General trends in CO dissociation on transition metal surfaces

Zhi-Pan Liu and P. Hu[a)]

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, United Kingdom

Dissociative adsorption is one of the most important reactions in catalysis. In this communication we propose a model aiming to generalize the important factors that affect dissociation reactions. Specifically, for a dissociation reaction, say AB→A+B, the model connects the dissociation barrier with the association barrier, the chemisorption energies of A and B at the final state and the bonding energy of AB in the gas phase. To apply this model, we have calculated CO dissociation on Ru(0001), Rh(111), Pd(111) (4d transition metals), Os(0001), Ir(111), and Pt(111) (5d transition metals) using density function theory (DFT). All the barriers are determined. We find that the DFT results can be rationalized within the model. The model can also be used to explain many experimental observations. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1372512]

Undoubtedly, the dissociation of molecules is one of the most important reactions in catalysis. It is the first step and often the rate-determining step in many catalytic processes. Therefore, dissociation reactions have been extensively studied both experimentally and theoretically in the last 50 years.[1–7] Following the detailed investigation of the simplest system, H_2 dissociation on metal surfaces,[2,3] the dissociation of heavier molecules, such as NO, CO, and N_2, on flat and stepped metal surfaces[4–6] have recently received more attention and some progress in understanding these reactions has been made. To date two factors[4] are found to affect the dissociation reactions. The first one is the electronic factor: It has been found experimentally that the reactivity of transition metals for dissociation reactions decreases from left to right in the periodic table.[7] Hammer and Norskov[4] have successfully correlated the reactivity of metal for dissociation reactions with the metal d band center. The second factor is the geometrical one: Both experimental and theoretical work shows that dissociation reactions occur much more efficiently on corrugated surfaces than on flat surfaces.[4,6] Despite these advances, a general model for dissociation reactions is still unavailable. In this communication we intend to generalize all the important factors that affect dissociation reactions in one model.

For any co-adsorption system of two adsorbates, say A and B, the total chemisorption energy of A and B, E_{A+B}, can be written[8] [Fig. 1(a)]

$$E_{A+B}=E_A+E_B-E_{\text{int}}, \tag{1}$$

where $E_A(E_B)$ is the chemisorption energy of A (B) in the co-adsorption structure (including both transition state like and final state like structures) without B (A), and E_{int} is defined as the interaction energy. The physical meanings of E_{A+B}, E_A, and E_B are self-evident, and E_{int} is a quantitative measure of the interaction between A and B in the coadsorption system, which is believed mainly due to a bonding competition effect[9,10] that results from the sharing atom of two

adsorbates on the surface.[4,6,11–13] If A and B do not share atoms in a coadsorption system, E_{int} will be very small.[10,11] Specifically, suppose that a dissociation reaction, AB→A+B, occurs on a catalyst. We can obtain the following equation for the transition state (TS) and the final state (FS) using Eq. (1):

$$E_{A+B}^{\text{TS}}=E_A^{\text{TS}}+E_B^{\text{TS}}-E_{\text{int}}^{\text{TS}}, \tag{2}$$

$$E_{A+B}^{\text{FS}}=E_A^{\text{FS}}+E_B^{\text{FS}}-E_{\text{int}}^{\text{FS}}. \tag{3}$$

The energy diagram for the dissociation reaction is illustrated in Fig. 1(b), where E_a^{dis} is the dissociation barrier with respect to molecule AB in the gas phase (direct dissociation) and E_a^{as} is the barrier of association reaction (A+B→AB), the reverse reaction of the dissociation. Obviously, the energy difference ΔE between E_a^{dis} and E_a^{as} can be written as

$$\Delta E=E_a^{\text{as}}-E_a^{\text{dis}}=E_{A+B}^{\text{FS}}-E_{AB}, \tag{4}$$

where E_{AB} is the AB bonding energy in the gas phase. Substituting (3) into (4), the dissociation barrier is

$$E_a^{\text{dis}}=E_a^{\text{as}}+E_{AB}-E_A^{\text{FS}}-E_B^{\text{FS}}+E_{\text{int}}^{\text{FS}}.$$

As discussed earlier, $E_{\text{int}}^{\text{FS}}$ is usually very small due to the large separation of two adsorbates A and B. Thus,

$$E_a^{\text{dis}}=E_a^{\text{as}}+E_{AB}-E_A^{\text{FS}}-E_B^{\text{FS}}. \tag{5}$$

Equation (5) shows that for the dissociation of molecule AB on a catalyst, its dissociation barrier depends on the association barrier as well as the total chemisorption energy of A and B at the FS (ΣE_X^{FS}, where $X=$A,B).

