equilibrium constants to determine ring-closing rate constants. These unidirectional rate constants can then be used to derive overall rate constants for the interconversion of cyclic forms, an approach that may be particularly useful in the study of biologically important sugars that may be available only as syrups or as solutions at anomeric equilibrium.

Thermodynamic and activation parameters can be estimated for each reaction, and the effects of temperature, pH, configuration, solvent, and catalysts can now be systematically examined. Although rate constants in the range 0.02–0.05 s^{-1} are difficult to estimate by ST NMR, various catalysts can be used to bring them into range, and intrinsic rate constants can be obtained by extrapolation. The extension of ST NMR methods to study pyranose or furanose anomerization of pentoses and hexoses may be feasible. D-Idose may be especially amenable to study since pyranose, furanose, hydrate, and aldehyde forms can be observed in the ^{13}C NMR spectrum of the 1-^{13}C-enriched derivative. Comparison of the unidirectional rate constants for α- and β-ribofuranose with those for α- and β-erythrofuranose would be particularly interesting, since in other systems, cyclizations to form furan rings involving secondary hydroxyls occur more readily than those involving primary hydroxyls.[17,25] Studies on the anomerization of the tetroses, aldose 5-phosphates, ketose phosphates, and their derivatives are in progress.

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Registry No. D-Erythrose, 583-50-6; D-threose, 95-43-2; 2,4-*O*-ethylidene-D-erythrose, 24871-55-4; α-threofuranose, 80877-72-1; β-threofuranose, 80877-73-2; α-erythrofuranose, 72599-80-5; β-erythrofuranose, 72599-81-6.

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The Concept of Lewis Acids and Bases Applied to Surfaces

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Abstract: The purpose of this paper is to apply the concept of Lewis acids and bases to provide an understanding of the influence of structure and composition on surface chemistry. The Lewis acid–base concept is briefly reviewed. The factors important for determining the strength of acid–base interactions, including orbital energies and orbital character, are illustrated with the aid of gas phase ion–molecule chemistry. The perturbational molecular orbital theory of acid–base interactions is adapted to the gas phase environment in order to show that changes in the ordering of base strength through a series of Lewis bases must be due to the criterion of maximum orbital overlap. The classification of metal surfaces as acid or base with respect to a molecular adsorbate is determined with the work-function change. The influence of surface composition modification by either electronegative or electropositive elements on CO adsorption is shown to follow an inductive effect analogous to that seen in molecules. On metal oxide surfaces and oxidized metal surfaces, the oxygen anions are assigned to be Lewis base sites and the electron-deficient metal atoms are assigned to be Lewis acid sites. For an oxygen monolayer on a metal surface, two types of structures are distinguished: the overlayer structure and the incorporation structure. Chemical and physical evidence is presented which indicates that the Lewis acid sites on a surface with an incorporation structure are localized. Finally, the chemical evidence from adsorption studies combined with the criterion of maximum orbital overlap indicates that it is the localized vs. delocalized character of the valence electronic states at the surface that determines adsorption selectivity changes.

I. Introduction: Lewis Acids and Bases

One of the ultimate goals for research into the chemical properties of solid surfaces is to establish an understanding of surface chemistry which is comparable to more traditional gas phase or solution phase organic and inorganic chemistry. Of particular importance in this endeavor is the need to establish the general principles or "rules of thumb" which can be used in practical situations to rationalize or predict the effects of structure and composition on surface chemistry. Such concepts as electronegativity, inductive effect, nucleophilicity, hard and soft, etc. which have proved useful for classifying and rationalizing traditional chemical phenomena will very likely be just as useful in surface chemistry. In fact, the same concepts of chemical bonding and chemical reactions currently used in traditional chemistry will most certainly be used in surface chemistry as well. The development of a chemical understanding of surfaces has been hampered by the generally heterogeneous nature of the solid surface. Experimentation on heterogeneous surfaces is analogous to performing solution phase chemistry on a complex mixture where any of a number of components may be responsible for observed chemical effects. In recent years the effort to describe and understand surface chemistry in molecular and atomic detail has been spurred (1) by the development of ultra-high-vacuum, clean-surface technology which allows a surface to be prepared and maintained in a well-defined structural and chemical state and (2) by the development of a variety of surface-sensitive spectroscopies which allow the structure and composition of the surface to be probed directly. With the accumulation of information on the chemical behavior of well-defined surfaces we can begin to apply the traditional chemical concepts to the solid surface.

The purpose of this paper is to apply the concept of Lewis acids and bases to the understanding of surface chemistry. The Lewis acid–base concept is one of the most generally useful classification schemes in traditional chemistry. It is a tool for systematizing reactive molecules and reactive sites on molecules that provides

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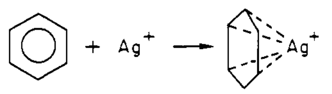
an insight into the nature of their reactivity. For an extensive review of the subject the reader is referred to ref 1. Briefly, a Lewis acid is an atom, molecule, or ion that tends to act as an electron acceptor while a Lewis base is an atom, molecule, or ion that tends to act as an electron donor. An acid and base interact by electron "donation" from the base to the acid. The result of this interaction is the formation of a chemical bond between the acid and base creating an "acid–base adduct" (see eq 1). In its

$$A + B = AB \qquad (1)$$

most general form, an acid–base interaction includes any degree of electron transfer (including only a simple polarization) of nonbonding, bonding, or antibonding electrons from the base to an empty nonbonding, bonding, or antibonding electronic state on the acid. The electronic states involved may be localized on a single atom or delocalized over several atoms in a molecule. Usually only closed-shell interactions are considered to be of an acid–base type, and usually a pair of electrons is involved.

Three examples of chemical reactions which illustrate the variety of bond-forming processes that can be viewed as acid–base interactions are listed in eq 2.[1] In eq 2a the bond is formed by

$$\begin{array}{llll} \text{base} & \text{acid} & \text{adduct} & \\ H_3N & + BF_3 \longrightarrow & H_3N\text{-}BF_3 & (2a) \\ 4CO & + Ni \longrightarrow & Ni(CO)_4 & (2b) \end{array}$$



(2c)

donation from the nitrogen nonbonding lone pair to an empty antibonding orbital in BF_3. The bonding in nickel tetracarbonyl is a combination of donation from the carbon nonbonding lone pair to an empty nickel d orbital along with back donation by nickel d electrons into the unoccupied π^* antibonding orbital of CO. Benzene behaves as a multisite, bonding π-electron donor into the unoccupied d orbitals on Ag^+.

The reactions listed in eq 2 illustrate several aspects of the Lewis acid–base interaction. The acceptor and donor orbitals may be localized primarily on single atoms within the acid or base molecule as is the case for BF_3 and NH_3 or they may be delocalized as is the case for the donor orbital in benzene. In the former instance the active atoms can be said to constitute sites on the molecule. Complex molecules may have multiple basic or acidic sites or even both together. In 2-hydroxyethylamine ($H_2NCH_2CH_2OH$), for example, both the nitrogen and the oxygen lone pair electrons form a basic site that may interact with a Lewis acid. In benzene where the donor orbital is delocalized over the ring, the acid interacts with the molecule as a whole so that no specific basic site is determined. Carbon monoxide is an example where a filled orbital is considered as an electron donor (4σ orbital) while simultaneously an unfilled orbital acts as an electron acceptor (π^* orbital) so that the molecule has both acid and base character.

