Activated Chemisorption: Internal Degrees of Freedom and Measured Activation Energies

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In activated chemisorption occurring both by direct impact from the gas and by conversion from a precursor on the surface, the measured activation energy can provide information about the mechanism of activation. If translational motion is dominant in promoting passage over the adsorption barrier, a single activation energy describes the reaction whether gas and surface are isothermal or hot gas strikes a cold surface. When internal degrees of freedom must be excited for chemisorption to occur, different activation energies characterize these two regimes of measurement.

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Although chemisorption has over the years received considerable attention, relatively little has been done to examine how the activation barrier is best overcome. There is a growing body of experimental work, however, to suggest that in activated chemisorption it is often the excitation of the gas which is important in bringing about the reaction.[1-6] The possibility therefore exists that chemisorption can occur in two ways: directly from the gas phase and also by conversion from a precursor weakly bound to the surface.[7] We show here that if both paths contribute, then by comparing the activation energy for adsorption of a hot Maxwellian gas striking a cold solid with the results for when gas and solid are at the same temperature, significant information about how the molecules should be excited to overcome the barrier most effectively may be obtained. This information is of interest both in its own right, and as an initial step towards eventual achievement of a more complete understanding of the detailed reaction paths taken by molecules dissociating at the surface.

Consider activated adsorption on a bare surface. The barriers are usually shown on a schematic potential diagram, such as in Fig. 1. Molecules from the gas phase may be chemisorbed directly on first striking the solid if they have enough energy to go over a barrier of height E_a above the potential for a molecule far from the surface. Those molecules which are not chemisorbed on first impact can still condense into a weakly bound precursor state. This state provides a reservoir from which molecules may be either chemisorbed by passing over a barrier of height E_c or desorbed back into the gas phase, over a barrier E_d.

The fraction s_a of the incoming molecules which is chemisorbed directly from the gas phase at temperature T_g, that is, the sticking coefficient, can be written in the usual way[8] as

$$s_a = s_a^0 \exp(-E_a/kT_g), \tag{1}$$

where s_a^0 denotes a weakly temperature-dependent prefactor, and k is Boltzmann's constant. In the fraction s_a we include, as an approximation, molecules that may have exchanged enough translational energy with the lattice to become trapped in the precursor, but retain the energy in internal degrees of freedom[9,10] in the gas at T_g and so may be able to be chemisorbed. Of those molecules that are not chemisorbed on striking the surface, a fraction s_m condenses into the molecular precursor, and comes to thermal equilibrium with the surface[11-13] on a time scale small compared to the lifetime of molecules in the precursor. The steady-state concentration n of molecules in the precursor state will be dictated by competition between conversion to the chemisorbed state, which occurs with a rate constant k_c, and desorption, characterized by the rate constant k_d, so that

$$n(k_c + k_d) = (1 - s_a)s_m p/(2\pi m k T_g)^{1/2}; \tag{2}$$

here $p/(2\pi m k T_g)^{1/2}$ is just the rate at which molecules strike unit area of the surface in unit time from gas at a pressure p. Inasmuch as the rate of chemisorption from the precursor is nk_c, the overall sticking coefficient at

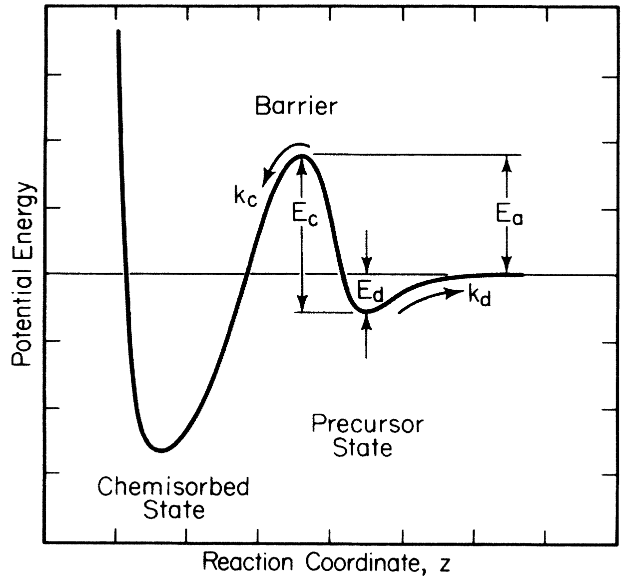

FIG. 1. Schematic one-dimensional potential-energy diagram for activated chemisorption occurring from the gas phase as well as from a precursor on the surface.

