DESORPTION KINETICS WITH PRECURSOR INTERMEDIATES *

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Several models are developed for desorption rates which proceed through precursor inter-mediate states. These include associative and dissociative chemisorption with one and two types of precursor states. It is shown that the presence of a precursor can lead to a $(1 - \theta)^{-1}$ factor in the rate expression, while distinct precursors over full and empty sites can produce an increase in the apparent order of the desorption processes from first to second and from second to third. These models predict broadening of flash desorption peaks at high coverage and shifts of peak temperature with coverage, effects which have in past experiments been interpreted as anomalous pre-exponential factors, coverage dependent activation energies, or multiple binding states. Experimental desorption kinetics are interpreted in terms of precursor states for several chemisorption systems. It is shown that these desorption rate expressions should be expected whenever sticking coefficients are independent of coverage.

1. Introduction

Recently it has been suggested that, since the existence of a precursor state is necessary to explain adsorption kinetics in many chemisorption systems, it may also be a factor in desorption kinetics [1,2,14]. Incentives to examine alternate rate expressions for desorption come from the frequent observation of anomalous pre-exponential factors, orders of desorption, and shapes of flash desorption spectra in chemisorption systems. King [2] considered a model involving two types of pre-cursors, one over a filled chemisorption site and one over an empty site. Modifying the successive site model of Kisliuk [3] for condensation, he obtained a rather complicated rate expression for which numerical calculations gave flash desorption spectra considerably different from normal first order kinetics. However, the model of King is rather complicated, and he did not attempt to generalize it.

We present here several kinetic models for desorption which include precursors states. These models are simple enough for curve fitting and provide a more physi-cal picture of the processes. All the models consider the precursor states to be

weakly bound (physically adsorbed or weakly chemisorbed) and to comprise only a small percentage of the adsorbate on the surface. We also assume that conversion between states on the surface is sufficiently fast compared to the desorption rate that all states on the surface are in equilibrium with each other.

We shall consider both the successive site models of Kisliuk and King and the kinetic models of Becker [4] and Ehrlich [5]. The kinetic models have the advantage of being easier to formulate and interpret since expressions are obtained directly as rates for various steps rather than as an infinite sum of probabilities. It has been shown previously that the Ehrlich and Kisliuk models give *exactly* the same coverage dependences for the simple first order case [6]. We shall show that
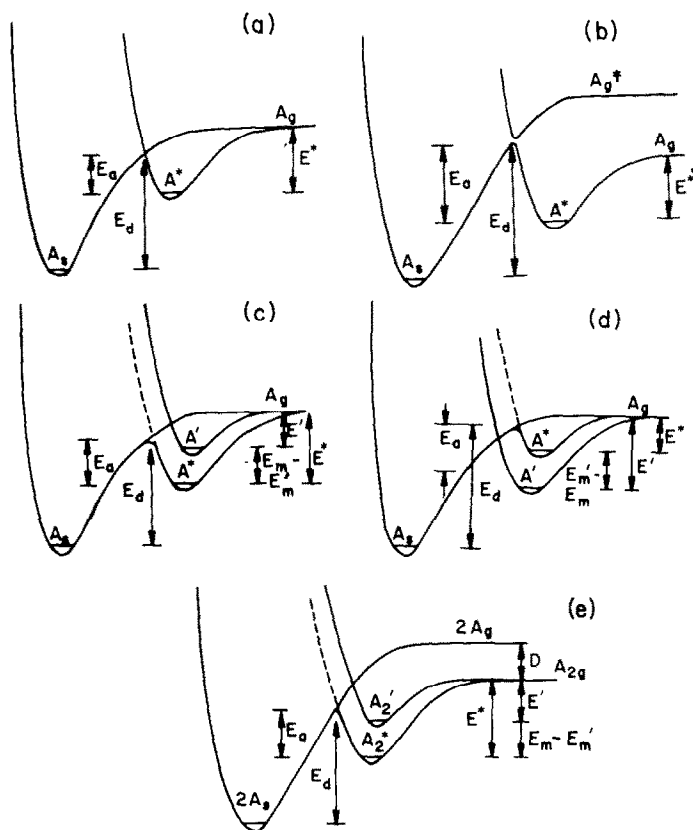

Fig. 1. One-dimensional potential energy curves for a chemisorbed molecule with precursors. (a) Normal single precursor situation. (b) Single precursor with a large activation energy for adsorption. (c) Empty and full site precursors with filled site precursor at higher energy. (d) Empty and full site precursor with empty site at higher energy. (e) Two precursors for dissociative adsorption.

detailed balancing requires that the kinetic and successive site models must also give identical coverage dependencies in desorption for first order processes.

