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## Chemisorption Theory: In Search of the Elephant

EVGENY SHUSTOROVICH

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Chemisorption deals with atomic and molecular processes on solid surfaces with interaction energies of regular chemical bonds. For transition-metal surfaces, the metal-adsorbate binding energies, measured as heats of chemisorption  $Q$ , typically fall in the range  $Q = 10\text{--}150$  kcal/mol.<sup>1</sup> Studies of chemisorption have become the central part of modern surface science.<sup>1-7</sup> The reasons for this are both intellectual and practical. The intellectual challenge stems from the fact that many fundamental issues of chemisorption remain open, frustrating current theoretical constructs.<sup>3-7</sup> The practical importance of chemisorption is that it sets the stage where various scenarios of heterogeneous chemical reactions, including most industrial catalytic processes, are played.<sup>1,2</sup> Understanding of chemisorption is a prerequisite for understanding of surface chemistry and heterogeneous catalysis.

Understanding means theory, and theoretical thinking is thinking by model structures. Historically, most theoretical modeling of chemisorption bonding was and is made on small metal clusters geometrically resembling a tiny piece of a metal surface, where an adspecies is treated as a ligand.<sup>3-5</sup> More recently, straightforward band-structure calculations of chemisorption on model metal slabs have begun to appear.<sup>4,8</sup> However, the premises of quantum chemistry of metal clusters and quantum physics of bulk metals are so different that they stubbornly resist being fused into a conceptually coherent framework.<sup>9</sup> At present there is no unified, or just generally accepted, theory of chemisorption, but

a variety of competing approaches developed to describe separate aspects of chemisorption.<sup>3-6,10</sup>

The main purpose of theory is to interrelate entities, and not to simply describe them. As an old story goes, six blind men described an elephant as a wall, a fan, a spear, a snake, a tree, and a rope (Figure 1a), depending on what part of the animal they had touched. This favorite story of theoretical folklore reminds us what can happen when one describes seemingly disparate

(1) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.

(2) King, D. A.; Woodruff, D. P., Eds. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; Elsevier: Amsterdam, Vol. 2, 1983; Vol. 3, 1984; Vol. 4, 1982.

(3) Rhodin, T. N.; Ertl, G., Eds. *The Nature of the Chemical Bond*; North-Holland: Amsterdam, 1979.

(4) Smith, J. R., Ed. *Theory of Chemisorption*; Springer-Verlag: West Berlin, 1980.

(5) Veillard, A., Ed. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; NATO ASI Series; Reidel: Dordrecht, 1986.

(6) Shustorovich, E.; Baetzold, R. C.; Muetterties, E. L. *J. Phys. Chem.* 1983, 87, 1100.

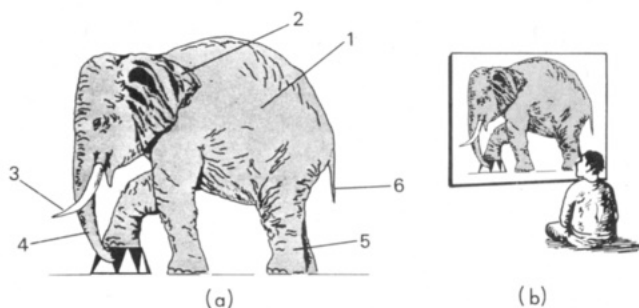
(7) Shustorovich, E. *Surf. Sci. Rep.* 1986, 6, 1.

(8) See, for instance: (a) Arlinghaus, F. J.; Gay, J. G.; Smith, J. R. In ref 4, Chapter 4. (b) Feibelman, P. J. *Phys. Rev. B* 1987, 35, 2626. (c) Soukiasian, P.; Rivan, R.; Lecant, J.; Wimmer, E.; Chubb, S. R.; Freeman, A. J. *Phys. Rev. B* 1985, 31, 4911. (d) Freeman, A. T.; Fu, C. L.; Wimmer, E. *J. Vac. Sci. Technol., A* 1986, 4, 1265. (e) Krakauer, H.; Freeman, A. J.; Wimmer, E. *Phys. Rev. B* 1983, 28, 610. (f) Umrigar, C.; Wilkins, J. M. *Phys. Rev. Lett.* 1985, 54, 1551. (g) Feibelman, P. J.; Hamann, D. R. *Surf. Sci.* 1985, 149, 48. (h) Hamann, D. R. *Bull. Am. Phys. Soc.* 1978, 23, 364. (i) Kleinman, L. *Phys. Rev. B* 1981, 25, 4960. (j) Bilander, D. M.; Kleinman, L. *Phys. Rev. B* 1983, 28, 5231. (k) Lang, N. D.; Kohn, W. *Phys. Rev. B* 1970, 1, 4555; 1971, 3, 1215. (l) Lang, N. D.; Williams, A. R. *Phys. Rev. B* 1978, 18, 616. (m) Norskov, J. K. *Phys. Rev. B* 1982, 26, 1583. (n) Norskov, J. K.; Holloway, S.; Lang, N. D. *Surf. Sci.* 1984, 137, 65. (o) Baetzold, R. C. *J. Am. Chem. Soc.* 1983, 105, 781. (p) Baetzold, R. C. *Phys. Rev. B* 1984, 29, 4211; 30, 6870. (q) Baetzold, R. C. *Surf. Sci.* 1985, 150, 193. (r) Baetzold, R. C. *J. Chem. Phys.* 1985, 82, 5729. (s) Baetzold, R. C. *Langmuir* 1987, 3, 189.

(9) Currently, Roald Hoffmann (private communication) is trying to bridge the cluster- and band-structure approaches via his crystal orbital overlap population (COOP) technique. Let us hope he will succeed.

(10) For an excellent analysis of theoretical issues in chemisorption, see: Einstein, T. L.; Hertz, J. A.; Schrieffer, J. R. In ref 4, Chapter 7.