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zero coverage, $s(0)$, is given by

$$s(0)=s_a[1-s_m k_c/(k_c+k_d)]+s_m k_c/(k_c+k_d). \quad (3)$$

For the rate constants to conversion and to desorption we write respectively

$$k_c=\nu_c\exp(-E_c/kT_s), \quad (4)$$

$$k_d=\nu_d\exp(-E_d/kT_s), \quad (5)$$

where ν indicates the appropriate frequency factor and T_s gives the temperature of the surface. In order for chemisorption from the gas to be activated, the barriers E_c and E_d must satisfy the condition $E_c>E_d$. However, we further assume, for the sake of clarity only, that the rate of desorption from the precursor actually far exceeds that of conversion,

$$k_d\gg k_c. \quad (6)$$

This validates the approximation $1\gg s_m k_c/(k_c+k_d)$, and the sticking coefficient now appears as

$$s(0)=s_a^0\exp(-E_a/kT_g) +s_m^0\exp[-(E_c-E_d)/kT_s], \quad (7)$$

where

$$s_m^0\equiv s_m\nu_c/\nu_d. \quad (8)$$

The first term on the right of Eq. (7) represents the contribution of molecules being chemisorbed directly from the gas phase. The second term gives the contribution of molecules in thermal equilibrium with the surface converting from the precursor. Here it is the competition between conversion of precursor into the chemisorbed state, over the barrier E_c, and desorption of precursor, over the barrier E_d, that yields the effective activation energy E_c-E_d.[14] Up to this stage the derivation has been fairly routine[15-17] and, except for the trivial simplifying assumption in Eq. (6), quite general.[18]

Assume now that it is the translational energy of the incoming molecules which is important in overcoming the barrier to chemisorption and consider chemisorption directly from the gas phase. Molecules approaching the surface are accelerated by the attractive potential for the precursor. Provided there is no exchange of energy or momentum with the surface during this first approach, the kinetic energy gained is available for continuing over the barrier to chemisorption, so that the incoming gas only has to have kinetic energy in excess of E_a in order to be chemisorbed. The one-dimensional diagram in Fig. 1, in which the potential energy is plotted as a function of the distance z from the surface, conveys the correct relation between the various barriers, namely

$$E_a=E_c-E_d. \quad (9)$$

For molecules being chemisorbed from the precursor, the activation energy, determined in the usual way from a semilogarithmic plot of the rate against $1/T$, always reflects the competing contributions from conversion and desorption so that the sticking coefficient simplifies to

$$s(0)=s_a^0\exp[-(E_c-E_d)/kT_g] +s_m^0\exp[-(E_c-E_d)/kT_s]. \quad (10)$$

Thus, for activated chemisorption in which translational motion is most effective in getting molecules over the barrier, a single activation energy E_c-E_d characterizes the rate of both direct chemisorption from the gas and conversion from the precursor, provided the temperature span of the experiments is limited so that the various prefactors remain essentially constant and other, higher energy, processes do not intrude. Measurements of chemisorption in which the temperature of the gas is changed, but the surface is maintained cold, will yield the same activation energy as studies of the adsorption rate with gas and surface at identical temperatures (or equivalently, with gas cold and the surface maintained at different high temperatures). The magnitude of the activation energy derived from such experiments will, in accord with Eq. (9), reflect the difference between the barriers to chemisorption and to desorption from the precursor state.

The situation is quite different when internal degrees of freedom must be excited, either in the incoming molecules or in the precursor, to facilitate chemisorption. Under these circumstances, a one-dimensional potential diagram, such as in Fig. 1, is not adequate[19] in conveying the relations between the different activation energies. For chemisorption in which the energy of activation goes into extending one of the internal dimensions r of the molecule, presumably through vibrational motion, the two-dimensional schematic in Fig. 2 is more appropriate. Now, in order for chemisorption to occur, the internal coordinate must exceed a critical value r^*. Equation (7) still describes the sticking coefficient, but the relations between the different barriers are changed.

For molecules being chemisorbed from the precursor, the net activation energy is as usual (E_c-E_d), but for direct chemisorption the situation is more complex. Now, as a molecule approaches the surface and is accelerated toward it by the precursor potential, the kinetic energy of motion so gained does not help *directly* in going over the barrier E_c to chemisorption. Chemisorption will only be assisted if during the collision with the surface, kinetic energy of translational motion is converted to excitation of the appropriate internal degree of freedom.[12] Consider what happens if such conversion is not competitive with trapping and subsequent thermalization of the molecules in the precursor state. For molecules from the gas phase to be chemisorbed directly, that is for their internal coordinate to exceed the critical value r^*, the molecules must have energy greater than E_a in the