Fig. 1 illustrates the assumed situations using curves of one-dimensional potential versus distance from the surface. Fig. 1a is the normal single precursor situation, while fig. 1b is appropriate for a large activation energy barrier to adsorption. The latter should be expected if the curve for the chemisorbed state rises above the vacuum level for the precursor, which would occur if the chemisorbed state is electronically excited compared to the precursor state. Distinct precursor states over full and empty chemisorbed states should produce curves such as figs. 1c and 1d. Molecules can only cross between curves if the precursor state is empty. Extensions of curves beyond crossing points are indicated with dashed lines, although molecules may remain in states even though the potential curves indicate the existence of lower energy states.

2. Models

2.1. Single precursor

The first model assumes that desorption proceeds through the reaction steps

$$A_s \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A* \overset{k*}{\longrightarrow} A_g \qquad . \tag{I}$$

Invoking the steady-state approximation for the precursor state A^* (valid for θ^* small), this sequence leads to the desorption rate expression

$$r_d = \frac{k^* k_d \theta}{k^* + k_a (1 - \theta)} . \tag{1}$$

If $k^* \gg k_a$, we obtain normal first-order kinetics with $r_d = k_d \theta$. If $k_a \gg k^*$, then

$$r_d = \frac{k^* k_d}{k_a} \frac{\theta}{(1 - \theta)} , \tag{2}$$

and the effect is to introduce k^*/k_a in the rate coefficient plus a $(1 - \theta)^{-1}$ coverage dependence. We assume the usual Arrhenius temperature dependences for the rate coefficients

$$k_d = k_0^d \exp(-E_d/RT) , \tag{3a}$$

$$k_a = k_0^a \exp(-E_a/RT) , \tag{3b}$$

$$k^* = k_0^* \exp(-E^*/RT) . \tag{3c}$$

As defined by fig. 1a, E_d is the activation energy barrier from the chemisorbed state to the precursor, E_a is the activation energy of chemisorption from the precursor, E^* is the desorption activation energy from the precursor, and the k_0's are the pre-

exponential factors. Eq. (2) becomes

$$r_d \simeq \frac{k_{do} k_0^*}{k_{a0}} \frac{\theta}{1-\theta} \exp\left(-\frac{E_d - E_a + E^*}{RT}\right).$$ (4)

From fig. 1a, we see that the activation energy for this process is the heat of adsorption as normally expected. For the case where normal kinetics is observed, the activation energy should be approximately equal to the heat of adsorption since $E^* - E_a$ should be small compared to E_d for loosely bound precursors.

One obtains the following relation between the flash desorption peak temperature, T_p, and the activation energy, $E = E_d - E_a + E^*$:

$$\frac{E}{RT_p^2} = \frac{1}{(1-\theta_p)^2} \frac{\nu_0}{\beta} \exp\left(-\frac{E}{RT_p}\right),$$ (5)

where θ_p is the coverage at the peak temperature, β is the constant heating rate, and ν_0 is the overall pre-exponential factor which is usually identified as a vibrational frequency, 10^{13} sec^{-1}. Since θ_p will be less than $1/2$ even for high coverages, the $(1-\theta)^{-2}$ factor will only produce a small shift in the peak temperature even at high initial coverages.

2.2. Empty and full site precursors

Another model for first-order desorption assumes two types of precursor states, one labelled A' which exists over a filled site and another A^* over an empty site:

$$A_s \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A^* \underset{k_m'}{\overset{k^*}{\xrightarrow{\hspace{1.5cm}}}} A_g \atop A' \quad k'$$ (II)

Letting θ be the coverage in the chemisorbed state and invoking the steady-state approximation for $[A^*]$ and $[A']$, we obtain

$$d[A^*]/dt = k_d \theta - k_a [A^*] + k_m' [A'](1-\theta) - k_m [A^*] \theta - k^* [A^*] \cong 0,$$ (6a)

$$d[A']/dt = k_m [A^*] \theta - k_m' [A'](1-\theta) - k' [A'] \cong 0.$$ (6b)

We write out these expressions to indicate the θ and $(1-\theta)$ factors on various terms which are required by the assumption of A' and A^* states being over full and empty chemisorbed sites. These will later be shown to agree with equilibrium requirements.

