is only in recent years that their influences on adsorption/desorption kinetics have been generally recognized [2]. In a previous paper [3] we noted that the theoretical studies to date of these systems have consisted solely of "statistical" treatments [4], thus neglecting the role played by particle dynamics in determining the detailed rate behavior. We sought in that earlier work to provide a formalism (adapted from the work of Chandler, Wolynes, and co-workers [5]), which would permit one to extract the dependence of adatom sticking probabilities on the structure of the weakly-bound precursor. The present paper represents somewhat of an extension of that investigation, although our particular interest here lies in obtaining, if possible, some dynamical justification for the conventional models used in the analysis of experimental kinetic data from systems thought to involve precursor states.

In section 2 we direct our attention to an elementary model system in which *both* chemisorbed and precursor states are qualitatively of the same nature, i.e., they involve either atomic or molecular adsorption, but not a dissociative process.

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One might expect that fairly simple rate laws would be sufficient in order to describe the "state-to-state" (chemisorbed $\rightleftharpoons$ precursor, precursor $\rightleftharpoons$ free) transitions. However, by the application of a multistate version of Chandler's theory, we are able to identify dynamical criteria that must be satisfied in order for the "naive" rate laws to be valid.

The catalytically more important case, namely a molecularly adsorbed precursor state coupled to a dissociated chemisorbed state, is examined in section 3. Here our interest resides in the nature of the temperature dependence of the adsorbate dissociation probability. The quite simple analysis of these dissociative systems which we present suggests that the primary temperature effects arise not, as is generally assumed, as a consequence of the relative heights of the barriers to dissociation and desorption, but rather they derive from the intrinsic variation with temperature of the probability of becoming trapped in the precursor state. We also show that by no means need these dissociation rates be simple functions of the system temperature.

2. Non-dissociative chemisorption

2.1. Multistate generalization of Chandler's theory

The theoretical framework for this part of the study of precursor state kinetics consists of a natural extension of the formalism described by Chandler and co-workers [5] that yields dynamical corrections to transition state theory. Since we have presented in our previous paper [3] (hereafter I) a simplified outline of the fundamental approach, the present section will indicate only the way in which that work is generalized so as to treat systems having an arbitrary number of states. Suppose, therefore, that one is interested in a system described by a potential which is comprised of a series of m wells (in I we examined the $m = 2$ case, i.e., a bistable potential). One may then define an $(m - 1)$-dimensional column vector of time-dependent state populations

$$\boldsymbol{N} = \boldsymbol{N}(t)\,.$$

(Since the total number of particles, N, is held fixed, only $m - 1$ individual populations are needed in order to specify the system.) Fluctuations of these populations away from their equilibrium values are therefore just

$$\delta \boldsymbol{N}(t) = \boldsymbol{N}(t) - \bar{\boldsymbol{N}}\,.$$

If, furthermore, the system obeys a simple, linear rate law, that is

$$\delta \dot{\boldsymbol{N}}(t) = -\boldsymbol{k}\, \delta \boldsymbol{N}(t)$$

(or equivalently $\delta \boldsymbol{N}(t) = \exp(-\boldsymbol{k}t)\, \delta \boldsymbol{N}(0)$), then one concludes that the fluctuation autocorrelation functions must also exhibit a simple exponential decay,

$$\langle \delta \boldsymbol{N}(0)\, \delta \boldsymbol{N}^{\mathrm{T}}(t)\rangle \propto \exp(-\boldsymbol{k}t)\,. \qquad (2.1)$$

(The l.h.s. of eq. (2.1) represents a matrix of autocorrelation functions; $\delta \boldsymbol{N}^{\mathrm{T}}(t)$ is the "vector transpose" of $\delta \boldsymbol{N}(t)$, i.e., $\delta \boldsymbol{N}(t)$ written as a row vector.) .

