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Site Densities in Unimolecular, Solid-Catalyzed Reactions

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Kinetic data may be used to determine the active site densities of solid catalysts for unimolecular reactions in which the surface step is the rate-determining step. The method presented does not depend upon prior knowledge of the entropy of activation of the surface step, and can be used to determine that quantity. Certain energetic and coverage assumptions must be made; it is shown, however, that making adequate assumptions is not an insurmountable problem. Twelve literature systems have been studied. The site densities obtained are much higher than the abnormally low values obtained earlier when it was assumed that the entropy of activation of the surface step is zero. On the average, the new calculated value and the value obtained by a nonkinetic method differ by 1.3 orders of magnitude. The entropy of activation for the surface step is shown to be significant. In some cases the value so obtained might not actually be the entropy of activation, but a measure of the complexity of the surface reaction.

We have earlier (*1*–*6*) calculated the concentration of active sites, the site density, for solid-catalyzed gas reactions, using transition state theory (TST) for many reactions and catalysts. We noted—especially concerning unimolecular reactions whose rate-determining step is the surface step—that often the site density is very low. The purpose of the present work is to investigate these unimolecular reactions further.

When the yield is small enough to allow neglect of the overall reverse reaction, the reaction can be given by

$$\mathrm{B(g)} + \mathrm{A(s)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{BA(s)} \xrightarrow{k_3} \mathrm{A(s)} + \text{products}, \quad (1)$$

where B is the reactant, A the surface site, and BA the adsorbed molecule before reaction. The TST equation for v, the rate of reaction (1) under zero-order conditions, i.e., when the surface is fully covered, is

$$v = L(kT/h)\exp(\Delta S_3/R)\exp(-\Delta E_3/RT), \quad (2)$$

where L is the site density, k and h are the Boltzmann and Planck constants, respectively, T is the temperature, R is the gas constant, and ΔS_3 and ΔE_3 are the activation entropy and energy, respectively, for the surface reaction. (We assume throughout this article that the partition function of the unoccupied site is unity.) When the rate is measured under zero-order conditions, the observed activation energy is ΔE_3. Therefore, we can combine v and ΔE_3 to determine L if we know ΔS_3.

Usually ΔS_3 is taken to be zero, since both BA and the activated complex for the surface step are adsorbed. The remainder of this article is devoted to an investigation of that assumption. We now derive an equation which enables us to calculate ΔS_3.

THEORY

After reaction (1) has begun, surface occupancy will increase until the steady state has been achieved. Then

$$\begin{aligned} d[\mathrm{BA}]/dt &= 0 \\ &= k_1[\mathrm{B}][\mathrm{A}] - (k_2 + k_3)[\mathrm{BA}]. \quad (3) \end{aligned}$$

Since $L = [\mathrm{A}] + [\mathrm{BA}]$ and the fraction of sites occupied, f, is $(1 - [\mathrm{A}]/L)$, Eq. (3)

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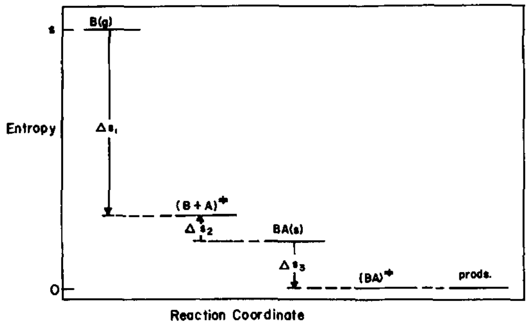

FIG. 1. Entropy scheme for reaction (1).

becomes

$$(k_2 + k_3)/k_1[\mathrm{B}] = (1 - f)/f. \tag{4}$$

Our evaluation of ΔS_3 is carried out in a three-step procedure. In this procedure Eq. (4) is related to the entropy-level diagram of reaction (1), Fig. 1.