The desorption rate expression now becomes

$$r_d = k^* [A^*] + k' [A']$$ (7a)

$$= \left\{ k^* + \frac{k' k_m \theta}{k_m'(1-\theta) + k'} \right\} \left\{ \frac{k_d \theta}{(k_a + k^*) + k_m k' \theta/[k_m'(1-\theta) + k']} \right\}.$$ (7b)

As in the single precursor model, we expect the effects of the precursor to be large when k^* and k' are relatively small. Letting k^* and k' be much less than k_m, k'_m, and k_a, this expression simplifies to

$$r_d = \frac{k^* k_d \theta}{k_a} + \frac{k' k_m k_d}{k'_m k_a} \frac{\theta^2}{1-\theta}. \tag{8}$$

Assuming Arrhenius expressions for each of the rate coefficients, this becomes

$$r_d = \frac{k_0^* k_{d0}}{k_{a0}} \exp\left(-\frac{E_d + E^* - E_a}{RT}\right)\theta$$

$$+ \frac{k_0' k_{m0} k_{d0}}{k'_{m0} k_{a0}} \exp\left(-\frac{E_d + E' + E_m - E'_m - E_a}{RT}\right)\frac{\theta^2}{1-\theta}. \tag{9}$$

From fig. 1c, we see that $E^* = E' + E_m - E'_m$. Therefore, both of these limiting rates will have the *same activation energy*, and only differences in the pre-exponential factors will determine which term is dominant. Note that the rate expression does not depend explicitly on whether the precursor is more strongly bound over the full or empty site (figs. 1c and 1d).

Now consider $k_a \ll k'$ or k^*. From eq. (7b)

$$r_d \simeq \left\{k^* + \frac{k' k_m \theta}{k'_m(1-\theta) + k'}\right\}\left\{\frac{k_d\theta}{k^* + k' k_m \theta / [k'_m(1-\theta)+k']}\right\} = k_d\theta , \tag{10}$$

and the precursor has no influence as expected.

2.3. Successive site precursors

The final first-order rate model we discuss is that of King [2], who modified the successive site precursor model originally proposed by Kisliuk [3] for condensation kinetics. They assume that the chemisorbed molecule has a rate of moving to a precursor state, whereupon it has a probability of hopping to a different site, readsorbing and desorbing. This model again considers two types of precursors, one over empty and one over full sites; and the probabilities are different over each type site. When these probabilities are summed to infinity, a convergent geometric series is found which reduces to

$$r_d = \nu_0\theta \exp\left(-\frac{E}{RT}\right)\left\{f_d + f_m\left(1 - \frac{S_0}{S^*}\frac{1}{1+K'\theta/(1-\theta)}\right)\right\}, \tag{11}$$

where f_d and f_m are probabilities of desorbing and moving from the precursor state above an empty site, S_0 and S^* are sticking probabilities into the chemisorbed and precursor state respectively. King showed that

$$K' = \frac{f'_d}{f_a + f_d} = \frac{1}{1 + r'_m/r'_d}\left(1 + \frac{r_m}{r_a + r_d}\right), \tag{12}$$

where the r's are rates of moving, adsorbing, and desorbing, and the primes indicate the rate over a filled site. It can be shown that K' is always less than unity.

There is one major assumption in deriving successive site models besides those usually stated. The derivation assumes that the fraction of full and empty sites surrounding the precursor go exactly as θ and $(1 - \theta)$. While this allows for a closed solution, it is never exactly true because there is a small discrete number of neighboring sites. Also, although the chemisorbed sites may be randomly distributed, the site from which the precursor comes out of the chemisorbed state must be empty, removing the "randomness" in this area. Since particles in a two-dimensional, random hopping model have a high probability of returning to their origin, this assumption is not insignificant. Further, for the desorption model of King to be thermodynamically consistent with the Kisliuk expression for adsorption, we shall show later that $f'_m/f'_d = f_m/f_d$, where the primes indicate the probabilities for a precursor over a filled site.

Although the above expression appears to be considerably different than either of the previous models, eq. (11), in fact, predicts a coverage dependence identical to the single site kinetic model. With the requirement that $f_m/f_a = f'_m/f'_a$, eq. (11) simplifies to

$$r_d = \nu_0 \exp\left(-\frac{E}{RT}\right)(f_d + f_m)\frac{\theta}{1 + (f_a f_m/f_d)(1 - \theta)}, \tag{13}$$

which clearly has the same coverage dependence as eq. (1).

King shows a numerical example of this model which appears to lead to a broadened, symmetric peak shifted to higher temperatures for first order desorption. The shift is obtained by assuming a lower than normal pre-exponential, and the symmetric peak (effectively second-order kinetics) can be obtained only by choosing parameters which violate detailed balancing requirements.

