JOURNAL OF CATALYSIS 78, 238–246 (1982)

A General Explanation for the Compensation Effect: The Relationship between $\Delta S^{\ddagger}$ and Activation Energy

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Received May 3, 1982; revised June 29, 1982

Changes in activation energy are often offset by a change in the pre-exponential factor for a group of similar reactions. I present a possible general explanation for this "compensation effect" by relating the entropy of transition to a change in the energy levels of the transition state. Reduction of the activation energy results in a "narrower" transition state. This energetic funneling dictates a decreasing (compensating) entropy.

INTRODUCTION

The kinetics of heterogeneous catalytic reactions are usually described using the Arrhenius equation developed for homogeneous systems. The dependence of the reaction rate on temperature is represented by

$$k = Ae^{-Ea/RT}, \qquad A \text{ is a constant} \quad (1)$$

where k is the rate constant, A is the pre-exponential (or frequency) factor, and Ea is the activation energy. Both Ea and A are considered constant, or at least independent, for a group of similar rate processes. Numerous studies, however, conclude that there can be an interrelationship between A and Ea (*1–6*). Often the change in one factor is offset by a change in the other. Most attempts to explain this compensation effect have dealt with the number or nature of the active sites, or alternately with the specific adsorption process. A more fundamental explanation may be possible. A lowering of the activation energy may indeed *require* a lowering of the entropy of transition.

I will analyze the relationship between the pre-exponential factor, A, and the energy of activation based on classical and statistical transition state theory. The statistical representation will be used to calculate the expected compensation for *ortho–para* hydrogen conversion.

BACKGROUND

In 1923, Constable described an increase in the pre-exponential term A with an increase in activation energy for ethanol dehydrogenation over copper oxide (*1*). Schwab has expressed the effect in a theta rule (*2*), viz:

$$\log A = aE + b, \qquad a \text{ and } b \text{ are constants} \quad (2)$$

Cremer suggested that the compensation effect could be explained by the effect of temperature on the distribution of active sites (*3*). Sosnovski suggested that two types of active sites (with differing activation energies) could explain the phenomena. Temperature changes the relative number of these sites, compensating for the change in the average measured activation energy (*4*). Sosnovski further explained the different activation on different crystalographic surfaces.

In a recent review article on the compensation effect, Galwey summarized the explanations for the compensation effect (*5*). He concluded that the most common explanations are "surface heterogeneity, in one form or another, and the occurrence of two or more concurrent reactions," and "no

0021-9517/82/110238-09$02.00/0

single theoretical explanation of compensation behavior has been recognized as having general application." The compensation effect has also been attributed to experimental error; inaccuracy or poor experimental technique (*6*).

I believe a general explanation is possible based on understanding the enthalpy–entropy relationship for changing activation energies. Galwey cites the effect of the heat of adsorption on the activation energy and the relationship between adsorption and rotational–vibrational freedom. This argument is expressed by Benson (*7*): "This compensation is perhaps more easily understood in the language of statistical mechanics, where we associate decreases in enthalpy (exothermic changes) with 'tighter' binding and consequently, with less entropy ('freedom of motion')."

Indeed, the entropy of an adsorbed molecule should decrease with increasing adsorption strength. However, the rate of reaction can be dominated by the surface reaction and not necessarily the indirect effect of the energetics of adsorption as indicated by Benson.

We want to focus on the entropy–enthalpy relationship of this transition. As the saddle height changes along the reaction coordinate, what happens to the energy states at the saddle? What effect will these energy states have on the entropy of transition?

To understand the effect of a change in the energy barrier (ΔEa) we consider a single transition giving rise to the activation energy. Galwey and Brown contended that the existence of isokinetic (compensation) behavior is due to a common surface intermediate or rate-controlling step for the set of catalysts investigated (*8*). To simplify the analysis of the (assumed) common transition, the energy levels of the state preceding the rate controlling surface transition are assumed to be fixed. These assumptions are only used to develop the arguments in this theory not to restrict the application of this approach.

