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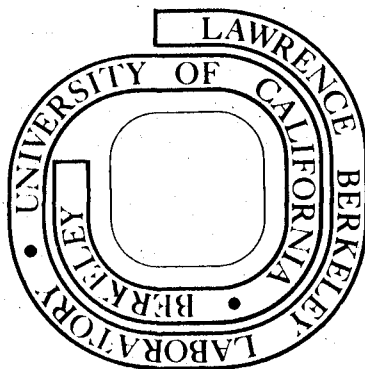
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PRE-EXPONENTIAL FACTORS IN SURFACE REACTIONS

by

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ABSTRACT

Pre-exponential factors for surface reactions have been estimated by use of transition state and hard sphere reaction models. We find that calculated values can be used to determine rate limiting steps in various surface reactions. In the case of H_2 - D_2 exchange, adsorption is the rate limiting step at high temperature while bond breakage becomes rate limiting at low temperature. Typical pseudo-first order pre-exponential factors for various rate limiting steps are: adsorption 10^2 - 10^4 sec^{-1} , diffusion 10^7 - 10^{11} sec^{-1} , surface reaction 10^{10} - 10^{13} sec^{-1} , desorption 10^{13} - 10^{16} sec^{-1} . The calculated values are compared to numerous examples of surface reactions compiled from the literature. In addition, conditions needed to apply these models to catalyzed reactions are discussed.

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Although surface reactions are important in many areas of science and technology, ^{detailed} kinetic information on these reactions has only recently become available. Studies of surface reactions using molecular beams and well-characterized surfaces (by atomic structure and composition) have yielded the rate constants, activation energies and pre-exponential factors for reactions where the surface served either as a catalyst or as one of the reactants.¹ These kinetic parameters are listed in Table I for the surface reactions that were investigated. On account of the experimental conditions that have fixed the surface concentrations of all but one of the reactants in many instances, the rate constant and the pre-exponential rate factors appear pseudo-unimolecular and are also tabulated in this manner. That is, the pre-exponential factor includes reactants with fixed concentrations throughout the reaction.

The pre-exponential factors that were determined by experiments are in the range of 10^2 - 10^{16} sec^{-1} , that is, they vary by fourteen orders of magnitude. Most of these values are small compared to those reported for gas phase unimolecular (10^{13} sec^{-1}) or bimolecular reactions. The typical pre-exponential for a bimolecular reaction is 10^{-11} $\text{molecule/cm}^3 \text{ sec}$ that becomes 10^3 sec^{-1} under pseudo-first order conditions with a reactant pressure of 10^{-7} torr. In fact, frequently when low pre-exponential factors were obtained in gas phase reaction studies the presence of surface reactions were suspected.²

Surface reactions can be viewed as composed of a series of consecutive steps starting with a) adsorption of an atom or molecule from the gas or liquid phases. The adsorption may be followed by b) diffusion of the reacting species on the surface among the various sites where bond

breaking may occur. Then the c) reaction takes place that includes bond scission and molecular rearrangement. These chemical processes are not readily separable by experiments at present. The product molecule then d) desorbs into the gas or liquid phase.

In this paper we compute the pre-exponential factor for each of these elementary surface reaction steps. We shall make order of magnitude estimates of the pre-exponential factor. Calculated pre-exponential factors vary from 10^2 to 10^{13} sec^{-1} depending upon whether the rate determining step is adsorption, surface diffusion, surface reaction or desorption. Thus, it should be possible to use these estimates to rule out certain reaction mechanisms and perhaps identify others. In addition, these models aid our understanding of the reaction mechanism and its variation with experimental conditions (reactant concentrations and surface site concentrations).

The pre-exponential factor (A_n) is defined for a reaction involving n specie as

$$k_n = A_n \exp(-E/RT) \quad (1)$$

when k_n , E , R and T have their usual meaning. We shall evaluate A_n employing transition state theories of Eyring³ in a fashion like that of Laidler.⁴

Experimental values of A_n can be obtained for surface reactions by knowledge of the rate of reaction per unit area or surface site, its temperature coefficient and the concentrations of surface species. Since the latter quantity is often not directly available, order of magnitude estimates of its value can be made from partition function ratios as illustrated in the appendix for conditions of low surface coverage (less

than 0.1 monolayer).

The rate of surface reactions involving two or more species are most easily analyzed for pseudo-first order conditions where the surface concentrations of all except one of the species are in excess and remain constant. This is the condition in most molecular beam-surface scattering experiments where some of the reactants are in the ambient background with sufficiently high pressures to assure excess concentrations on the surface. The flux, or surface concentration of the beam species is then varied.