First, let S be the molar entropy of the gas at the desired P and T. We introduce TST equations for k_1, k_2, and k_3 into Eq. (4) by assuming that the gas loses all its gas phase entropy upon adsorption, i.e., $\Delta S_1 = -S$. Then $\Delta S_2 = \Delta S_3 = 0$. It follows that

$$k_1 = [(kT/h)/F]\exp(-\Delta E_1/RT), \tag{5}$$

$$k_2 = (kT/h)\exp(-\Delta E_2/RT), \tag{6}$$

$$k_3 = (kT/h)\exp(-\Delta E_3/RT), \tag{7}$$

where F is the partition function of the gas; only the translational and rotational components need be considered. (The configurational factor for the molecule is neglected in Eq. (5) and in similar equations below because the change in molecular configuration upon adsorption is very likely close to zero.) Combining Eqs. (4)–(7) we have

$$\frac{\exp(-\Delta E_2/RT) + \exp(-\Delta E_3/RT)}{(c_g/F)\exp(-\Delta E_1/RT)} = (1 - f)/f. \tag{8}$$

The units for F are such that c_g, the number of reactant molecules per cubic centimeter, replaces [B].

Second, we revise the assumption of the previous paragraph so that ΔS_3, according to Fig. 1, may be negative; then, still assuming that $\Delta S_2 = 0$, $\Delta S_1 = -S - \Delta S_3$. The adsorption rate constant then increases by the factor $\exp(-\Delta S_3/R)$ and the surface step rate constant decreases by the factor $\exp(+\Delta S_3/R)$. When Eqs. (6) and (7) are thus modified, we have instead of Eq. (8)

$$\frac{\exp(-\Delta E_2/RT) + \exp(\Delta S_3/R)\exp(-\Delta E_3/RT)}{(c_g/F)\exp(-\Delta S_3/R)\exp(-\Delta E_1/RT)} = (1 - f)/f. \tag{9}$$

Solving for $\exp(\Delta S_3/R)$,

$$\exp(\Delta S_3/R) = \frac{-\exp(-\Delta E_2/RT) \pm \{\exp(-2\Delta E_2/RT) + 4[(1 - f)/f](c_g/F)\exp[-(\Delta E_3 + \Delta E_1)/RT]\}^{1/2}}{2\exp(-\Delta E_3/RT)}. \tag{10}$$

Only the positive sign has physical significance.

Third, we revise our assumptions once again so that, as in the previous case, $\Delta S_3 \leq 0$, but now $\Delta S_2 \geq 0$. This is the most general set of assumptions. Then $\Delta S_3 = -S - \Delta S_2$; that is, ΔS_3 will be larger by ΔS_2 (a positive quantity) than the value given by Eq. (10). Our procedure is to carry out calculations using Eq. (10), that is, assuming $\Delta S_2 = 0$. We believe ΔS_2 normally would be very small. Then, after the calculations have been made, we shall make qualitative conclusions concerning the results for the case in which ΔS_2 is greater than zero.

In order to determine ΔS_3, the values of

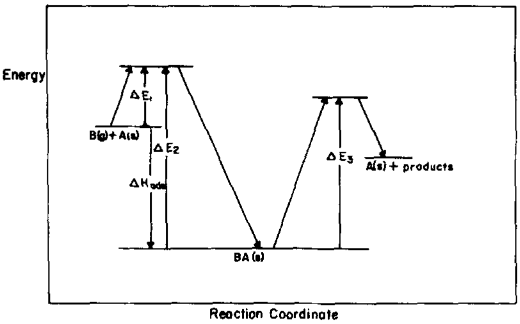

FIG. 2. Energy scheme for reaction (1).

several quantities on the right side of Eq. (10) must be ascertained. Of the three energies in Eq. (10), ΔE_3 is the experimentally determined activation energy for a zero-order reaction. The other quantities with which we must be concerned are ΔE_1, ΔE_2, and f.