From the Lewis acid–base point of view a molecule adsorbed on a surface is just another example of eq 1 and 2. The surface may be the acid or the base or have both types of character simultaneously. The interaction may be localized at a single atomic site or delocalized over several surface atoms. Several types of sites may coexist on the surface at the same time. In this paper we shall discuss molecular adsorption on surfaces from the Lewis acid–base point of view. The factors which determine the strength of the acid–base interaction will be illustrated with examples from gas phase ion–molecule chemistry to lay the groundwork for this discussion. The examples will be interpreted with use of a perturbational molecular orbital theory of acid–base interactions. The treatment of adsorption on surfaces will focus primarily on four aspects: (1) the assignment of the surface as the acid or base species in molecular adsorption; (2) the identification of the acid and base sites on the surface; (3) the influence of chemical modifiers on the metal surface acid–base character through the inductive effect; and (4) the role of localized vs. delocalized surface electronic structure in selective adsorption.

Table I. Effect of Fluorination on Proton Affinities and Ionization Potentials of Primary Amines

amine	PA[a]	IP[a]	amine	PA[a]	IP[a]
$CH_3CH_2NH_2$	214.0	202.9	$F_2CHCH_2NH_2$	205.9	216.3
$FCH_2CH_2NH_2$	210.2	210.1	$F_3CCH_2NH_2$	200.3	224.3

amine	PA	fluorinated amine	PA
$CH_3CH_2NH_2$	214.0	$CF_3CH_2NH_2$	200.3
$CH_3(CH_2)_2NH_2$	215.2[b]	$CF_3(CH_2)_2NH_2$	209.0
$CH_3(CH_2)_3NH_2$	215.7[b]	$CF_3(CH_2)_3NH_2$	212.3

[a] From ref 6. [b] Corrected from ref 7.

II. Acid–Base Strength: Inductive Effects and Ordering

The strength of an acid–base chemical bond can be defined as the change in enthalpy, ΔH, associated with the formation of an adduct from the isolated species as in eq 2. A measure of base strength can be obtained from the ΔH for forming a complex with a particular Lewis acid, e.g., H^+ or BF_3. In this way a series of bases may be compared. In recent years the heats of adduct formation for a large number of Lewis bases with the bare proton, H^+, have been measured in the gas phase with the technique of ion cyclotron resonance.[2] These studies have revealed several correlations that are important to note.

Within a homologous series of bases such as the primary amines or alcohols there is a nearly linear correlation between the heat of adduct formation with H^+ (termed the proton affinity, PA) and the first ionization potential of the base.[3] Since the first ionization potential is, in some sense, a measure of the intrinsic ability of the base to give up electrons, this correlation is not surprising. Independently, several research groups have shown that changes in both the ionization potential and the proton affinity through the series of primary amines or alcohols is caused largely by changes in the polarizability of the hydrocarbon chain.[4,5] Evidently polarization of the hydrocarbon chain serves to stabilize a positive charge to a similar degree whether the positive charge is due to addition of a proton or to removal of an electron.

For ethylamine, $CH_3CH_2NH_2$, replacement of hydrogens on the methyl carbon with the more electron withdrawing fluorine atom serves to lower the proton affinity and the ionization potential through the series of molecules shown in Table I.[6] This is the so-called "inductive effect". The fluorines are thought to destabilize the protonated base by withdrawing electron density from the nitrogen. This effect operates over a distance of several carbon–carbon bond lengths as can be seen by comparing the proton affinities of the fluorinated propyl- and butylamines with their corresponding hydrocarbon analogues in the lower portion of Table I. The effect is not due to a lowering of the hydrocarbon chain polarizability since fluorine has a slightly larger polarizability than hydrogen.[6] The inductive effect is an old idea for chemists but one which has proved very useful for understanding and even predicting a broad range of phenomena in organic and inorganic chemistry.

The ordering of base strengths is not unique but depends on the choice of a reference acid. For example, in aqueous solution, ammonia (NH_3) is a stronger base than triethylphosphine, $P(Et)_3$, when H^+ is the reference acid while just the opposite is true when CH_3Hg^+ is the reference acid.[8] Reversals in the base strength

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(1) W. B. Jensen, "The Lewis Acid-Base Concepts-An Overview", Wiley, New York, 1980.

(2) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971).

(3) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6252 (1974).

(4) B. E. Mills, R. L. Martin, and D. A. Shirley, *J. Am. Chem. Soc.*, **98**, 2380 (1976).

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(6) R. H. Staley, M. Taagepera, W. G. Henderson, I. Koppel, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 326 (1977).

(7) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972).

Table **II.** Ionization Potentials, Electron Affinities, Orbital Energies, and Acid-Base Bond Dissociation Energies

molecule	IP_1 $(EA_1)^a$	IP_2 $(EA_2)^{a,d}$	orbital energy^a	D-$(B\text{-}H^+)^b$	D-$(B\text{-}Li^+)^c$	D-$(B\text{-}CpNi^+)^b$
			Bases			
H_2O	12.6	28.5	−16.6	170	34.0	<40
CH_3OH	10.8	24.1	−14.1	182	38.1	45.7
CH_3CN	12.2	23.2	−14.9	187	43.6	53.3
CH_3-OCH_3	9.98	22.1	−13.0	190	39.5	47.0
NH_3	10.2	23.4	−13.5	202	39.1	52.4
C_2H_4	10.5	23.1	−13.6	169	NA	NA
C_6H_6	9.24	16.9	−11.2	181	37.9	>74
			Acids^e			
H^+	(13.6)	(0.75)	−10.4			
Ni^+	(8.7)	(1.3)^f	−6.9			
Li^+	(5.4)	(0.82)	−4.2			

[a] Values in electron volts. [b] Values in kcal/mol from ref 11. [c] Values in kcal/mol from ref 12 and 13. [d] IP_2 determined from gas phase Auger data according to eq A3. Data from ref 15-18. [e] Acid data from ref 14. [f] Estimated from ref 8, p 52.

ordering such as this led Pearson to propose a supplementary classification of Lewis acids and bases which he called "hard and soft".[9] This supplementary classification has proved very useful for rationalizing and predicting acid–base chemistry in solution.[10] In solution the influence of the solvent complicates any understanding of acid–base interactions. However, reversals in base strength ordering also occur for gas phase acid–base adduct formation where the interactions should be determined by the intrinsic properties of the atoms, molecules, or ions involved. This is evident from Table II which lists data for the heat of adduct formation for a series of bases with three, cation reference acids: H^+, Li^+, and the (cyclopentadienyl)nickel cation. Note, for example, that benzene is nearly the weakest base when H^+ is the reference acid while it is the strongest base when $CpNi^+$ is the reference acid. The base strength ordering also reverses for ammonia and acetonitrile, CH_3CN, depending on whether the reference acid is H^+ or $CpNi^+$.

