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Entropy Effects in the Chemisorption of CO on (100) Pd, Ni and Cu Single Crystal Surfaces

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Experimental data for the chemisorption of CO on the (100) surface of Pd, Ni and Cu are used to calculate the activation entropy of the adsorption–desorption equilibrium within the framework of the absolute rate theory of chemisorption. It is shown that the activation entropy (i.e., the pre-exponential of the rate coefficient for the elementary surface reaction) is quite anisotropic on the same crystallographic orientation of these three different face-centered cubic metals even at a constant surface coverage of CO. The activation entropy is also found to vary widely on the Ni (100) surface as the CO coverage increases from 0.50 to 0.655.

INTRODUCTION

When the absolute rate theory formulation is used to predict the rates at which various elementary gas-surface reactions occur (e.g., adsorption, desorption or heterogeneously catalyzed surface reactions obeying either Langmuir–Hinshelwood or Rideal–Eley kinetics), there are generally two uncertainties present. These uncertainties are the following: (a) the activation energy of the elementary surface reaction; and (b) the entropy of activation to the surface reaction, i.e., the pre-exponential factor of the reaction rate coefficient. In view of the fact, a bond-energy bond-order (BEBO) model has recently been formulated which allows estimates to be made of heats of adsorption and activation energies to adsorption, desorption and surface reaction (*1–4*) it is very important to be able to make estimates of the activation entropy. If reliable estimates of the entropy of activation may be made, then the combined use of absolute rate theory with the BEBO model allows a *prediction of the rates of elementary surface reactions* (*4*). As will be seen below, the activation entropy is intimately connected with values of the partition functions of reactants and the reaction transition state, and thus can be used to glean valuable insight into the microscopic details of the various surface reactions.

The absolute rate theory will be applied to the general case of the reversible adsorption of an AB molecule on a surface S. Then the results will be applied specifically to the elegant data of Tracy for CO adsorption on the (100) surface of Pd, Ni and Cu (*5–7*). The effects of surface coverage will be examined for the Ni (100) surface.

MODEL DESCRIPTION

At equilibrium, for the reversible adsorption of an AB molecule the rates of adsorption and desorption are equal, i.e.,

$$R_{a,\mathrm{AB}} = R_{d,\mathrm{AB}}. \tag{1}$$

Using absolute rate theory these rates may be written explicity as follows (*1, 4*):

$$R_{a,\mathrm{AB}} = \eta\langle\kappa_a\rangle\left(\frac{q^{\ddagger}}{q}\right)_a(1-\theta_{\mathrm{AB}})n_s\frac{P_{\mathrm{AB}}}{(2\pi m_{\mathrm{AB}}kT)^{1/2}} \times \exp(-E_a/kT) \tag{2}$$

and

$$R_{d,\mathrm{AB}} = \langle\kappa_d\rangle \left(\frac{q^+}{q}\right)_d \theta_{\mathrm{AB}} n_s \left(\frac{kT}{h}\right) \times \exp(-E_d/kT), \quad (3)$$

where η is the symmetry number (unity for a heteronuclear diatomic molecule); $\langle\kappa_a\rangle$ and $\langle\kappa_d\rangle$ are the transmission coefficients for the adsorption and desorption reactions, respectively; $(q^+/q)_a$ and $(q^+/q)_d$ are the ratios of the partition functions state to the reactants for the adsorption and desorption reactions, respectively; θ_{AB} is the fractional surface coverage of the AB molecule; n_s is the concentration of surface sites; P_{AB} in the gas phase equilibrium pressure of AB; m_{AB} is the mass of the AB molecule; k and h are the Boltzmann and Planck constants, respectively; T is the absolute temperature; and E_a and E_d are the activation energies to adsorption and desorption, respectively. In Eq. (2), $(q^+/q)_a$ is the ratio of the product of eight vibrational partition functions to the product of two translational, two rotational and four vibrational partition functions, i.e., one vibrational degree of freedom along the "adsorption coordinate" has been removed from the transition state and one translational degree of freedom has been removed from the reactants. In Eq. (3), $(q^+/q)_d$ is the ratio of the product of eight vibrational partition functions (again with the one along the "desorption coordinate" removed) to the product of nine vibrational partition functions. If the following definition is made

$$Q \equiv \left\langle\frac{\kappa_d}{\kappa_a}\right\rangle \left(\frac{q^+{}_d}{q^+{}_a}\right) \left(\frac{q_a}{q_d}\right), \quad (4)$$

then by combining Eqs. (1–4) the following expression is obtained

$$Q = \left(\frac{1-\theta_{\mathrm{AB}}}{\theta_{\mathrm{AB}}}\right) \frac{P_{\mathrm{AB}}}{(2\pi m_{\mathrm{AB}} kT)^{1/2}} \times \exp\left(\frac{E_d - E_a}{kT}\right). \quad (5)$$

It is clear from Eqs. (4 and 5) that large values for Q are a result of an entropy effect favoring desorption whereas (relatively) smaller values of Q favor the adstate.

