group was staggered, except for **1–3**, where both staggered and eclipsed forms were used.

Basis sets A, B, and C yielded total RHF energies of respectively (thioacetone) ($N = 30$) –512.709 103, ($N = 52$) –513.966 854, ($N = 70$) –514.000 128 au (1 au = 627.5 kcal/mol); (methyl ethyl thioketone) ($N = 37$) –551.637 418, ($N = 65$) –552.940 938, ($N = 83$) –552.974 289 au. Basis A yielded the following RHF energies (all in au) for 1–4: (**1**, staggered, $N = 80$) –819.322 491; (**1**, eclipsed, $N = 80$) –819.317 254, (**2**, staggered, $N = 76$) –498.294 136, (**2**, eclipsed, $N = 76$) –498.288 907, (**3**, staggered, $N = 80$) –829.319 224, (**3**, eclipsed, $N = 80$) –819.314 474, (**4**, staggered, $N = 76$) –498.290 552.

The RPA calculations included all possible single excitations, excluding those out of the core MOs, supported by the MO basis. For thioacetone, bases A, B, and C yielded 120, 384, and 600 configurations, respectively, while for methyl ethyl thioketone there were 195, 615, and 885 configurations. For **1–4**, the RPA calculations included 1023 configurations for each molecule.

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Electrostatic Effects in Interactions between Hard (Soft) Acids and Bases[†]

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Abstract: Recent theoretical deduction of the principle of hard and soft Lewis acids and bases (HSAB) by Parr and Pearson is commented upon and extended to explicitly include the electrostatic effects accompanying the formation of a chemical bond. The present explanation of the HSAB principle is based on a modified energy expression for an atom-in-a-molecule, suggested by the density functional theory, and the chemical potential (electronegativity) equalization principle.

This article comments upon and extends the recent remarkable theoretical deduction by Parr and Pearson[1] of the Principle of Hard and Soft Acids and Bases (HSAB).[2]

According to this principle hard Lewis acids prefer to coordinate to hard Lewis bases, and soft acids to soft bases, with the soft–soft interactions being largely covalent and the hard–hard interactions predominantly ionic. In an attempt to quantify and theoretically justify the HSAB principle Parr and Pearson have introduced the concept of *absolute hardness*:

$$\eta = \tfrac{1}{2}(\partial^2 E/\partial N^2)_Z = \tfrac{1}{2}(\partial \mu/\partial N)_Z = -\tfrac{1}{2}(\partial \chi/\partial N)_N = \tfrac{1}{2}(I - A) \quad (1)$$

where $E = E(N,Z)$ is the energy, N is the number of electrons, Z is the atomic number of the donor (or acceptor) atom, $\mu = (\partial E/\partial N)_Z$ is the chemical potential, and $\chi = -\mu = {}^1/_2(I + A)$ is the electronegativity; here I and A are the ionization potential and electron affinity of the species in question. The absolute hardness, positive by the stability criterion,[3] is large for hard species and small for soft ones. It is one of the three *stiffness moduli* defining the *stiffness matrix* of the second derivatives of $E(N,Z)$.[4] With use of the energy expression (superscript degree refers to the isolated reactants)

$$E(N) = E^\circ + \mu^\circ(N - N^\circ) + \eta(N - N^\circ)^2 = E^\circ + \mu^\circ \Delta N + \eta(\Delta N)^2 \quad (2)$$

for an atom-in-a-molecule, and the chemical potential (electronegativity) equilization principle[5] (to determine ΔN) gives the stabilization energy for the A–B complex:[1]

$$\Delta E = (E_A - E_A^\circ) + (E_B - E_B^\circ) = [(\mu_A^\circ - \mu_B^\circ)\Delta N] + [(\eta_A + \eta_B)(\Delta N)^2] = \left[-\tfrac{1}{2}\frac{(\mu_B^\circ - \mu_A^\circ)}{\eta_A + \eta_B}\right] + \left[\tfrac{1}{4}\frac{(\mu_B^\circ - \mu_A^\circ)^2}{\eta_A + \eta_B}\right] = -\tfrac{1}{4}\frac{(\mu_B^\circ - \mu_A^\circ)^2}{\eta_A + \eta_B} \quad (3)$$