Adsorption

Let us consider the change in surface concentration (n_s) of molecules with a gas phase concentration (n). We take a surface of area (a), where θ is the fraction of surface covered by molecules. The average gas phase velocity of the molecules (\bar{c}) enables us to calculate a volume swept out per unit time of the gas phase molecules that will strike the surface $1/4 \bar{c} \cdot a$. The number of collisions per unit time with uncovered surface is given by the pre-exponential part of equation (2).

$$a \frac{dn_s}{dt} = 1/4 \bar{c} a (1-\theta) n \exp(-E/RT) \quad (2)$$

A Boltzmann factor must be multiplied by the right side of the equation (1) to account for the fraction of molecules having activated adsorption with activation energy E . This situation can apply when adsorption requires an activation energy as in H_2 - D_2 exchange reaction on Cu.⁵ This is determined by the rate dependence of surface reaction on beam temperature. The pre-exponential factor giving the rate of formation of adsorbed surface molecule per unit area, when these molecules are colliding with uncovered surface and are removed rapidly by reaction is:

$$A_1 = 1/4 \bar{c} (1-\theta) \quad (3)$$

Note that the units of Eq. (3) are length/time.

Let us consider adsorption as the rate limiting step of a reaction involving gas phase and surface reactant species. We will apply Eq. (3) to the case where product molecules are detected in the gas phase of volume V . First, we replace $1-\theta$ by θ in Eq. (3) since reaction is considered to take place only when the gas phase species collides directly with a surface species as in the Eley-Rideal type reaction. Thus, $A_1 = 1/4 \bar{c} \theta$ for this case. Under steady state conditions for the product species formed on the surface

$$V \frac{d(\text{product})}{dt} = k^{\text{pseudo}} n \cdot \underline{a} \quad (4)$$

where the pre-exponential part of k^{pseudo} equals $1/4 \bar{c} \theta$. Thus, the effective pseudo-first order pre-exponential for product formation becomes

$$A_1 = 1/4 \bar{c} \theta \underline{a}/V \quad (5)$$

which has the units of reciprocal time. This expression applies to the rate of product formation as detected after desorption into the gas phase of volume V for an Eley-Rideal reaction mechanism.

Desorption

Desorption of an adsorbed molecule can be considered a unimolecular process where the surface bond has vibrational frequency ν_0 , which typically

$$k = \nu_0 \exp(-E/RT) \quad (6)$$

has the value 10^{13} sec^{-1} . For this step $A_1 = \nu_0$. If a molecule is dissociated on the surface, a bimolecular association reaction must take place prior to molecular desorption. This step may be rate limiting and will be treated below in the section on surface reaction kinetics.

Diffusion

Surface diffusion may be treated for a surface species of concentration n_s by a random walk type of analysis.⁶ The frequency (f) of jumps of distance d is given by

$$f = \nu e^{-E_D/RT} \quad (7)$$

where ν is the surface vibration frequency and E_D , the diffusion energy, is averaged over the various surface regions.

The random walk expression is

$$t = \frac{3 \langle x^2 \rangle}{fd^2} \quad (8)$$

where t is the time required to diffuse a distance $\langle x^2 \rangle^{1/2}$. We calculate a surface diffusion velocity ($v = \langle x^2 \rangle^{1/2}/t = fd^2/3\langle x^2 \rangle^{1/2}$). Thus, the surface area swept out by diffusing species having a molecular diameter (b) is $v \cdot b$. The collision number of diffusing species with active sites of density N_s is $v \cdot b \cdot N_s$. We evaluate the diffusion distance as the average separation between active sites. Thus this approximation gives $\langle x^2 \rangle^{1/2} = N_s^{-1/2}$. Combining the collision number with a Boltzmann factor to account for collisions with sufficient energy for reaction (E), we obtain

$$\begin{aligned} \frac{-dn_s}{dt} &= v \cdot b \cdot N_s \cdot n_s \exp(-E/RT) \\ k &= \frac{vd^2b}{3} N_s^{3/2} \exp(-(E+E_D)/RT) \end{aligned} \quad (9)$$

The pre-exponential factor is

$$A_1 = \frac{vd^2b}{3} N_s^{3/2} \quad (10)$$

As in gas phase collision theory, a steric factor is sometimes multiplied by the right side of equation (10) to account for the required orientation of the reactants.

Surface Reactions

The transition state theory may be used to express the pre-exponential factor for Nth order reaction of i specie as

$$A_n = \frac{KT}{h} \times \frac{Q^\ddagger}{\prod_{i=1}^N Q_i} \quad (11)$$

where K = Boltzmann Constant

T = temperature

h = Planck's constant

Q_i = partition function for reactant species i

Q^\ddagger = partition function for transition state

The total partition function for a mobile surface polyatomic species containing n atoms is

$$Q_i = q_T^2 q_R q_V^{3n-3} \quad (12)$$

where q_T , q_R and q_V are the translational, rotational and vibrational partition functions, respectively. The total partition function for the transition state species is calculated by Eq. (12), except one vibrational component along the bond being broken is removed. The significant component of Q_i is the translational partition function q_T

$$q_T = \frac{\sqrt{2\pi MKT}}{h} \quad (13)$$

which typically has the value 10^8 cm^{-1} . Vibrational partition functions have typical values near unity and free rotational partition functions have values near 10. Vibrational partition function components will be neglected for surface species since their magnitude is near unity.

