JOURNAL OF CATALYSIS **45**, 94–105 (1976)

Preexponential Factors in Surface Reactions

R. C. BAETZOLD[1] AND G. A. SOMORJAI

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

Received April 8, 1976

Preexponential 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 there are two reaction branches, and adsorption and/or surface reactions are the rate limiting steps. Typical pseudo first-order preexponential 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^{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.

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 preexponential 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 1 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 preexponential rate factors appear pseudo-unimolecular and are also tabulated in this manner. That is, the preexponential factor includes reactants with fixed concentrations throughout the reaction.

The preexponential factors that were determined by experiments are in the range of 10^2–10^{16} sec^{-1}; that is, they vary by 14 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 preexponential for a bimolecular reaction is 10^{-11} cm^3/molecule sec that becomes 10^3 sec^{-1} under pseudo first-order conditions with a reactant pressure of 10^{-4} Torr. In fact, frequently when low preexponential 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. (b) The adsorption may be followed by diffusion of the reacting species on the surface among the various sites where bond breaking may occur. (c) Then the reaction takes place that includes bond scission and molecular rearrangement. These chemical processes are not readily separable by experi-

---

[1] Permanent address: Eastman Kodak Laboratories, Rochester, New York.

TABLE 1

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

Reaction	A^a	E_a(kcal/mole)	Reaction probability	Reference
$H + D_2 \xrightarrow{Pt} HD$ (<600 K)	2×10^5 (sec^{-1})	4.5	$\sim 10^{-1}$	*7*
$H + D_2 \xrightarrow{Pt} HD$ (>600 K)	1×10^2 (sec^{-1})	0.6	$\sim 10^{-1}$	*7*
$D + O_2 \xrightarrow{Pt} D_2O$ (700 K)	—	12	—	*20*
$CO + O \xrightarrow{Pt} CO_2$ (700 K)	—	20	$\sim 10^{-3}$	*21*
$C_2H_4 + O_2 \xrightarrow{Ag} CO_2$ (800 K)	—	8	$<10^{-2}$	*22*
$2H \xrightarrow{\text{graphite}} H_2$ (800–1000 K)	1.06×10^{-2} cm²/atom sec	15.9	10^{-3}–10^{-2}	*11*
$H_2 \xrightarrow{Ta} 2H$ (1100–2600 K)	—	75	4×10^{-1}	*23*
$HCOOH \xrightarrow[\text{decomp}]{Ni} CO_2$ (<455 K)	10^{12} (sec^{-1})	20.7	—	*12*
$HCOOH \xrightarrow[\text{decomp}]{Ni} CO_2$ (>455 K)	5.8×10^3 (sec^{-1})	2.5	~ 0.9	*12*
$C + O_2 \to CO$ (1000–2000 K)	2.5×10^7 (sec^{-1})	30	10^{-3}–10^{-2}	*14*
$C + O_2 \to CO$ (1000–2000 K)	3×10^{12} (sec^{-1})	50	10^{-3}–10^{-2}	*14*
$C + 4H \to CH_4$ (500–800 K)	1.27×10^{-18} cm⁴/atom sec	3.3	10^{-3}–10^{-2}	*11*
$2C + 2H \to C_2H_2$ (>1000 K)	1.59 cm²/atom sec	32.5	10^{-3}–10^{-2}	*11*
$Ge + O_2 \to GeO$ (750–1100 K)	10^{16} (sec^{-1})	55	2×10^{-2}	*24*
$Ge + O \to GeO$ (750–1100 K)	10^{16} (sec^{-1})	55	3×10^{-1}	*25*
$Ge + O_3 \to GeO$ (750–1100 K)	10^{16} (sec^{-1})	55	5×10^{-1}	*17*
$Ge + Cl_2 \to GeCl_2$ (750–1100 K)	10^7 (sec^{-1})	25	3×10^{-1}	*12*
$Ge + Br_2 \to GeBr_2$ (750–1100 K) $\searrow GeBr_4$	10^7 (sec^{-1})	20	3×10^{-1}	*26*
$Si + Cl_2 \to SiCl_2$ (1100–1500 K)	10^8 (sec^{-1})	40	3×10^{-1}	*12*
$Ni + Cl_2 \to NiCl$ (900–1400 K)	10^7 (sec^{-1})	30	8×10^{-1}	*13*

[a] For bimolecular reactions, the preexponential factor also includes the surface concentration of one of the reactants that is held constant during the experiments.

ments at present. (d) The product molecule then desorbs into the gas or liquid phase.