Evgeny Shustorovich was born in Moscow, USSR, and graduated from the Moscow Institute of Fine Chemical Technology in 1956 as an engineer and synthetic organic chemist. He received his Ph.D. in Quantum Chemistry from the Institute of Chemical Physics, Academy of Sciences, USSR, in 1960 and his Dr.Sci. in Physical Chemistry from the Institute of Organoelement Compounds, Academy of Sciences, USSR, in 1967. After immigrating to the U.S. in 1977, he worked at Cornell University with Roald Hoffmann and then in 1979 joined the Eastman Kodak Co. in Rochester, NY. His current research interests are in the area of theory of chemisorption and heterogeneous catalysis.



**Figure 1.** (a) An elephant according to six blind men: (1) wall; (2) fan; (3) spear; (4) snake; (5) tree; (6) rope. (b) Theorist's dream: the elephant model (from ref 7).

phenomena without understanding how they interrelate as parts of the whole. Whenever the theorist contemplates experimental puzzles, he always dreams of recognizing their elephant features (Figure 1b). The search for the elephant is the most exciting game the theorist can play.

Given the slow progress of quantum-mechanical models of chemisorption, a practical alternative appears to be phenomenological modeling. Critical here is the choice of basic assumptions and mathematical formalism. As Einstein put it, nature is the realization of the simplest conceivable mathematical ideas, and the creativity of modeling resides in mathematics. We are free to set rules of the game but the rules must be rigid: it is their rigidity alone that makes the game possible. Below we will describe such a phenomenological approach to an elephant model of chemisorption. It is based on bond-order conservation (BOC) and makes use of Morse potentials (MP). This BOC-MP model<sup>7,11,12</sup> explicitly interrelates a variety of chemisorption phenomena such that all the interrelations are expressed in terms of observables only—the heats of chemisorption and various constants (thermodynamic, structural, numerical, etc.). The scope of the model includes the preferred adsorbate sites,<sup>11a,d</sup> the activation barriers for adsorbate migration,<sup>11a,d</sup> dissociation,<sup>11b,f</sup> and recombination,<sup>11f</sup> various coverage and coadsorption effects such as overlayer phase transitions and island formation,<sup>11c</sup> and promotion and poisoning,<sup>11e</sup> as well as total energy profiles of various surface reactions.<sup>12</sup>

The aim of this Account is to give a flavor of the BOC-MP modeling, its formalism, and major applications. We will concentrate on issues of general interest and on conclusions that are analytically straightforward and experimentally well tested. For the rest of the story and all details, the reader is referred to the original publications.<sup>7,11,12</sup>

### BOC-MP Model of Chemisorption

**The Game and Its Rules.** We consider chemisorption of an adsorbate X, atomic A or molecular AB, on transition-metal M surfaces. High coordination of the M atoms (up to 12 nearest neighbors in the close-packed lattices such as fcc and hcp) makes the M-M and M-A forces quasi-spherical when the total energy  $E$  depends

on the bond distance  $r$  only. Here the main supportive arguments are the following: (i) Both transition and simple  $s^1$  (1A and 1B group) metals have the same densely packed (hcp, fcc, bcc) crystal lattices.<sup>1</sup> (ii) The d-orbital anisotropy is averaged out and for many purposes, the d band may be effectively represented by a degenerate s-type band.<sup>13</sup> (iii) For various cases of transition and simple metallic binding, including chemisorption, there exists an apparently universal relation between  $E$  and  $r$ .<sup>13a,14</sup>

Migration and dissociation of an adsorbate X involve changes in its coordination mode  $M_n-X$  (where  $n$  is the coordination number) and in the M-X distances  $r$  accompanied by changes in the  $M_n-X$  total energy  $E$ . To describe these processes, one should use a model potential relating  $E$  to  $r$  or some convenient function of  $r$ , for example, the two-center M-A bond order  $x$

$$x = \exp[-(r - r_0)/a] \quad (1)$$

which is an exponential function of the M-A distance  $r$  ( $r_0$  and  $a$  are constants). The possible chemisorption sites should correspond to the total energy  $E$  minima so that the model potential must include both attractive and repulsive forces. For two-center interactions, the simplest general potential of this kind is the Morse potential,<sup>15</sup> including only linear and quadratic terms in  $x$ , namely

$$E(x) = -Q(x) = -Q_0(2x - x^2) \quad (2)$$

where  $Q_0$  is the M-A equilibrium bond energy. The total energy  $E(x)$  (eq 2) has only one minimum at the equilibrium distance  $r_0$  when the bond order  $x = 1$ , by definition (eq 1).

Now the question is how to describe many-center  $M_n-A$  interactions in the Morse-type fashion. The simplest scheme is pairwise additivity of all the two-center M-A contributions to  $Q$  and  $x$ , namely

$$Q_n = \sum_{i=1}^n Q_i \quad (3)$$

and

$$x_n = \sum_{i=1}^n x_i \quad (4)$$

Here the simplest way to proceed is to keep the Morse parameters ( $Q_0$ ,  $r_0$ ,  $a$ ) the same for both the isolated M-A bond and each additive M-A contribution within  $M_n-A$  so that these contributions would differ by their bond orders  $x_i$  ( $i = 1, 2, \dots, n$ ) only. Experimentally,  $Q_n$  increases less than linearly with  $n$

$$Q_0 < Q_n < nQ_0, \quad n > 1 \quad (5)$$

which requires imposing some constraints on the allowed values of  $x_i < 1$  (if  $x_i = 1$ , then  $Q_n = nQ_0$ ). The simplest assumption is that the total bond order  $x$  (eq 4) does not change with  $n$ ; namely,  $x$  is conserved and normalized to unity

$$x = \sum_{i=1}^n x_i = x_0 = 1 \quad (4')$$

(11) (a) Shustorovich, E. *J. Am. Chem. Soc.* **1984**, *106*, 6479. (b) Shustorovich, E. *Surf. Sci.* **1985**, *150*, L115. (c) Shustorovich, E. *Surf. Sci.* **1985**, *163*, L645. (d) Shustorovich, E. *Surf. Sci.* **1985**, *163*, L730. (e) Shustorovich, E. *Surf. Sci.* **1986**, *175*, 561. (f) Shustorovich, E. *Surf. Sci.* **1986**, *176*, L863. (g) Shustorovich, E. *Surf. Sci.* **1987**, *181*, L205. (h) Shustorovich, E. *Surf. Sci.* **1987**, *187*, L627.