To further understand each term in Eq. (5), we have systematically investigated CO dissociation on Ru(0001), Rh(111), Pd(111)(4d), and Os(0001), Ir(111), Pt(111)(5d), using density function theory. Calculation details are described in Refs. 14–18. Transition states of all reactions were searched by constraining the C–O distance, using the so-called constrained minimization technique.[9,15,16] The TS is identified when (*i*) the force on the atoms vanishes and (*ii*) the energy is a maximum along the reaction coordinate, but a minimum with respect to all remaining degrees of freedom.

[a)]Author to whom correspondence should be addressed. Electronic mail: p.hu@qub.ac.uk
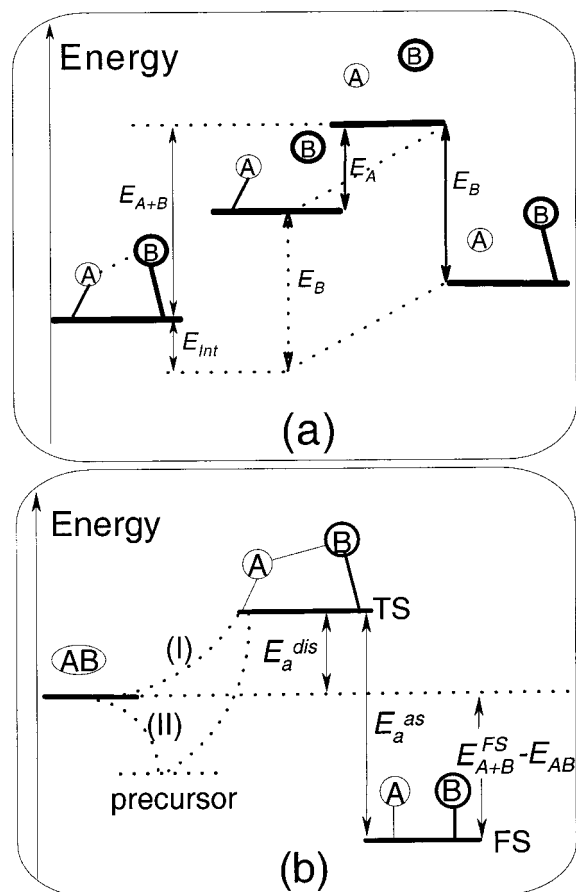
FIG. 1. (a) The energy diagram of a co-adsorption system of A and B. (b) The energy diagram of the dissociation of molecule AB. (I) and (II) are direct and precursor-mediated dissociation, respectively. All the terms are defined in the text.

The lowest energy TSs for CO dissociation on different transition metal surfaces have been shown in Fig. 2 and their structural parameters are listed in Table I. Although all the metal surfaces investigated are close packed, it can be seen
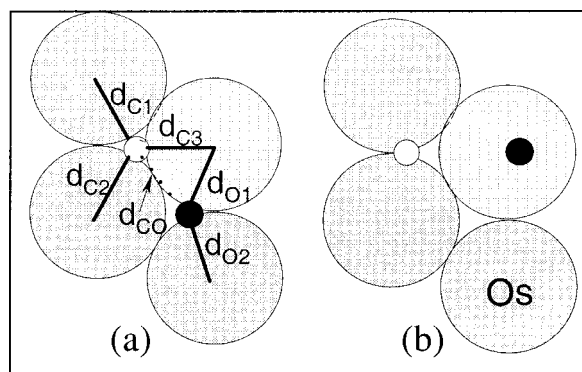

FIG. 2. The lowest energy TS structures for CO dissociation on $4d$ and $5d$ transition metals. The big circles are the metal atoms and the hatched one is the surface atom that bonds with the C and the O simultaneously. The small white circle is the C atom and the small black one is the O atom. (a) Illustrates the TSs on all the metals except Os(0001). (b) Shows the TS on Os(0001). Bond distances between the C and three nearest metal atoms are labeled as d_{C1}, d_{C2} and d_{C3}, respectively. Bond distances between the O and two nearest metal atoms are labeled as d_{O1} and d_{O2}, respectively. The distance between the C and the O is labeled as d_{CO}. They are listed in Table I.