We have tabulated the expressions for pre-exponential factors for the

various rate limiting steps in Table II. Note that pseudo-first order pre-exponential values are listed which are most useful for comparison to molecular beam experimental results. Expressions for reactions with various rate limiting steps are presented in which only translational partition functions are considered. Note that for these reactions the Nth order pre-exponential decreases by a factor of $10^{-16} \text{ cm}^{-2} \text{ molecule}^{-1}$ for each increase in reaction order by one. We assume that n_s , the surface concentration of the reactant species in excess, is constant as a function of temperature in making the estimations of values in Table II. This assumption, of course, depends upon the experimental conditions and system of interest and therefore these relative values are intended only for comparison with each other.

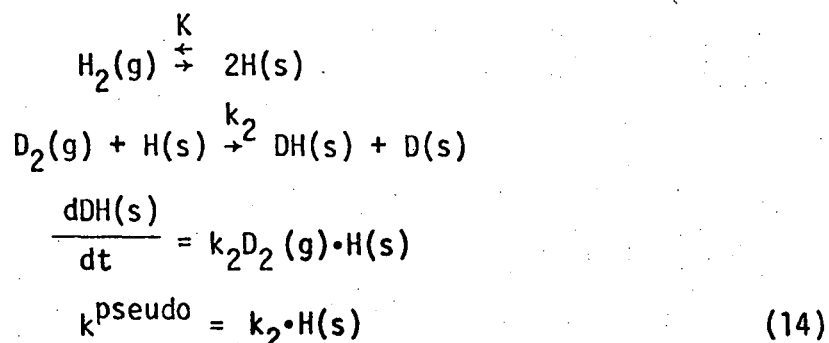
Application of Eq. (13) assumes free particle motion for the reactant molecules. In those cases where this condition is not met, the calculated pre-exponential factor for the rate of reaction will be too high. Surface diffusion will be the more likely slow step in that case.

III Comparison of Computed and Experimental Values of the Pre-Exponential Factor, A_n .

The surface reaction $\text{D}_2 + \text{H} \rightarrow \text{DH} + \text{D}$ has been studied on stepped Pt surfaces using a modulated molecular beam technique.⁷ In the reaction a beam of D_2 molecules is directed at the surface which contains excess H atoms, formed from H_2 background gas, of constant concentration. The rate of HD formation on the surface is monitored from its concentration in the gas phase. Pseudo-first order pre-exponential factors of $2 \pm 1 \times 10^5 \text{ sec}^{-1}$ and $1 \times 10^2 \text{ sec}^{-1}$ were measured below and above 600K respectively. These values may be compared to gas phase reaction data. Converting the experimental gas

phase value⁸ $k_2 = 3 \times 10^{-11} \exp(-6.5 \text{ kcal/RT}) \text{ cm}^3/\text{molecule sec}$ to a pseudo first order pre-exponential factor ($P_{D_2} = 6 \times 10^{-7} \text{ torr}$, 600K) we find $A_1 = 7 \text{ sec}^{-1}$.

The high temperature surface reaction may be classified as an Eley-Rideal type mechanism in which a gas phase molecule of D_2 reacts with an H species adsorbed to the surface.



Taking the pre-exponential part of Eq. (14) as $A_2 H(s)$ and employing Eq. (5), we arrive at the effective pseudo first-order pre-exponential

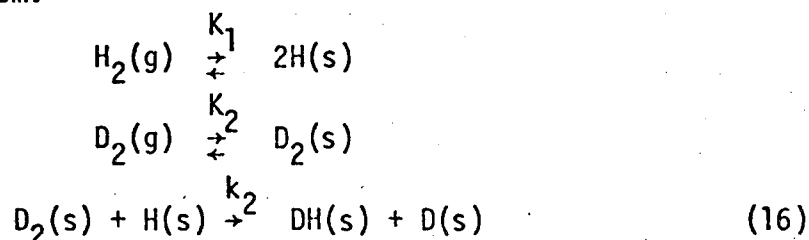
$$A_1 = A_2 H(s) \frac{a}{V} = 1/4 \bar{c} \theta a/V \quad (15).$$

In the molecular beam experiments, we estimate $a/V = 1 \text{ cm}^{-1}$ and $\theta = .01$ to $.1$ under the experimental conditions. These parameters give $A_1 = 2 \times 10^4 \theta \text{ sec}^{-1}$. The volume V calculated for this beam type experiment is that between the catalyst and mass spectrometer. In static type experiments where product molecules not in a beam are detected, the volume V is taken as the volume of the container. This would give a value of a/V much less than 1 cm^{-1} and could significantly decrease the pre-exponential factor.