(12) Shustorovich, E.; Bell, A. T. *J. Catal.*, in press.

(13) See, for instance: (a) Abel, G. C. *Phys. Rev. B* **1985**, *31*, 6184. (b) Skriver, H. L. *Phys. Rev. B* **1985**, *31*, 1909. (c) Haydock, R. *Philos. Mag.* **1977**, *35*, 845; **1978**, *38*, 155.

(14) (a) Rose, J. H.; Smith, J. R.; Ferrante, J. *Phys. Rev. B* **1983**, *28*, 1835. (b) Rose, J. H.; Smith, J. R.; Guinea, F.; Ferrante, J. *Phys. Rev. B* **1984**, *29*, 2963. (c) Ferrante, J.; Smith, J. R. *Phys. Rev. B* **1985**, *31*, 3427.

(15) Morse, P. M. *Phys. Rev.* **1929**, *34*, 57.

for any  $n \geq 1$  (cf. eq 1). The BOC at unity in its pairwise additive form is our major model assumption. For various linear three-center A...B...C interactions, such a form ( $x_{AB} + x_{BC} = 1$ ) was already assumed<sup>16</sup> and shown to be very accurate, both computationally<sup>17</sup> and experimentally.<sup>18</sup> In a sense, we simply postulate the similar BOC for many-center  $M_n$ -A (spherical) interactions. Within the BOC framework, Morse potentials prove to be very efficient to describe the energetics of chemisorption, which ultimately originates from the zero-energy gap between the occupied and vacant parts of the metal band.<sup>11g</sup>

The last question concerns the values of  $n$  in  $M_n$ -A. The simplest assumption is to limit  $n$  to nearest-neighbor metal atoms. For instance, for A/fcc(100), the maximum  $n = 4$  can be reached in the hollow site but  $n = 2$  and 1 in the two-fold bridge and on-top sites, respectively. The last assumption reflects the known efficiency of the nearest-neighbor approximation in many problems of metallic binding.<sup>10,13a</sup>

In summary, our model assumptions are as follows:

(1) Each two-center M-A interaction is described by the Morse potential (eq 1 and 2).

(2) For a given  $M_n$ -A,  $n$  two-center M-A interactions are additive.

(3) Along a migration path up to dissociation, the total  $M_n$ -X bond order is conserved and normalized to unity. (The analytic form of BOC depends on X; namely, eq 4' for adatoms X = A or eq 8 for ad molecules X = AB.)

(4) For a given  $M_n$ -A,  $n$  is limited to nearest neighbors.

Assumptions 1-4 are the rules of the game. They are the simplest logical possibilities.<sup>19</sup> The rest is straightforward algebra. The most definitive results have been obtained for chemisorption on flat symmetric surfaces with a regular unit mesh  $M_n$ , say, an equilateral triangle  $M_3$  for fcc(111) or hcp(001), a square  $M_4$  for fcc(100), etc. Consider the major findings.

### Heats of Chemisorption and Activation Barriers

**Atomic Chemisorption.** We begin with atomic chemisorption where at low adsorbate coverages the model interrelations are exact. The  $M_n$ -A bond energy  $Q_n$  monotonically increases with  $n$  as

$$Q_A = Q_n = Q_{0A}(2 - 1/n) \quad (6)$$

where  $Q_{0A}$  is the maximum M-A two-center bond energy (cf. eq 2). The value of  $Q_n$  reaches the absolute

(16) (a) Johnston, H. S.; Parr, C. *J. Am. Chem. Soc.* **1963**, *85*, 2544. (b) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(17) See, for instance: (a) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7692, 7694. (b) Dunning, T. H., Jr.; Harding, L. B.; Bair, R. A.; Eades, R. A.; Shepard, R. L. *J. Phys. Chem.* **1986**, *90*, 344.

(18) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, NY, 1979; pp 341-360.

(19) Another version of bond-order conservation, known as the bond-energy/bond-order (BEBO) method, has been applied to chemisorption bonding and surface reactivity by Weinberg and Merrill (Weinberg, W. H.; Merrill, R. P. *J. Vac. Sci. Technol.* **1973**, *10*, 89; *Surf. Sci.* **1972**, *33*, 493; **1973**, *39*, 206; **1974**, *41*, 312; *J. Catal.* **1973**, *28*, 459; **1975**, *40*, 268). The basic assumptions and mathematical formalism of the BOC-MP and BEBO methods are quite different, however. Most important, in the BEBO method, following Lewis and Pauling, the bond order  $x$  is defined as the number of shared electron pairs, so that  $x$  may be smaller than, equal to, or larger than unity, reflecting fractional, single, or multiple A-B bonding, respectively. Furthermore, the BEBO method makes use of the power function  $E(x) = -Qx^p$ , where  $p$  is some empirical constant.

maximum in the hollow  $n$ -fold site so that the observed heat of atomic chemisorption  $Q_A$  can be identified with  $Q_n$ . The immediate conclusion from eq 6 is that on flat symmetric surfaces, adatoms will always prefer the highest coordination sites in the hollow depressions. Indeed, on surfaces in question, adatoms as varied as H, C, N, O, S, Se, Te, P, As, F, Cl, Br, and I, as well as Na and Cd, have been invariably found in the hollow sites of maximum coordination.<sup>1,7,20</sup>

From eq 6, it also follows that the energy differences between various hollow sites are very small, typically of the order of several percent, in broad agreement with experiment.<sup>21</sup> (For example, for  $n = 3$ ,  $Q_3 = 1.67Q_0$  and for  $n = 4$ ,  $Q_4 = 1.75Q_0$ ; the anisotropy  $\Delta Q/Q = 0.08/1.67 \approx 0.05$ .) Finally, from eq 6, one can calculate the activation barrier  $\Delta E$  for lateral migration of A. The lowest energy pathway between two adjacent unit meshes  $M_n$  will obviously be hollow  $\rightarrow$  bridge ( $n = 2$ )  $\rightarrow$  hollow, where the barrier  $\Delta E_n$  is the energy difference  $Q_n - Q_2$ ; that is

$$\Delta E_n = \frac{n-2}{4n-2} Q_n \quad (7)$$

In other words, the migration barrier  $\Delta E_n$  linearly depends on  $Q_n$  and the coefficient  $k = (n-2)/(4n-2)$  is a structural constant. For  $n = 3-5$ , the theoretical values of  $k$  fall within the narrow range  $k = 0.10-0.17$ , in excellent agreement with experiment, in particular for adatoms H, O, N, C, and S on various W, Pt, and Ni surfaces.<sup>22</sup>