III. Perturbational Molecular Orbital Theory: Orbital Energies and Overlap

It is helpful to refer to a perturbational molecular orbital theory of acid–base interactions developed initially by Klopman[14] and later extended by Jensen[1] in order to understand the factors which influence the strength of an acid–base interaction and the ordering in base strength. The incipient reaction of an acid and a base is treated as a perturbation on the ground-state properties of the separated species. The perturbation energy is the sum of three terms:

$$\Delta E^{\text{pert}} = \Delta E^{\text{ch}} + \Delta E^{\text{orb}} + \Delta E^{\text{repl}} \tag{3}$$

an electrostatic term, ΔE^{ch}, due to the Coulomb attraction between cation acids and anion bases, an electron transfer (covalent bond) term, ΔE^{orb}, and a repulsive term, ΔE^{repl}, due to the electron–electron repulsion between the filled orbitals of each moiety. The notation here follows that of Jensen.[1]

The electrostatic, Coulomb attraction in Klopman's theory is given by[14]

$$\Delta E^{\text{ch}} = \sum_{\text{rs}} \frac{Q_{\text{r}} Q_{\text{s}}}{R_{\text{rs}}} \tag{4}$$

This is a pairwise interaction between each atom r with charge Q_r on the base and each atom s with charge Q_s on the acid at a distance R_{rs}. For gas phase species the contributions to the electrostatic term include permanent dipole, charge-induced dipole, and polarization in addition to the charge–charge interactions. We expect electrostatic interactions to be very weak for neutral acid–base adducts such as a molecule bonded to a surface. Rather, it is the electron transfer covalent bonding that produces a stable adduct between neutral acids and bases.

The electron transfer covalent bonding term, which accounts for the attractive interactions between the filled orbitals on one species and the empty orbitals on the other, is represented by a second-order orbital perturbation:

$$\Delta E^{\text{orb}} = \sum_{\substack{\text{m}\\ \text{base}}}^{\text{occ}} \sum_{\substack{\text{n}\\ \text{acid}}}^{\text{unocc}} - \sum_{\substack{\text{n}\\ \text{acid}}}^{\text{occ}} \sum_{\substack{\text{m}\\ \text{base}}}^{\text{unocc}} \frac{2(\sum_{\text{rs}} C_{\text{r}}^{\text{m}} C_{\text{s}}^{\text{n}} \beta_{\text{rs}})^2}{E_{\text{m}} - E_{\text{n}}} \tag{5}$$

This expression is derived by first calculating the pairwise perturbation produced on one occupied orbital Ψ_m of the base by one unoccupied orbital Ψ_n of the acid within the complete neglect of differential overlap (CNDO) approximation. A new perturbed molecular orbital Ψ_{mn} results:

$$\Psi_{\text{mn}} = a\Psi_{\text{m}} + b\Psi_{\text{n}}$$

where a and b are variational parameters and $a^2 + b^2 = 1$ for the CNDO approximation. Ψ_m and Ψ_n are expressed as sums of atomic orbitals ϕ_i:

$$\Psi_{\text{m}} = \sum_{\text{r}} C_{\text{r}}^{\text{m}} \phi_{\text{r}} \qquad \Psi_{\text{n}} = \sum_{\text{s}} C_{\text{s}}^{\text{n}} \phi_{\text{s}}$$

For Ψ_m originally doubly occupied the interaction energy is expressed as the energy difference between the perturbed orbital Ψ_{mn} and the isolated orbital Ψ_m.

$$\Delta E^{\text{orb}} = \int \Psi_{\text{mn}}(1)\Psi_{\text{mn}}(2)\mathcal{H}\Psi_{\text{mn}}(1)\Psi_{\text{mn}}(2)\, d\tau_1\, d\tau_2 - \int \Psi_{\text{m}}(1)\Psi_{\text{m}}(2)\mathcal{H}\Psi_{\text{m}}(1)\Psi_{\text{m}}(2)\, d\tau_1\, d\tau_2$$

where $\mathcal{H}$ is the total Hamiltonian operator for the interacting system. For the simple case where the only transmolecular interactions taken into account are those involving atoms r and s and following a variational minimization of the energy with respect to a and b:[14]

$$\Delta E^{\text{orb}} = E_{\text{n}} - E_{\text{m}} + [(E_{\text{m}} - E_{\text{n}})^2 + 4(C_{\text{r}}^{\text{m}} C_{\text{s}}^{\text{n}} \beta_{\text{rs}})^2]^{1/2} \tag{6}$$

E_m and E_n are the orbital energies of Ψ_m and Ψ_n, respectively. β_{rs} is the resonance integral between atomic orbitals ϕ_r and ϕ_s.

$$\beta_{\text{rs}} = \int \phi_{\text{r}}(\text{i})\mathcal{H}'\phi_{\text{s}}(\text{i})\, d\tau_{\text{i}}$$

where $\mathcal{H}'$ is the perturbation Hamiltonian representing the interaction between the acid and base:

$$\mathcal{H}' = \frac{Q_{\text{r}} + 2(C_{\text{r}}^{\text{m}})^2}{R_{\text{ri}}} + \frac{Q_{\text{s}}}{R_{\text{si}}}$$

In the limit of the initial interaction between the acid and base where $4\beta^2 \ll (E_m - E_n)^2$ eq 6 reduces to the usual perturbation result:

$$\Delta E^{\text{orb}} = \frac{2(C_{\text{r}}^{\text{m}} C_{\text{s}}^{\text{n}} \beta_{\text{rs}})^2}{E_{\text{m}} - E_{\text{n}}} \tag{7}$$

Summation of eq 7 over all interacting pairs of occupied and unoccupied orbitals and over all pairs of interacting atoms r and s gives eq 5.

Generally, E_m is identified with the highest occupied molecular orbital (HOMO) of the base, while E_n is the energy of the lowest unoccupied molecular orbital (LUMO) of the acid. Neglecting the Coulomb interaction between the orbitals these energies may be estimated:[14]

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(8) J. E. Huheey, "Inorganic Chemistry-Principles of Structure and Reactivity", 1st ed., Harper and Row, New York, 1971, p 228.

(9) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(10) See, for example, the articles in "Hard and Soft Acids and Bases", R. G. Pearson, Ed., Dowden, Stroudsburg, 1973.

(11) R. R. Corderman and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 3998 (1976).

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(13) R. L. Woodin and J. L. Beauchamp, *J. Am. Chem. Soc.*, **100**, 501 (1978).

(14) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).

$$-E_m = \mathrm{IP}_2{}^m - a^2(\mathrm{IP}_2{}^m - \mathrm{IP}_1{}^m) \quad (8a)$$

$$-E_n = \mathrm{EA}_1{}^n - b^2(\mathrm{EA}_1{}^n - \mathrm{EA}_2{}^n) \quad (8b)$$

$\mathrm{IP}_1{}^m$ and $\mathrm{IP}_2{}^m$ are the first and second ionization potentials of orbital m, respectively. $\mathrm{EA}_1{}^n$ and $\mathrm{EA}_2{}^n$ are the first and second electron affinities of orbital n, respectively. The variational parameters, a and b, are a measure of the electron transfer—$a^2 = 1$ and $b^2 = 0$ for no electron transfer and $a^2 = {}^1/_2$ and $b^2 = {}^1/_2$ for complete covalent bond formation. Orbital energies calculated according to eq 8 take into account electron pair repulsions that are neglected if only the first ionization potential or first electron affinity is used to estimate the orbital energies. Following Klopman, an "intrinsic" orbital energy may be defined by use of values of a and b appropriate for an intermediate degree of electron transfer, $a^2 = {}^3/_4$ and $b^2 = {}^1/_4$. Orbital energies calculated by use of these values in eq 8 are listed in Table II for a variety of bases and for H^+, Li^+, and Ni^+. The second ionization potentials for the bases have been determined from gas phase Auger data (see Appendix I).