TABLE I. Structural parameters of the TSs for CO dissociations on $4d$ and $5d$ transition metals. d_{C1}, d_{C2}, d_{C3}, d_{O1}, d_{O2}, and d_{CO} are labeled in Fig. 2. The unit of distance is Å.

	d_{C1}	d_{C2}	d_{C3}	d_{O1}	d_{O2}	d_{CO}
Ru	1.970	1.901	1.950	2.084	2.151	1.838
Rh	1.921	1.909	1.954	2.094	2.066	1.897
Pd	1.883	1.987	1.942	2.095	2.010	2.007
Os	1.901	1.900	2.434	1.821	3.275	2.253
Ir	2.064	1.905	2.000	2.060	2.278	1.870
Pt	2.139	1.893	1.987	2.110	2.133	1.930

that the TS structures can be quite different, especially in CO dissociation on Os(0001). Nevertheless, there are obvious common features at the TSs: (1) long stretched distance between the C and the O at the TSs (Table I), which are usually called ''late TSs,'' and (2) sharing of bonding with a metal atom between the C and the O (Fig. 2), implying the existence of bonding competition effect. Our TS geometry on Pt(111) is qualitatively consistent with the estimation from previous work.[5] All the reaction barriers and each term in Eq. (5) have been determined and are shown in Table II.

It can be seen that E_a^{dis} vary considerably from 0.55 to 2.21 eV on these metals (Table II), but there is a correlation between E_a^{dis} and ΣE_X^{FS} in each row of the periodic table investigated. This appears to be evident by the linear regression fitting E_a^{dis} against ΣE_X^{FS} (for $4d$ and $5d$ metals), shown in Fig. 3. For $4d$ metals, we obtain $E_a^{dis} = -0.98\Sigma E_X^{FS} + 12.98$ while for $5d$ it is $E_a^{dis} = -1.35\Sigma E_X^{FS} + 17.30$. A similar phenomenon has been observed by Hammer for NO dissociation.[4] Hammer suggested that the apparent long distance between N and O atoms at the TS is the reason for the linear relationship (TSs behave like FSs). In fact, these results can be qualitatively explained using Eq. (5). Apparently, the slope for $4d$ metals (-0.98) agrees well with the theoretical prediction (-1) of Eq. (5) assuming that E_a^{as} is constant. On the other hand, the slope of -1.35 for $5d$ metals is substantially lower than -1, indicating that E_a^{as} varies in an opposite trend with ΣE_X^{FS}. As can be seen in Table II, on going from left to right in $5d$ metals of the periodic table, E_a^{as} increases just in contrast to ΣE_X^{FS}. It is this variation of E_a^{as} that lowers the slope of a $5d$ metal curve to -1.35. In

TABLE II. The energy components of CO dissociations on $4d$ and $5d$ transition metal surfaces. ΣE_X^{FS}, E_{int}^0, E_a^{as} and E_a^{dis} are defined in the text. The energy unit is eV.