**Molecular Chemisorption.** Now we turn to the more complex and interesting case of molecular AB chemisorption. Here, BOC for  $M_n$ -AB reads as

$$\sum_{i=1}^n (x_{Ai} + x_{Bi}) + x_{AB,n} = 1 \quad (8)$$

which, unlike eq 4' for  $M_n$ -A, depends on the nature of the adsorbate AB. The most important model conclusion is that the heat of molecular  $M_n$ -AB chemisorption  $Q_{AB}$  is *not* an independent quantity but relates to heats of chemisorption of the coordinated atoms ( $Q_A$  and  $Q_B$ ) and the A-B gas-phase dissociation energy  $D_{AB}$ . The simplest case corresponds to AB perpendicular to a surface with the A end down when, to first approximation, the  $M_n$ -B bond order can be neglected ( $x_{Bi} = 0$  in eq 8). For the on-top coordination M-A-B, we then have

$$Q_{AB} \leq \frac{Q_{0A}^2}{Q_{0A} + D_{AB}} \quad (9)$$

where the inequality sign reflects neglect of a small negative contribution from the M-B interaction. In the same approximation, for the  $n$ -fold  $M_n$ -AB coordination, we arrive at

$$Q_{AB,n} \leq \frac{Q_{0A}^2}{(Q_{0A}/n) + D_{AB}} \quad \text{for } D_{AB} > \frac{n-1}{n} Q_{0A} \quad (10)$$

Here, however, the neglected negative  $M_n$ -B contribution is larger in absolute value than the one for M-B so that  $Q_{AB}$  may be either larger or smaller than  $Q_{AB,n}$  and *all* the  $M_n$ -AB chemisorption sites tend to be *close*

(20) (a) Van Hove, M. A. In ref 3, Chapter 4. (b) Somorjai, G. A.; Van Hove, M. A. *Struct. Bonding (Berlin)* **1979**, *38*, 1.

(21) See Table 5 in ref 7.

(22) See Table 6 in ref 7.

Table I  
Initial Heats of Chemisorption  $Q_{AB}$  on Some Close-Packed Metal Surfaces ( $n = 3$ )<sup>a</sup>

surface	coord type	AB	exptl values of			$Q_{AB}$	
			$Q_A$	$Q_B$	$D_{AB}$ <sup>b</sup>	calcd	exptl
Ni(111)	$\eta^1$	CO	171		257	29 <sup>c</sup>	27
Pt(111)	$\eta^1$	NO	116		150	22 <sup>c</sup> -26 <sup>d</sup>	27
Pd(111)	$\eta^1$	NO	130		150	27 <sup>c</sup> -32 <sup>d</sup>	31
Pt(111)	$\eta^1$	NH <sub>3</sub>	116		279	13 <sup>c</sup>	12-15
Ni(111)	$\eta^1$	NH <sub>3</sub>	135		279	18 <sup>c</sup>	20
Pt(111)	$\eta^1$	OH <sub>2</sub>	85		220	11 <sup>c</sup>	12
Pt(111)	$\eta^1$	O=CH <sub>2</sub>	85		176	11 <sup>c</sup>	11
Pt(111)	$\eta^2$	O <sub>2</sub>	85	85	119	11 <sup>e</sup>	9
Ru(001)	$\eta^2$	O=C(CH <sub>3</sub> ) <sub>2</sub>	100	67	179	15 <sup>f</sup>	16
Ni(111)	$\eta^2$	H <sub>2</sub> C=CH <sub>2</sub>	171	171	355	14 <sup>e</sup>	13

<sup>a</sup> See text for notations and ref 7 and 11f for sources of the experimental values of  $Q_A$ ,  $Q_B$ , and  $Q_{AB}$ . All energies in kcal/mol. <sup>b</sup> Reference 31. <sup>c</sup> Equation 9. <sup>d</sup> Equation 10 for  $n = 2$ . <sup>e</sup> Equation 12. <sup>f</sup> Equation 11.

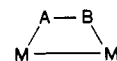
in energy, the approximation  $Q_{AB} \approx Q_{AB,n}$  becoming more accurate the larger the value of  $D_{AB}$ .

A good example is CO with the very large dissociation energy  $D_{CO} = 257$  kcal/mol. Registries of CO have been studied on various flat surfaces of hcp Re, Ru, and Os and fcc Cu, Ag, Au, Ni, Pd, Pt, Ir, and Rh.<sup>23</sup> As ground chemisorption states, the on-top sites are typical but the hollow ( $n = 3$ ) sites are exceptionally rare [and have never been found for  $n > 3$ , say, for fcc(100),  $n = 4$ , or bcc(100),  $n = 5$ ], which is in sharp contrast to the preferred hollow sites for adatoms (see above). The most important pattern, however, is that the energy differences among the on-top, bridge, and hollow sites are so small that at higher coverages and temperatures, some (or all) of these sites may coexist.<sup>23</sup> For example, for CO/Pt(111),  $Q_{CO}$  decreases in the order on-top > bridge > hollow but within  $\Delta Q < 1$  kcal/mol.<sup>24a</sup> Since  $Q_{CO} = 32$  kcal/mol, the differences  $\Delta Q/Q$  do not exceed 3%, which makes all the CO sites on Pt(111) practically isoenergetic. A similar difference of  $\Delta Q < 1$  kcal/mol was found for CO/Ni(100),<sup>25a</sup> CO/Ni(110),<sup>25b</sup> and CO/Ni(111).<sup>26</sup> For CO/Ni(111), the  $Q_{CO}$  order hollow > bridge > on-top<sup>26</sup> is reversed compared with that for CO/Pt(111), which demonstrates the lack of correlation between  $Q_{CO}$  and  $n$ .<sup>27</sup> Because the energy profile of AB migration has several minima corresponding to the values of  $Q_{AB}$  in different coordination sites, the activation barrier  $\Delta E_{AB}$  will be larger than  $\Delta Q_{AB}$  [unlike adatoms, where there is only one (global) minimum and, thus,  $\Delta E = \Delta Q$ ; see eq 7]. For example, for CO/Pt(111),  $\Delta E_{CO} = 7$  kcal/mol<sup>24b</sup> is conspicuously larger than  $\Delta Q_{CO} \leq 1$  kcal/mol.<sup>24a</sup> Thus, for weakly bound molecules like O<sub>2</sub> on stepped surfaces, where the anisotropy  $\Delta Q$  may become comparable with  $Q$ , the migration activation barrier  $\Delta E$  can even exceed  $Q$ , as found, for example, for O<sub>2</sub>/Pt(112).<sup>25c</sup>