From this point it is a fairly simple matter to perform the few algebraic manipulations that yield the explicit expression for the rate matrix in terms of the individual state populations,

$$\boldsymbol{k}^{\mathrm{T}} = [\langle \delta \boldsymbol{N}(0)\, \delta \boldsymbol{N}^{\mathrm{T}}(t)\rangle]^{-1}\, \langle \delta \dot{\boldsymbol{N}}(0)\, \delta \boldsymbol{N}^{\mathrm{T}}(t)\rangle \,.$$

If indeed the assumed linear rate law is valid for the system of interest, then one will find that plots of the elements of $\boldsymbol{k}$ versus time exhibit the same plateau behavior noted in the studies of the two-state case. That is, the matrix elements will attain constant values on a time scale which is longer than some initial fast relaxation time, but much shorter than the time required for complete equilibration to be reached. Insofar as this paper is concerned, the crucial point will be that confirmation of the validity of the rate law and the observation of plateau behavior are totally equivalent.

2.2. Three-state case

Since the particular precursor state kinetic model of interest to us here is described by $m = 3$, we shall elaborate at this point on some of the details of that specific case. If the three distinct states are separated spatially such that

state 1: $0 \leqslant x(t) \leqslant q_1$,
state 2: $q_1 < x(t) \leqslant q_2$,
state 3: $q_2 < x(t)$

(see fig. 1), then the (normalized) reduced population vector may be written in terms of standard step functions as

$$\boldsymbol{N}(\mathrm{t}) = \begin{pmatrix} N_1(t) \\ N_2(t) \end{pmatrix} = \begin{pmatrix} \theta(q_1 - x(t)) \\ \theta(q_2 - x(t))\, \theta(x(t) - q_1) \end{pmatrix} \equiv \begin{pmatrix} \theta_1(t) \\ \theta_2(t) \end{pmatrix} .$$

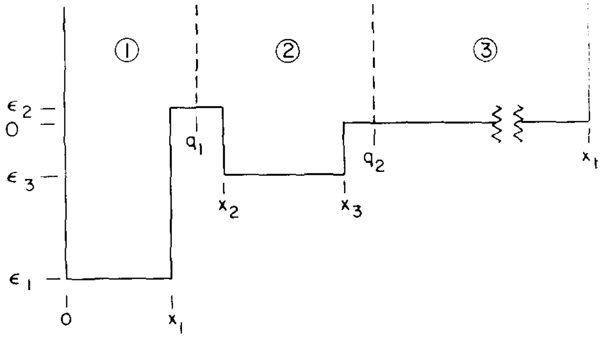

Fig. 1. Square-well model potential which includes a precursor state.

Using this form for $\boldsymbol{N}(t)$ one can easily construct the elements of 2 × 2 rate constant matrix (assuming that the correlations of the form $\langle \delta N_i(0)\, \delta N_j(t)\rangle$ are slowly decaying),

$$(k)_{1,1} = -\chi_1^{-1}\langle \dot{x}(0)\, \delta(q_1 - x(0))\, \theta_1(t)\rangle - \chi_3^{-1}\langle \dot{x}(0)\, \delta(q_2 - x(0))\, \theta_1(t)\rangle\,,$$

$$(k)_{1,2} = -(\chi_2^{-1} + \chi_3^{-1})\langle \dot{x}(0)\, \delta(q_2 - x(0))\, \theta_1(t)\rangle$$
$$+ \chi_2^{-1}\langle \dot{x}(0)\, \delta(x(0) - q_1)\, \theta_1(t)\rangle\,,$$

$$(k)_{2,1} = -\chi_1^{-1}\langle \dot{x}(0)\, \delta(q_1 - x(0))\, \theta_2(t)\rangle$$
$$-\chi_3^{-1}\langle \dot{x}(0)\, \delta(q_2 - x(0))\, \theta_2(t)\rangle\,,$$

$$(k)_{2,2} = -(\chi_2^{-1} + \chi_3^{-1})\langle \dot{x}(0)\, \delta(q_2 - x(0))\, \theta_2(t)\rangle$$
$$+ \chi_2^{-1}\langle \dot{x}(0)\, \delta(x(0) - q_1)\, \theta_2(t)\rangle\,,$$

where χ_1, χ_2, and χ_3 are the equilibrium mole fractions of particles in states 1, 2, and 3, respectively. Note that in the limit $t \to 0$, the above result reduces to the corresponding transition state theory expression,

$$(k^{\mathrm{TST}})_{1,1} = (2\chi_1)^{-1}\langle |\dot{x}(0)|\, \delta(x(0) - q_1)\rangle = k^{\mathrm{TST}}_{1\to 2}\,,$$