Alternatively, the transition state model could be used through Eq. (11) to evaluate the pre-exponential. Taking values of translational and rotational partition functions as $q_T = 2.8 \times 10^8 \text{ cm}^{-1}$ and $q_R = 6.8$ for D_2 , we calculate $A_1 = 7 \times 10^3 \theta \text{ sec}^{-1}$ providing qualitative agreement with the results of Eq. (15) as shown in Table III.

A surface reaction controlled rate leads to calculated pre-exponential factors agreeing with experimental values for the low temperature branch.

Consider the mechanism:



A rate expression for this mechanism may be written as

$$\begin{aligned} \frac{d\text{HD}(\text{s})}{dt} &= k_2 \text{H}(\text{s}) \text{D}_2(\text{s}) = k_2 \sqrt{K_1 \text{H}_2(\text{g})} \text{D}_2(\text{s}) \\ k^{\text{pseudo}} &= k_2 \sqrt{K_1 \text{H}_2(\text{g})} \end{aligned} \quad (17)$$

This expression gives a pseudo first order rate constant varying by the square root of the H_2 pressure as observed experimentally. We calculate k_2 using Eq. (11) and express K_1 in terms of partition functions of the specie involved. Considering all translational and rotational components we obtain the expression

$$k^{\text{pseudo}} = \frac{KT}{h} \frac{q_{\text{R,DH}(\text{s})}}{q_{\text{R,D}_2(\text{s})}} \frac{q_{\text{T,D}_2\text{H}(\text{s})}^2}{q_{\text{T,D}_2(\text{s})}^2} \frac{\sqrt{\text{H}_2(\text{g})}}{q_{\text{T,H}_2(\text{g})}^{3/2} q_{\text{R,H}_2(\text{g})}} \exp(-(E+\Delta H/2)/RT) \quad (18)$$

ΔH = heat of dissociative chemisorption of H_2 . The pre-exponential part of this expression is evaluated in Table III ($A = 5 \times 10^5 \text{sec}^{-1}$) and agrees well with experiment. In this calculation we have used $T = 600\text{K}$ and $P_{\text{H}_2} = 6 \times 10^{-7}$ torr. We note that other possible rate limiting steps such as desorption, adsorption or diffusion to step sites give the following pre-exponential factors: adsorption = 10^4sec^{-1} , desorption = 10^{13}sec^{-1} and diffusion = 10^{11}sec^{-1} for $N_s = 10^{14} \text{cm}^{-2}$. Only the adsorption step gives values close to experiment.

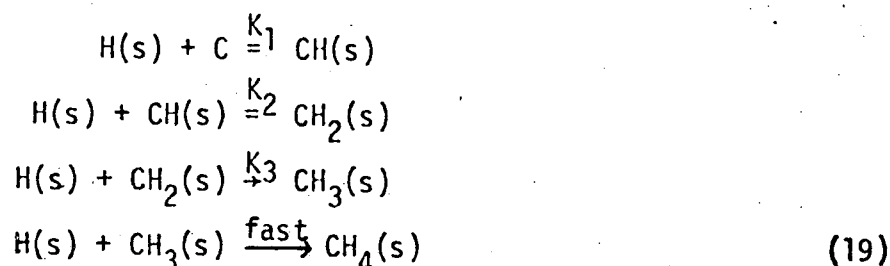
The catalytic hydrogenolysis of cyclohexane giving n-hexane and other

products on stepped and kinked Pt surfaces has been recently studied.⁹ Besides n-hexane, formation of other saturated hydrocarbons takes place under reaction conditions as well as the simultaneous dehydrogenation to form benzene. A pre-exponential factor of $1.3 \times 10^{10} \text{ sec}^{-1}$ may be determined from the experimental data at 300K as shown in the appendix. Our calculations suggest diffusion of cyclohexane to the active sites is the rate limiting step of this reaction. This is based upon agreement of the pre-exponential value calculated using equation (18) with the experimental value. An active site density for n-hexane formation of $2.7 \times 10^{13} \text{ cm}^{-2}$ gives a calculated value agreeing with experiment. The experimental active site density was $4 \times 10^{14} \text{ cm}^{-2}$. In view of the fact that n-hexane is a minority product, this agreement is considered satisfactory.