From eq 10, it immediately follows that in the upright  $M_n$ -AB geometry AB will be coordinated to  $M_n$  through the atom whose heat of chemisorption is larger, namely,

$M_n$ -A-B if  $Q_A > Q_B$ . For example, since  $Q_A$  increases in the order O < N < C (reflecting the number of unpaired valence electrons), one can predict that monocoordination ( $\eta^1$ ) of CO should always occur via C and NO via N, in full agreement with experiment.<sup>1,23</sup> Some examples of the CO and NO heats of chemisorption are given in Table I. We see that eq 10 gives the values of  $Q_{AB}$  with a typical error 10-15%. The coordinations via oxygen (M-O-C or M-O-N) would have been less favorable by 10-15 kcal/mol.<sup>11d</sup>

If AB is coordinated parallel to a surface, via both A and B (dicoordination  $\eta^2$ ), the bridge mode



appears to be the general prototype with the bonding energy

$$Q_{AB} = \frac{ab(a+b) + D_{AB}(a-b)^2}{ab + D_{AB}(a+b)} \quad (11)$$

where

$$a = Q_{OA}^2(Q_{OA} + 2Q_{OB}) / (Q_{OA} + Q_{OB})^2$$

and

$$b = Q_{OB}^2(Q_{OB} + 2Q_{OA}) / (Q_{OA} + Q_{OB})^2$$

For a homonuclear A<sub>2</sub> ( $a = b = 3/4 Q_{OA}$ ), eq 11 reduces to

$$Q_{A_2} = \frac{9/2 Q_{OA}^2}{3Q_{OA} + 8D_{A_2}} \quad (12)$$

By comparing eq 10 and 11, one can get an idea which coordination,  $\eta^1$  or  $\eta^2$ , is more favorable. Although one should be careful with numbers (since the equations have been obtained in somewhat different approximations), some periodic trends can be discerned. For example, for CO the estimates show<sup>11g</sup> that on late transition metals, the monocoordination  $\eta^1$  (via C) is always preferred, in full agreement with experiment.<sup>23</sup> However, the  $\eta^1$  vs  $\eta^2$  energy differences are not great ( $\Delta Q < 5$  kcal/mol<sup>11f</sup>) and decrease as one traverses from right to left along the transition-metal series so that in the middle of the period, the  $\eta^1$  and  $\eta^2$  energies seem to converge and may even be reversed. This model conclusion is consistent with the recent findings that at low CO coverages the  $\eta^2$  coordination is slightly more favorable than the  $\eta^1$  one for CO/Cr(110),<sup>28</sup> CO/Mo-

(23) For a recent review, see: (a) Hoffmann, F. M. *Surf. Sci. Rep.* 1983, 3, 107. (b) Biberian, J. P.; Van Hove, M. A. *Surf. Sci.* 1982, 118, 443; 1984, 138, 361. (c) Ishi, S.; Ohno, Y.; Viswanathan, B. *Surf. Sci.* 1985, 161, 349.

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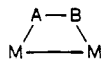
(26) Tang, S. L.; Lee, M. B.; Yang, Q. Y.; Beckerle, J. D.; Ceyer, S. T. *J. Chem. Phys.* 1986, 84, 1876.

(27) However, there is a definitive correlation between  $n$  and the C-O stretching frequency,<sup>23a</sup> which can also be explained by our model.<sup>7,11d</sup>

(28) Shinn, N. D.; Madey, T. E. *J. Chem. Phys.* 1985, 83, 5928.

(100),<sup>29a</sup> and CO/Fe(100).<sup>29b</sup> For O<sub>2</sub>/Pt(111), where O<sub>2</sub> is known to be chemisorbed parallel to a surface, we used eq 12 only. The calculated value  $Q_{O_2} = 11$  kcal/mol agrees well with the experimental value 9 kcal/mol.<sup>30</sup>

In eq 9–12, A and B may be both atoms and atomic groups (quasi-atoms) so that the model can treat not only diatomic but also polyatomic molecules and molecular fragments coordinated via one ( $\eta^1$ ) or two ( $\eta^2$ ) atoms. For example, CH<sub>x</sub> fragments can be treated as a quasi-diatom AB, where B is H<sub>x</sub> and  $D_{CH_x} = 81, 183,$  and  $293$  kcal/mol for  $x = 1, 2,$  and  $3,$  respectively.<sup>31</sup> For the perpendicular coordination  $M_n-CH_x$ , eq 9 and 10 can be applied directly, where  $D_{AB}$  now stands for  $D_{CH_x}$ . For the parallel coordination



eq 11 and 12 can also be used but scaling of the parameters  $a, b,$  and  $D_{AB}$  will now depend on the nature of A and B. For example, if H<sub>2</sub>C=CH<sub>2</sub> is coordinated via both C atoms, then  $A = B = CH_2$ . In this case,  $Q_{0A}$  in eq 12 stands for the atomic carbon value of  $Q_{0C} = Q_C/(2 - 1/n)$  (cf. eq 6) and  $D_{A_2}$  for the total energy of all bonds formed by each C atom; namely,  $D_{A_2} = 355$  kcal/mol.<sup>11g,31</sup> Chemisorption of rather complex admolecules, say, formaldehyde (O=CH<sub>2</sub>), can still be described by eq 11 where  $D_{AB}$  has the meaning of the C=O bond energy (178 kcal/mol<sup>31</sup>) and the parameters  $a$  and  $b$  relate to an atom O and a "quasi-atom" CH<sub>2</sub>, respectively.<sup>11g</sup>