THE ENTHALPY–ENTROPY RELATIONSHIP OF THE TRANSITION STATE

According to transition state theory as proposed by Eyring, the reaction rate constant is given by:

$$k_r = K\frac{kT}{h} e^{\Delta S\ddagger/R} e^{-\Delta H\ddagger/RT} = \frac{kT}{h} e^{-\Delta F\ddagger/RT} \quad (3)$$

where

K = transmission coefficient
k = Boltzmann's constant
h = Planck's constant
$\Delta S\ddagger$ = entropy difference between reactants and the transition state
$\Delta H\ddagger$ = enthalpy difference between reactants and the transition state
$\Delta F\ddagger$ = free energy difference between reactants and the transition state.

In statistical mechanics the rate constant is defined as:

$$k_r = K\frac{kT}{h}\frac{Z\ddagger}{\prod_i Z_{ri}} e^{-\Delta E\ddagger/RT} \quad (4)$$

where

$\Delta E\ddagger$ = energy difference between reactants and the transition state
$Z\ddagger$ = partition function of the transition state
Z_{ri} = partition function of the *i*th reactant.

Transition state theory assumes all energy levels have equal reactivity. Tolman suggested that the rate constant is more complex and will differ for each energy level (*9*). As was pointed out by Benson, this means (*7*):

$$k_r = \frac{\sum_j g_j e^{-\epsilon_j/RT} k_j}{\sum_j g_j e^{-\epsilon_j/RT}} \quad (5)$$

where

g_j = the degeneracy in the jth energy level
ϵ_j = the energy in the jth energy level
k_j = the individual rate constant for the jth level.

In transition state theory (Eq. (3)) a compensation effect will be seen if $Ke^{\Delta S\ddagger/R}$ decreases with decreasing $\Delta H\ddagger$. Similarly, in the statistical mechanical representation (Eq. (4)) $KZ\ddagger$ has to decrease with $\Delta E\ddagger$. Tolman's representation (Eq. (5)) suggests we may have to consider the changes in degeneracy and energy levels in conjunction with the relative rate constants for each energy level.

In general the total entropy per mole of a given state is given by (*10, 11*)

$$S = R \ln Z + RT \frac{\partial \ln Z}{\partial T}. \quad (6)$$

The second term in Eq. (6) is equal to the ratio of the internal energy to the temperature (E/T). The net result is that the free energy,

$$F = RT \ln Z; \qquad S = R \ln Z + E/T. \quad (7)$$

As the activation energy changes from one catalyst to another, there may be a change in the energy states of the activated complex. For a decrease in activation energy, the energy difference between the levels may either remain the same or increase. Indeed for a harmonic oscillation an increase is expected. Activation energy represents the difference between zero point energies; however, the other accessible energy states may not decrease by the same amount or may not retain their degeneracy. Stated differently, with a decreasing activation energy, certain energy states may split their degeneracy or may change the energy level separation between the states. The analysis of the uniform shift (Ea and ΔS independent) assumed the degeneracies are constant and the effect of splitting the degeneracies without changing the energy spacing should be considered. We will consider these two effects independently as illustrated in Fig. 1.

The initial transition state (I) is shown on the left with two states with lowered activation energies shown on the right. The first state (A) has an increased energy level separation. The state to the far right (B) has a split in the degeneracy of the energy levels.

The analysis is facilitated by isolating the effects in stages:

(A) The effect on $\Delta S\ddagger$ of equal and unequal shifts in the energy levels.
(B) Increasing (unequal) separations between energy levels.
(C) Splitting of the degeneracies of the energy levels.

Ortho–para hydrogen transitions with a change in the barrier to rotation of the adsorbed species are used as an example of compensating behavior. Possible changes in the transition probability are then discussed. Finally, if compensation occurs, isokinetic behavior has been suggested. The specific shifts in energy levels (for vibration or rotation of the adsorbed species) that will result in isokinetic behavior are presented.