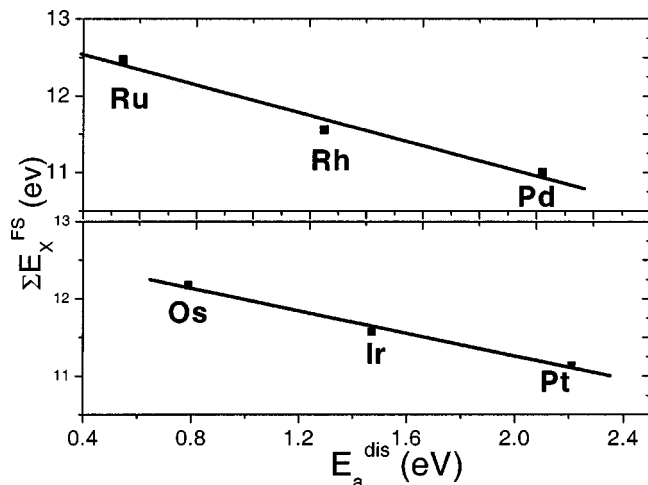|	CO→C+O		
$4d$	Ru(0001)	Rh(111)	Pd(111)
ΣE_X^{FS}	12.47	11.56	11.00
E_{int}^0	0.36	0.65	1.13
E_a^{as}	**1.87**	**1.59**	**1.79**
E_a^{dis}	**0.55**	**1.25**	**2.03**
$5d$	Os(0001)	Ir(111)	Pt(111)
ΣE_X^{ES}	12.18	11.58	11.14
E_{int}^0	0.27	0.45	1.11
E_a^{as}	**1.74**	**1.82**	**2.12**
E_a^{dis}	**0.79**	**1.47**	**2.21**

FIG. 3. ΣE_x^{FS} vs E_a^{dis} on $4d$ and $5d$ metal surfaces for CO dissociations.

fact, even for $4d$ metals E_a^{as} is not constant either. The E_a^{as} on Rh is about 0.2 eV lower than that on Ru and Pd, resulting in the point of Rh being slightly away from the linear line ($E_a^{dis} = -0.98\Sigma E_X^{FS} + 12.98$) for $4d$ metals. Nevertheless, the changes in E_a^{as} are much less pronounced than that in ΣE_X^{FS}, leading to the apparent linear relationship between the dissociation barrier and the FS chemisorption energy.[19] In other words, to a large extent the dissociation reaction barrier is determined by the FS atomic chemisorption energy for these systems. This is consistent with the empirical Bronsted–Polanyi relationship, which indicates the change in reaction barrier can be correlated with the change in the heat of reaction as long as the reaction mechanism is unchanged.[20] It should be stressed that the Bronsted–Polanyi relationship is only qualitatively correct because E_a^{dis} not only depends on ΣE_X^{FS}, but also is related to the E_a^{as} [Eq. (5)]. As shown in Table II for CO dissociation on all the close-packed metal surfaces investigated, even with the same reaction mechanism E_a^{as} is not constant and hence the relationship between E_a^{dis} and ΣE_X^{FS} is not exactly linear.

Since the dissociation barrier also depends on the association barrier [Eq. (5)], it is worth discussing the origin of the association barrier. Using Eqs. (2) and (3), we can write E_a^{as} as

$$E_a^{as} = E_{A+B}^{FS} - E_{A+B}^{TS} = \Delta E_A + \Delta E_B + \Delta E_{int}, \qquad (6)$$

where $\Delta E_A = E_A^{FS} - E_A^{TS}$; $\Delta E_B = E_B^{FS} - E_B^{TS}$, and $\Delta E_{int} = E_{int}^{TS} - E_{int}^{FS} \approx E_{int}^{TS}$. Obviously, all three terms strongly depend on the TS geometry. $\Delta E_A(\Delta E_B)$ is further related to the chemisorption energy of A (B) at the FS.[21] As E_A^{FS} and E_B^{FS} increase, ΔE_A and ΔE_B should increase. E_{int}^{TS} measures the bonding competition effect at the TS geometry, which is metal dependent. To screen off the TS geometry effect on E_{int}^{TS}, and then to estimate the quantitative trend of bonding competition effect on different metals, we performed the following calculations: (i) optimizing the C and the O in a separate $p(2 \times 2)$ unit cell (both at hcp hollow sites), respectively, and calculating their chemisorption energies, namely E_C and E_O; and (ii) calculating the total chemisorption energy, E_{C+O}, of a C and O coadsorption, in which the C is at