The ring opening of cyclopropane to propane at high pressure has been studied on Pt stepped surfaces.¹⁰ The experimental pre-exponential factor of 10^{12} sec^{-1} is derived in the appendix. This value would be consistent with desorption of product, diffusion of reactant or bond breakage as the rate determining step. We would expect a pre-exponential factor of $10^{12}-10^{13} \text{ sec}^{-1}$ for desorption of product. The calculated pre-exponential factor for a diffusion-controlled reaction is $2.6 \times 10^{11} \text{ sec}^{-1}$, where we have used the experimental active site density of $2 \times 10^{14} \text{ cm}^{-2}$ in Eq. (10). Alternatively, the unimolecular bond breakage would have a pre-exponential of $10^{12}-10^{13} \text{ sec}^{-1}$. We cannot choose the rate limiting step in this circumstance. Experiments varying the active site density would be helpful to test the diffusion limited path.

Rate constants for the surface reaction of C and H_2 leading to CH_4 and C_2H_2 formation have been recently measured.¹¹ A model for methane

formation is:



The rate expression for this mechanism is

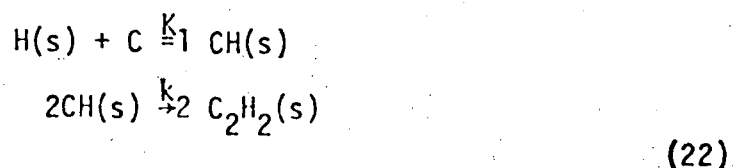
$$\frac{d(\text{CH}_4\text{(s)})}{dt} = K_1 K_2 K_3 (\text{H(s)})^3
 \tag{20}$$

Employing Eq. (11) we write the pre-exponential factor

$$A_3 = \frac{KT}{h} \frac{q_T^2, \text{CH}_3\text{(s)}}{q_T^6, \text{H(s)}}
 \tag{21}$$

The pre-exponential factor calculated from this expression (4.4×10^{-20} cm⁴/atom sec) compares well with experiment as shown in Table III.

The reaction leading to acetylene formation is modelled as:



The rate expression becomes

$$\begin{aligned}
 & \frac{d(\text{C}_2\text{H}_2\text{(s)})}{dt} = K_1^2 K_2 (\text{H(s)})^2 \\
 & A_2 = \frac{KT}{h} \frac{q_T^2, \text{C}_2\text{H}_2\text{(s)}}{q_T^4, \text{H(s)}}
 \end{aligned}
 \tag{23}$$

for which the pre-exponential term of 1.4×10^{-2} cm²/atom sec is also given in Table III is determined. In each case there is rough agreement between experiment and calculation indicating that a surface reaction step is most likely controlling the reaction. Other possible mechanisms could also be considered in analyzing these reactions.

Many gas-solid reactions¹²⁻¹⁴ have been classified as diffusion-

controlled on the basis of their pre-exponential factors. Those cases shown in Table III where values of the pre-exponential factor of 10^7 - 10^8 sec^{-1} are measured fall into this category. The authors of this work assume diffusion of products to sites for desorption is rate limiting and postulate desorption site densities of 10^9 - $10^{11}/\text{cm}^2$. The expression employed by these workers to evaluate A_1 differs somewhat from Eq. (10). Using Eq. (10), it is clear that increasing the active site density, as with kinked or stepped surfaces, would give larger pre-exponential factors. The other variable of importance in determining the pre-exponential factor is ν . Vibration frequencies would be expected to vary with the reciprocal square root of the specie's mass.

These are examples of bimolecular and higher order surface reactions which appear to be limited by an elementary surface reaction step. In the case of H_2 desorption from nickel¹⁴, shown in Table III, the calculated A_1 factors would be in closer agreement with experiment if the surface translational partition function of H were decreased. This would be the case for a severely hindered type of motion of H on the surface. Other reactions studied include decomposition of acetic acid¹⁵ which has pre-exponential factors suggesting a unimolecular reaction at low temperature and an Eley-Rideal mechanism at elevated temperature. The oxidation of germanium yielding the oxide has a large pre-exponential factor.¹⁷ Desorption of the oxide is considered the rate limiting step, but this step would yield normally a value of $A = 10^{13} \text{sec}^{-1}$ according to Eq. (11). This reaction may involve a transition state very loosely bound with much more motion than the reactant oxide molecule. This would account for a partition function ratio greater than 1 and applying Eq. (11) to this

situation could yield values of A_1 in excess of 10^{13} sec^{-1} . These effects have been observed⁸ in gas phase reactions such as $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ which has an experimental pre-exponential factor of $2 \times 10^{18} \text{ sec}^{-1}$.