A. The Effect of Equal and Unequal Energy Level Shifts

As the activation energy changes, we can express the new energy levels ($\epsilon_i \rightarrow \epsilon_i'$) with two parameters: a uniform shift in all energy levels, $\alpha = \epsilon_0' - \epsilon_0$; and the difference

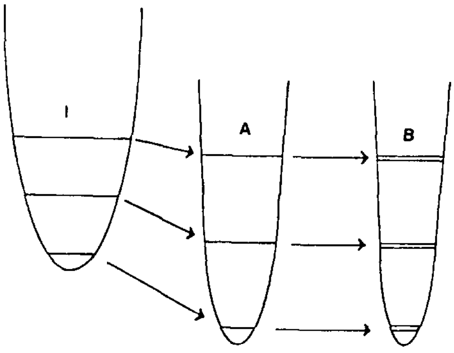

FIGURE 1

in the shift for the individual energy levels, B_i. Therefore the new energy levels (ϵ_i') become:

$$\epsilon_i' = \epsilon_i + \alpha + B_i \qquad \text{with } B_0 = 0.$$

The difference in the transition entropy ($\Delta S^{\pm}$) can be expressed with Eq. (7). The energy and partition function of the transition and the state preceding it are used. The preceding state is used as energy reference. The change in the molar transition entropy $\Delta(\Delta S^{\pm})$ of one transition (with transition state energy levels ϵ_i) compared to the new transition (with transition state energy levels ϵ_i') is:

$$\Delta(\Delta S\ddagger) = R \ln \left(\frac{Z\ddagger'}{Z\ddagger}\right) + \frac{\Sigma n_i'\epsilon_i' - \Sigma n_i\epsilon_i}{T}. \tag{8}$$

In Eq. (8), n_i, n_i' equal the number of the moles in the i'th and i'th energy level and the partial molar energy E and E' equal $\Sigma\epsilon_i n_i$ and $\Sigma\epsilon_i' n_i'$, respectively ($\Sigma n_i = \Sigma n_1' = n_0$). A partial molar representation is used for the adsorbed state as suggested by Hill (*12*). Then:

$$\frac{Z\ddagger'}{Z\ddagger} = \frac{\Sigma g_i' e^{-\epsilon_i'/kT}}{\Sigma g_i e^{-\epsilon_i/kT}} = e^{-\alpha/kT}\frac{\Sigma g_i' e^{-(\epsilon_i+B_i)/kT}}{\Sigma g_i e^{-\epsilon_i/kT}}$$

$$\underset{\text{defn}}{=\!=\!=} e^{-\alpha/kT}\frac{Z\ddagger(B)}{Z\ddagger(0)} \tag{9}$$

and

$$\frac{\Sigma n_i'\epsilon_1' - \Sigma n_i\epsilon_i}{T} = \frac{\Sigma n_i'\alpha + \Sigma n_i'(\epsilon_i + B_i) - \Sigma n_i\epsilon_i}{T}$$

$$= \frac{n_0\alpha}{T} + \frac{\Sigma n_i'(\epsilon_i + B_i) - \Sigma n_i\epsilon_i}{T}. \tag{10}$$

Therefore from Eq. (8):

$$\Delta(\Delta S\ddagger) = -\frac{R\alpha}{kT} + R \ln \left(\frac{Z\ddagger(B)}{Z\ddagger(0)}\right) + \frac{n_0\alpha}{T} + \frac{\Sigma n_i'(\epsilon_1 + B_1) - \Sigma n_i\epsilon_i}{T}$$

$$\Delta(\Delta S\ddagger) = R \ln \frac{Z\ddagger(B)}{Z\ddagger(0)} + \frac{\Sigma n_i'(\epsilon_1 + B_i) - \Sigma n_i\epsilon_i}{T}. \tag{11}$$