In this paper we compute the preexponential factor for each of these elementary surface reaction steps. We shall make order of magnitude estimates of the preexponential factor. Calculated preexponential 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 (reactant concentrations and surface site concentrations).

The preexponential factor (A_n) is defined for a reaction involving n specie as

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

when k_n, E, R, and T have their usual meaning. We shall evaluate A_n employing transition state theories of Eyring (*3*) in a fashion like that of Laidler (*4*). A list of symbols is also shown in the appendix.

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 specie are most easily analyzed for pseudo first-order conditions where the surface concentrations of all except one of the specie 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 their constant 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 $\frac{1}{4}\bar{c}\cdot a$. The number of collisions per unit time with uncovered surface is given by the preexponential part of Eq. 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 Eq. 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 preexponential 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

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

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, $A_1 = \frac{1}{4}\,\bar{c}\,\theta$ for this case. Under steady state conditions for the product species formed on the surface

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

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

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

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*). We assume that the molecule adsorbs on a random site, then diffuses to the active site where the reaction occurs. The frequency (f) of jumps of distance d is given by

$$f = \nu e^{-E_D/RT}, \tag{7}$$

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

$$t = \frac{3\langle x^2\rangle}{fd^2}, \tag{8}$$

where t is the time required to diffuse a distance $\langle x^2\rangle^{\frac{1}{2}}$. We calculate a surface diffusion velocity ($v = \langle x^2\rangle^{\frac{1}{2}}/t = fd^2/3\langle x^2\rangle^{\frac{1}{2}}$). 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 $\langle x^2\rangle^{\frac{1}{2}} = N_s^{-\frac{1}{2}}$. Combining the collision number with a Boltzmann factor to account for collisions with sufficient energy for reaction (E), we obtain

$$\begin{aligned} \frac{-dn_s}{dt} &= v \cdot b \cdot N_s \cdot n_s \exp(-E/RT) \\ k &= \frac{\nu d^2 b}{3} N_s^{\frac{3}{2}} \exp[-(E + E_D)/RT]. \end{aligned} \tag{9}$$

The preexponential factor is

$$A_1 = \frac{\nu d^2 b}{3} N_s^{\frac{3}{2}}. \tag{10}$$

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

Surface Reactions

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

$$A_n = \frac{KT}{h} \times Q^{\ddagger} \Big/ \prod_{i=1}^{N} Q_i, \tag{11}$$

where K = Boltzmann constant, T = temperature, h = Planck's constant, Q_i = partition function for reactant species i, and $Q^{\ddagger}$ = partition function for transition state.

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

$$Q_i = q_T^2 q_R q_v^{3n-3}, \tag{12}$$

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

$$q_T = \frac{(2\pi MKT)^{\frac{1}{2}}}{h}, \tag{13}$$

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 preexponential factors for the various rate limiting steps in Table 2. Note that pseudo first-order preexponential 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 preexponential decreases by a

TABLE 2

Values of Preexponential Factors

Rate limiting step	Expression for A_n	Pseudo first-order A_n (sec^{-1})	Typical value (sec^{-1})
Adsorption	$\frac{1}{4}\bar{c}\theta a/V$	$\frac{1}{4}\bar{c}\theta a/V$	10^2–10^4
Desorption	ν_0	ν_0	10^{13}
Surface diffusion	$\frac{\nu d^2 b N_s^{1/2}}{3}$	$\frac{\nu d^2 b N_s^{1/2}}{3}$	10^7–10^{12a}
Surface reaction control			
Order			
$N = 1$	KT/h	KT/h	10^{13b}
$N = 2$	KT/hq_T^2	$\frac{KT}{hq_T^2} n_s$	10^{9b}
$N = 3$	KT/hq_T^4	$\frac{KT}{hq_T^4} n_s^2$	10^{5b}
$N = 4$	KT/hq_T^6	$\frac{KT}{hq_T^6} n_s^3$	10^{1b}

[a] N_s varies from 10^{11} to 10^{14} sites/cm^2.

[b] Values are $n_s = 10^{12}$ atoms/cm^2, $KT/h = 10^{13}$ sec^{-1}, $\nu = 10^{13}$ sec^{-1}, $d = 3 \times 10^{-8}$ cm, $b = 3 \times 10^{-8}$ cm, $c = 4 \times 10^4$ cm/sec.

factor of 10^{-16} cm^{-2} 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 2. 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 preexponential factor for the rate of reaction will be too high. Surface diffusion will be the more likely slow step in that case.

