

NOTE

An Explanation of the Compensation Effect in Catalysis

The compensation effect is observed in both homogeneous and heterogeneous catalysis when the experimental Arrhenius parameters, A and E , obey a simple linear relationship (1), where a and b are constants

$$\ln A = aE + b. \quad [1]$$

The effect is noted generally either for the same reaction and a group of similar catalysts, or for the same catalyst and a family of similar reactions, and although known for 70 years has no satisfactory theoretical explanation.

Conner (1), using the simple transition state kinetic equations

$$k_{\text{exp}} = kT/h \cdot K^\ddagger \quad [2]$$

$$k_{\text{exp}} = kT/h \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}, \quad [3]$$

showed that when the experimental rate constant, k_{exp} , and thus the constant, K^\ddagger , for equilibrium between reactants and the transition state, is effectively constant, ΔS^\ddagger , will vary in a linear fashion as a function of ΔH^\ddagger . Since kT/h is a constant $\ln A$ and E are given by the following equations, where c , d , and e are constants:

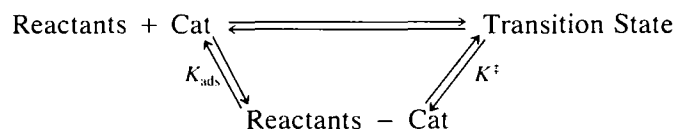
$$\ln A = c\Delta S^\ddagger + d \quad [4]$$

$$E = \Delta H^\ddagger + e. \quad [5]$$

Galwey (2) has raised various objections to the validity of this treatment in deriving equation (1), but our only major one is that the E values usually extend over far too wide a range for it to be a general explanation, as Conner claims (1). We have now concentrated on this major problem because there is a recent report (3) showing an excellent compensation effect over a difference of more than 100 kJ mol⁻¹ in E values for neopentane hydrogenolysis on various Pd-zeolite catalysts. Furthermore, we have also noted recently a compensation effect over a similar range for the very simple reaction of cyclopentene hydrogenation using as catalysts Pt dispersed on doped oxide supports of varying basicities (4).

The following extension of Conner's treatment provides a more general solution. The cornerstone of the Arrhenius rate equation and transition state theory in kinetics is

physical equilibrium, i.e., the energy and matter in a given system under specified conditions, T and P , etc., are always at their most probable distributions. Consideration of the following scheme for catalysis shows that if there is equilibrium between free reactants and complexed or chemisorbed reactants, then the free reactants plus catalyst are also in physical equilibrium with the transition state complex:



Now the kinetic equation for conversion of the reactants is valid,

$$k_{\text{exp}} = kT/h \cdot K_{\text{ads}} \cdot K^\ddagger, \quad [6]$$

and this may be expanded as before to give

$$k_{\text{exp}} = kT/h \cdot e^{(\Delta S_{\text{ads}}^\circ + \Delta S^\ddagger)/R} \cdot e^{-(\Delta H_{\text{ads}}^\circ + \Delta H^\ddagger)/RT}. \quad [7]$$

The sum, $\Delta H_{\text{ads}}^\circ + \Delta H^\ddagger$, gives approximately the experimental E values, and the main variable is by far $\Delta H_{\text{ads}}^\circ$ and not ΔH^\ddagger . As the adsorption strength increases and therefore E decreases there is a corresponding decrease in $\Delta S_{\text{ads}}^\circ + \Delta S^\ddagger$ and thus in the value of A . That Eq. [1] can hold over such a wide range of E values is now understood.

In statistical thermodynamics the entropy of a system is governed by two terms, the amount of heat required to produce a given temperature and a partition function expressing the most probable distribution of this heat over various degrees of freedom. The second term varies to much the same extent on going from weaker to stronger chemisorption; the main contribution, loss of translational freedom of the free adsorbate, is the same. The distribution function is solely responsible for the free energy of the system, so $\Delta G_{\text{ads}}^\circ$ changes very little and variations in $\Delta H_{\text{ads}}^\circ$ are therefore almost entirely compensated by corresponding variations in $\Delta S_{\text{ads}}^\circ$, as expressed by

$$\Delta H_{\text{ads}}^\circ - T\Delta S_{\text{ads}}^\circ = \Delta G_{\text{ads}}^\circ \approx \text{Constant}. \quad [8]$$

Equation [8] is a particular example of a general property inherent in the fundamental relation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, already discussed briefly by Benson (5) and in more detail by Conner (1) using statistical arguments as applied to the transition state relation, $\Delta S^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