$$(k^{\mathrm{TST}})_{1,2} = -(2\chi_2)^{-1}\langle |\dot{x}(0)|\, \delta(x(0) - q_1)\rangle = -k^{\mathrm{TST}}_{2\to 1}\,,$$

$$(k^{\mathrm{TST}})_{2,1} = -(2\chi_2)^{-1}\langle |\dot{x}(0)|\, \delta(x(0) - q_1)\rangle$$
$$+ (2\chi_3)^{-1}\langle |\dot{x}(0)|\, \delta(x(0) - q_2)\rangle = -k^{\mathrm{TST}}_{1\to 2} + k^{\mathrm{TST}}_{3\to 2}\,,$$

$$(k^{\mathrm{TST}})_{2,2} = [(2\chi_2)^{-1} + (2\chi_3)^{-1}]\langle |\dot{x}(0)|\, \delta(x(0) - q_2)\rangle$$
$$+ (2\chi_2)^{-1}\langle |\dot{x}(0)|\, \delta(x(0) - q_1)\rangle = k^{\mathrm{TST}}_{2\to 3} + k^{\mathrm{TST}}_{3\to 2} + k^{\mathrm{TST}}_{2\to 1}\,.$$

In comparing $\boldsymbol{k}$ to $\boldsymbol{k}^{\mathrm{TST}}$, one is struck by the curious fact that two of the terms appearing in $\boldsymbol{k}$ seem incorrect. Specifically, terms of the form

$$\langle \dot{x}(0)\, \delta(q_2 - x(0))\, \theta_1(t)\rangle\,,$$

which are zero in the short-time limit, intuitively should be expected to vanish at all t if the correct rate constants are to be extracted from $\boldsymbol{k}$. But just what does the vanishing of this correlation function mean in terms of the dynamics of particles moving in the tristable potential described above? Quite simply, in order for the rate law to be valid, i.e., for plateau behavior of the elements of $\boldsymbol{k}$ to be observed, particles located at $x = q_2$ at $t = 0$ must not pass directly into state 1 on a time scale shorter than the system equilibration time. This condition implies either that energy dissipation must be sufficiently rapid within state 2 that particles will be immediately trapped or that the barrier separating states 1 and 2 must be high enough that particles are only reflected back into state 2 (or, of course, a combination of these factors).

A somewhat more rigorous argument of why these dynamical restrictions must be present in a system obeying the simple, linear rate law follows closely along the lines of Chandler's original argument for the existence of plateau values. If these values are to be attained in a bistable system, it is necessary that the one independent state population not be coupled to other "slow" system variables. In an extension of this requirement to a multistate system, however, one must demand in addition that there be no coupling along the $m - 1$ independent populations themselves. Thus, in our three state case $N_1(t)$ and $N_2(t)$ must necessarily be uncoupled if plateau values are to be observed. But the dynamical conditions which would prevent such a coupling from appearing are just those indicated above, namely rapid energy dissipation and/or a high activation barrier. One is led, therefore, to identify the vanishing of the above correlation function with the establishment of plateau behavior and hence with the confirmation of the rate law as written.

2.3. Examples

As a demonstration of the importance of the considerations indicated above, we have determined state-to-state rate constants for an ensemble of particles moving in the one-dimensional potential shown in fig. 1. This particular potential function is intended to model the adsorption/desorption either of atomic species or of molecular species which are not dissociatively chemisorbed. Although the parameters describing the potential (see table 1) have been chosen somewhat arbitrarily, they reflect reasonable guesses for the interactions involved in adsorption which proceeds via a precursor state. As in I, we have accounted for the motion of the surface (and thus for energy transfer with the surface) by using a Brownian dynamics description of the adatom motion parameterized by a characteristic energy relaxation time.

Representative results of these calculations are displayed in table 2. The variable parameters are the height and width of the (activation) barrier separating the inner and precursor wells and energy relaxation times for particles moving in these wells. One may readily see that the criteria suggested in section 2.2 for the existence of

Table 1
Parameters for the sample calculations of section 2.3

Inner well depth = $-10\,000$ K (~20 kcal mol^{-1})
Precursor well depth = -2500 K (~5 kcal mol^{-1})
Inner well width = $3a_0$ [a] (~1.5 A)
Precursor well width = $4a_0$ (~2.0 A)

Outer system bound [b] = $200a_0$
Particle mass = 28 amu
System temperature = 300 K

[a] a_0 = Bohr radius.