Comparison of Computed and Experimental Values of the Preexponential Factor, A_n

The surface reaction $D_2 + H \rightarrow DH + D$ 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 preexponential factors of $2 \pm 1 \times 10^5$ sec^{-1} and 1×10^2 sec^{-1} were measured below and above 600 K, respectively. These values may be compared to gas phase reaction data. Converting the experimental gas phase value (*8a*) $k_2 = 3 \times 10^{-11} \exp(-6.5\ \text{kcal}/RT)$ cm^3/molecule sec to a pseudo first-order preexponential factor ($P_{D_2} = 6 \times 10^{-7}$ Torr, 600 K), we find $A_1 = 7$ 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.

$$H_2(g) \overset{K}{\leftrightarrows} 2H(s)$$

$$D_2(g) + H(s) \xrightarrow{k_2} DH(s) + D(s)$$

$$\frac{d\text{DH}(s)}{dt} = k_2 D_2(g) \cdot H(s) \tag{14}$$

$$k^{\text{pseudo}} = k_2 \cdot H(s).$$

Taking the preexponential part of Eq. 14 as $A_2\mathrm{H(s)}$ and employing Eq. 5, we arrive at the effective pseudo first-order preexponential

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

In the molecular beam experiments, we estimate $a/V = 1\ \mathrm{cm}^{-1}$ and $\theta = .01$ to $.1$ under the experimental conditions. These parameters give $A_1 = 2 \times 10^4\,\theta\ \mathrm{sec}^{-1}$. 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 $1\ \mathrm{cm}^{-1}$ and could significantly decrease the preexponential factor.

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

A surface reaction controlled rate leads to calculated preexponential factors that also agrees with experimental values for the high temperature or the low temperature branch. Consider the mechanism:

$$\mathrm{H_2(g)} \overset{K_1}{\rightleftarrows} \mathrm{2H(s)}$$

$$\mathrm{D_2(g)} \overset{K_2}{\rightleftarrows} \mathrm{D_2(s)}$$

$$\mathrm{D_2(s)} + \mathrm{H(s)} \xrightarrow{k_2} \mathrm{DH(s)} + \mathrm{D(s)} \qquad (16)$$

A rate expression for this mechanism may be written as

$$\frac{d\mathrm{HD(s)}}{dt} = k_2\mathrm{H(s)D_2(s)}$$

$$= k_2(K_1\mathrm{H_2(g)})^{\frac{1}{2}}\mathrm{D_2(s)}. \qquad (17)$$

$$k^{\mathrm{pseudo}} = k_2(K_1\mathrm{H_2(g)})^{\frac{1}{2}}$$

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

$$k^{\mathrm{pseudo}} = \frac{KT}{h}\,\frac{q_{R,\mathrm{DH(s)}}}{q_{R,\mathrm{D_2(s)}}}\,\frac{q^2{}_{\mathrm{T,D_2H(s)}}}{q^2{}_{\mathrm{T,D_2(s)}}}$$

$$\times \frac{(\mathrm{H_2(g)})^{\frac{1}{2}}}{q^{\frac{3}{2}}{}_{\mathrm{T,H_2(g)}}\,q_{R,\mathrm{H_2(g)}}}$$

$$\times \exp(-(E + \Delta \mathrm{H}/2)/RT). \qquad (18)$$

ΔH = heat of dissociative chemisorption of H_2. The preexponential part of this expression is evaluated in Table 3 ($A = 5 \times 10^5\ \mathrm{sec}^{-1}$) and agrees well with experiment. In this calculation we have used $T = 600$ K and $P_{H_2} = 6 \times 10^{-7}$ Torr. We note that other possible rate limiting steps such as desorption, adsorption, or diffusion to step sites give the following preexponential factors: adsorption $= 10^4\ \mathrm{sec}^{-1}$, desorption $= 10^{13}\ \mathrm{sec}^{-1}$, and diffusion $= 10^{11}\ \mathrm{sec}^{-1}$ for $N_s = 10^{14}\ \mathrm{cm}^{-2}$. Only the adsorption step or the surface reaction controlled step gives values close to experiment.

Recently Wachs and Madix (*8b*) have reanalyzed the experimental data dealing with HD formation in the molecular beam (*7*). They considered two parallel reaction paths and found pseudo first-order rate constants $8 \times 10^4 \exp(-5.2\ \mathrm{kcal}/RT)\ \mathrm{sec}^{-1}$ and $3 \times 10^2 \exp(-2.7\ \mathrm{kcal}/RT)\ \mathrm{sec}^{-1}$. A reaction mechanism consisting of HD formation at the step or terrace of the Pt crystal was associated with each reaction path. We would like to point out that the preexponential factors determined in each analysis are in rough agreement. Thus, we believe the reaction models for which we have calculated preexponential factors, as described above, are consistent with both experimental sets of data.