Therefore n_i' is independent of α (using Eq. (9) and realizing $Z\ddagger(0) = Z\ddagger$), viz:

$$\frac{n_i'}{n_i} = \frac{e^{-\epsilon_i'/kT}/Z\ddagger'}{e^{-\epsilon_i/kT}/Z\ddagger'} = \frac{e^{-\alpha/kT}e^{-(\epsilon_i+B_i)/kT}Z\ddagger(0)}{e^{-\epsilon_i/kT}e^{-\alpha/kT}Z\ddagger(B)}$$

$$n_i' = n_i \frac{e^{-(\epsilon_i+B_i)/kT}Z\ddagger(0)}{e^{-\epsilon_i/kT}Z\ddagger(B)}.$$

All the terms in Eq. (11) are independent of the parameter α. The entropy of the transition is independent of any uniform shift in the energy levels and depends only on the shift between energy levels. This analysis assumed that the degeneracies, g_i, were constant—splitting degeneracies even without shift in the energy levels will be considered later.

B. The Effect of the Energy Level Separation ($I \rightarrow A$)

As we change the depth of the energy well for the transition state, the energy separation between individual energy states will increase. This was indicated by Hinshelwood (*10, 11*), and recently Cremer (*3*). Cremer noted that the vibrotational transition would be less accessible for a lower activation energy. Rotational transitions can also be limited. For example, molecular hydrogen adsorbed on Zn0 does not exhibit $J = 2$ transitions. This is explained by a high barrier to rotation for the adsorbed hydrogen (*12–15*).

The effect of changing the energy separation is found by taking the partial derivative of $\Delta(\Delta S\ddagger)$ with respect to B_i. Using Eq. (8) for $\Delta(\Delta S\ddagger)$, the partial derivative (at constant $B_{k\neq j}$, T, e_j, n_j) equals:

$$\frac{\partial\Delta(\Delta S\ddagger)}{\partial B_j} = \frac{R\partial \ln(Z\ddagger'/Z\ddagger)}{\partial B_j} + \frac{1}{T}\frac{\partial(\Sigma n_i'\epsilon_i')}{\partial B_j}. \tag{12}$$

From Eq. (9) with constant degeneracy ($g_i' = g_i$), since $\partial e^{-(\epsilon_i+B_i)kT}/\partial B_j < 0$ the first term in (12) is negative. Substituting for ϵ_i' in the second term:

$$\frac{\partial(\Sigma n_i'\epsilon_i')}{\partial B_j} = \frac{\partial(\Sigma n_i'(\epsilon_i + \alpha + B_i))}{\partial B_j}.$$

Since $\partial n_i'/\partial B_j < 0$ and $\partial n_i' B_i/\partial B_j < 0$ therefore:

$$\frac{\partial\Delta(\Delta S\ddagger)}{\partial B_j} < 0.$$

If the separation increases ($B_j > 0$) then the transition entropy $\Delta(\Delta S\ddagger)$ decreases.

C. The Effect of the Splitting of the Degeneracy ($A \rightarrow B$)

We saw above that the entropy depends on the separation of the energy levels. Let us consider only a split of the degeneracy of a single energy level (j) without an increase in the energy level separation. This jth level has degeneracy g_j and population n_j. If the energy separation is neglected, the new energy levels will have degeneracies $g_j \Rightarrow g_{1j}$ and g_{2j} where $g_{1j} + g_{2j} = g_j$, and population n_{1j}, n_{2j}. The relative population n_{1j}, n_{2j} will be proportioned to the new degeneracies (e.g., $n_{1j} = n_j g_{1j}/g_j$).

We can write the entropy difference from the thermodynamic probabilities W (with g_j) and W' (with g_{1j} and g_{2j}).

$$S - S' = k \ln W/W'. \qquad (13)$$

W can be expressed in terms of the degeneracy and population for identical particles.

$$W = \frac{\Pi_i g_i^{n_i}}{\Pi_i n_i!}. \qquad (14)$$

With all the states identical except j we can write the entropy difference as:

$$S - S' = k \ln \left[\frac{g_j^{n_j} n_{ij}! n_{2j}!}{n_j! g_{1j}^{n_{1j}} g_{2j}^{n_{2j}}}\right] \qquad (15)$$