K_{ads} is, of course, the Langmuir adsorption coefficient or a combination of such coefficients, as discussed later in more detail. It is worth emphasizing that Eq. [6] can be abbreviated to the relation $k_{\text{exp}} = K_{\text{ads}} \cdot k_{(\text{true})}$, where $k_{(\text{true})}$ is the rate constant for the transformation of the adsorbed complex. The temperature coefficient of the logarithm of this equality affords the activation energy relation, $E_{\text{exp}} = E_{(\text{true})} + \Delta H_{\text{ads}}^\circ$, which has long since been developed and widely accepted (6) without having recourse to transition-state rate equations. However, the incorporation of Langmuir adsorption theory into the transition state equations is a novel significant feature which not only encompasses this activation energy relation for catalysis but also greatly illuminates the validity of Conner's approach (1) with its emphasis on the role that entropy plays in causing the compensation effect. For example, if the rate-limiting step becomes adsorption of the reactants rather than transformation of the adsorbed complex $K_{\text{ads}} \cdot K^\ddagger$ is simply replaced by K_{ads}^\ddagger . This can be regarded as one kinetic extreme, the other being strictly zero-order reactions with respect to all reactants, where $K_{\text{ads}} = 1$, and only K^\ddagger is required. Conner's treatment (1) covers both these extremes where there will still be compensation, but only over a limited range according to the relation, $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

The introduction of the composite constant, $K_{\text{ads}} \cdot K^\ddagger$, is a significant novel feature because of the range and flexibility afforded by K_{ads} . Now in terms of the Langmuir adsorption equations for one reactant, X , or two reactants, X and Y , competing for the same sites, the general transition state rate equations may be developed:

$$\text{rate} = kT/h \cdot \theta_X \cdot K^\ddagger = kT/h \cdot \frac{C_X P_X}{1 + C_X P_X} \cdot K^\ddagger \quad [9]$$

$$\begin{aligned} \text{rate} &= kT/h \cdot \theta_X \theta_Y \cdot K^\ddagger \\ &= kT/h \cdot \frac{C_X P_X C_Y P_Y}{(1 + C_X P_X + C_Y P_Y)^2} \cdot K^\ddagger. \quad [10] \end{aligned}$$

The corresponding expressions for the rate constants, k_{exp} , for the various limiting cases show that K_{ads} is given by C_X or 1 for Eq. [9], and by $C_X C_Y$ or C_X/C_Y for Eq. [10]. The quotient C_X/C_Y arises when X is weakly adsorbed and Y is strongly adsorbed.

With noncompetitive adsorption in the case of cyclopentene hydrogenation (4) which is zero order and first order in olefin and hydrogen pressures respectively, the rate of reaction is given by

$$\text{rate} = kT/h \cdot \theta_{\text{H}_2}^2 \cdot K^\ddagger. \quad [11]$$

The Langmuir relation for weak dissociative adsorption of H_2 is $\theta_{\text{H}} = C_{\text{H}_2} \cdot P_{\text{H}_2}^{1/2}$, so Eq. [11] can be written as

$$k_{\text{exp}} = kT/h \cdot C_{\text{H}_2}^2 \cdot K^\ddagger. \quad [12]$$

Here K_{ads} is $C_{\text{H}_2}^2$ where C_{H_2} is the Langmuir coefficient for dissociative adsorption of H_2 .

The heat and entropy of adsorption of H_2 are thus shown to be important variables in producing the compensation effect noted (4). In the limit as $\Delta H_{\text{ads}}^\circ \rightarrow 0$ and E assumes its maximum value the mechanism of H_2 activation during hydrogenation will become increasingly Eley-Rideal in character (7).

The application of the present development of Eyring's transition state theory in explaining compensation effects is even more apt when we come to homogeneous catalysis where site uniformity is to be expected (8). Now K_{ads} can be replaced by an equivalent K_c for complex formation between reactants and catalyst. Further developments will require statistical theories as discussed by Conner (1) and a detailed knowledge of the energy levels of the adsorbed or solution complexes. This is a really formidable task, but it is the only way whereby Eq. [8] may be adequately explored.

The theory outlined here to explain Eq. [1] (*theta rule*) and isokinetic temperature (2) has so far only emphasized variations in adsorption strengths as the factor mainly responsible. However, variations in the densities of active sites from catalyst to catalyst in the same family may be another important factor because the *theta rule* is obeyed generally when A values are expressed, as is most often the case (4, 9), per g or per m^2 rather than per site. It is quite likely that the densities of sites from one catalyst to another vary exponentially as a function of their intrinsic free energies. The number of such sites, n , per g, or per m^2 , can then be expressed by the simple function, $n = n^0 \cdot e^{-\Delta G/RT}$, where the superscript zero refers to one catalyst chosen as a standard, and $\Delta G = G - G^0$ is the free energy difference with reference to this standard. The composite constant, $K_{\text{ads}} \cdot K^\ddagger$, may then be elaborated to contain this additional exponential free energy term. However, the rates in Ref. (3) are expressed as TOF (turn over frequency) per dispersed metal atom in the zeolites, which can be construed realistically as TOF per site, so $K_{\text{ads}} \cdot K^\ddagger$ as defined in Eq. [7] may be a sufficient explanation for this very important example of compensation (3).

In conclusion, while the application of transition state theory to surface reactions and catalysis with detailed intensive probing of the microscopic states of the adsorbed complexes is a subject of considerable current interest (10, 11), no one has hitherto discussed the equilibrium constant in the Eyring equation, when applied to

kinetics in the field of catalysis, as a composite constant, embracing a variety of free energy exponential terms, as we have done here.

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Received July 14, 1993; revised October 6, 1993