a hcp hollow site and the O at the neighboring hcp site[22] (thus they share bonding with metal atoms) and both are fixed in structure (i). Then we define $E_{int}^0 = E_C + E_O - E_{C+O}$ as the *standard interaction energy*. All E_{int}^0 are listed in Table II. It can be seen that as the metal d occupancy increases (from left to right in the periodic table), E_{int}^0 is increased. In contrast, ΣE_X^{FS} is reduced with the increase of d occupancy[4] (Table II). Therefore, it is these two opposite trends that result in the overall small change in E_a^{as} [Eq. (6)] compared with that in E_a^{dis}. For example, for $5d$ metals the change in E_a^{as} is 0.38 eV (larger than $4d$ metals), while the change in E_a^{dis} is higher up to 1.41 eV (Table II). It should be noted that the above discussion of bonding competition effect and ΣE_X^{FS} is based on the fact that the reactions studied here possess late TSs. In this case, it is the bonding competition effect, not the bonding and antibonding states between the C and the O, that greatly influences the E_{int}^{TS}.

Based on the understanding presented here, we can explain many observations for dissociation reactions. For example, the two important factors that affect the dissociation barrier, namely the electronic and geometrical factors,[23] can be rationalized within the present model. The electronic effect on the dissociation barrier, i.e., the increase of the dissociation barrier from left to right in the periodic table, mainly results from the variation of ΣE_X^{FS}, as shown in Fig. 2. This chemisorpion energy trend also affects E_a^{as} and finally affects E_a^{dis}, but to a much less extent for systems with late TSs. The geometrical effect on the dissociation barriers, i.e., lower dissociation barriers on steps,[6] kinks, and defects than that on terraces,[4] is mainly a consequence of change in E_a^{as}, particularly in E_{int}^{TS}. On these corrugated surfaces, the reaction can achieve such TS structures that two reactants do not share bonding with metal atoms (the dissociation path has been changed at the corrugated surfaces). As a result, the bonding competition between the two reactants is small at the TSs, resulting in a small $\Delta E_{int}(E_{int}^{TS})$. Thus, the association barriers, E_a^{as}, will be small [Eq. (6)], leading to finally lower dissociation barriers.

It is worth mentioning the effect of AB bonding energy in the gas phase, E_{AB}, on the dissociation barrier. It can be seen in Eq. (5) that the higher the E_{AB} is, the larger the dissociation barrier, which is obvious from chemical intuition. What is not apparent is whether a dissociation reaction should be a nonactivated one (no dissociation barrier) or an activated one and whether a dissociation reaction should occur through the precursor-mediated mechanism (molecules adsorb molecularly first and then dissociate). The present model can provide some clues to the answers to these questions. In Eq. (5), if $E_a^{as} + E_{AB} > \Sigma E_x^{FS}$, the reaction is certainly an activated process; if $E_a^{as} + E_{AB} < \Sigma E_x^{FS}$, then the reaction would occur without a barrier (nonactivated), otherwise the reaction should follow a precursor-mediated mechanism [Fig. 1(b)].

In summary, this work represents one of the first attempts to generalize a model for dissociation barriers. Specifically, a model to connect the dissociation barrier to the association barrier, chemisorption energies at the FS, and the bonding energy of the molecule is proposed. Using the present model many observations can be rationalized.

[1] G. R. Darling and S. Holloway, Rep. Prog. Phys. **58**, 1595 (1995).

[2] J. Harris and S. Andersson, Phys. Rev. Lett. **55**, 1583 (1985).

[3] B. Hammer and J. K. Norskov, Surf. Sci. **343**, 211 (1995).

[4] B. Hammer and J. K. Norskov, Adv. Catal. **45**, 71 (2000).

[5] Y. Morikawa, J. J. Mortensen, B. Hammer, and J. K. Norskov, Surf. Sci. **386**, 67 (1997).

[6] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Tornqvist, and J. K. Norskov, Phys. Rev. Lett. **83**, 1814 (1999).

[7] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surface* (Interscience, New York, 1996).

[8] A similar equation was used by Hammer as follows, $E_{ts}=E_{rebond}+E_{int}$ in B. Hammer, Phys. Rev. Lett. **83**, 3681 (1999); B. Hammer, Surf. Sci. **459**, 323 (2000).