Since $n_{1j} + n_{2j} = n_j$ we can rewrite this as:

$$S - S' = k \ln \left[\left(\frac{g_j}{g_{1j}}\right)^{n_{1j}} \left(\frac{g_j}{g_{2j}}\right)^{n_{2j}} \frac{n_{1j}! n_{2j}!}{(n_{1j} + n_{2j})!}\right] \qquad (16)$$

It is easily seen that $S - S'$ is a symmetric function with a maximum for an equal split in degeneracies. In this case ($g_{1j} = g_{2j} = g_j/2$); with no energy difference, the states will be equally populated ($n_{1j} = n_{2j} = n_j/2$), then

$$\left(\frac{g_j}{g_{1j}}\right)^{n_{1j}} \left(\frac{g_j}{g_{2j}}\right)^{n_{2j}} \frac{n_{1j}! n_{2j}!}{(n_{1j} + n_{2j})!} = \frac{2^{n_j}((n_j/2)!)^2}{n_j!} > 1 \qquad \text{for } n_j > 1.$$

Therefore

$$S - S' > 0.$$

The entropy decreases, $S > S'$ with a splitting degeneracy.

As the activation energy decreases, both the splitting of the energy levels and the energy separation can lead to an entropy decrease. King and Benson have shown the splitting of the energy levels for hydrogen as a function of the barriers to rotation (*16*). Increased coupling between the surface and adsorbed molecules will further split the energy levels of a surface species. The stronger the coupling of a surface intermediate (transition state) with the surface, the greater the split. In effect the lower the energy of the transition complex relative to the reacting species, the more the possibility for energy level separation and splitting. The entropy of the transition to that state will tend to decrease.

In the extreme, the overall degeneracy in individual levels will decrease. Certain energy states will become relatively inaccessible. Hindered rotation and vibrational coupling with the surface will decrease the internal degrees of freedom of a surface species. Lowering the relative energy (decreasing the activation energy) increases the surface interaction and therefore the vibrational and rotational coupling. As the number of accessible internal energy states decrease, the partition function and entropy will decrease. This limits the energy available for molecular rearrangement and reaction. In effect, the energy is being funneled through fewer accessible energy states. This energetic funneling is manifest in the entropy of transition.

CALCULATION OF THE COMPENSATION EFFECT: ortho–para HYDROGEN

The energy levels for molecular hydrogen on a surface have been calculated by King and Benson using a Hindered Rotor Model (*17*). This model was supported by experimental chromatographic separation factors. *Ortho–para* conversion can occur by a molecular mechanism (*16*). The conversion is induced by a paramagnetic surface site. Catalysts with different barriers to hindered rotation (V_0) will have different activation energies for the *ortho–para* conversion on the surface (disregarding sorption reaction control). We will consider five different catalysts with varying barriers to rotation (V_0—0; 0.5; 1, 1.5; 2 kcal/mole). We will calculate the entropy change of the *ortho* to *para* transition states and the activation energy difference for these five catalysts based on King and Benson's model.

Schematically the energy states we are considering are shown in Fig. 2. A barrier to rotation splits the *ortho* energy states into an upper, doubly degenerate, state and a lower, singly degenerate, energy state. To avoid assuming specific zero point energy we shall consider the change in the transition entropy $\Delta(\Delta S\ddagger)$ and the difference in the activation energy ΔEa for one catalyst compared to another. The change in the transition entropy is calculated at 77°K using Eq. (11). The activation energy is estimated from the energy level difference (E_R) for the reactants and products using the empirical Polanyi relationship ($Ea = \alpha E_R$) with $\alpha = 1$. The results are shown in Table 1. At this temperature (77°K) little compensation due to entropy differences is seen for a change in the barrier to rotation from 1.5 → 2 kcal/mole or from 1.0 → 2 kcal/mole. However, the net effect of going from 0.5 to 2 kcal/mole is reduced by one-third from the expected increase due to the lowered activation energy alone. These first three transitions correspond to $I \rightarrow A$ in Fig. 1. The $V_0 = 0 \rightarrow V_0 = 2$ kcal/mole also takes into account the splitting of degeneracies in the *ortho* state. Interestingly, little net effect would be seen by going from 0 → 0.5 kcal/mole where the decreasing activation energy (ΔEa = 114 cal/mole) is almost totally compensated for by the change in entropy ($\Delta(\Delta S\ddagger)$ = 4 cal/mole °K).