[b] Particles do not reflect and return within the time over which plateau values are established.

Table 2

Activation barrier width ($x_2 - x_1$) (Å)	Activation barrier height (ϵ_2) (kcal/mole)	Relaxation time, inner well (ps)	Relaxation time, precursor well (ps)	Plateau values established?	$k_{2\to1}/k_{2\to1}^{\mathrm{TST}}$
0.26	3.5	0.15	0.60	No	–
0.26	4.0	0.15	0.60	Yes	0.80
0.26	4.5	0.15	0.60	Yes	0.79
0.26	3.5	0.15	1.5	No	–
0.26	4.0	0.15	1.5	Yes	0.80
0.53	3.0	0.15	0.60	No	–
0.53	3.5	0.15	0.60	Yes	0.72
0.53	3.0	0.15	1.5	No	–
0.53	3.5	0.15	1.5	No	–
0.53	4.0	0.15	1.5	Yes	0.72
0.53	3.0	0.060	0.60	No	–
0.53	3.5	0.060	0.60	Yes	0.57
0.53	4.0	0.060	0.60	Yes	0.56
0.53	0.0	0.025	0.25	No	–
0.53	0.0	0.025	0.10	Yes	0.36

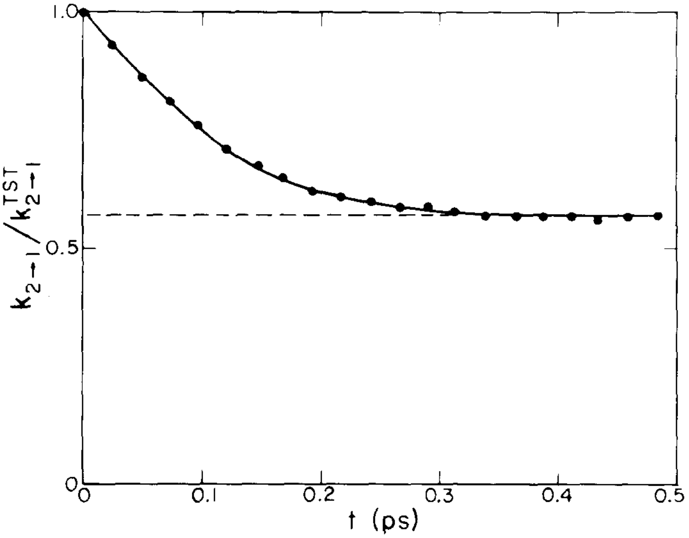

Fig. 2. Example of a rate constant which exhibits plateau behavior. This result was obtained using the parameters given in the twelfth line of table 2.

plateau values and consequently of a simple, linear rate law are indeed supported by these examples. By raising or widening the activation barrier or by increasing the rate at which energy is dissipated in the adsorbed states, we are, in general, able to produce conditions under which the linear rate laws apply. It should be noted in particular that, except for the case of unrealistically fast energy transfer, there must exist an actual barrier of a few kcal mol^{-1} in height separating the inner and precursor states in order for plateau behavior of the rate constants to be observed. (An example of such behavior is illustrated in fig. 2, a plot of the time evolution of the rate constant for transfer from the precursor state into the inner chemisorptive well.) If instead the separating barrier does not describe a truly activated kinetic process, then one should not view the precursor well described here as representing a discrete, identifiable state of the system. Again, however, we remind the reader that such a result applies only to the case of an undissociated chemisorbed species.

3. Dissociative chemisorption

A very large class of catalytically important adsorption processes cannot be described in terms of the above model inasmuch as they involve dissociation upon passage from the precursor state into the more tightly bound chemisorbed state. Since such an event characteristically involves the elongation and subsequent rupture of a bond oriented more or less in the plane of the surface, the actual dissociation may be viewed as being "orthogonal" to the concurrent adsorption/desorption. The potential function depicted in fig. 1 does not, of course, really reflect this sort of dynamical behavior, so a somewhat different approach must be adopted.

