JOURNAL OF CATALYSIS 56, 358–362 (1979)

Entropies of Adsorption in Heterogeneous Catalytic Reactions

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Received July 12, 1978; accepted October 4, 1978

Langmuir–Hinshelwood (or Hougen–Watson) rate expressions are frequently used to correlate kinetic data. The equilibrium adsorption constants contained in these equations can be utilized to abstract values for standard enthalpies and entropies of adsorption. By using limiting, model cases to describe dissociative, dual-site adsorption, we have shown that the values obtained for $\Delta S_a{}^0$ must conform to certain rules in order to have any physical meaning and thereby support the proposed reaction model. Rules proposed earlier by Boudart, Mears, and Vannice for nondissociative adsorption have also been found to be applicable to dissociative adsorption.

INTRODUCTION

Langmuir–Hinshelwood rate expressions are still frequently used today to describe catalytic reactions on solid surfaces. In many cases, quite satisfactory agreement is obtained between these expressions and experimental data despite the assumptions pertaining to ideal surfaces involved in the derivation of Langmuir–Hinshelwood (L–H) or Hougen–Watson (H–W) rate equations. However, surface rate processes other than those represented by L–H or H–W kinetics can have the same mathematical form, and, in addition, real, nonuniform surfaces may alter the simple interpretation afforded by these kinetic equations (*1*). Methods to assess the validity of these L–H rate expressions, when used, are therefore quite useful. Boudart originally suggested that an examination of the equation of the equilibrium adsorption constants contained in the L–H or H–W rate equations could provide valuable information regarding the standard entropy of adsorption, $\Delta S_a{}^0$, with meaningless values of $\Delta S_a{}^0$ making the proposed reaction model suspect (*2*). Boudart *et al.* later studied entropies of adsorption in greater detail, and provided two firm rules and two guidelines to determine whether the reported equilibrium constants had any physical meaning, and could thereby support the proposed rate model (*3*). Since this earlier paper restricted itself to nondissociative adsorption, we wanted to address the more complicated dissociative adsorption process and to determine if a similar set of rules could be established for L–H or H–W rate equations involving dissociative, dual-site, adsorption. This paper is a consequence of that examination.

DISCUSSION

The procedure commonly used to apply L–H or H–W equations to experimental data involves first the postulation of a

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0021-9517/79/030358-05$02.00/0

series of elementary steps and then the use of reasonable simplifying assumptions, such as a rate determining step and/or a most abundant surface intermediate, to obtain agreement with the experimentally determined rate law. Such expressions are of the form

$$k \prod_i C_i^{\alpha_i}/(1 + \sum_i K_i^m C_i^m)^n$$

where C_i represents the concentration of species i, K_i represents an adsorption equilibrium constant, $m = 1$ for nondissociative adsorption and $\frac{1}{2}$ for dual-site, dissociative adsorption, and n is most frequently 1 or 2. The adsorption equilibrium constant can be expressed as $K = e^{\Delta S_a^0/R} e^{-\Delta H_a^0/RT}$ where ΔH_a^0 is the standard enthalpy of adsorption and ΔS_a^0 is the standard entropy of adsorption. In particular, the value of the latter thermodynamic quantity can especially, as mentioned, provide significant insight into the validity of the proposed reaction model.

Restricting themselves to nondissociative adsorption, Boudart *et al.* showed that two strong rules could be stated regarding values of ΔS_a^0: Rule I: ΔS_a^0 must be negative, and Rule 2: ΔS_a^0 must have an absolute value smaller than S_g^0, the standard entropy in the gas phase (*3*). Violation of either of these two rules indicates inconsistencies in the proposed kinetic model, and the constants appearing to represent values of K have no physical meaning in the Langmuirian sense. Two less stringent rules were offered as guidelines, and can be combined and summarized as follows:

$$10 \leq -\Delta S_a^0 \leq 12.2 - 0.0014\Delta H_a^0.$$

The lower limit was established by estimating the loss of free volume upon adsorption at the standard state coverage of $\theta = \frac{1}{2}$, while the upper limit was a consequence of comparison between entropies of chemisorption obtained from the literature and a linear relationship between ΔS_a^0 and ΔH_a^0 observed by Everett for physical adsorption (*4*).

These rules have proven useful during the past decade and we felt it would be beneficial if such a set of rules were also found applicable to dissociative adsorption. In this paper we have examined dissociative adsorption which involves two sites, with the simplest process involving diatomic molecules:

$$A_{2(g)} \rightarrow 2A_{(a)}.$$

In this case $\Delta S_a^0 = 2S_{A(a)}^0 - S_{A_2(g)}^0$ where $S_{A(a)}^0$ is the standard entropy of species A in the adsorbed standard state and $S_{A_2(g)}^0$ is the absolute entropy of species A_2 in the standard state gas phase. If the standard state in the gas phase is chosen to be 1 atm, for Langmuirian adsorption the standard state in the adsorbed phase is one-half surface coverage ($\theta = \frac{1}{2}$). It is quickly seen that adsorption with dissociation is not so straightforward as nondissociative adsorption, due to the increase in the number of species upon adsorption.