The catalytic hydrogenolysis of cyclohexane giving *n*-hexane and other products

TABLE 3

Experimental and Calculated Preexponential Values

Reaction	Reference	Experimental pseudo first-order A (sec^{-1})	Calculated pseudo first-order A (sec^{-1})	Expression for A	Suggested mechanism
			Catalytic reactions		
$D_2 + H \rightarrow DH + D$		2×10^5 below 600 K	5×10^5	$\frac{KT}{h} \frac{q_{R,DH(s)} q_{T^2,D_2H(s)} (H_2(g))^{\frac{1}{2}}}{q_{R,D_2(s)} q_{T^2,D_2(s)} q_{T^{\frac{3}{2}},H_2(g)} q_{R,H_2(g)}}$	Reaction limited
	7	1×10^2 above 600 K	$2 \times 10^4 \theta$	$(\bar{c}/4)\theta a/V$	Adsorption limited
cyclohexane → n-hexane	*9*	1.3×10^{10}	5×10^{10}	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
cyclopropane → propene	*10*	1×10^{12}	3×10^{11}	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
$HCOOH \rightarrow CO_2$	*15*	$1 \times 10^{12} < 455$ K	10^{12}–10^{13}	ν_0	Reaction limited
		$5.8 \times 10^3 > 455$ K	10^4	$(\bar{c}/4)a/V$	Adsorption limited
$2H \overset{Ni}{\rightarrow} H_2$	*16*	1 cm^2/atom sec[a]	.001 cm^2/atom sec[a]	$\frac{KT}{h} \frac{1}{q_{T^2}}$	Reaction limited
$2H \xrightarrow{graphite} H_2$	*11*	1.06×10^{-2} cm^2/atom sec[a]	.001 cm^2/atom sec[a]	$\frac{KT}{h} \frac{1}{q_{T^2}}$	Reaction limited
			Gas-solid reactions		
$C + 4H \rightarrow CH_4$	*11*	1.3×10^{-18} cm^4/atom sec[a]	4.4×10^{-20} cm^4/atom sec[a]	$\frac{KT}{h} \frac{1}{q_{T^4}}$	Reaction limited
$2C + 2H \rightarrow C_2H_2$	*11*	1.59 cm^2/atom sec[a]	1.7×10^{-2} cm^2/atom sec[a]	$\frac{KT}{h} \frac{1}{q_{T^2}}$	Reaction limited
$Ge + Cl_2 \rightarrow GeCl_2$	*12*	10^7	10^7 for $N_s = 1 \times 10^{11}$	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
$Si + Cl_2 \rightarrow SiCl_2$	*12*	10^8	10^8 for $N_s = 5 \times 10^{11}$	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
$Ni + Cl_2 \rightarrow NiCl_2$	*13*	10^7	10^7 for $N_s = 1 \times 10^{11}$	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
$C + O_2 \rightarrow CO$	*14*	2.5×10^7	10^7 for $N_s = 1 \times 10^{11}$	$\nu_0 d^2 b N_s^{\frac{1}{2}}/3$	Diffusion limited
		3×10^{12}	10^{12}–10^{13}	ν_0	Desorption limited
$Ge + O_3 \rightarrow GeO$	*17*	1×10^{16}	$10^{13} Q\ddagger/Q$[b]	$\frac{KT}{h} \frac{Q\ddagger}{Q}$	Desorption limited

[a] Reported as an Nth order rate constant.

[b] See text for explanation of $Q\ddagger/Q$.

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 preexponential factor of 1.3×10^{10} sec^{-1} may be determined from the experimental data at 300 K 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 preexponential value calculated using Eq. 18 with the experimental value. An active site density for *n*-hexane formation of 2.7×10^{13} cm^{-2} gives a calculated value agreeing with experiment. The experimental active site density was 4×10^{14} 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 preexponential 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 preexponential factor of 10^{12}–10^{13} sec^{-1} for desorption of product. The calculated preexponential factor for a diffusion-controlled reaction is 2.6×10^{11} sec^{-1}, where we have used the experimental active site density of 2×10^{14} cm^{-2} in Eq. 10. Alternatively, the unimolecular bond breakage would have a preexponential of 10^{12}–10^{13} 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:

$$\begin{aligned} H_2(g) &\overset{K_1}{=} 2H(s) \\ C + H_2(g) &\overset{K_2}{=} CH_2(s) \\ CH_2(s) + 2H(s) &\xrightarrow{k_3} CH_4(s). \end{aligned} \quad (19)$$