2.4. Dissociative adsorption

Dissociative adsorption models can also be formulated assuming precursor intermediates. The simplest model, analogous to Model I, results from the sequence

$$2A_g \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A_2^* \overset{k^*}{\longrightarrow} A_{2s} \tag{III}$$

By the staeady-state approximation,

$$d[A_2^*]/dt = k_d\theta^2 - k_a[A_2^*](1 - \theta)^2 - k^*[A_2^*] \doteq 0, \tag{14}$$

$$r_d = k^*[A_2^*] = \frac{k^* k_d \theta^2}{k^* + k_a(1 - \theta)^2}. \tag{15}$$

The two limiting cases for this model are

$$r_d = k_d \theta^2 , \tag{16}$$

$$r_d = \frac{k^* k_d}{k_a} \frac{\theta^2}{(1 - \theta)^2} . \tag{17}$$

Eq. (16) describes the normal second-order kinetics while eq. (17) shows a $(1 - \theta)^{-2}$ dependence of the adsorption rate due to the precursor. In a flash desorption experiment the activation energy can be determined using this model from the following relation between T_p and coverage:

$$\frac{E\beta}{RT_p^2} = 2 \frac{k_0^* k_{d0}}{k_{a0}} \frac{\theta_p}{(1 - \theta_p)^3} \exp\left(-\frac{E}{RT_p}\right). \tag{18}$$

A second model, analogous to Model II, is

(IV)
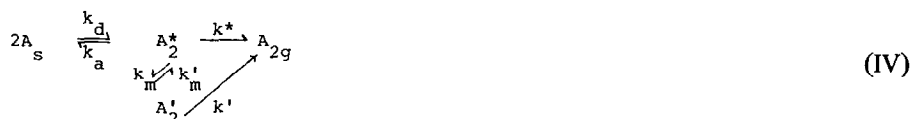
where A_2^* exists over an empty site and A_2' exists over a filled site. By the steady state approximation,

$$d[A_2^*]/dt = k_d\theta^2 - k_a[A_2^*](1 - \theta) - k_m'[A_2^*] \theta$$

$$+ k_m'[A_2'](1 - \theta) - k_2^*[A_2^*] \doteq 0 , \tag{19a}$$

$$d[A_2']/dt = k_m[A_2^*] \theta - k_m'[A_2'](1 - \theta) + k'[A_2'] \doteq 0 . \tag{19b}$$

Then

$$r_d = k^*[A_2^*] + k'[A_2'] \tag{20a}$$

$$= \left(\frac{k_m k' \theta}{k' + k_m'(1 - \theta)} + k^*\right)\left(\frac{k_d\theta^2}{k^* + k_a(1 - \theta) + k'k_m\theta/[k' + k_m'(1 - \theta)]}\right) . \tag{20b}$$

If the term in the first bracket is large compared to k_a, we obtain normal desorption kinetics. However, for k^* and k' small,

$$r_d = \frac{k^* k_d\theta^2}{k_a(1 - \theta)} + \frac{k' k_m k_d}{k_m' k_a} \frac{\theta^3}{(1 - \theta)^2} , \tag{21}$$

which predicts the possibility of third order desorption kinetics for dissociative adsorption. Again, using fig. 1e, both terms have the same activation energy.

3. Discussion

We shall next consider the implications of these precursor models for adsorption kinetics and adsorption equilibrium. Then we shall discuss the relative magnitudes

of rate constants expected for various processes. Finally, we shall consider examples of theoretical flash desorption spectra and attempt to fit several experimental spectra using these expressions.

3.1. Condensation and adsorption equilibrium

Statistical considerations [7] require a Langmuir isotherm at equilibrium for any adsorption—desorption process involving a definite number of sites for adsorption, a maximum of one gas molecule adsorbed on each site, and no lateral interactions between adsorbed molecules. Since these assumptions are inherent in all these models, the adsorption and desorption rates must yield a Langmuir isotherm at equilibrium.