TABLE 1

Change in V_0 (kcal/mole)	$e^{\Delta Ea/RT}$	$e^{\Delta(\Delta S\ddagger/R)}$	Net effect
1.5 → 2	1.18	0.96	1.13
1.0 → 2	1.58	0.90	1.42
0.5 → 2	3.66	0.66	2.38
0 → 2	7.63	0.33	2.5

ISOKINETIC BEHAVIOR AND THE REQUIRED SHIFT IN THE ENERGY LEVELS

If we assume that compensation occurs by a shift in the energy levels, the existence of an isokinetic temperature implies a specific dependence of the shift on the activation energy. At the isokinetic temperature (T_{ik}) the ratio of rates is unity from Eq. (4) with the same state preceding the transition

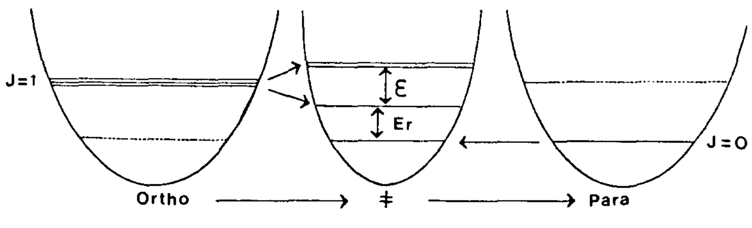

FIGURE 2

for any two cases x and y:

$$1 = \frac{Z_x\ddagger}{Z_y\ddagger}\, e^{-(\Delta E_x\ddagger - \Delta E_y\ddagger)/RT_{ik}}$$

and

$$\frac{Z_y\ddagger}{Z_x} = e^{-\Delta Ea/RT_{ik}} \tag{17}$$

where

$$\Delta E_a \underset{\text{defn}}{=\!=\!=} \Delta E_x\ddagger - \Delta E_y\ddagger = Ea)_x - Ea)_y.$$

The partition function consists of the product of a number of terms, one for each of the modes of energy distribution within the transition state. The primary modes of energy within an adsorbed species are electronic, vibration, and rotation. The partition function of the activated complex is the product of all the individual partition functions for each of the vibrational, electronic, and rotational modes of energetic freedom. Compensation can be "shared" among a combination of energy distributions. As an example, for M modes sharing the compensation equally, the compensation for each mode would be the Mth root of the shift for a single mode. Consider the extreme case where compensation is accounted for either by M vibrational or N rotational modes of energy sharing the compensation equally. A simple approach is used involving harmonic oscillator or rigid rotor approximations for the energy states of vibration or rotation, respectively. The purpose of this analysis is to show a possible dependence of energy levels on activation energy that will give rise to isokinetic behavior.

For compensation by n modes of rotational energy, the partition function for each of the energy modes is inversely proportional to the energy required for the $J = 0 \rightarrow J = 1$ transition (ϵr_0). All the other energy levels (Er_J, the energy of the Jth level) for the rigid rotor are functions of this lowest energy separation ($Er_J = [J(J + 1)]/2\ \epsilon r_0 + Er_0$). For two sets of n rotational modes sharing the compensation equally, from Eq. (17):

$$\frac{Z^{\ddagger}_{\text{rot}}\big|_y}{Z^{\ddagger}_{\text{rot}}\big|_x} = \frac{\epsilon r_0|_x}{\epsilon r_0|_y} = e^{-\Delta Ea/nRT_{ik}}. \tag{18}$$

The analysis gives a simple result, the energy spacing ($\epsilon r_0|_x \rightarrow \epsilon r_0|_y$) depends exponentially on the shift in the activation energy. Note that, as proved above, a decreasing activation energy ($\Delta Ea > 0$, $Ea|_x > Ea|_y$) requires an increasing energy level spacing.