Table I lists some representative data corroborating the application of eq 9–12 to polyatomic molecules. Also, from eq 9–12, it clearly follows that the molecular heat of chemisorption  $Q_{AB}$  rapidly decreases as the gas-phase dissociation (total bond) energy  $D_{AB}$  increases,  $Q_{AB}$  being typically smaller than  $Q_A$  ( $Q_B$ ) by a factor of 5–10 or even 15. For this reason, the periodic changes in  $Q_{AB}$  for molecules such as CO, CH<sub>3</sub>, NH<sub>3</sub>, NO, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> are small and irregular compared with the large and systematic variations in  $Q_A$  observed for the relevant multiple-bonded adatoms A.<sup>6,7</sup>

**Dissociation and Recombination Barriers.** If AB approaches a surface from the gas phase, the activation barrier  $\Delta E^*_{AB,g}$  for dissociation  $AB_g \rightarrow A_s + B_s$  explicitly depends on the chemisorption energies of the (atomic or molecular) fragments,  $Q_A$  and  $Q_B$ ; namely

$$\Delta E^*_{AB,g} = D_{AB} - (Q_A + Q_B) + \frac{Q_A Q_B}{Q_A + Q_B} \quad (13)$$

For homonuclear dissociation  $A_{2,g} \rightarrow A_s + A_s$ , eq 13 simply becomes

$$\Delta E^*_{A_2} = D_{A_2} - \frac{3}{2}Q_A \quad (14)$$

Obviously, the dissociation barrier  $\Delta E_{AB,s}$  from a chemisorbed state will be larger just by the amount of the molecular heat of chemisorption  $Q_{AB}$

$$\Delta E^*_{AB,s} = \Delta E^*_{AB,g} + Q_{AB} \quad (15)$$

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Table II  
Observed Range of  $k$  for A<sub>2</sub> Dissociation<sup>a</sup>

A <sub>2</sub>	surface	exptl values of			$k^b$
		$Q_A$	$D_{A_2}$	$\Delta E^*_{A_2}$	
H <sub>2</sub>	Fe(111)	62	103	~0	1.66
	Ni(111)	63		2	1.60
	Ni(110)	62		~0	1.66
	Cu(100)	58		5	1.69
N <sub>2</sub>	W(110)	155	228	~10	1.41
	Fe(110)	138		8	1.57
	Fe(100)	140		2.5	1.60
	Fe(111)	139		-0.8	1.63
O <sub>2</sub>	Pt(111)	85	119	-1	1.43

<sup>a</sup> See text for notations and Table 11 in ref 7 for sources of the experimental values of  $Q_A, D_{A_2},$  and  $\Delta E^*_{A_2}$ . All energies in kcal/mol. <sup>b</sup> From  $\Delta E^*_{A_2} = D_{A_2} - kQ_A$  (to be compared with the theoretical value  $k = 1.5$  in eq 14).

For the reverse reaction of recombination of chemisorbed A and B, the activation barrier is (cf. eq 13)

$$\Delta E^*_{A-B} = \frac{Q_A Q_B}{Q_A + Q_B} \quad (16)$$

Clearly, if  $Q_A \gg Q_B$ ,  $\Delta E^*_{A-B}$  will be close to  $Q_B$ , the heat of chemisorption of the weaker bound partner. If  $Q_A = Q_B$ , we simply have  $\Delta E^*_{A-A} = \frac{1}{2}Q_A$ .

How do these interrelations fit the experiment? Equation 14 establishes the linear correlation between the dissociation barrier  $\Delta E^*_{A_2}$  and the atomic heat of chemisorption  $Q_A$  with the slope of  $k = \frac{3}{2}$ .<sup>32</sup> As seen from Table II for diatomic molecules H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> dissociated on a variety of metal surfaces (Fe, Ni, Cu, W, Pt, etc.), the experimental values of  $k$  lie within the range  $k = 1.4$ – $1.7$ , i.e., within 10–15% of the theoretical value of  $k = 1.5$ . For heteronuclear molecules AB, both diatomic and triatomic, eq 13 and 16 seem to work well, as illustrated by examples in Table III. In particular, as eq 16 predicts, the recombination barrier  $\Delta E^*_{O-CO}$  is very sensitive to  $Q_{CO}$  but insensitive to  $Q_O$  (since  $Q_O \gg Q_{CO}$ ).

One should add that the activation recombination barrier  $\Delta E^*_{A-B}$  cannot be smaller than  $\Delta H = \Delta H_{AB} - \Delta H_{A+B}$ , the difference between the enthalpies of the reactant AB ( $-\Delta H_{AB} = D_{AB} + Q_{AB}$ ) and the products A and B ( $-\Delta H_{A+B} = Q_A + Q_B$ ). Thus, the BOC barrier (eq 16) is only the *necessary* (minimal energy) condition for recombination, which may be *sufficient* if

$$\frac{Q_A Q_B}{Q_A + Q_B} \geq \Delta H = Q_A + Q_B - D_{AB} - Q_{AB} \quad (17)$$

(but not sufficient if  $Q_A Q_B / (Q_A + Q_B) < \Delta H$ ). The overwhelming majority of admolecules satisfy the criterion of eq 17 and only a few do not, in particular, carbyne (CH) and formyl (HCO).<sup>11h</sup> This dissatisfaction results from the weakness of the forming A–B bond (81 kcal/mol for C–H<sup>31</sup> and a meager 17 kcal/mol for H–CO<sup>31</sup>), which makes the enthalpy factor decisive. In such cases, the recombination barrier may be assumed to be the enthalpy difference,  $\Delta E^*_{A-B} = \Delta H$ .<sup>11h</sup>

**Mapping of Surface Reactions.** We see that the BOC method provides reasonably accurate estimates of the heats of chemisorption  $Q$  and the dissociation and recombination barriers  $\Delta E^*$  for AB molecules and

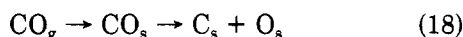
(32) Unlike similar linear relations between the activation barriers and the heats of reactions (Brønsted, Polanyi, Frumkin–Temkin–Semenov, etc.), eq 14 is not a postulate but a rigorous corollary of the general principle (BOC).