Model I is a direct extension of the original precursor model proposed by Ehrlich [5] for condensation. It yields a rate of adsorption equal to

$$r_d = \frac{s^* \mathcal{F}}{1 + (k^*/k_a)/(1-\theta)} = \frac{k_a(1-\theta)\,s^* \mathcal{F}}{k^* + k_a(1-\theta)} \,, \tag{22}$$

where $\mathcal{F} = P(2\pi\mu RT_g)^{-1/2}$ is the flux to the surface and s^* is the sticking·coefficient into the precursor. With adsorption equilibrium, $r_a = r_d$, this model predicts

$$\frac{k^* k_d \theta}{k^* + k_a(1-\theta)} = \frac{k_a(1-\theta)\,s^* \mathcal{F}}{k^* + k_a(1-\theta)} \,, \tag{23}$$

or

$$\theta = KP/(1 + KP) \,, \tag{24}$$

which is the Langmuir isotherm with

$$K = \frac{k_a}{k_d k^*} \frac{s^*}{(2\pi MRT_g)^{1/2}} \,. \tag{25}$$

The activation energy in K is $E_a - E_d - E^*$ which, from fig. 1a, is exactly equal to the heat of adsorption.

The two precursor model can be shown to yield the following expression for the rate of adsorption:

$$r_a = \frac{k_a(1-\theta)\,\mathcal{F}\{s^* + s' k_m' \theta/[k' + k_m'(1-\theta)]\}}{k^* + k_a + k_m k'\theta/[k_m'(1-\theta) + k']} \,, \tag{26}$$

where s' and s^* are sticking coefficients over full and empty chemisorbed states respectively. Detailed balancing requires that

$$s^*/s' = k^* k_m'/k' k_m \,. \tag{27}$$

In adsorption equilibrium, eqs. (7b), (26), and (27), give the Langmuir isotherm once again with the constant K again defined by eq. (25).

The successive site models of Kisliuk and King, for which r_d is given by eq. (11)

and

$$r_a = \frac{s^* f_a (1 - \theta) \mathscr{F}}{f_a + f_d - \theta (f_a + f_d - f_d')} \, ,$$ (28)

gives at equilibrium

$$\mathscr{F} = \frac{k_d}{s^* f_a} \frac{\theta}{(1 - \theta)} [f_d + \theta (f_m f_d' - f_d f_m')] \, .$$ (29)

By setting $f_m/f_d = f_m'/f_d'$ one obtains again the Langmuir isotherm. K is given by eq. (25) after noting that $f_a/f_d = k_a/k^*$.

Thus we see that all of these models are consistent with thermodynamics. Since thermodynamics requires a relation between rate expressions for adsorption and desorption in any experiment, it is necessary that, if the sticking coefficient is independent of coverage, then the desorption rate *must* have a $(1 - \theta)^{-1}$ factor. This applies only if both measurements are carried out at the *same temperature* because the rate coefficients in these expressions are temperature dependent. Since adsorption measurements are usually made at low temperatures where desorption rates are negligible, this requirement can seldom be tested directly. However, the absence of a precursor in condensation at low temperature implies the absence of a precursor expression for desorption, and the presence of a precursor in condensation suggests that these expressions might be anticipated in desorption.

3.2. Pre-exponential factors

In the two precursor models, II and IV, the desorption rate is the sum of two terms which represent desorption from the full and empty sites. Since the activation energies for both terms will be the same, the relative magnitudes of the pre-exponential factors, the k_0's, will determine which term is dominant.

We first note that the k_0's should as a first approximation be vibrational frequencies. These may in general be expected to be lower in the weakly bound precursor than in the chemisorbed states because the force constants are lower. A simple estimation indicates that the vibrational frequency should be roughly proportional to the square root of the interaction energy. Therefore, for a chemisorbed state with a binding energy of 30 kcal/mole and a precursor state with 300 cal/mole, the pre-exponential factors might be 10^{13}/sec and 10^{12}/sec respectively. However, since in all rate expressions involving several terms these will always occur as ratios with the same number of factors for precursor and chemisorbed states, the difference in vibrational frequencies alone will not yield anomalous pre-exponential factors. In fact, if the pre-exponentials are equal in eq. (9), the rate expression will revert to the $\theta/(1 - \theta)$ coverage dependence of the single precursor model.

The processes involving a conversion between precursor and chemisorbed states should in general not be expected to be simply a vibrational frequency since they involve a crossing between distinct potential energy surfaces and this will require an

electronic transition. As illustrated in fig. 1b, the curves corresponding to A_s and A^* states continue beyond their crossing points, and the adsorbate can only cross to the other curve if symmetry and energy considerations are satisfied. The shapes of potential surfaces, bond symmetry requirements, and matrix elements for curve crossing are not understood in detail for any chemisorption system. However, it should be expected that the k_0's for these processes should be vibrational frequencies multiplied by electronic and steric factors that may be far from unity. Therefore, we see that, while the different coverage dependences of the rate in these precursor models can broaden the curves, the existence of precursor intermediates with different bonding characteristics could lead naturally to an anomalous pre-exponential factor which produces still more broadening.