Part of the rationale for choosing to make a closer examination of such systems arises as a result of the widespread use of a rather questionable model [6], namely that the temperature dependence of the dissociation rate may be predicted solely on the basis of an estimate of the height of the barrier separating the chemisorbed and precursor states. If such a description is indeed valid, then the dissociation probability may be written as a branching ratio,

$$\begin{aligned} P_{\mathrm{dis}}(T) &= P_{\mathrm{s}} \frac{k_{\mathrm{dis}}}{k_{\mathrm{dis}} + k_{\mathrm{desorb}}} \\ &= P_{\mathrm{s}} \frac{\omega_{\mathrm{dis}} \exp[-\beta E_{\mathrm{dis}}]}{\omega_{\mathrm{dis}} \exp[-\beta E_{\mathrm{dis}}] + \omega_{\mathrm{desorb}} \exp[-\beta E_{\mathrm{desorb}}]} \\ &= P_{\mathrm{s}} \left[1 + \left(\frac{\omega_{\mathrm{desorb}}}{\omega_{\mathrm{dis}}} \right) \exp[-\beta \Delta E] \right]^{-1}, \end{aligned} \tag{3.1}$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$, $\Delta E = E_{\mathrm{desorb}} - E_{\mathrm{dis}}$, and P_{s} is the probability of sticking in the precursor well. But since empirically we expect the ratio of the frequencies for desorption and dissociation to be on the order of 0.1 or less, eq. (3.1) predicts that

P_{dis} should exhibit only a fairly weak temperature dependence. How, therefore, can this prediction be explained in light of the fact that often a quite strong dependence on the system temperature is observed [7,8]? It appears unlikely that an explanation can be given which retains the notion that the sticking coefficient is a constant over an appreciable range of temperatures. Therefore, we seek to show that sticking probabilities in the precursor state may themselves afford the bulk of the observed temperature effects.

Some insight into the significance of temperature-dependent sticking is suggested by results reported recently by White and co-workers [8] concerning the dissociative chemisorption of nitrous oxide on a ruthenium single crystal. In that paper they indicated that once the molecular species becomes trapped in the weakly-bound precursor state, dissociation proceeds rapidly yielding chemisorbed O_2. One might suspect, therefore, that the measured initial dissociation rate of N_2O would be given, to a reasonable approximation, simply by the rate of adsorption of the molecule. This hypothesis may be easily tested through an examination of the overall sticking probability for a potential function having a single shallow well, a situation which can be described by the potential shown in fig. 1 if E_2 is taken to be large and positive. (The two-state version of Chandler's theory described in I is quite sufficient for this particular calculation.)

In fig. 3 we have displayed the results of a sample calculation of the sticking coefficient as a function of temperature for a system in which only precursor trapping is possible. Note first that the characteristic concave structure of the curves reflects essentially the same temperature dependence seen by White in the dissociation rates. (A very similar result has also been reported by Grimmelmann et al. [9] for xenon sticking on platinum, although in that case the single potential well is not a precursor state, but rather a simple physisorbed one.) Second, a comparison of the curves calculated for differing well depths and rates of energy dissipation suggests that while the depth of the potential well influences most strongly the magnitude of the sticking probability, the curve shapes display a definite dependence upon the characteristic energy relaxation times. These observations imply that from a measurement of sticking probabilities over a range of temperatures, one may extract useful information about precursor state structure which might otherwise remain hidden in gross kinetic data.

But does one recover the complete temperature variation of the dissociation probability by equating it to the sticking coefficient's temperature dependence? A fairly simple argument indicates that the answer may be no. We begin with a somewhat more general expression for the dissociation probability than that given in eq. (3.1), namely

$$P_{dis} = \int_0^\infty dt\, k_{dis} \exp(-k_{dis}t)\, h(t) , \tag{3.2}$$

where $\exp(-k_{dis}t)$ represents the fraction of undissociated species and $h(t)$ is a