Table III  
Dissociation and Recombination Barriers  $\Delta E^*$  for Some Surface Reactions<sup>a</sup>

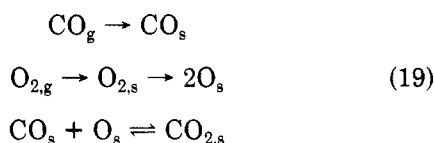
reaction	surface	exptl values of			$\Delta E^*$	
		$D_{AB}$	$Q_A$	$Q_B$	calcd	exptl
$\text{CO}_g \rightarrow \text{C}_s + \text{O}_s$	Ni(111)	257	171	115	40 <sup>b</sup>	30–40 <sup>c</sup>
$\text{CO}_{2,g} \rightarrow \text{CO}_s + \text{O}_s$	Rh(111)	127	32	102	17 <sup>b</sup>	17
$\text{CO}_s + \text{O}_s \rightarrow \text{CO}_{2,g}$	Rh(111)		32	102	24 <sup>d</sup>	27
	Pd(111)		34	87	24 <sup>d</sup>	25
	Pt(111)		32	85	23 <sup>d</sup>	25
	Ag(110)		6.5	60–80	5.8–6.0 <sup>d</sup>	5.3 <sup>e</sup>
	Rh(111)		26	128	22 <sup>d</sup>	21
$\text{NO}_s + \text{N}_s \rightarrow \text{N}_2\text{O}_s^f$	Rh(100)		25	131	21 <sup>d</sup>	21
	Pt(111)		27	116	22 <sup>d</sup>	20

<sup>a</sup> See text for notations and ref 7 and 11f for sources of the experimental values of  $Q_A$ ,  $Q_B$ , and  $\Delta E^*$ . All energies in kcal/mol. <sup>b</sup> Equation 13. <sup>c</sup> Reference 41. <sup>d</sup> Equation 16. <sup>e</sup> Reference 42. <sup>f</sup> Followed by nonactivated decomposition  $\text{N}_2\text{O}_s \rightarrow \text{N}_{2,g} + \text{O}_s$ .

molecular fragments. Combined with the knowledge of the AB total bond (gas-phase dissociation) energies, this allows one to construct potential energy profiles of surface reactions. For example, from the data in Tables I and III, we can immediately describe the reaction profiles of



or



We can go much further and map complex processes, including several competing pathways.

As an example, let us consider hydrogenation of CO over the platinum-group metals. The process shows distinct periodic regularities; namely, methane ( $\text{CH}_4$ ) has been produced on Ni, Pd, and Pt but methanol ( $\text{CH}_3\text{OH}$ ) only on Pd and Pt.<sup>33–40</sup> One can wonder what might be possible pathways for  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  synthesis and how they depend on metal composition. Here, there are two questions of special interest: (i) why the C–O bond cannot be retained on nickel catalysts, and (ii) how does C–O bond cleavage occur, directly from CO or from partially hydrogenated species  $\text{H}_x\text{CO}$  (hydrogen-assisted C–O cleavage)?

We have calculated<sup>12</sup> total energy profiles of conceivable elementary steps leading to  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ . The major results are the following:

For Ni(111), the activation barrier  $\Delta E^*_{\text{CO}_s}$  for direct dissociation  $\text{CO}_s \rightarrow \text{C}_s + \text{O}_s$  is 67 kcal/mol, which corresponds to  $\Delta E^*_{\text{CO}_g} = 40$  kcal/mol, in excellent agreement with the molecular beam estimate of 30–40

kcal/mol.<sup>41</sup> The hydrogen-assisted C–O cleavage  $\text{CO}_s + \text{H}_s \rightarrow \text{HCO}_s \rightarrow \text{COH}_s \rightarrow \text{C}_s + \text{OH}_s$  would occur with the higher activation energy of 87–90 kcal/mol (which includes isomerization of formyl  $\text{HCO}_s$  into hydroxycarbonyl  $\text{COH}_s$ , which requires 14 kcal/mol). The results are consistent with the fact that carbidic carbon  $\text{C}_s$  is formed on Ni while heated either in clean CO or in  $\text{H}_2 + \text{CO}$ , but with  $\text{H}_2$  the CO dissociation proceeds much faster,<sup>34</sup> most probably due to the scavenging of  $\text{O}_s$  by  $\text{H}_s$ .<sup>36</sup> Once  $\text{C}_s$  is formed, the progressive hydrogenation  $\text{C}_s + \text{H}_s \rightarrow \text{CH}_s + \text{H}_s \rightarrow \text{CH}_{2,s} + \text{H}_s \rightarrow \text{CH}_{3,s} + \text{H}_s \rightarrow \text{CH}_4$  takes place where the activation recombination barrier  $\Delta E^*_{\text{H}_x\text{C-H}}$  monotonically decreases with  $x$ ; namely,  $\Delta E^*_{\text{H}_x\text{C-H}} = 63, 33, 12,$  and  $6$  kcal/mol for  $x = 0, 1, 2,$  and  $3$ , respectively. Thus, the activation energy of carbide formation and that for carbide hydrogenation are very close (67 vs 63 kcal/mol), in agreement with the observation that under  $(\text{CO} + \text{H}_2)/\text{Ni}$  reaction conditions, the specific rates of carbon formation and removal are very near, leading to a constant carbide coverage.<sup>34b</sup> These barrier calculations also suggest that for methanation on Ni, the rate-limiting step is either the C–O dissociation or the first (carbidity) carbon hydrogenation, again in agreement with experiment.<sup>34,35</sup> One can add that if the C–O bond could somehow survive up to the formation of methoxide  $\text{CH}_3\text{O}_s$ , it will be cleaved as  $\text{CH}_3\text{O}_s \rightarrow \text{CH}_{3,s} + \text{O}_s$  because the competitive hydrogenation to methanol,  $\text{CH}_3\text{O}_s + \text{H}_s \rightarrow \text{CH}_3\text{OH}$ , requires a much larger activation barrier (13 vs 26 kcal/mol, respectively).