3.3. Flash desorption spectra

In figs. 2a–c, we have plotted theoretical flash desorption curves for the first order models for several limiting cases. For all calculations we chose the activation
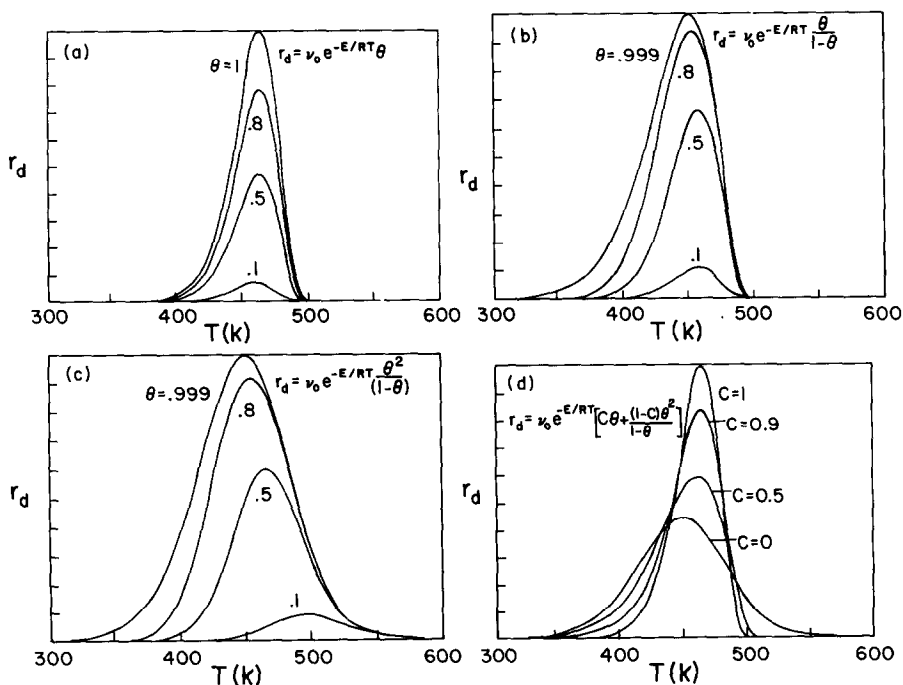

Fig. 2. Calculated flash desorption spectra assuming E_d = 26 kcal/mol, $\nu_0 = 10^{13}$/sec, and β = 100 K/sec. (a) Normal first-order desorption. (b) Limiting case for single precursor, eq. (2). (c) Limiting case for empty and full site precursors, eq. (9). (d) Saturation ($\theta = 1$) spectra for empty and full site precursors showing effects of relative sizes of terms in eq. (9).

energy and heating rate to be 26 kcal/mole and 100 K/sec respectively. The overall pre-exponential ν_0 was taken as 10^{13}/sec. Model I with a single precursor (fig. 2b) gives peaks that shift by about 12 K. For this model, the binding energies which would be calculated assuming normal desorption kinetics will be lower by about 0.7 kcal/mole. The major effect of this model is to broaden the peaks near saturation.

Figs. 2c and 2d show curves predicted by Model II, the empty and full site precursor model. Desorption curves as in fig. 2c result when

$$r_{\mathrm{d}} = K_2 \frac{\theta^2}{1 - \theta} \exp\left(-\frac{E}{RT}\right)$$

is the limiting rate. Fig. 2d shows the range of curves that can be expected for the expression.

$$r_{\mathrm{d}} = \left(K_1\theta + K_2 \frac{\theta^2}{1 - \theta}\right) \exp\left(-\frac{E}{RT}\right)$$

as K_1 and K_2 vary, keeping $K_1 + K_2 = 10^{13}$/sec. We see that the effect of increasing the precursor is to broaden the curves but not to change the peak temperature or the calculated activation energy by more than a few percent.

Figs. 3a–c show the limiting curves for the second order models with the same activation energies and pre-exponentials taking $\nu_0^{(2)}\eta_0 = 10^{13}$/sec^{-1}. These expressions, unlike those for the nondissociative models, give peak temperatures shifted by more than 35 K from those expected for normal kinetics with identical activation energies (an activation energy variation of $\sim$2 kcal/mole). Also, the precursor is seen to greatly affect the shift in peak temperature with coverage. Again, the curves are broadened, and, with the $\theta^3/(1 - \theta)^2$ coverage dependence, one obtains curves which are quite assymetric and tail off slowly at high temperatures.