We first investigate the relation between ΔE_1 and ΔE_2. The enthalpy of adsorption (see Fig. 2) is the difference between these two quantities. We can then write

$$\begin{aligned}\Delta H_{\text{ads}} &= \Delta E_1 - \Delta E_2 \\ &= \Delta G_{\text{ads}} + T\Delta S_{\text{ads}}. \quad (11)\end{aligned}$$

The standard state for the adsorbed molecule is a half-filled surface; and since we are assuming ΔS_2 to be zero, we have (see Fig. 1)

$$-\Delta S_{\text{ads}} = S + R \ln 2 + \Delta S_3. \quad (12)$$

From statistical mechanics, $S = R \ln (F/c_g) + R(g + \frac{7}{2})$, where g is 0 and $\frac{1}{2}$ for linear and nonlinear molecules, respectively. Then ΔE_2 is given by

$$\begin{aligned}\Delta E_2 = \Delta E_1 - \Delta G_{\text{ads}} &+ RT[\ln(F/c_g) \\ &+ g + 4.19 + \Delta S_3/R]. \quad (13)\end{aligned}$$

We eliminate ΔE_2 by combining Eqs. (10) and (13); but in so doing we introduce a new variable, ΔG_{ads}. The advantage of this procedure is that we know enough about ΔG_{ads} so that it is in effect not a variable. Thus, in order for the surface coverage to be significant ΔG_{ads} should be negative. As we shall see, our results are almost insensitive to ΔG_{ads} when it is negative.

We have solved Eqs. (10) and (13) for ranges of ΔE_1 and f values. We have estimated what these ranges should be in the following way: For ΔE_1, we noted that the average activation energy is $\sim 12RT$ for 19 widely varying first-order reactions (see Tables V–VIII, Ref. (*6*)). Some of these reactions are surface reactions, which tend to have larger activation energies than adsorption reactions; to allow for this effect and normal variation, we chose $5 \pm 4RT$ as the range for ΔE_1. For f, since we use data in near-zero order reactions, we chose values between 0.80 and 0.99.

Since the value of ΔS_3 obtained in this way does not depend upon L, we can calculate L using Eq. (2). In the next section we compare this value with the value of the site density obtained by independent means. To the extent that ΔS_2 is greater than zero, $|\Delta S_3|$ and therefore L are decreased. We thus obtain a minimum value of L if $\Delta S_3 = 0$, an intermediate value if $\Delta S_3 < 0$ and $\Delta S_2 > 0$, and a maximum if $\Delta S_3 < 0$ and $\Delta S_2 = 0$.

RESULTS

Our procedure is to solve Eqs. (2), (10), and (13) for ΔS_3 and $\log L$. We then compare these results with the values of $\log L$ reported using non-TST methods.

But since the calculation of ΔS_3 involves assumptions concerning f, ΔG_{ads}, and ΔE_1, we must examine those assumptions first. We observe what effect varying these three quantities has on the calculated value of $\log L$. The reaction used is the decomposition of cumene (isopropylbenzene) to benzene and propylene over silica–alumina catalyst containing 10 wt% alumina. We previously described the experimental conditions and results (*2*).

This reaction is Example 1 of Table 1. Figure 3 shows how the calculated value of $\log L$ varies with ΔG_{ads}, ΔE_1, and f. We make the following conclusions concerning the question of assuming values for these