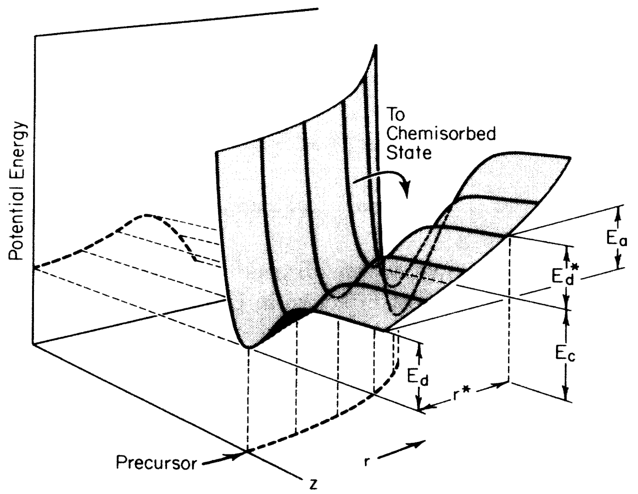

FIG. 2. Potential-energy schematic for chemisorption in which an internal coordinate r of the molecule is extended to overcome the activation barrier; z = distance from surface. For the chemisorbed state, only a small region close to the top of the barrier is shown.

appropriate internal degree of freedom. We now have

$$E_a + E_d = E_d^\ddagger + E_c, \tag{11}$$

where $E_d^\ddagger$ is the desorption energy for precursor molecules with the internal coordinate at the critical value r^* for chemisorption. The sticking coefficient at zero coverage therefore becomes

$$s(0) = s_a^0 \exp[-(E_c + E_d^\ddagger - E_d)/kT_g] + s_m^0 \exp[-(E_c - E_d)/kT_s]. \tag{12}$$

For molecules in the precursor state the desorption energy should not depend sensitively upon the internal degrees of freedom of the molecules; that is, we can expect

$$E_d^\ddagger \approx E_d, \tag{13}$$

so that the activation energy E_a for chemisorption from the precursor reduces to

$$E_a \approx E_c. \tag{14}$$

We conclude that when internal degrees of freedom must be excited for activated chemisorption to take place, coversion from the precursor is favored over direct chemisorption from the gas phase: Coversion from the precursor has an effective activation energy $E_c - E_d$, compared with the barrier of roughly E_c to direct chemisorption. For experiments in which gas and surface are at the same temperature, direct chemisorption should therefore be relatively unimportant, and the sticking coefficient, at low temperatures at least, can be approximated by

$$s(0) \approx s_m^0 \exp[-(E_c - E_d)/kT]. \tag{15}$$

If measurements are made with a hot gas on a surface maintained so cold that the second term on the right in Eq. (12) accounting for conversion from the precursor does not contribute, then the activation energy for chemisorption will be found as $\approx E_c$. In contrast, experiments with cold gas on a hot surface at different temperatures will yield an activation energy $E_c - E_d$, just as in Eq. (15), provided that thermalization of gas condensed into the precursor is rapid.

In the studies of activated chemisorption reported so far,[1-6,20-28] measurements have not been done to reveal differences in activation energies determined under these different conditions. Nevertheless, two general conclusions follow immediately from the present analysis. (1) If excitation of internal molecular motions is a prerequisite to activated chemisorption, then different activation energies characterize chemisorption from the gas and from the precursor. A proper interpretation of measured rate parameters therefore presupposes knowledge of the mechanism by which activated chemisorption occurs. (2) In activated chemisorption, measurements on a cold surface done by variation of the gas temperature should be compared with the results of studies with cold gas on a surface at different temperatures, or better, with rates measured when gas and surface are isothermal. Differences in activation energies obtained under these two different regimes indicate that internal molecular degrees of freedom, not translation, are important in promoting the chemisorption process.

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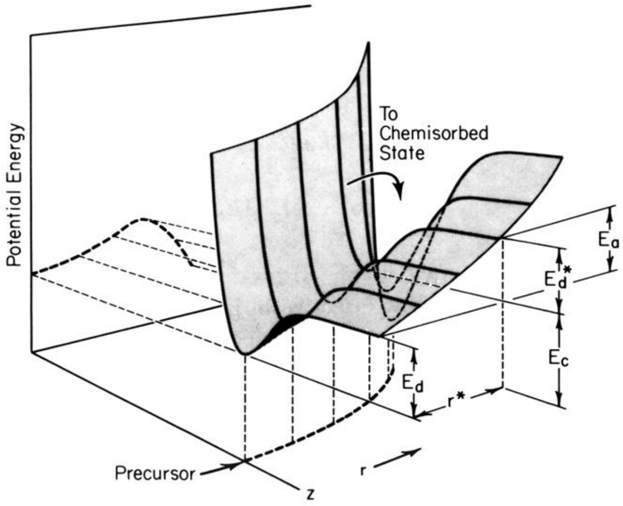

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