For vibrational energy modes, the result is somewhat more complex. The partition function depends on the energy level spacing (ϵv_0 for the 0–1 transition) as: $Z_{\text{vibration}} = (1 - e^{-\epsilon v_0/kT})^{-1}$. For M vibrational modes sharing the compensation equally Eq. (17) becomes:

$$\frac{1 - e^{-\epsilon v_0/kT_{ik}|_x}}{1 - e^{-\epsilon v_0/kT_{ik}|_y}} = e^{-\Delta Ea/MRT_{ik}}.$$

This can be rearranged to give the relationship between $\epsilon v_0|_y$ and $\epsilon v_0|_x$, viz;

$$\epsilon v_0|_y = kT_{ik} \ln(1 - (1 - e^{-\epsilon v_0|_x/kT_{ik}})e^{\Delta Ea/MRT_{ik}})^{-1}. \tag{19}$$

CHANGE IN THE TRANSITION PROBABILITY

The above effects were evaluated assuming that all the energy states have an equal reaction rate constant (transition probabilities). Additional effects could arise from changes in transition probabilities.

In Eq. (5) we have expressed the possible variation in rate constants for differing energy levels. Intuitively, we might believe that energy states with higher vibrational (and rotational) energy may have a higher probability of transition. The lowering of the activation energy may not correspond to the transition through the more reactive energy states. With a concurrent increase in energy level separation (due to the narrowing of the potential well), the more reactive states will not have as much of a decrease in individual activation energy as the less reactive energy states.

For spectroscopic transitions, the Franck–Condon principle states that there will be no change in radius for a diatomic transition. The transition on the surface from reacting species to transition state will be facile if both states have similar geometry. As we decrease the activation energy the geometric overlap may change. The transition state may be "sterically narrower" and provide less of a chance for transition. Fewer states of the reacting species will spend less relative time in configurations resembling the transition state. Kazanski utilized this principle in his study of the potential curves of surface species (*18*). Infrared overtones coupled with vibrational and fluorescent spectra were used to determine surface energy states. A similar excitation (transition) may be necessary to cross to or from the transition state.

CONCLUSIONS

Two changes in the transition state for reaction were considered. As a consequence of lowering the activation energy, a splitting or increased separation of the energy levels give rise to a decreasing entropy of transition. Shifts in the relative transition probability for different energy states can also compensate for any decrease in activation energy. There will be no compensation if the transition state has the same shape and position along the reaction profile.

These effects are not independent but depend on the relative population of the energy levels. As temperature increases, the relative population shifts to higher energy states. If the higher energy states are less perturbed than the lower energy states (which are shifted to reflect the lowered activation energy), the compensation effect will become less pronounced at higher temperatures. Eventually the effect of the relative population of the higher energy levels will obscure the entropy difference that will be seen with a narrow distribution of energy states. Indeed, specific shifts in the energy levels that give rise to isokinetic behavior were derived.

The arguments presented here do not necessarily apply only to heterogeneous catalysis. Nor is a compensation only found for heterogeneous reactions (*19*). Explanations of compensation due to specific surface properties cannot explain the general phenomena.

Transition state theory was used to express the dependence of the entropy (and related partition functions) on a change in energy states. However, the general argument does not depend on transition state theory.

As we lower the barriers between reacting states, the energy saddle between these states can become narrower. The energy separation between levels can increase and the degeneracy of the levels can decrease. Higher energy states may be expected to have higher probability for reaction. The specific overlap of the energy states within the reaction profile may decrease. In effect this energetic pinch is reflected in the entropy of reaction. In catalysis we may have to pay for a lowering of the activation energy by an energetic funneling of the reaction. The entropy loss due to the funneling can compensate for the absolute energy gain.

ACKNOWLEDGMENTS

I would like to recognize the important contributions of Professor John Ragle and Nilesh Shah. Their discussions, comments, and checking of these theories were greatly appreciated.

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