TABLE 1

Calculated Entropies

Ex.	Reaction	Catalyst	Data				Results[a]		Ref.
			P (atm)	T (°K)	ΔE_3 (kcal mol^{-1})	v (molecules cm^{-2} s^{-1})	ΔE_2[b] (kcal mol^{-1})	$-\Delta S_3$ (cal °K^{-1})	
1	cumene → $C_6H_6 + C_3H_6$	SiO_2/Al_2O_3	1.0	623	24.0	7.7×10^{12}	41.0	21.0	*2*
2	*tert.* butylbenzene → $C_6H_6 + C_4H_8$	SiO_2/Al_2O_3	6.87×10^{-4}	373	17.9	6.6×10^{7}	29.0	27.5	*7*
3	1-butene isom.	ZrO_2	0.13	373	14.0	2.2×10^{13}	23.9	24.2	*8*
4	*cis*-butene isom.	ZnO	0.10	593	30.5	9.0×10^{11}	40.4	15.8	*9*
5	neopentane isom. (80%); cracking (20%)	Pt/Au/Aerosil	4.8×10^{-2}	573	34.0	1.4×10^{13}	42.9	14.6	*10*
6	cyclohexane → $C_6H_6 + 3H_2$	Pt/Al_2O_3	1.0	423	15.8	9.7×10^{13}	26.6	23.5	*11*
7	$C_2H_5OH \rightarrow C_2H_4 + H_2O$	TiO_2	0.1	473	19.0	1.8×10^{9}	29.8	21.3	*12*
8	iso-$C_3H_7OH \rightarrow C_3H_6 + H_2O$	$ZnMoO_4$	1.0	573	23.5	2.2×10^{14}	35.4	19.7	*13*
9	iso-$C_3H_7OH \rightarrow C_3H_6 + H_2O$	η-Al_2O_3	1.0	548	27.8	1.6×10^{13}	36.6	14.9	*14*
10	*sec.*-$C_4H_9OH \rightarrow CH_3COC_2H_5 + H_2$	Cu/Al_2O_3	5×10^{-2}	486	12.5	1.2×10^{13}	28.6	31.6	*15*
11	*tert.*-$C_4H_9OH \rightarrow$ *iso*-$C_4H_8 + H_2O$	$SiO_2/Al_2O_3/MgO$	0.4	393	22.0	1.5×10^{13}	28.7	14.8	*16*
12	$2CO \rightarrow 2C(ads) + O_2$	Ni/Al_2O_3	1.0	573	32.8	2.8×10^{12}	34.8	4.5	*17*

[a] Assumptions: For all examples, $\Delta E_1 = 6000$ cal/mol, $\Delta G_{ads} = -1000$ cal/mol; for Ex. 1, $f = 0.91$ and for Examples 2–12, $f = 0.99$. See text for effect on log L when these assumptions are changed.

[b] Decreasing the value assumed for ΔG_{ads} causes ΔE_2 to increase by almost the same amount; increasing ΔE_1 causes ΔE_2 to increase by almost one-half the increase in ΔE_1.

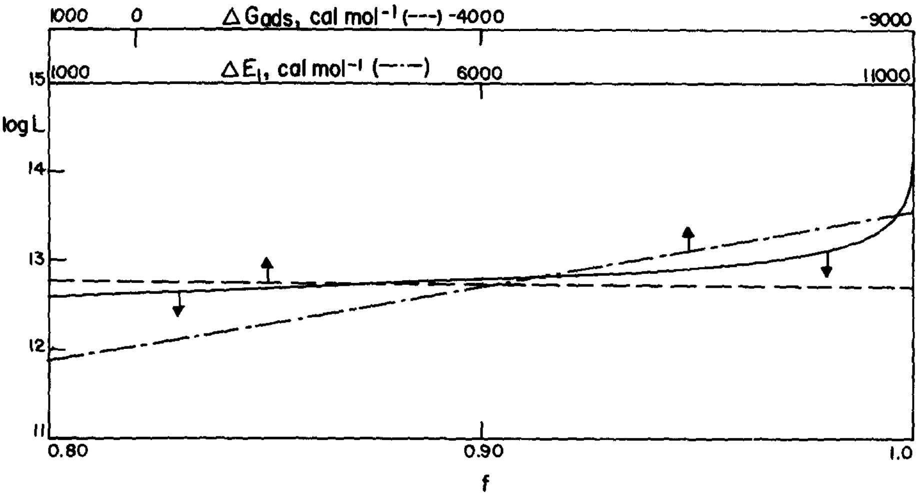

FIG. 3. Dependence of $\log L$ upon values assumed for ΔG_{ads}, ΔE_1, and f for Example 1, Table 1.

three quantities: (1) There is virtually no dependence of $\log L$ on ΔG_{ads} if that quantity is negative. Since positive values are in any case not likely, the assignment of a value to ΔG_{ads} is not critical. (2) In ranges of interest, $\log L$ is linear in ΔE_1; with a 5-kcal/mol increase in ΔE_1, $\log L$ increases about 0.8. Extending this result to other