3.4. Fits of precursor models to experimental data

3.4.1. N_2 on (100)W
Condensation kinetics have probably been examined in more detail [6,8–10] for this system than for any other. From sticking coefficient measurement between 190 and 600 K, the quantity k^*/k_a from eq. (15) has been shown [8] to be consistent with an Arrhenius temperature dependence with an activator energy of 830 cal/mole. Using this expression to extrapolate to desorption temperatures, we can predict the flash desorption spectrum of N_2 from (100)W, since k^*/k_a must be the same for condensation and desorption by detailed balancing.

In fig. 3d are shown the experimental flash desorption spectra for N_2 on (100)W and calculated spectra assuming E_d constant at 86 kcal/mole with experimentally measured values for other parameters. It is seen that the agreement is essentially quantitative. For the fit shown in fig. 3d we used the extrapolated k^*/k_a measured below 600 K. A higher value was obtained at higher temperatures which gives a narrower peak than observed. The spectra could not be fit [6,8] assuming normal
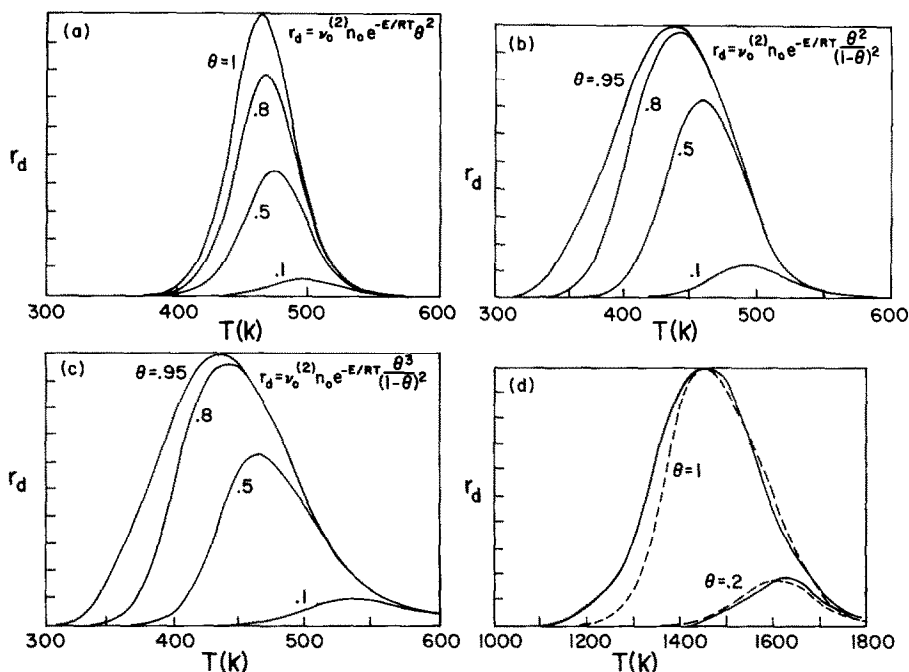
Fig. 3. (a) through (c) are calculated flash desorption curves for dissociative desorption assuming E_d = 26 kcal/mol, $\nu_0^{(2)} n_0$ = 10^{13}/sec, and β = 100 K/sec with the coverages indicated. (a) Normal dissociative desorption. (b) Limiting case for single site precursor model, eq. (17). (c) Limiting case for empty and full site precursor model, eq. (21). (d) Fit to experimental data (solid curves) for N_2 desorption from (100)W using k^*/k_a = 0.2 exp($-830/RT$), E_d = 86 kcal/mol and $\nu_0^{(2)} n_0$ = 10^{13}/sec, eq. (15).

second order kinetics with constant ν_0 and E_d. Good fits were obtained assuming $E_d = 80 - 5.5\,\theta$ or using a model which predicts a variation of ν_0 with coverage because of atom recombination considerations. However, the agreement between adsorption and desorption kinetics required by detailed balancing shows that the data are all consistent with a constant activation energy of desorption.

3.4.2. CO on (100) Pt

This system exhibits a single major peak which broadens significantly near saturation. McCabe and Schmidt [11] showed that this spectrum could be fit assuming a linear variation of E_d with coverage of the form $E_d = 26 - 2.5\,\theta$. Fig. 4b shows experimental and calculated spectra assuming constant E_d with the $\theta^2/(1-\theta)$ coverage dependence limit from eq. (9). The experimental peak is still somewhat broader than that calculated using this expression, but the agreement is better than that obtained assuming a coverage dependent E_d. The expression used assumed only that the first order term in the rate expression eq. (9) was negligible; no other para-

meters were allowed to vary and the pre-exponential ν_0 was assumed to be 10^{13}/sec. By allowing this to vary, the fit could easily have been made quantitative. The sticking coefficient for CO on (110) Pt at 300 K is independent of θ at low coverages. This suggests that the model used in fig. 4a could be valid.