We have not included steric effects in this discussion because of the difficulty in estimating this term. Under normal conditions steric effects would reduce the calculated pre-exponential factor. For molecules possessing essentially free rotation and translation on the surface, the effect should be minimal and included in Eq. (10). On the other hand, when large bulky molecules diffuse in the rate limiting step to a special site, the effect could be important. Considerable time might be required for achieving the proper orientations for reaction on the surface. Possibly one of the causes of the wide product distribution noted earlier for the hydrogenolysis reaction of cyclohexane is a steric effect. The relative orientation of the cyclohexane molecule with respect to the active site geometry during reaction would determine the distribution of products formed in this case. Alternative explanations would suggest the product distribution results from reaction at different types of active sites. It would be interesting to study this reaction on active sites with different geometries in an attempt to observe such an effect.

Summary

Pre-exponential factors have been calculated for a variety of surface reactions that are controlled by an elementary step including adsorption, surface diffusion, surface reactions or desorption. The calculated values are comparable to experimental results whenever A_n was available or calculable. Pre-exponential factors of surface reactions are clearly often different than for gas phase reactions and may be

used to indicate the slowest step in a surface reaction. Pseudo-first order pre-exponential factors of 10^2 - 10^5 sec^{-1} can be associated with surface reaction control or slow adsorption. Pre-exponential factors for diffusion-controlled reactions vary from 10^7 - 10^{12} sec^{-1} depending upon the density of active sites. Desorption or unimolecular reaction controlled surface reactions have factors typically greater than 10^{12} sec^{-1} . In the gas phase, the pre-exponential factors are typically 10^{13} sec^{-1} for first order reactions, 10^{-12} - $10^{-10} \text{ cm}^3/\text{molecule sec}$ for second order reactions and 10^{-37} - $10^{-31} \text{ cm}^6/\text{molecule}^2 \text{ sec}$ for third order reactions.¹⁸ The values measured for surface reaction can deviate significantly from gas phase values depending upon the rate limiting step, the detailed mechanism and the reactant concentrations. It appears that the statistical models useful for gas phase kinetics and employed here can reproduce most experimental pre-exponential factors. There have been reactions reported¹⁹ where other effects such as changes in symmetry leading to the activated state are necessary to explain pre-exponential factors. These reactions appear to be in the minority of those examined to date.

The pre-exponential factors of diffusion controlled reactions may be altered in a non-linear fashion by changing the active site density as suggested by Eq. (10). Such behavior has been observed as a function of step density for cyclohexene dehydrogenation.⁷ In the case of the $\text{D}_2 + \text{H} \rightarrow \text{DH} + \text{D}$ reaction on stepped Pt surfaces there does not seem to be the opportunity for non-linear changes in pre-exponential factors by changes in the active site concentration. A more profitable strategy towards increasing the rate would be to look for other types of active sites where the microscopic activation energy (E) is smaller.

Appendix I

Calculation of the pre-exponential factors for hydrogenolysis of cyclohexane⁹ and cyclopropane¹⁰ requires the experimental rate of product formation, reactant concentration and activation energy. These experimental data are as follows:

<u>Reaction</u>	<u>Reactant Concentration</u>	<u>Rate</u>	<u>Eact.</u>
CYCLOHEXANE HYDROGENOLYSIS	4×10^{10} molecules cm^{-3}	7.5×10^9 molecules/sec cm^2	3 kcal
CYCLOPROPANE HYDROGENOLYSIS	9.2×10^{19} molecules cm^{-3}	2×10^{16} molecules/sec cm^2	12.2 kcal

In each reaction we consider that the reactant (R) must be adsorbed prior to the reactive step, the fraction of surface coverage by reactant is less than unity and that excess hydrogen atoms are available for the reaction.



For this mechanism, we have

$$\text{rate} = \frac{-d(R(s))}{dt} = k(R(s)) = kK_s(R(g)) \quad (A2)$$

Since the surface concentration of reactant, $R(s)$, is unknown we must express the overall rate constant k^{overall} in terms of the gas phase concentration, $R(g)$. This gives equation A3 where E is the overall activation energy

$$k^{\text{overall}} = kK_s = \frac{\text{rate}}{R(g)} = A \cdot B \exp(-E/RT) \quad (A3)$$

We wish to separate the pre-exponential part of k (A) from the pre-exponential part of K_s (B) in Eq. (A3). To do this we express B in terms of the partition functions appropriate for this equilibrium. This gives equation A4.

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$$A = \frac{\text{rate}}{(R(g))} \times \frac{q_T^3}{q_T^2} \exp(-E/RT) \quad (A4)$$

The gas phase concentration of reactant is known and Eq. (A4) may be used to calculate the pre-exponential factor for each of the reactions. This procedure gives the experimental pre-exponential factors listed in Table III.