TABLE 2

Comparison of TST and Non-TST Methods of Determining Site Density

Ex.[a]	Catalyst	Non-TST Method[b]	log L		
			Non-TST	Calculated, TST	
				$\Delta S_3 = 0$	$\Delta S_3 > 0$
1	SiO_2/Al_2O_3	ESR count of surface perylene cations (*18*, *19*)	12.3		
		Surface titration of adsorbed NH_3 (*20*)	13.7	8.0	12.8
		Amount of KI oxid. on surface (*21*)	12.0		
		Ion exchange of surface Al^{3+} (*22*)	~13		
2	SiO_2/Al_2O_3	Heterogeneous part of C_6H_6 ads. isotherm	12.4	5.4	11.4
3	ZrO_2	CO_2 poisoning of reaction	13.2	8.7	13.9
4	ZnO	NH_3 ads. on acidic sites	14.4	10.1	13.6
		CO_2 ads. on basic sites	14.3		
5	Pt/Au/Aerosil	Number of exposed Pt's	~15	13.0	16.2
6	Pt/Al_2O_3	Number of exposed Pt's	~15	9.2	14.3
7	TiO_2	Irreversible ads. of C_2H_5OH	14.4	5.0	9.7
8	$ZnMoO_4$	NH_3 ads. on acidic sites	14.7	10.2	14.5
9	η-Al_2O_3	CO_2 adsorption	14.0	11.2	14.5
		Acetic acid adsorption	14.3		
10	Cu/Al_2O_3	Number of exposed Cu's	15.2	5.7	12.6
11	$SiO_2/Al_2O_3/MgO$	*n*-Butylamine titration	13.8	12.5	15.7
12	Ni/Al_2O_3	Number of exposed Ni's	14.7	11.9	12.9

[a] The example numbers refer to the systems of Table 1.

[b] The non-TST method is reported in the reference of Table 1, except where references appear in parenthesis after the phrase describing the method.

systems and other temperatures, we can use the rule that the increase in log L is approximately $(100/T)$ per kilocalorie increase in ΔE_1. (3) The value of log L calculated increases by about 0.7 when f increases from 0.80 to 0.99; the increase is more rapid when $f > 0.99$.

From the kinetic parameters determined earlier for Example 1 (*2*) we estimate that f is near 0.9 at the conditions given. If $\Delta E_1 =$ 6000 cal/mol, log L is about 12.8, the value given in Table 2. If $\Delta S_3 = 0$, then using Eq. (2) log L is calculated to be 8.0. In Table 2 are listed several non-TST determinations of the site density on similar silica–alumina catalysts; the average of these values is also about 12.8. If, however, ΔS_2 is not zero but positive, the calculated value of log L is less than 12.8.

The results for Examples 2–12 are also given in Tables 1 and 2. For these examples the value of $f = 0.99$ was used because the reactions were reported to be near zero order. Except for Example 7, the calculated value of log L agrees fairly well with the non-TST value. For the 12 examples, the average difference between the calculated and non-TST value of log L is 4.9 when ΔS_3 is taken to be zero; when the above method of calculating ΔS_3 is used, the average difference is 1.3, even though Example 7 is included. Some calculated values of log L are greater and some smaller than the non-TST values. If we take the sign of the difference into account, the average difference is still 4.9 when $\Delta S_3 = 0$ but only 0.6 when ΔS_3 is calculated.

Probably the value of ΔS_3 thus determined cannot always be used to determine the entropy of the adsorbed complex. A nonzero value of this quantity could well be an indication that the reaction is complicated, possibly consisting of several surface steps, as in the cyclohexane dehydrogenation of Example 6 (*11*). But where ΔS_3 is negative and is the entropy of activation of the surface step, it is very likely that the surface molecule lost translational entropy but retained some rotational entropy: $|\Delta S_3|$ is either the same as or less than the gas phase rotational entropy.

Interestingly, one would predict a priori for Example 12 that $|\Delta S_3|$ would be small in this simple reaction, where the rate-determining step has been taken to be scission of the carbon–oxygen bond (*17*); a small value is just what we find.

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