The third term in eq 3, ΔE^{repl}, is due to Jensen[1] and represents the repulsive interactions between the filled orbitals of both reactants:

$$\Delta E^{\text{repl}} = -\sum_{rs} [2 \sum_{m}^{\text{occ}} (C_r{}^m)^2 + 2 \sum_{n}^{\text{occ}} (C_s{}^n)^2]\beta_{rs}S_{rs} \quad (9)$$

S_{rs} is the overlap integral $\int \phi_r(i)\phi_s(i)\, d\tau_i$. β_{rs} is the resonance integral and $C_r{}^m$ and $C_s{}^n$ are the coefficients in the LCAO representation of Ψ_m and Ψ_n.

The phenomenological effect of the three types of interactions in eq 3 can be determined by the examination of the bond dissociation energy data, $D(\text{B–A}^+)$, in Table II for the three reference acids H^+, Li^+, and $CpNi^+$. Several features of the data should be noted. (1) The order of bond dissociation energies is $D(\text{B–H}^+) > D(\text{B–CpNi}^+) > D(\text{B–Li}^+)$ with $D(\text{B–H}^+)$ very much larger than the other two. (2) The bond energies for Li^+ adducts are relatively constant across the series of bases while $D(\text{B–H}^+)$ and $D(\text{B–CpNi}^+)$ span a range of more than 30 kcal/mol. (3) There are dramatic changes in the ordering of base strengths between the H^+ and $CpNi^+$ reference acids. For example, the bond-dissociation energy for benzene with H^+ is 21 kcal/mol lower than that for ammonia, but with $CpNi^+$ it is more than 21 kcal/mol higher than that for ammonia. Recent semiempirical[13] and ab initio[19] calculations have shown that the interactions in Li^+ adducts are mainly electrostatic and repulsive (ΔE^{ch} and ΔE^{repl}). The negligible covalent bonding is evidently due to the high energy of the Li^+ acceptor orbital that produces a large mismatch between donor and acceptor energies. In contrast, the very large values of $D(\text{B–H}^+)$ reflect the strong electrostatic and covalent attractions resulting from the small size and low acceptor-orbital energy (see Table II) characteristic of a bare proton as well as the absence of electron–electron repulsion. The influence of covalent bonding in H^+ adducts is illustrated by the 32 kcal/mol difference in $D(\text{B–H}^+)$ for H_2O and NH_3 where the parameters that determine the electrostatic attraction (polarizability, dipole moment) are approximately the same. Finally, the greater stability of $CpNi^+$ adducts compared to Li^+ adducts is predominantly due to covalent bonding. The larger ionic radius and more numerous valence and core electrons in $CpNi^+$ tend to reduce the electrostatic attraction and increase the repulsion in comparison to Li^+. Yet, the bond energies in $CpNi^+$ adducts are larger than those in Li^+ adducts by an average of ~15 kcal/mol across the series of bases listed in Table II. From these considerations we conclude that the combination of ΔE^{ch} and ΔE^{repl} alone produces relatively low and constant acid–base bond energies. The covalent bonding contributes substantially to the stability of the acid–base adducts and must be mainly responsible for both the wide range of $D(\text{B–A}^+)$ values for H^+ and $CpNi^+$ as well as the dramatic reversals in the base-strength ordering for these two reference acids.

Equation 5 can be used as a basis for discussing the factors that determine the strength of covalent bonding: orbital energy and orbital overlap. If we restrict our consideration of orbital energies to the HOMO of the base, E_m, and the LUMO of the acid, E_n, the data in Table II indicate that generally the donor orbital is lower in energy than the acceptor orbital. Thus eq 5 correctly predicts that the base strength increases through the homologous series H_2O–CH_3OH–CH_3OCH_3 and that the magnitude of the increase becomes larger as the acceptor-orbital energy on the acid decreases. However, the orbital energies alone cannot account for the low values of the proton bond dissociation energies observed for ethylene and benzene. They also cannot account for reversals in the base-strength ordering with different reference acids. Both of these effects can be understood from consideration of the resonance integral, β_{rs}.

The resonance integral, β_{rs}, is usually assumed to be proportional to the overlap integral, S_{rs}, of the atomic orbitals.[20] The validity of this assumption can be seen from the form of the defining equations. Within the context of perturbational molecular orbital theory, which is only appropriate for describing the incipient reaction of an acid and base, the resonance integral expresses the tendency for the separated, unperturbed orbitals to overlap and form a chemical bond without rehybridization or charge redistribution. For example, consider the overlap of the unperturbed nitrogen lone pair orbital on ammonia with the acceptor orbital on H^+. Neglecting phase effects, we expect the unperturbed orbitals to produce a substantial overlap integral at some distance since they are both small, localized orbitals. Therefore formation of a covalent bond requires minimal rehybridization energy. By contrast the unperturbed π electrons on ethylene and benzene cannot produce a substantial overlap integral with H^+ because their orbitals are large and delocalized compared to the acceptor orbital on H^+. Substantial, destabilizing charge redistribution in the ethylene and benzene must occur for a covalent bond to form. For adduct formation with $CpNi^+$, due to the nickel d orbitals, a strong interaction is favored by a donor orbital which is delocalized and able to form π bonds. Thus, benzene forms the most stable adduct with $CpNi^+$ of the bases listed in Table II. We conclude, therefore, that *it is the overlap of the unperturbed orbitals and the magnitude of charge redistribution that is necessary to bring about efficient overlap which are responsible for the dramatic reversals in base-strength ordering for different reference acids*. Localized donor orbitals form strong covalent bonds with localized acceptor orbitals. π-Donor orbitals form strong covalent bonds with π-acceptor orbitals. In essence, this is a restatement or extension of the "principle of maximum overlap" which was formulated by Pauling[21] to introduce the idea of orbital hybridization. It can be considered as a gas phase analogue of the classification "hard and soft" developed by Pearson.[9]

Since the perturbational molecular orbital theory is formulated in terms of the unperturbed electronic properties of the interacting species, it cannot provide reliable quantitative predictions for acid–base association energies where the final state electronic structure is drastically altered from the initial, unperturbed state. Unfortunately, this is precisely the case for a molecule adsorbed on a clean metal surface. The valence electronic structure in the initial state is an energy band of closely spaced, very delocalized orbitals while in the final adsorbed state it is much more localized and more well-defined in energy. Nevertheless, the perturbation theory should be useful for obtaining a qualitative understanding of the acid–base *trends* in a series of surfaces or in a series of

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molecules adsorbed on a given surface under two situations: (1) when the valence-orbital energy or orbital geometry differs from one species to another in a regular fashion through the series (e.g., the orbital energies in the series H_2O–CH_3OH–CH_3OCH_3) and (2) when the orbital energy or geometry is so dissimilar for the species in question that this dominates their differing chemistry (e.g., the donor-orbital geometry in ammonia compared to benzene or the orbital energy in water vs. ammonia). An example of a series of surfaces in class 1 is a metal surface with varying amounts of an electronegative impurity such as carbon, nitrogen, or oxygen. As the surface concentration of the impurities increases, the valence-orbital energies associated with the metal atoms should decrease due to an inductive effect, and the orbital geometry should become more localized as the surface transforms into the corresponding carbide, nitride, or oxide. An example of situation 2 would be to compare the adsorption of benzene and ammonia on clean metals and oxidized metals. The differences in orbital geometry should be the dominant factor in the determination of the relative adsorption energies. According to the orbital overlap criterion, benzene should always adsorb more strongly on a clean metal surface and ammonia more strongly on an oxidized surface. In what follows we shall utilize the concept of Lewis acids and bases and the results of the perturbation theory to explain the effects of surface composition on adsorption.