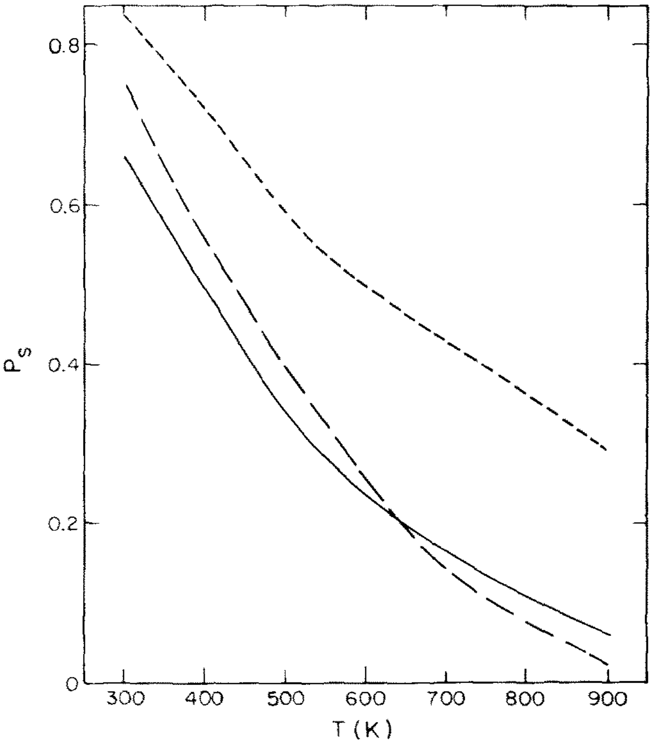

Fig. 3. Plot of precursor sticking probability versus temperature. The three curves correspond to precursor well depths and characteristic energy relaxation times of 2 kcal mol^{-1} and 1.5 ps (solid curve), 2 kcal mol^{-1} and 0.75 ps (lower dashed curve), and 4 kcal mol^{-1} and 1.5 ps (upper dashed curve).

function which describes the probability of being located in the molecularly adsorbed precursor well. Eq. (3.1) is easily derived from the above expression if one assumes $h(t)$ to be of the form

$$h(t) = P_s \exp(-k_{\mathrm{des\,or\,b}}t) \,.$$

Again we note that if such a description is valid, then the temperature dependence of P_{dis} should be nearly identical with the corresponding temperature dependence of the precursor sticking probability. However, what if there exists some critical time t_c during which desorption does not occur (e.g., a mean-first-passage time through the precursor well)? In this case $h(t)$ is better represented by

$$h(t) = P_s \exp(-k_{\mathrm{des\,or\,b}}t) + (1 - P_s)\,\theta(t_c - t) \,,$$

where $\theta(t_c - t)$ is, as before, just the standard step function. Substitution of this expression into eq. (3.2) and subsequent integration then yields a more complicated dissociation probability,

$$P_{\text{dis}} = P_{\text{s}} \frac{k_{\text{dis}}}{k_{\text{dis}} + k_{\text{desorb}}} + (1 - P_{\text{s}})[1 - \exp(-k_{\text{dis}} t_{\text{c}})] \ ,$$

which would be expected to exhibit a correspondingly more intricate temperature dependence. Although we certainly do not claim that this result necessarily represents the best description of dissociation in the presence of concurrent desorption, it does point to the fact that conventional analyses of such events may prove to be even less satisfactory in that they omit what is quite likely the major source of temperature effects, the temperature variation of the sticking probability.

4. Summary

In this study we have attempted to elucidate some additional features of adsorption/desorption via a weakly-bound precursor state. Particular emphasis has been placed on identifying those assumptions commonly adopted in order to explain experimental data that appear to be of questionable validity when viewed within the context of adsorbate dynamics. First, it was shown that although arbitrary nondissociative adsorption processes need not obey simple, linear rate laws, chemisorbed $\rightleftharpoons$ precursor and precursor $\rightleftharpoons$ free kinetics *may* be well defined if the gas–solid system meets certain requirements. Since, of course, in the three-dimensional case energy dissipation can occur through motion lateral to the surface, the simple rate laws may be more generally applicable than the one-dimensional calculations would indicate. Still, one must be aware that rate expressions *do* contain hidden dynamical assumptions which unless recognized can invalidate an entire kinetic analysis.

Second, in section 3 we identified a fairly serious flaw in the commonly used model of dissociative chemisorption, that the probability of sticking in the molecularly adsorbed precursor state is assumed to be independent of temperature. Even the quite elementary calculation presented herein reveals a non-negligible variation of the sticking coefficient as the system temperature is changed. In fact, it appears that the temperature dependence of the sticking may actually provide the principal temperature effect seen in adsorbate dissociation rates. Our simple example also suggests that one might be able to probe at least the gross structural features of precursor states by examining these changes in the sticking probabilities. But again, the most significant finding of this work is that purely statistical models may not yield reasonable descriptions of these particular types of adsorption/desorption processes.

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