It is possible to apply the formulation given above to the experimental data of Tracy (*5–7*) for CO adsorption on the (100) surface of Pd, Ni and Cu. In explicity performing this calculation, it is possible to evaluate q_a which appears in Q, i.e.,

$$q_a = q^2_{t,\mathrm{CO}} q^2_{r,\mathrm{CO}} q_{v,\mathrm{CO}} q^3_{v,\mathrm{Me}} \quad (6)$$

where $q^2_{t,\mathrm{CO}}$ is the square of the translational partition function of gaseous CO, $q^2_{r,\mathrm{CO}}$ is the square of the CO rotational partition function, and $q_{v,\mathrm{CO}}$ and $q^3_{v,\mathrm{Me}}$ are the vibrational partition function for CO and the cube of the vibrational partition function for an atom in the metal lattice. It is assumed that the CO interacts with a single surface metal atom which possesses three degrees of vibrational freedom although this is clearly not a restrictive assumption (*1*); it is merely done for convenience. It is easy to evaluate Eq. (6) since it is known that

$$q_t{}^2 = \frac{2\pi mkT}{h^2},$$

$$q_r{}^2 = \frac{8\pi^2 IkT}{h^2}, \quad (7)$$

and

$$q_v = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right]^{-1},$$

where I is the moment of inertia of the CO molecule, and ν is a vibrational frequency. For the metal lattice $h\nu/k$ is taken to be the surface Debye temperature, i.e., 220 K for Ni, 186 K for Cu and 140 K for Pd (*8*).

Results and Discussion

Values for both Q and Q/q_a may be calculated from Eqs. (5 and 6) using the experimental isosteres of Tracy for the equilibrium (reversible) adsorption of CO on (100) Pd, Ni and Cu (*5–7*). These values are shown in Table 1 together with the conditions for which they apply. Q was defined in Eq. (4), and q_a was defined in Eq. (6). The appropriate expression for q_d is the following:

$$q_d = (q^s_{v,\mathrm{Me}})^3 (q^s_{v,\mathrm{CO}}) (q^s_{v,\mathrm{Me-CO}}) (q^b_{v,\mathrm{Me-CO}})^4, \quad (8)$$

where the superscript s refers to stretching

TABLE 1

ENTROPY PARAMETERS FOR CO ADSORPTION ON (100) Pd, Ni AND Cu

Surface and CO coverage[a]	Pd (100) $\theta_{CO} = 0.50$	Ni (100) $\theta_{CO} = 0.50$	Ni (100) $\theta_{CO} = 0.61$	Ni (100) $\theta_{CO} = 0.64$	Ni (100) $\theta_{CO} = 0.655$	Cu (100) $\theta_{CO} = 0.50$
Q, cm^{-2}	1.22×10^{15}	2.75×10^{19}	9.78×10^{20}	8.26×10^{19}	1.94×10^{23}	1.92×10^{19}
Q/q_a	2.23×10^{-6}	0.137	4.88	0.412	961	0.234

[a] $T = 300$ K except for Cu (100) where $T = 155$ K.

vibrations, and the superscript b refers to bending vibrations. It might be expected *a priori* that $\langle \kappa_d/\kappa_a \rangle$ $(q_d^+/q_a^+) \sim 1$, i.e., the potential energy curve for the adsorption–desorption "reaction" is approximately symmetric about the saddle point in the curve where the transition state is positioned, and the transition state for the adsorption reaction is not unlike the one for the desorption reaction. Since $1/q_d$ is clearly less than unity, it would be expected that Q/q_a is also less than unity [see Eq. (4)]. The half-monolayer coverages for all three metal surfaces have a Q/q_a less than unity as would be expected. The entropy effect favors adsorption on Pd to a rather greater extent than adsorption on Ni which in turn is slightly favored over Cu. However, the results for the compressed structures of CO on Ni are interesting. There is an oscillatory behavior of Q/q_a which, as expected, tends to discourage the high coverage compressed adsorbate. However, a CO coverage of 0.64 is more favorable from an entropy point of view that a coverage of 0.61. A precipitous change in the entropy is noted upon slightly increasing the CO coverage from 0.64 to 0.655. For CO adsorption on Ni (100) at $\theta_{CO} =$ 0.61 and 0.655, it is clear that $\langle \kappa_d/\kappa_a \rangle$ $(q_d^+/q_a^+) > 1$, i.e., the entropy term favors desorption at the expense of adsorption as pointed out above.

These results point up the care which must be exercised in applying rate theory to adsorption–desorption reactions. The considerable differences in entropy contributions to CO adsorption on the (100) crystal plane of the fcc metals Pd, Ni, and Cu are demonstrated as well as the critical dependence on CO coverage on Ni (100). However, it should be emphasized that these calculated results are not unreasonable in view of typical known values of the various partition functions, i.e., $1 \lesssim q_v \lesssim 1.5$, $10 \lesssim q_r \lesssim 50$, and $10^8 \lesssim q_t \lesssim 3 \times 10^8$. Using these values it is found that $10^{15} \lesssim Q \lesssim 5 \times 10^{22}$ assuming $\langle \kappa_a \rangle \sim \langle \kappa_d \rangle$, and $10^{-6} \lesssim Q/q_a \lesssim 5 \times 10^4$. The entropy effects in the absolute rate formulation may be assessed further as other data of reversible adsorption become available.

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