Appendix II

Values of rotational and translational partition functions employed
in this work were:

<u>Species</u>	<u>Translation (cm^{-1})</u>	<u>Rotation</u>
D ₂	2.8×10^8	6.8
H ₂	1.4×10^8	3.4
cyclohexane	9.1×10^8	-
cyclopropane	4.5×10^8	-
CH ₄	1.3×10^8	-
CH ₂	1.2×10^8	-

Table I

Pre-exponential Factors, Activation Energies and Reaction Probabilities
for Several Surface Reactions Studied by Molecular Beam Scattering

Reaction	A*	E _a (kcal/mole)	Reaction Probability	Reference
$\text{H} + \text{D}_2 \xrightarrow{\text{Pt}} \text{HD} (<600 \text{ K})$	$2 \times 10^5 \text{ (sec}^{-1}\text{)}$	4.5	$\sim 10^{-1}$	7
$\text{H} + \text{D}_2 \xrightarrow{\text{Pt}} \text{HD} (>600 \text{ K})$	$1 \times 10^2 \text{ (sec}^{-1}\text{)}$	0.6	$\sim 10^{-1}$	7
$\text{D} + \text{O}_2 \xrightarrow{\text{Pt}} \text{D}_2\text{O} (700 \text{ K})$	-	12	-	20
$\text{CO} + \text{O} \xrightarrow{\text{Pt}} \text{CO}_2 (700 \text{ K})$	-	20	$\sim 10^{-3}$	21
$\text{C}_2\text{H}_4 + \text{O}_2 \xrightarrow{\text{Ag}} \text{CO}_2 (800 \text{ K})$	-	8	$< 10^{-2}$	22
$2\text{H} \xrightarrow{\text{graphite}} \text{H}_2 (800-1000 \text{ K})$	$1.06 \times 10^{-2} \text{ cm}^2/\text{atom sec}$	15.9	$10^{-3}-10^{-2}$	11
$\text{H}_2 \xrightarrow{\text{Ta}} 2\text{H} (1100-2600 \text{ K})$	-	75	4×10^{-1}	23
$\text{HCOOH} \xrightarrow[\text{decomp}]{\text{Ni}} \text{CO}_2 (<455 \text{ K})$	$10^{12} \text{ (sec}^{-1}\text{)}$	20.7	-	12
$\text{HCOOH} \xrightarrow[\text{decomp}]{\text{Ni}} \text{CO}_2 (>455 \text{ K})$	$5.8 \times 10^3 \text{ (sec}^{-1}\text{)}$	2.5	~ 0.9	12
$\text{C} + \text{O}_2 \longrightarrow \text{CO} (1000-2000 \text{ K})$	$2.5 \times 10^7 \text{ (sec}^{-1}\text{)}$	30	$10^{-3}-10^{-2}$	14
$\text{C} + \text{O}_2 \longrightarrow \text{CO} (1000-2000 \text{ K})$	$3 \times 10^{12} \text{ (sec}^{-1}\text{)}$	50	$10^{-3}-10^{-2}$	14
$\text{C} + 4\text{H} \longrightarrow \text{CH}_4 (500-800 \text{ K})$	$1.27 \times 10^{-18} \text{ cm}^4/\text{atom sec}$	3.3	$10^{-3}-10^{-2}$	11
$2\text{C} + 2\text{H} \longrightarrow \text{C}_2\text{H}_2 (>1000 \text{ K})$	$1.59 \text{ cm}^2/\text{atom sec}$	32.5	$10^{-3}-10^{-2}$	11
$\text{Ge} + \text{O}_2 \longrightarrow \text{GeO} (750-1100 \text{ K})$	$10^{16} \text{ (sec}^{-1}\text{)}$	55	2×10^{-2}	24

Table I (continued)

Reaction	A*	E _a (kcal/mole)	Reaction Probability	Reference
Ge+O → GeO (750-1100 K)	10 ¹⁶ (sec ⁻¹)	55	3x10 ⁻¹	25
Ge+O ₃ → GeO (750-1100 K)	10 ¹⁶ (sec ⁻¹)	55	5x10 ⁻¹	17
Ge+Cl ₂ → GeCl ₂ (750-1100 K)	10 ⁷ (sec ⁻¹)	25	3x10 ⁻¹	12
Ge+Br ₂ → GeBr ₂ (750-1100 K) ↘ GeBr ₄	10 ⁷ (sec ⁻¹)	20	3x10 ⁻¹	26
Si+Cl ₂ → SiCl ₂ (1100-1500 K)	10 ⁸ (sec ⁻¹)	40	3x10 ⁻¹	12
Ni+Cl ₂ → NiCl (900-1400 K)	10 ⁷ (sec ⁻¹)	30	8x10 ⁻¹	13

* For bimolecular reactions, the pre-exponential factor also includes the surface concentration of one of the reactants that is held constant during the experiments.