The rate expression for this mechanism is

$$\frac{dCH_4(s)}{dt} = k_3[H(s)]^2[CH_2(s)]. \quad (20)$$

Employing Eq. 11, we write the preexponential factor

$$A_3 = \frac{KT}{h} \frac{q^2{}_{T,CH_4(s)}}{q^4{}_{T,H(s)}q^2{}_{T,CH_2(s)}}. \quad (21)$$

The preexponential factor calculated from this expression (4.4×10^{-20} cm^4/atom sec) compares well with experiment as shown in Table 3.

The reaction leading to acetylene formation is modeled as

$$\begin{aligned} H_2(g) &\overset{K_1}{=} 2H(s) \\ H(s) + C_2 &\overset{K_2}{=} C_2H(s) \\ C_2H(s) + H(s) &\xrightarrow{k_2} C_2H_2(s). \end{aligned} \quad (22)$$

The rate expression becomes

$$\frac{d[C_2H_2(s)]}{dt} = k_2[C_2H(s)][H(s)]$$

$$A_2 = \frac{KT}{h} \times q^{\frac{1}{2}}{}_{T,H(s)} \times \frac{q^2{}_{T,C_2H_2(s)}}{q^2{}_{T,C_2H(s)}}, \quad (23)$$

for which the preexponential term of 1.7×10^{-2} cm^2/atom sec also given in Table 3 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 reactions (*12–14*) have been classified as diffusion-controlled on the basis of their preexponential factors. Those cases shown in Table 3 where values of the preexponential 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}/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 preexponential factors. The other variable of importance in determining the preexponential 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 nickel (*14*), shown in Table 3, 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 acid (*15*) which has preexponential 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 preexponential factor (*17*). Desorption of the oxide is considered the rate limiting step, but this step would yield normally a value of $A = 10^{13}$ 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 observed (*8a*) in gas phase reactions such as $C_2H_6 \rightarrow 2CH_3$ which has an experimental preexponential factor of 2×10^{18} 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 preexponential factor. For molecules possessing essentially free rotation and translation on the surface, the effects 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

Preexponential 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. Preexponential 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 preexponential factors of 10^2–10^5 sec^{-1} can be associated with surface reaction control or slow adsorption. Preexponential 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 preexponential factors are typically 10^{13} sec^{-1} for first-order reactions, 10^{-12}–10^{-10} cm^3/molecule sec for second-order reactions, and 10^{-37}–10^{-31} cm^6/molecule^2 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 preexponential factors. There have been reactions reported (*19*) where other effects such as changes in symmetry leading to the activated state are necessary to explain preexponential factors. These reactions appear to be in the minority of those examined to date.

The preexponential factors of diffusion controlled reactions may be altered in a nonlinear 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 $D_2 + H \rightarrow DH + D$ reaction on stepped Pt surfaces, there does not seem to be the opportunity for nonlinear changes in preexponential 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 preexponential factors for hydrogenolysis of cyclohexane (*9*) and (*10*) requires the experimental rate of product formation, reactant concentration, and activation energy. These experimental data are as follows:

Reaction	Reactant concentration (molecules cm^{-3})	Rate (molecules/sec cm^2)	$E_{act.}$ (kcal)
Cyclohexane hydrogenolysis	4×10^{10}	7.5×10^{9}	3
Cyclopropane hydrogenolysis	9.2×10^{19}	2×10^{16}	12.2

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

$$R(g) \overset{K_s}{\rightleftarrows} R(s)$$
$$R(s) \xrightarrow{k} \text{product} \qquad (A1)$$

For this mechanism, we have

$$\text{rate} = \frac{-d[R(s)]}{dt} = k[R(s)]$$
$$= kK_s[R(g)]. \qquad (A2)$$

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 Eq. A3 where E is the overall activation energy

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

We wish to separate the preexponential part of k (A) from the preexponential 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 Eq. A4.

$$A = \frac{\text{rate}}{[R(g)]} \times \frac{q_T^3}{q_T^2} \exp(E/RT). \qquad (A4)$$

The gas phase concentration of reactant is known, and Eq. A4 may be used to calculate the preexponential factor for each of the reactions. This procedure gives the experimental factors listed in Table 3.