Arguing in the same spirit as before, and assuming a stable surface for adsorption, let us consider two limiting cases. The first case adheres strongly to all the assumptions associated with adsorption on a Langmuirian surface, i.e., a localized, noninteracting adsorbate on a uniform surface. Restricting our discussion now to diatomic molecules, this represents a system whose only available modes of motion are vibrational. Describing the adsorbed state in this manner will produce maximum values for the entropy loss upon adsorption.

The second case involves the description of the adsorbate as an ideal two-dimensional gas of species A, and would yield minimum values for the adsorption entropy change. Realistically, we would expect values to lie between these two extremes, especially since Everett has mentioned that the tenets describing Langmuirian adsorption can allow some migration of adsorbed species between sites (*5*).

TABLE 1

Entropy Values for Diatomic Molecules (cal/gmole °K)[a,b]

Gas, A_2	$S_{A_2,g}^0$	ΔS_{diss}^0	$S_{A,g}^0$	$S_{A,a(tr)}^0$	ΔS_a^0[c]
H_2	31.2	23.6	27.4	9.9	−11.4
N_2	45.8	27.5	36.6	15.1	−15.6
O_2	49.0	27.9	38.5	15.4	−18.2
F_2	48.6	27.2	37.9	15.7	−17.2
Cl_2	53.3	25.6	39.5	17.0	−19.4
Br_2	58.6	25.0	41.8	18.6	−21.5
I_2	62.3	24.0	43.2	19.5	−23.3
CO	47.3	28.9	38.1	15.1 (ave)	−17.1

[a] Standard state: 1 atm and 298.16°K.

[b] $\Delta S_a^0 = 2S_{A,a}^0 - S_{A_2}^0$; $S_{A,a(tr)}^0 = R \ln MTa + 65.8$ e.u. (for a two-dimensional gas).

[c] Assuming the adsorbed state is a two-dimensional gas.

Considering the first case of immobile, localized adsorption, the configurational entropy term, $-R \ln \theta/1 - \theta$, is equal to zero (*5*), and the only important entropy term is that associated with vibrational entropy

$$S_v = R[h\nu/kT(e^{h\nu/kT} - 1)^{-1} - \ln(1 - e^{-h\nu/kT})].$$

When $h\nu/kT = 1$, $S_v = 1$ entropy unit (cal/gmole °K); and if the universal frequency of 10^{13} sec^{-1} is chosen to approximate ν, which is a lower limit suggested by DeBoer (*6*), each vibrational degree of freedom will contribute about 1 e.u. Therefore, at most reaction temperatures the total entropy of an adsorbed, dissociated diatomic molecule (two atoms) will be less than 10 e.u. Of course, at higher frequencies S_v will approach a limiting value of zero. Since the minimum value of $S_{A_2(g)}^0$ is far greater than 10 e.u., even at 298.2°K as shown in Table 1, the first two rules proposed for nondissociative adsorption are found to also apply to dissociative adsorption, i.e.,

$$0 < -\Delta S_a^0 < S_{A_2(g)}^0.$$

In the second case, where the adsorbed state is described as a two-dimensional gas, two different thermodynamic paths can be followed to calculate the entropy change of the gas upon adsorption. One path corresponds to a two-step adsorption process:

$$A_{2(g)} \xrightarrow{\Delta S_{diss}} 2A_{(g)} \xrightarrow{2\Delta S_{A(a)}^0} 2A_{(a)},$$

while the other path is a one-step process:

$$A_{2(g)} \xrightarrow{\Delta S_a^0} 2A_{(a)},$$

where $\Delta S_a^0 = \Delta S_{diss} + 2\Delta S_{A(a)}$.

The first step in the two-step process corresponds to the entropy of dissociation, which represents the entropy involved in the severing of the chemical bond plus the change in the partition functions between a diatomic molecule and two separated atoms. These values have been calculated and can be found in general reference books (*7*). For diatomic gases the entropy of dissociation at 298.2°K is typically 26 ± 2 e.u., as shown in Table 1. Values of $S_{A_2(g)}^0$ and $S_{A(g)}^0$ can be calculated, and have also been tabulated (*7*). The translational entropy of an ideal two dimensional gas is $S_{A(a)tr} = R \ln MTa + 65.8$ cal/°K mole where M is the atomic weight of species A, T is the absolute temperature in °K, and a is the area per adsorbed species in cm^2 (*8*). Since our standard state coverage is $\theta = \frac{1}{2}$ and site densities are typically near 10^{15} cm^{-1}, a reasonable value of 20 Å^2/atom can be determined. This value was used to calculate $S_{A(a)tr}^0$; however, this calculation actually overestimates the absolute entropy in the adsorbed state since for a real gas the cross-sectional area of the atom itself must be subtracted from the value of a. This correction can reduce the entropy of the adsorbed gas significantly (*9*).