IV. The Classification of Surfaces as Lewis Acids and Lewis Bases: Inductive Effects

A surface is classified as an acid (electron acceptor) or a base (electron donor) according to the direction of the net electron transfer which results in the formation of the chemical bond to an adsorbate molecule. For situations where the adsorbate molecule is associatively adsorbed on top of the first atomic layer of the solid, the direction of the net electron transfer can be determined experimentally from measurements of the work-function change, $\Delta\phi$. A positive $\Delta\phi$ indicates net electron transfer from the surface to the adsorbed molecule (basic surface) while a negative $\Delta\phi$ indicates net electron transfer from the molecule to the surface (acidic surface). For dissociative adsorption the sign of the work-function change may not indicate the correct direction of net electron transfer since any atomic species formed as a result of dissociation may penetrate into or beneath the surface of the metal.

A clean metal surface may act as either an acid or a base, depending on the nature of the adsorbate molecule. This is illustrated by the clean Ni(111) surface. The surface acts as a Lewis base toward carbon monoxide, producing a positive work-function change.[22] For adsorbed acetylene, benzene, and ammonia, the work-function change is negative, indicating that the surface behaves as a Lewis acid toward these molecules.[23,24] This dual character is a consequence of the continuum of allowed electronic states at the Fermi energy so that the highest occupied electronic states and the lowest unoccupied electronic states have essentially the same energy. Thus empty states for electron accepting as well as filled states for electron donation are both equally accessible energetically for interactions with an adsorbed molecule. In fact, both electron donating and accepting may occur simultaneously with a single adsorbate molecule as is believed to be the case with carbon monoxide adsorbed on many metal surfaces.[25] However, even for CO, the work-function change indicates that a net electron transfer takes place. For most metals the surface acts as a base toward CO.

Classifying the surface as acidic or basic with respect to a particular adsorbate molecule is useful for understanding the role of surface composition changes in modifying the heat of adsorption of the molecule. Here we wish to make a direct analogy with the inductive effect observed in molecular Lewis acids and bases. In the example discussed previously, the "composition" of ethylamine was modified by replacing hydrogen atoms at the methyl position by the more electronegative fluorine atom. This resulted in a reduction in the amine base strength as measured by the proton affinity. On a metal surface the introduction of oxygen, carbon, or other electronegative elements onto the surface should produce an analogous inductive effect, making the nearby metal atoms less basic or more acidic. On the other hand, the introduction of electropositive species such as alkali metal atoms should produce a more basic or less acidic surface. The change in basic or acidic character will be reflected in the heats of adsorption as well as the surface reactivity of molecular acids and bases before and after the introduction of the modifying element. Thus the classification of a surface as acid or base toward an adsorbed molecule combined with the concept of an inductive effect provides a rule of thumb for predicting the outcome of surface-composition modifications.

The available data on the effect of surface composition on heats of adsorption support the concept of an inductive effect for surfaces. For example, the effect of oxygen pretreatment on the heat of adsorption of carbon monoxide has been studied on Ni(111),[22] Ni(100),[26] Ni(110),[27,28] Ir(110),[29] Fe(100),[30,31] Ru(001),[32] and Pd(001).[33] In all cases, the surface acts as a base toward CO at all coverages as judged by the work-function change for CO adsorbed on the clean surface. A surface inductive effect due to the presence of oxygen on the surface should reduce the basicity of the surface metal atoms and weaken the CO–chemisorption bond. In all cases pretreatment with oxygen produces a lowering in the CO heat of adsorption consistent with a surface inductive effect. In the other direction pretreatment of the Fe(100)[31] and Fe(110)[34] surfaces with potassium, an electropositive element, increases the heat of adsorption of CO, again consistent with a surface inductive effect. Another example is the effect of oxygen pretreatment of Ni(111) on the heat of adsorption of ammonia. The work-function change for adsorption of NH_3 on clean Ni(111) is negative, indicating that the surface is acidic toward ammonia.[24] Oxygen pretreatment increases the heat of adsorption of NH_3 consistent with an increase in surface acidity as expected for an inductive effect.[35] The effect has even been observed with physisorbed xenon on W(111)[36] and Mo(100).[37] The work-function change is negative for xenon adsorbed on both surfaces, and the xenon heat of adsorption is increased by the presence of the surface oxygen.

Studies of surface pretreatment or coadsorption of elements other than oxygen are less common. A few investigations with carbon or sulfur as surface modifiers have been performed with results that are consistent with a surface inductive effect caused by an electronegative element. For example, pretreatment of the Ni(110)[38] and Fe(100)[31] surfaces with carbon decreased the heat of adsorption of CO. Similarly, pretreatment of the Ni(111),[39] Fe(100),[31] and Pt(110)[40] surfaces with sulfur also decreased the heat of adsorption of CO. In each case the surfaces were not simply blocked to further adsorption by the carbon or sulfur, but

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each exhibited an effect on CO heat of adsorption observable at low coverage of carbon or sulfur.

Very recently Kiskinova and Goodman have reported on the adsorption of CO on Ni(100) surfaces modified by preadsorbed chlorine, sulfur, or phosphorus.[41] These modifiers cover a range of electronegativities (3.0, 2.5, and 2.1, respectively, on the Pauling scale). They show an increased inductive effect on the CO heat of adsorption with increasing electronegativity, a trend which is also observed with molecular acids and bases.

Properties other than heats of adsorption may also be influenced by surface inductive effects. In particular the vibrational frequency of the CO stretching mode in adsorbed carbon monoxide is strongly influenced by the presence of coadsorbates. The origin of this influence is the subject of some controversy, but in at least a few cases the degree of surface back donation into the antibonding π^* orbital of CO is believed to play a role in determining the stretching frequency.[42,43] The back donation (the metal acting as a base) in turn is influenced by the nature and concentration of coadsorbed species. Both raising[44,45] and lowering[43] of the CO frequency by coadsorbates have been reported, and in most cases, the change in frequency is in the direction expected for a simple inductive effect.

While the concept of a surface inductive effect is supported by the experimental data available for heats of adsorption of CO, its generality has not been established. In particular, there are few examples where surface pretreatment *increases* the heat of adsorption of a molecular acid or base. The inductive effects of potassium on CO adsorption[31,34] and oxygen on ammonia[35] or xenon adsorption[36,37] are the only cases known to the author. In addition, since oxygen, carbon, and sulfur are much more electronegative than the metals studied, it is not surprising that a substantial inductive effect is observed. Other surface modifiers such as boron, silicon, and phosphorus have electronegativities closer to those of most metals and may not produce a substantial inductive effect. Indeed, the work of Kiskinova and Goodman[41] suggests that surface modification by phosphorus is less pronounced than that for more electronegative elements. Clearly further exploratory work in this area is needed.

Another important issue is the role of the surface inductive effect in chemical reactions on surfaces. Qualitative prediction of changes in surface reactivity due to surface composition modifiers may be gained by use of the concept of the inductive effect. Kiskinova and Goodman showed that poisoning of the Ni(110) activity for CO hydrogenation by Cl, S, or P was directly correlated to both the surface concentration and the electronegativity of the poison.[41] In the language used here, the poisoning was directly correlated with the reduction in surface basicity caused by the inductive effect. Demuth has also noted enhanced activity for acetylene decomposition on oxygen-pretreated Ni(111).[46] Work function change measurements indicate that the surface is acidic toward acetylene so that the reactivity change is in the direction expected for an inductive effect.