Table II

Values of Pre-exponential Factors

Rate Limiting Step	Expression for A_n	Pseudo-First-Order A_n (sec^{-1})	Typical Value (sec^{-1})	
Adsorption	$1/4\bar{c}\theta_a/V$	$1/4\bar{c}\theta_a/V$	10^2-10^4	
Desorption	v_0	v_0	10^{13}	
Surface Diffusion	$\frac{vd^2bN_s^{1/2}}{3}$	$\frac{vd^2bN_s^{3/2}}{3}$	10^7-10^{12+}	
Surface Reaction Control	Order			
	$N = 1$	KT/h	KT/h	10^{13*}
	$N = 2$	KT/hq_T^2	$\frac{KT}{hq_T^2}n_s$	10^9*
	$N = 3$	KT/hq_T^4	$\frac{KT}{hq_T^4}n_s^2$	10^5*
	$N = 4$	KT/hq_T^6	$\frac{KT}{hq_T^6}n_s^3$	10^1*

* Values chosen are $N_s = 10^{12}$ atoms/cm², $KT/h = 10^{13}$ sec⁻¹, $v = 10^{13}$ sec⁻¹, $d = 3 \times 10^{-8}$ cm, $b = 5 \times 10^{-8}$ cm, $c = 4 \times 10^4$ cm/sec.

+ N_s varies from 10^{11} to 10^{14} sites/cm².

Table III

Experimental and Calculated Pre-exponential Values

- Catalytic Reactions -					
Reaction	Reference	Experimental Pseudo-First Order A (sec ⁻¹)	Calculated Pseudo-First Order A (sec ⁻¹)	Expression for A	Suggested Mechanism
D ₂ +H→DH+D	7	2x10 ⁵ below 600 K 1x10 ² above 600 K	5x10 ⁵ 2x10 ⁴⁰	$\frac{KT}{h} \frac{q_{R,DH(s)} q_{T,D_2H(s)}^{1/2} q_{H_2(g)}^{1/2}}{q_{R,D_2(s)} q_{T,D_2(s)}^{3/2} q_{H_2(g)} q_{R,H_2(g)}}$	Reaction limited
cyclohexane→ n-hexane	9	1.3x10 ¹⁰	5x10 ¹⁰	$(\pi/4) a_s/V$ $v_o d^2 b N_s^{3/2}/3$	Adsorption limited Diffusion limited
cyclopropane→ propene	10	1x10 ¹²	3x10 ¹¹	$v_o d^2 b N_s^{3/2}/3$	Diffusion limited
HCOOH→CO ₂	15	1x10 ¹² <455 K 5.8x10 ³ >455 K	10 ¹² -10 ¹³ 10 ⁴	$\frac{KT}{h} \frac{1}{q_T}$ $(\pi/4) a_s/V$	Reaction limited Adsorption limited
2H \xrightarrow{Ni} H ₂	16	1cm ² /atom sec [†]	.001cm ² /atom sec [†]	$\frac{KT}{h} \frac{1}{q_T^2}$	Reaction limited
2H $\xrightarrow{\text{graphite}}$ H ₂	11	1.06x10 ⁻² cm ² /atom sec [†]	.001cm ² /atom sec [†]	$\frac{KT}{h} \frac{1}{q_T^2}$	Reaction limited
- Gas-Solid Reactions -					
C+4H→CH ₄	11	1.3x10 ⁻¹⁸ cm ⁴ /atom sec [†]	4.4x10 ⁻²⁰ cm ⁴ /atom sec [†]	$\frac{KT}{h} \frac{1}{q_T^4}$	Reaction limited
2C+2H→C ₂ H ₂	11	1.59cm ² /atom sec [†]	1.7x10 ⁻² cm ² /atom sec [†]	$\frac{KT}{h} \frac{1}{q_T^2}$	Reaction limited
Ge+Cl ₂ →GeCl ₂	12	10 ⁷	10 ⁷ for N _s = 1x10 ¹¹	$v_o d^2 b N_s^{3/2}/3$	Diffusion limited
Si+Cl ₂ →SiCl ₂	12	10 ⁸	10 ⁸ for N _s = 5x10 ¹¹	$v_o d^2 b N_s^{3/2}/3$	Diffusion limited
Ni+Cl ₂ →NiCl ₂	13	10 ⁷	10 ⁷ for N _s = 1x10 ¹¹	$v_o d^2 b N_s^{3/2}/3$	Diffusion limited
C+O ₂ →CO	14	2.5x10 ⁷ 3x10 ¹²	10 ⁷ for N _s = 1x10 ¹¹ 10 ¹² -10 ¹³	$v_o d^2 b N_s^{3/2}/3$ v_o	Diffusion limited Desorption limited*
Ge+O ₃ →GeO	17	1x10 ¹⁶	10 ¹³ q [†] /q*	$\frac{KT}{h} \frac{q^{\dagger}}{q}$	Desorption limited

† Reported as an Nth order rate constant.

* See text for explanation of q[†]/q.

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