At 298.2°K and our standard state of 1 atm pressure, values of these various entropy terms for typical diatomic gases are listed in Table 1. Even in the less restrictive case of a two-dimensional gas, the overall standard entropy of adsorption is negative. However, no entropy contribution of vibrational motion perpendicular to the surface was included in this calculation. This contribution is typically expected to be small, less than 3 e.u. per atom as discussed earlier. This expectation would seem to be especially true for these highly reactive atoms. The diatomic molecules in Table 1 have bond dissociation energies ranging from 35 to 255 kcal/gmole, and a strong interaction between the adsorbent surface and these molecules is required to initiate dissociation. This same strong interaction should continue between the free radicals formed and the surface, particularly at monolayer coverages near one-half. The adsorption of hydrogen on nickel is an example (*10*). Vibrational frequencies determined by infrared spectroscopy also support this contention as Pliskin and Eischens have reported wave numbers around 2100 cm^{-1} for hydrogen adsorbed on Pt at temperatures of 35 to 350°C (*11*). This corresponds to a frequency of 6.3×10^{13} sec^{-1}. Even consideration of this possible entropy contribution is not sufficient to cause the standard entropy of adsorption to become positive, but it must be remembered that the area correction mentioned previously will tend to cancel this contribution. We are then left with the conclusion that despite the model chosen to describe dissociative adsorption, the entropy change still must be negative.

Again, we have shown that $0 < -\Delta S_a^0 < S_{A_2(g)}^0$. Therefore, we conclude that the two rules proposed earlier for nondissociative adsorption are also applicable to dissociative adsorption onto dual sites. Also, it is interesting to note that the standard entropy change calculated assuming a two-dimensional gas, which can be considered to be a minimum value for ΔS_a^0, is typically near -10 cal/gmole A °K (or -20 e.u. per A_2) as shown in Table 1. This value agrees well with that estimated previously for nondissociative adsorption (*3*). However, as a conservative estimate which should include all molecules, we propose that the original value of -10 e.u. per molecule be maintained. Realistically, we would expect that ΔS_a^0 values would lie between these two extremes, but we feel that the first case better approximates the chemisorption process on a Langmuirian surface.

A survey of the literature was conducted to find reported L–H or H–W rate expressions invoking dual-site dissociative

TABLE 2

Molecules Postulated to Exhibit Dissociative Dual-Site Adsorption[a]

Compound	T_{ave} (°K)	$\Delta H_a^0 \left(\frac{\text{kcal}}{\text{gmole}}\right)$	ΔS_a^0 (e.u.)	Reference
CH_3Cl	573	−4.7	−27.3	*12*
O_2	757	−24.5	−17.1	*13*
O_2	913	−18.0	−13.0	*14*
O_2	603	−0.02	−0.74	*15*
O_2	698	−20.4	−23.0	*16*
H_2	411	−7.8	−20.8	*17*

[a] Standard state: 1 atm.

adsorption which allowed the determination of K values at different temperatures. Only six papers provided equilibrium adsorption constants from which values of standard entropies could be obtained which satisfied Rules I and II. These values are listed in Table 2. One value of ΔS_a^0 appears to be too low. Of the remaining five values, four are below Everett's correlation while one is somewhat above it. Although data are few, we see no reason to reject the fourth guideline suggested earlier:

$$-\Delta S_a^0 \leq 12.2 - 0.0014\ \Delta H_a^0.$$

Although we have discussed only diatomic molecules, these arguments should hold for any dual-site dissociative adsorption process resulting in the formation of two surface species. We feel our argument, based on the choice of identical atomic species on the surface, represents a limiting case for two reasons. First, multi-atom radicals will be larger, thereby reducing the area per species and the entropy in the adsorbed state if a two-dimensional gas is assumed to exist. Second, for multi-atom species, rotational entropy contributions are possible and adsorption on the surface can do nothing but hinder this rotational motion thereby providing an additional entropy loss compared to that calculated for a diatomic molecule. We have not considered situations where more than two sites are required.

CONCLUSION

We have used two different models, that of immobile, localized adsorption and that of a two-dimensional gas, to describe limiting behavior for dissociative, dual-site adsorption on a Langmuirian surface. Both models show that the standard entropy of adsorption must be negative and must be less than the total entropy of the gas phase molecule. In addition, a minimum value for ΔS_a^0 of -10 e.u. per species is indicated. Finally, from an examination of data from the literature, calculated entropy values are found to be close to or smaller than those predicted by Everett's correlation between enthalpies and entropies for physical adsorption. Therefore, the original rules and guidelines proposed by Boudart, *et al.*:

Rule:

$$0 < -\Delta S_a^0 < S_g^0$$

Guideline:

$$10 \leq -\Delta S_a^0 \leq 12.2 - 0.00014\ \Delta H_a^0 \text{ (per molecule)}$$

are applicable to dissociative, dual-site adsorption as well as nondissociative adsorption.

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