Finally, many questions regarding the origin of the inductive effect remained unanswered. Calculations by Benziger and Madix suggest that for sulfur on Fe(100) there is a strong direct interaction with other adsorbates.[31] However, experimental studies of some systems suggest that through-metal interactions over several bond lengths are important. Kiskinova and Goodman discuss their results in terms of the electron density at the surface.[41] Spectroscopic measurements and calculations are needed to determine the importance of the orbital character of charge-density changes.

V. Surface Sites as Lewis Acids and Bases

An interesting possibility would be to classify the various adsorption sites on a metal surface (e.g., atop a single atom, bridged between two atoms, threefold hollow, fourfold hollow, etc.) according to their acidic or basic character. In principle, such an assignment would allow the prediction of adsorption sites for molecules with the complementary character. However, because of the large number of electronic states closely spaced in energy at a metal surface substantial charge reorganization occurs during chemisorption[47] so that the acidic or basic character of a site is not well-defined.

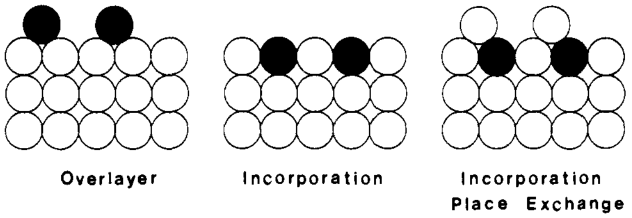

Figure 1. A schematic drawing of the overlayer and incorporation structures for oxygen adsorbed on a surface. The view is a cross section perpendicular to the surface. The filled circles represent the oxygen atoms and the open circles represent the metal atoms.

A more promising case for assigning acid or base character to specific sites on a surface can be made for metal oxide or oxidized metal surfaces. These surfaces will be the main focus of this section. Because of the large electronegativity of oxygen relative to most metals substantial electron transfer from metal to oxygen accompanies surface oxidation and metal oxide formation. The metal oxides have a gap between their HOMO and LUMO energies which stabilizes the charge distribution relative to the pure metal, lowers their polarizability relative to the pure metal, and inhibits charge reorganization during chemisorption. On metal oxides we expect that the electron-rich oxygen anions will show basic, electron-donating character while the electron-deficient metal cations will show acidic, electron-accepting character. In addition, we also expect the electronic-acceptor and -donor orbitals to be much more localized on a metal oxide surface than on a clean metal surface. These expectations have been the basis for interpretation of much of the surface chemistry of metal oxides in terms of acid and base sites on the surface.[48]

An intermediate case between the metal oxide and clean metal surface is the metal surface with a monolayer or submonolayer amount of oxygen contamination on it. The nature of such a surface will depend strongly on the details of its structure. For the purpose of this discussion, two types of surface structures can be distinguished: (1) an overlayer structure where the oxygen molecule dissociates into atoms which are located on top of the first metal atomic layer and (2) an incorporation structure where the oxygen penetrates into or below the surface, forming a surface oxide phase (see Figure 1).

We shall first consider the Lewis acid–base properties of the overlayer structure. Several pieces of evidence suggest that overlayer oxygen atoms should be anionic Lewis bases. Because of the electronegativity difference between oxygen and most metals we expect that chemisorbed oxygen atoms will have a partial negative charge. The several oxygen–metal surface structures that have been established as overlayers by LEED intensity analysis (0 on Fe(001),[49] Ni(111),[50] and Ni(100)[51]) show a positive work-function change that is consistent with electron transfer from metal to oxygen. X-ray photoelectron spectroscopy (XPS) measurements also suggest that chemisorbed, overlayer oxygen atoms have a partial negative charge. For instance, the oxygen (1s) binding energies are the same for the overlayer on Ni(111) and NiO, indicating that the oxygen electronic environments are

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similar.[52] Since NiO is a basic oxide it would seem that the oxygen overlayer on Ni(111) should also be basic. Chemical evidence for adsorbed oxygen acting as a Lewis base on the Ag(110) surface was reported by Madix and co-workers in temperature-programmed reaction studies of adsorbed formic acid.[53] The interaction of formic acid with the surface is activated for abstraction of the acidic proton by adsorbed basic oxygen forming surface hydroxyl and adsorbed formate species. A similar activation by oxygen of copper surfaces toward the adsorption of methanol and formation of a surface methoxide[54] may also be interpreted as an abstraction of the acidic proton by basic oxygen.

We expect that the electron-donor orbital associated with the oxygen anion is localized on a single atom site. Recent self-consistent electronic structure calculations for oxygen adsorbed on Ni(100) show that the conduction electron charge density transferred to oxygen is localized at the oxygen site.[47] The chemical evidence from formic acid adsorption on oxygen-pretreated Ag(110) also supports a localized basic site.[53] According to the overlap criterion discussed in section III, abstraction of a proton, which is a highly localized electron acceptor, would be favored by a highly localized electron donor.

The presence of overlayer oxygen atoms will reduce the number of metal atoms at the surface available for chemisorption of an additional molecule. The available surface metal atom sites will be altered from their clean metal chemistry, becoming more acidic and less basic due to the inductive effect. An interesting question concerns whether the electronic structure associated with the surface-metal atoms is localized or delocalized. No metal–metal bonds have been broken so that the surface-metal atoms are still coupled strongly the bulk metal electronic structure. For example, XPS measurements of the Ni($2P_{3/2}$) binding energy detect no shift during the initial stages of oxidation.[52,55] This has been interpreted to mean that the holes produced by charge transfer to oxygen are delocalized over the bulk of the metal.[55] Thus, it appears that the acceptor orbital produced by electron transfer to the adsorbed oxygen is delocalized. According to the overlap criterion the interaction of this delocalized Lewis acid should be greater with delocalized Lewis bases than with localized Lewis bases.

At the present time an interpretation of the acid–base behavior of oxygen-modified metal surfaces in terms of a pure overlayer structure must be approached with some caution. Some adsorbed oxygen structures which were thought to be pure overlayers may not be. For example, with oxygen adsorbed on the Ni(100) surface both a low coverage and a high coverage ordered structure were thought to be overlayers by LEED analysis.[51] More recently there is evidence that at higher coverage the oxygen atoms are nearly coplanar with the first layer of nickel.[56,57] Provided the oxygen atoms are accessible to an adsorbing molecule they would still be considered as basic surface sites. However, the metal-atom acid sites would be transformed into that characteristic of an incorporation structure as discussed in the next section. For an extensive review of the interaction of oxygen with metal surfaces see ref 58.

VI. The Oxygen-Incorporation Structure: Localized Lewis Sites

The incorporation structure presents a different situation. There will still be electron transfer to the oxygen from the metal. However, depending on the details of the surface structure, the oxygen anions may not be accessible as chemisorption sites. If the oxygen atoms penetrate below the first metal layer, for example, they will be sterically blocked from interacting directly with an adsorbed molecule (see Figure 1). Surface-oxygen atoms which are sterically accessible should be localized Lewis base sites similar to those of the overlayer oxygen atoms. On the other hand, the chemical nature of the metal atoms within the incorporation layer should be substantially altered from either the clean surface or the overlayer oxygen surface. The incorporation structure can result in reconstruction of the top metal layer, breaking metal–metal bonds and/or displacing metal atoms from their clean surface positions. In addition to the charge transfer which produces an electron deficiency in the metal atoms at the surface, because of the structural rearrangements the metal atoms in the incorporation layer will be electronically decoupled from the bulk metal. Without the strong coupling to the bulk, the holes produced by electron transfer to the oxygen will be localized on the metal atoms in the incorporation layer, resulting in localized Lewis acid sites at the surface. This type of structure should more properly be considered as a surface oxide phase distinct from either the clean metal surface or the bulk metal oxide surface. Because of the localized character of the Lewis acids on this surface, the adsorption properties and surface chemistry will differ dramatically from the clean surface or the oxygen overlayer surface.