LIST OF SYMBOLS

A_n = Preexponential factor for a reaction involving n specie
k_n = Rate constant for reaction involving n specie
k^{pseudo} = Pseudo first-order rate constant
E = Activation energy for reaction
R = Gas constant
T = Temperature, °K
$\bar{c}$ = Average gas phase velocity of molecules
a = Surface area
n_s = Surface concentration of molecules
n = Gas phase concentration of molecules
θ = Surface coverage
V = Volume of gas phase
ν_0 = Vibrational frequency of surface bond
f = Frequency of jumps of molecules on surface
E_D = Activation energy for surface diffusion
d = Jump distance on surface
$\langle x^2 \rangle^{\frac{1}{2}}$ = Average diffusion distance
v = Velocity of surface diffusion
b = Molecular diameter
N_s = Active site density on surface
K = Boltzmann's constant
h = Planck's constant
Q = Partition function for reactant species i
$Q^{\ddagger}$ = Partition function for transition state
q_T = Translational partition function
q_R = Rotational partition function
q_V = Vibrational partition function
M = Mass of molecule

APPENDIX II

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

Species	Translation (cm^{-1})	Rotation
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	—

REFERENCES

1. Somorjai, G. A., "Accounts of Chemical Research," 9, 248 (1976).
2. Benson, S. W., "The Foundations of Chemical Kinetics," p. 256. McGraw-Hill, New York, 1960.
3. Eyring, H., *J. Chem. Phys.* **3**, 107 (1935).
4. Laidler, K. J., "Chemical Kinetics," McGraw-Hill, New York, 1950.
5. Balooch, M., Cardillo, M. J., Miller, D. R., and Stickney, R. E., *Surf. Sci.* **46**, 358 (1974).
6. Somorjai, G. A., "Principles of Surface Chemistry," Chapter 3. Prentice-Hall, Englewood Cliffs, New Jersey, 1972.
7. Bernasek, S. L., and Somorjai, G. A., *J. Chem. Phys.* **62**, 3149 (1975).
8. (*a*) Benson, S. W., "The Foundations of Chemical Kinetics," Table XII.5. McGraw-Hill, New York, 1960. (*b*) Wachs, I. E., and Madix, R. J., to be published.
9. Blakely, D. W., and Somorjai, G. A., *J. Catal.*, **42**, 181 (1976).
10. Kahn, D. R., Petersen, E. E., and Somorjai, G. A., *J. Catal.* **34**, 294 (1974).
11. Balooch, M., and Olander, D. R., *J. Chem. Phys.* **63**, 4772 (1975).
12. Madix, R. J., Reactive scattering from solid surfaces *in* "Physical Chemistry of Fast Reactions," (D. O. Hayward, Ed.), Vol. 2. Plenum, New York, 1976.
13. McKinley, J. D., *J. Chem. Phys.* **40**, 120 (1964).
14. Olander, D. R., Jones, R. H., Schwartz, J. A., and Siekhaus, W. J., *J. Chem. Phys.* **57**, 421 (1972).
15. McCarty, J., Falconer, J., and Madix, R. J., *J. Catal.* **30**, 235 (1973).
16. Lapujoulade, J., and Neil, K. S., *Surf. Sci.* **35**, 288 (1973).
17. Madix, R. J., Parks, R., Susu, A. A., and Schwartz, J. A., *Surf. Sci.* **24**, 288 (1971).
18. Benson, S. W., "The Foundations of Chemical Kinetics," Tables XII.5 and XII.9. McGraw-Hill, New York, 1960.

19. Jelend, W., and Menzel, D., *Surf. Sci.* **42**, 485 (1974).

20. Smith, J. N., and Palmer, R. L., *J. Chem. Phys.* **56**, 13 (1972).

21. Bonzel, H. P., and Ku, R., *Surf. Sci.* **33**, 91 (1975).

22. Smith, J. N., Palmer, R. L., and Vroom, D. A., *J. Vac. Sci. Technol.* **10**, 5027 (1968).

23. Krakowski, R. A., and Olander, D. R., *J. Chem. Phys.* **49**, 5027 (1968).

24. Anderson, J. B., and Boudart, M., *J. Catal.* **3**, 216 (1964); Madix, R. J., and Boudart, M., *J. Catal.* **7**, 240 (1967).

25. Madix, R. J., and Susu, A. A., *Surf. Sci.* **20**, 377 (1970).

26. Madix, R. J., and Susu, A. A., *J. Vac. Sci. Technol.* **9**, 915 (1972).