[9] A. Alavi, P. Hu, T. Deutsch, P. L. Silverstrelli, and J. Hutter, Phys. Rev. Lett. **80**, 3650 (1998).

[10] K. Bleakley and P. Hu, J. Am. Chem. Soc. **121**, 7644 (1999).

[11] J. J. Mortensen, B. Hammer, and J. K. Norskov, Surf. Sci. **414**, 315 (1998).

[12] C. J. Zhang, P. Hu, and M.-H. Lee, Surf. Sci. **432**, 305 (1999).

[13] E_{int} may contain other terms, such as the Pauli repulsion. The Pauli repulsion contribution to E_{int} is important only when A and B are very close (Ref. 11). For the systems concerned in this communication, the distances between A and B are usually large. In addition, the distances between A and B at the TSs determined in this study are similar. Therefore, one may expect that the Pauli repulsion contribution to E_{int} will not change dramatically from one system to another. In other words, the Pauli repulsion will not considerably affect the reactivity difference for the systems investigated in this study.

[14] A generalized gradient approximation was utilized in all the calculations (Ref. 17). The electronic wave functions were expanded in a plane wave basis set and the ionic cores were described by ultrasoft pseudopotentials (Ref. 18). Ru(0001), Rh(111), Pd(111), Os(0001), Ir(111), and Pt(111) were modeled by three layers slabs with all layers fixed at their bulk positions. The surface relaxation was checked and found to be rather small (less than 0.1 eV). The vacuum region between slabs was 10 Å and a cutoff energy of 340 eV was used. $3\times3\times1\mathbf{k}$ point sampling for $p(2\times2)$ unit cell and $3\times2\times1\mathbf{k}$ point sampling for $p(2\times3)$ unit cell have been used in calculations. Convergence check has been performed by increasing $\mathbf{k}$ point sampling up to $4\times4\times1$ for $p(2\times2)$ slab and $3\times3\times1$ for $p(2\times3)$ slab. Previous work (Refs. 15 and 16) also show that this setup affords enough accuracy. All the total energy calculations were performed using CASTEP [M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992)].

[15] A. Michaelides and P. Hu, J. Am. Chem. Soc. **122**, 9866 (2000).

[16] C. J. Zhang and P. Hu, J. Am. Chem. Soc. **122**, 2134 (2000).

[17] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedeson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[18] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[19] The effect of the approximate linear relationship between E_a^{dis} and ΣE_X^{FS} with a slope around -1 is quite dramatic in some sense. For instance, if ΣE_X^{FS} lowers down by 0.5 eV, then the barrier will increase by 0.5 eV [such chemisorption energy difference can be easily achieved if sulphur sits at the neighboring site of reaction center (Refs. 11 and 12)]. Thus a little sulphur addition should suppress the local reactivity of metal surface. The same explanation is also applicable for the self-poisoning phenomenon (coverage effect), in which as the coverage of the fragments increases, the dissociation reaction rate decreases quickly due to the considerable decrease in ΣE_X^{FS}.

[20] See, e.g., R. A. van Santen and M. Neurock, Catal. Rev. Sci. Eng. **37**, 557 (1995).

[21] E_A^{TS} can be approximated as $E_A^{TS}=E_0 f(r_0-r^{TS})$, where E_0 is the chemisorption energy of A at the optimized position, r_0, and r^{TS} is the TS position of A which is near r_0. Usually $E_0=E_A^{FS}$, thus $\Delta E_A=E_A^{FS}-E_A^{TS}=E_A^{FS}[1-f(r_0-r^{TS})]$.

[22] E_{int}^0, which is a measure of the bonding competition effect, depends mainly on how two adsorbates sharing bonding with the top layer metal atoms. Metal atoms in the second layer have little effect on E_{int}^0. For example, E_{int}^0 for C on a hcp site and O on a neighboring hcp site on Pt(111) is calculated as 1.10 eV (Table II), which is very similar to that for C on a hcp site and O on a neighboring fcc site (1.19 eV).

[23] A. Logadottir, T. H. Rod, J. K. Norskov, B. Hammer, S. Dahl, and C. J. H. Jacobsen, J. Catal. **197**, 229 (2001).