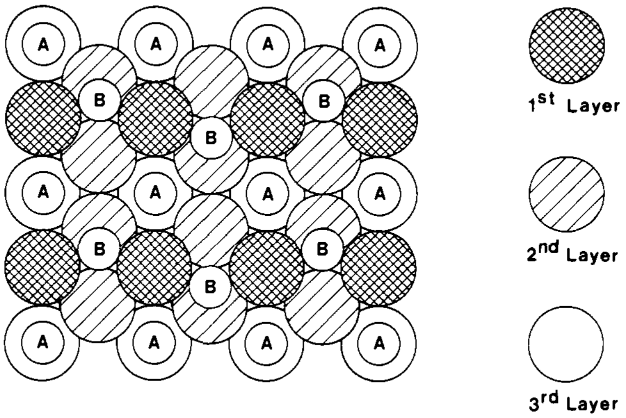

Figure 2. A schematic drawing of the oxygen-induced Ni(110)–(2 × 1) surface structure according to ref 60–62. The possible locations for the oxygen atoms are A according to ref 61 and B according to ref 62.

With two exceptions the surfaces used to study the influence of oxygen pretreatment on adsorption and surface chemistry have been simple overlayer structures. The two exceptions are the Ni(110) surface exposed to oxygen at room temperature and the Mo(100) surface exposed to oxygen above 900 K. Several models for the structure of the oxygen-induced (2 × 1) surface of Ni(110) have been proposed. An overlayer model deduced from a LEED intensity analysis[59] appears to be incorrect based on recent ion-scattering data.[60] Instead, the surface is reconstructed into a missing row model with the metal atoms in the positions originally proposed by Germer and MacRae[61] (see Figure 2). The location of the oxygen atoms is still uncertain. Position A in Figure 2 was proposed by Germer and MacRae, but there is no specific evidence that favors this location. Verheij et al.[62] proposed position B based on low-energy ion-scattering data. However, their measurements were performed with the sample at 250 °C where the oxygen location may not be the same as at room temperature. In any event, the reconstructed surface has a very open structure so that the oxygen atoms are most likely in essentially the same plane as the top layer of nickel atoms. Therefore, this surface can be classified as an incorporation structure.

Work-function change and LEED-pattern changes provide evidence of an incorporation structure on the Mo(100) surface when oxygenated above 900 K.[63] At low oxygen concentrations, less than 0.8 monolayers, the work-function change is negative,

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(52) P. R. Norton, R. L. Tapping, and J. W. Goodale, *Surf. Sci.*, **65**, 13 (1977).

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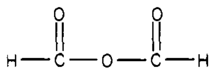
indicating that the oxygen atoms have penetrated the top layer of metal atoms. Recent XPS measurements of the molybdenum core level binding energies show oxidation-state changes on initial exposure to oxygen consistent with incorporation of oxygen into the top metal layer.[64] At higher oxygen exposures, with surface concentrations above one monolayer, the LEED beams show pronounced, energy-dependent broadening indicative of small, random-sized, ordered domains separated by steps.[63] These steps must be due to surface reconstruction resulting from oxygen incorporation. At very large oxygen exposures MoO_2 is formed at the surface as judged by XPS measurements of the molybdenum core level shift[64] and by Raman spectroscopy of the surface.[65]

The adsorption and surface chemistry observed on the oxidized Mo(100) and Ni(110) surfaces are consistent with those of the model of localized Lewis acid and base sites on the surface. Johnson and Madix[28] have studied the adsorption and thermal decomposition of formic acid to CO, CO_2, H_2O, and H_2 on Ni(110) as a function of surface-oxygen concentration. They have also examined the thermal desorption of CO, H_2, H_2O, and CO_2 from the same surfaces. The results of the CO thermal-desorption measurements are in agreement with a more acidic/less basic surface following oxygen treatment. However, the character of the changes in the CO desorption spectrum[28] is qualitatively different from that observed for desorption of CO from oxygenated Ni(111) where the surface is known to have an overlayer structure.[22] On Ni(111) a single CO desorption peak is observed which shifts to lower temperature with increasing surface-oxygen concentration. This continuous change in the CO desorption peak temperature must be characteristic of a simple inductive effect. In contrast, while the clean Ni(110) surface produces a single CO desorption peak similar to Ni(111), the presence of oxygen on the surface produces a new low-temperature CO desorption peak. With increasing oxygen concentration this low-temperature state increases in size while the higher-temperature, clean-surface state decreases. This new low-temperature CO state signals the creation of sites on the surface which are distinctly less basic or more acidic than those of the clean surface.

The change in mechanism for formic acid decomposition between the clean and oxidized Ni(110) surfaces and hence the selectivity for CO or CO_2 product formation can be rationalized by a change in the character of the surface electronic structure from delocalized to localized. On the clean Ni(110) surface Falconer and Madix[66] have proposed that the decomposition of formic acid proceeds via an adsorbed formic anhydride intermediate:



$$\mathrm{H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H}$$

They note that the anhydride does not form in solution but may be stabilized on the surface by multiple atom chelating action. In fact, the anhydride may lie flat on the surface forming a π complex which extends over several metal atoms. Such a surface-bonding scheme would be favored by a delocalized surface-electron structure according to the overlap criterion discussed previously. On the other hand, the key surface intermediate in the decomposition of formic acid on the oxidized surface is a formate species, HCOO.[28] Based on the strength of the formate–proton interaction it is not difficult to see that a formate species would be stabilized by the presence of *localized* acidic sites on the oxidized Ni(110) surface. Thus a change in the surface chemical reaction mechanism and hence a change in product selectivity can be understood in terms of the localized or delocalized character of the surface electronic structure.

Walker, Henry, and Stair[67,68] have examined the adsorption selectivity of a Mo(100) pretreated at 1023 K to produce 1.5 monolayers of oxygen atoms incorporated into the surface. A series of Lewis bases was chosen to compare the tendency of this surface to adsorb localized nitrogen lone pair donor bases with delocalized π-electron donor bases. The nitrogen lone pair bases examined were ammonia, monomethylamine, dimethylamine, trimethylamine, pyridine, and 2,6-di-*tert*-butylpyridine. The π-electron donors examined were ethylene, propylene, benzene, and toluene. With the surface at room temperature all of the nitrogen bases adsorbed readily, bonding to the surface via the nitrogen lone pair.[68] In fact, they were all so strongly chemisorbed by the oxidized molybdenum surface that they could not be thermally desorbed intact from the surface. In contrast, the π-electron-donor bases did not adsorb on this surface at room temperature even with exposures of 10^{12} langmuirs at 1 atm.[67] The clearest example of the preference by this surface for the nitrogen lone pair is a comparison of benzene and pyridine adsorption since both molecules have similar π-electron systems while pyridine also has the nitrogen lone pair. Pyridine adsorbs strongly while benzene does not adsorb at room temperature. This result is in striking contrast to the situation with clean metal surfaces such as Ni(111) and Pt(111). On clean Pt(111) and Ni(111) ammonia[69,24] and benzene[70,23] produce the work-function changes expected for adsorption of an electron donor. Ammonia adsorbs weakly on both surfaces, desorbing at room temperature or just above.[71,72] Benzene adsorbs strongly and will not desorb prior to decomposition on either surface.[73] What we have here is a classic example of a reversal in base-strength ordering with a change in the Lewis acid, in this case a surface. As discussed in section III, the change in base-strength ordering can be understood in terms of the criterion of maximum orbital overlap. The delocalized electron-acceptor orbitals of the clean metal surface overlap best with the π-electron-donor Lewis bases while the localized acid sites on the oxidized molybdenum surface overlap best with the lone pair donor bases.