3.4.3. CO on (111) Pt

King [12] used this system as an example of a possible fit to his precursor model. A fit to the experimental spectrum using eq. (2) shown in fig. 4b) does not give a peak nearly wide enough to fit the experimental spectrum. King, in effect, allowed the pre-exponential factors in eq. (13) to vary in order to fit experimental results. Clearly, almost any of our models could be made to fit if several parameters are adjusted. However, we suggest that this system is probably not a situation where precursor intermediates give reasonable agreement with experiment. In fact, the heat of adsorption measurements of Ertl, Neumann, and Streitt [13] gave a decrease of E_d with θ. McCabe and Schmidt [11] showed that a linear coverage dependence of E_d of the form 29.6—6.5 θ (kcal/mole) gave reasonable fit to the desorption spectra.
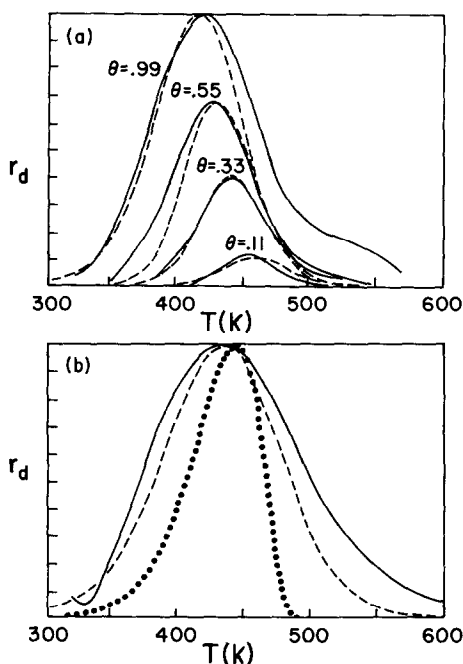

Fig. 4. Comparison of experimental data (solid curves) with precursor models (dashed lines). (a) CO on (110) Pt. The coverage dependence is taken as $\theta^2/(1-\theta)$, E_d = 24 kcal/mol, ν_0 = 10^{13}/sec and β = 100 K/sec for the theoretical spectra. (b) CO on (111) Pt. Dotted curve is the calculated spectra using eq. (2) with ν_0 = 10^{13}/sec, and β = 100 K/sec. Dashed line uses $\theta^2/(1-\theta)$ rate dependence and ν_0 = 10^{10}/sec.

4. Summary

All of the precursor models can lead to $(1 - \theta)$ or $(1 - \theta)^2$ factors in the denominator of the desorption rate expressions. Such terms are required by detailed balancing if the sticking coefficient (at the desorption temperature) is independent of coverage. Several of these models can also lead to an increase in the order of the desorption rate, although the conditions under which this occurs are more restrictive. A higher order in θ is obtained if desorption occurs only over a full precursor site.

The kinetic and successive site versions of the two precursor model lead to different expressions. One can show that the successive site model can only give a $(1 - \theta)$ factor in the denominator while the kinetic two precursor model can lead to an increase in the desorption order. Since all rate parameters in the model should be temperature dependent, the kinetic model has the advantage that these coefficients should have Arrhenius temperature dependences. The various probabilities in the successive site model involve groupings of rate coefficients which may have no simple temperature dependencies. Temperature independence of these parameters would require that all systems exhibiting precursor effects at low temperatures in condensation must exhibit precursor effects in desorption.

It is not clear how many chemisorption systems exhibit desorption kinetics which are affected by precursor considerations. We suggest that this is quite plausible for N_2 on (100)W, possible for CO on (110) Pt, and less likely for CO on (111) Pt. Systems which exhibit coverage independent sticking coefficients are likely candidates, and these considerations should be added to possible explanation of experimental desorption spectra.

It should be noted that thus far the only evidence of weakly bound precursor intermediate states in chemisorption comes from the interpretation of the coverage dependence of sticking coefficients. While such states probably exist, their properties are undoubtedly more complex than these models imply. For example, physically adsorbed or weakly chemisorbed states may be on sites different than chemisorbed states, and occupation of them may influence the properties of the other. However, it is questionable whether any of these states will, in fact, be "on top of" chemisorbed sites. More direct information, such as in molecular beam scattering and lifetime experiments, is needed to characterize precursor states.

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