Hydrogenation of CO on Pd looks rather different.<sup>12</sup> First of all, on Pd(111) the formation of carbidity carbon requires prohibitively high activation barriers, namely, 100 kcal/mol for  $\text{CO}_s \rightarrow \text{C}_s + \text{O}_s$  or 110–113 kcal/mol for  $\text{CO}_s + \text{H}_s \rightarrow \text{C}_s + \text{OH}_s$ . The progressive hydrogenation  $\text{CO}_s + \text{H}_s \rightarrow \text{HCO}_s \rightarrow \text{H}_2\text{CO}_s \rightarrow \text{H}_3\text{CO}_s$  occurs with much lower barriers of 57, 18, and 39 kcal/mol, respectively. Once methoxide  $\text{CH}_3\text{O}_s$  is formed, its hydrogenation to  $\text{CH}_3\text{OH}$  is slightly preferred ( $\Delta E^*_{\text{H}_3\text{CO-H}} = 18$  kcal/mol) over the C–O bond cleavage to  $\text{CH}_{3,s} + \text{O}_s$  (23 kcal/mol). The similarity of the two activation energies is consistent with the fact that on Pd powder, the selectivities to  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  are about the same ( $\sim 50\%$  of each product<sup>37</sup>) but supported Pd catalysts can selectively produce either  $\text{CH}_4$  or  $\text{CH}_3\text{OH}$ , depending on the reaction conditions and the nature of the support.<sup>38,39</sup> The results for Pt<sup>12</sup> are

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very similar to those for Pd.

Summing up, the BOC model calculations project that C-O bond cleavage occurs directly on Ni to produce carbidic carbon followed by progressive hydrogenation up to the formation of CH<sub>4</sub>. There is no way to retain the C-O bond and form CH<sub>3</sub>OH. By contrast, the assistance of hydrogen in C-O bond cleavage is critical for Pd (and Pt). Here, the C-O bond rupture is not likely to occur before methoxide CH<sub>3</sub>O<sub>s</sub> is formed, after which both decomposition to CH<sub>3,s</sub> + O<sub>s</sub> and hydrogenation to CH<sub>3</sub>OH can proceed with similar activation barriers. These projections are in agreement with the selectivities observed experimentally for CO hydrogenation over Ni, Pd, and Pt.<sup>33-40</sup>

### Concluding Remarks

The analytic BOC-MP model explicitly interrelates many seemingly disparate chemisorption phenomena, including surface reactivity, which reveals the essential "elephantness" of chemisorption. Let us stress again that the BOC-MP model is based on a few well-defined assumptions and within these assumptions, the model interrelations are rigorous and (for atomic chemisorption at the zero-coverage limit) even exact. Moreover, these interrelations are expressed in terms of observa-

bles only (the heats of chemisorption and various constants), which makes comparison with experiment direct and unambiguous. The latter is critical in developing any serious theoretical model, which should be falsifiable (in the Popperian sense), and the BOC-MP model is of this kind.

The scope of the BOC-MP modeling can be further extended to embrace, in principle, any aspect of chemisorption and surface reactivity, provided the model projections retain their rigor and simplicity. The latter is naturally more difficult to achieve the more complex the ad molecules become. But this job is worth trying. The chemical appeal of the BOC-MP model is that it is a truly "back-of-the-envelope" model, which can be directly used by the practitioners in the field.

*This work began during my collaboration with the late Earl L. Muetterties. He strongly believed in the comprehensible chemical order in chemisorption and kept encouraging me to look for general analytic modeling. It is hard to express the depth of my gratitude to Earl. I wish to thank Roald Hoffmann, John T. Yates, Jr., Gerhard Ertl, Michel Boudart, Alexis T. Bell, Jay B. Benziger, Robert J. Madix, and Sylvia T. Ceyer for exciting discussions and illuminating comments. My special thanks are to Roger C. Baetzold, whose parallel work on theory of chemisorption gave me much insight.*

## Topological Control of the Structures of Molecules and Solids

JEREMY K. BURDETT

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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One of the challenges that often faces chemists is the organization and understanding of the enormous wealth of molecules and solids whose structures have been determined. Oftentimes there is a clear dependence of structure on electron count, observations that have led to the famous counting rules associated with the names of Hückel,<sup>1</sup> Walsh,<sup>2</sup> Sidgwick, Powell, Nyholm, and Gillespie,<sup>3</sup> Woodward and Hoffmann,<sup>4</sup> and Wade.<sup>5</sup> Simple one-electron orbital methods have been extremely useful in constructing such models.<sup>6-8</sup> The success of Hückel's rule in polyene chemistry, the one-electron molecular orbital model behind the Woodward-Hoffmann rules, and the utility of extended-Hückel ideas to probe the properties of molecules of all types are clear evidence that imaginative use of very simple molecular orbital ideas can help us understand large tracts of chemistry. In this Account we show that there is a simple idea, drawn from the field of topology, that unifies many of these orbital problems. It ties together observations from many different areas of chemistry and provides a larger window with which to look at molecular and solid-state structure.

Jeremy Burdett was educated at the Universities of Cambridge and Michigan and has been on the faculty of The University of Chicago since 1978. His interests lie in understanding the relationship between the geometrical and electronic structure of molecules and solids and how it controls molecular and solid-state properties.

### Some Structural Diversity

Figure 1 shows calculated energy difference curves<sup>9,10</sup> as a function of the number of relevant electrons for ten different structural problems. They have been calculated by using the simplest possible one-electron molecular orbital modes. The Hückel method was employed for homoatomic systems, the angular overlap model was used for heteroatomic systems,<sup>6</sup> and the Hückel implementation of tight-binding theory was employed for solids. In all cases the results of the calculation faithfully mimic the experimental observations. The most striking feature of this figure is that the curves are all extremely similar in shape but the examples as diverse as chemistry itself.

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