In addition to the chemical evidence from adsorption studies, physical measurements related to the surface polarizability confirm that the valence electronic structure of the oxidized molybdenum surface is more localized than the clean surface.[74] For a spherical metal particle the classical polarizability is proportional to the volume of the metal particle, $\alpha_{cl} \propto R^3$, where R is the particle radius. Recent free electron gas calculations show that the polarizability of metal particles and metal films is further reduced with respect to the classical result for very small sizes due to quantum effects.[75] Thus the polarizability is an experimental measure of the spatial extent of the valence electronic states. A measure of the surface polarizability can be obtained from the energy shifts in Auger lines and core levels of xenon physically adsorbed on the surface.[74] In particular Wagner has defined a quantity he calls the "Auger parameter" which is just the difference in the measured kinetic energies of an X-ray excited core level electron and an X-ray excited Auger electron.[76] The change in the Auger parameter between a rare gas atom in the gas phase and adsorbed on the surface is a direct measure of the polarization by the surface in response to the creation of the positive rare gas ion and hence a measure of the surface polarizability. Indeed, measurements of the Auger parameter for xenon physisorbed on Mo(100) confirm that reduction in the surface polarizability is detectable even for submonolayer surface-oxygen concentrations.[74] Therefore, the valence electronic states at an oxygenated Mo(100) surface are spatially more localized than those for the clean surface

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in agreement with the chemical evidence.

The preceding discussion implies that orbital overlap is an important criterion for determining the strength of the chemisorption bond and that the nature of the orbital in an adsorbing molecule which is preferred by the surface can be substantially altered by modifying the surface composition. In fact, the initial chemisorption experiments reported for the oxygen pretreated molybdenum surface suggest that adsorption selectivity for molecular Lewis bases is controlled by the geometric structure of the electronic states at the surface.[65,68] It remains to be shown whether surface composition modifiers less electronegative than oxygen will produce similar adsorption selectivity as well as whether it can be produced with other metals. It will also be important to investigate adsorption selectivity with molecular Lewis acids and with molecular Lewis bases other than nitrogen bases and π-electron donors in order to evaluate the generality of the overlap criterion.

VII. Summary and Conclusion

The concept of Lewis acids and bases was briefly reviewed. The dependence of base-strength ordering on the nature of the reference acid was demonstrated for both the solution phase and gas phase environments. By adapting the equations of perturbational molecular orbital theory to the gas phase environment, we showed that a reversal in base-strength ordering must be due to changes in the orbital overlap of the electron donor with the electron acceptor. This was seen to be a consequence of the principle of maximum orbital overlap.

The classification of surface–adsorbate interactions as acid–base was established by using the sign of the work-function change which accompanies simple adsorption. The surface acid–base adduct was shown to exhibit an inductive effect similar to that seen in molecules. The production of localized Lewis acid sites was demonstrated for oxygen-incorporation structures on Mo(100) and Ni(110) by using chemical evidence as well as measurements of the surface polarizability.

The most interesting conclusion from this discussion is that the spatial extent of electronic states at the surface, that is whether they are delocalized over two or more surface atoms or localized mainly on a single surface atom, may be the determining factor in adsorption and surface chemical reaction selectivity. In essence, the description of surface electronic structures as localized or delocalized is merely a supplementary classification scheme on top of the primary classification as acid or base. It may serve to provide both qualitative predictions and rationalizations of a wide variety of surface chemical phenomena in the same way that the classifications "hard and soft" have provided for a qualitative understanding of solution phase Lewis acid–base chemistry.

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Appendix I. Calculation of the Second Ionization Potential

The production of a doubly ionized molecule can be decomposed into two steps:

$$M \rightarrow M^+(C) + e^- \tag{A1}$$

$$M^+(C) \rightarrow M^{2+}(VV) + e^- \tag{A2}$$

The notations $M^+(C)$ and $M^{2+}(VV)$ indicate that the hole or holes are located in a core level, C, or in valence orbitals, VV. The free electrons are to be considered at rest at infinite separation from the positive ion. The energy associated with (A1) is just the core level binding energy for the gas phase molecule measured by X-ray photoelectron spectroscopy, BE(C). The energy of (A2) is just the negative of the Auger electron kinetic energy arising from the (CVV) Auger process, –KE(CVV). For the case where the doubly ionized cation, $M^{2+}(VV)$, is equivalent to the cation produced by removing the two highest-energy electrons from neutral M, the second ionization potential can be written:

$$IP_2 = BE(C) - KE(CVV) - IP_1 \tag{A3}$$

where IP_1 is the first ionization potential.

Registry No. $CH_3CH_2NH_2$, 75-04-7; $CH_3(CH_2)_2NH_2$, 107-10-8; $CH_3(CH_2)_3NH_2$, 109-73-9; $CF_3CH_2NH_2$, 753-90-2; $CF_3(CH_2)_2NH_2$, 460-39-9; $CF_3(CH_2)_3NH_2$, 819-46-5; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CN, 75-05-8; CH_3OCH_3, 115-10-6; NH_3, 7664-41-7; C_2H_4, 74-85-1; C_6H_6, 71-43-2.

Atom–Atom Potential Analysis of the Packing Characteristics of Carboxylic Acids. A Study Based on Experimental Electron Density Distributions

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Abstract: Information contained in electron density distributions, derived from X-ray diffraction data, was exploited to improve the electrostatic parameters of atom–atom potential functions of the carboxyl group and thus to obtain a better estimate of the Coulomb intermolecular energies. The proton affinities of the carbonyl oxygen atom of the amide and carboxyl groups were compared in terms of electrostatic potential energy around these atoms and correlated with hydrogen-bonding properties. Energy calculations were undertaken to account for various characteristic packing motifs of carboxylic acid molecules, including the geometry of the catemer motif, order–disorder of the carboxyl dimer, preferred stacking of carboxyl dimers, the role played by C–H···O(carbonyl) interactions in stabilizing overall packing, characteristic packing of substituted benzoic acids, and the stability of the observed crystal structures of oxalic acid and formic acid, via the generation and analysis of ensembles of alternative crystal structures.

1. Introduction

In a previous paper we demonstrated the role played by intermolecular Coulomb potentials in determining the molecular packing modes of amides in the crystal;[1] the atomic electrostatic properties used in that study were derived from low-temperature X-ray diffraction data. The aim of the present work is to account in a similar manner for some of the characteristic molecular packing modes of carboxylic acids.

Crystal packing of carboxylic acids has been studied in terms of atom–atom potentials by several groups, notably Derissen and Smit[2] and Hagler and Lifson.[3] The latter derived a force field

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