here ΔN is the electron transfer from B (donor atom of a base) to A (acceptor atom of an acid). This expression immediately explains the soft–soft preference of the HSAB principle, since then both η_A and η_B are small and stabilization of the complex large. It does not explain, however, the hard–hard preference (large denominator). To resolve this apparent paradox Parr and Pearson attributed stability of the hard–hard interaction to the ionic bond which should be favorable in this case. Equation 3, supplemented by an extra-stabilization expected from the equalization of ionization potentials of atoms-in-a-molecule, offers a "proof" of the HSAB principle.[1]

A major defect of this deduction, and—as we shall demonstrate—the reason for the hard–hard paradox, is that, while including second-order effects due to electron transfer in energy expressions 2 and 3, it neglects important *first-order contributions*

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due to perturbing external potential of the partner of a given atom-in-a-molecule. It should be noticed that the main implications for the HSAB principle are the same from the first-order stabilization energy, $\Delta E^{(1)} \equiv (\mu_A{}^\circ - \mu_B{}^\circ)\Delta N = 2\Delta E$ [see eq 3], with the hardness being used only in determining changes in the chemical potentials due to electron transfer.

In order to explicitly include the major effects of the chemical bond formation, we apply the *full second-order expansion* of the energy $E(N,Z)$ of an atom-in-a-molecule:[6]

$$E(N,Z) = E^\circ + \left(\frac{\partial E}{\partial N}\Delta N + \frac{\partial E}{\partial Z}\Delta Z\right) + \tfrac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}(\Delta N)^2 + 2\frac{\partial^2 E}{\partial N \partial Z}\Delta N \Delta Z + \frac{\partial^2 E}{\partial Z^2}(\Delta Z)^2\right] \equiv E^\circ + (\mu^\circ \Delta N + \upsilon^\circ \Delta Z) + [\eta(\Delta N)^2 + 2\alpha \Delta N \Delta Z + \beta(\Delta Z)^2] \quad (4)$$

where $\upsilon = V_{ne}/Z < 0$ is the electron–nuclear attraction per unit nuclear charge, $\alpha = {}^1/_2(\partial\mu/\partial Z)_N = {}^1/_2(\partial\upsilon/\partial N)_Z < 0$, and $\beta = {}^1/_2(\partial\upsilon/\partial Z)_N < 0$.

The formation of the chemical bond is well-known to constitute a relatively small perturbation of only the outer (valence) part of the electron density distribution, with the inner (core) part remaining practically unchanged. Therefore, for the purpose of determining first-order stabilization energy in the acid–base complex, the *frozen-core approximation* can be adopted. We thus interpret the quantities N, Z, and υ in eq 4 accordingly as the average number of *outer electrons*, *charge of atomic core*, and the *outer electron core attraction energy per unit core charge*.

The increase in the core charge ($\Delta Z > 0$) of an atom-in-a-molecule is essential to account for the fact that in the A–B complex, outer electrons of an atom core are in the presence of *both atomic cores*. It is well-known that this lowering of the effective external potentials of atoms-in-a-molecule results in an overall *contraction of atomic density distributions*, which manifests itself, e.g., in the positive change of the electronic kinetic energy, $\Delta T = T(R_e) - T(\infty) = D_e$ (dissociation energy) at the equilibrium bond length, R_e. In our model expression (eq 4) we model this contraction effect by increasing core charges of both partners in the A–B complex.

The magnitude of ΔZ_X, for an atom-in-a-molecule will depend on the nature of its partner, Y. The donor or acceptor atoms of *soft species* (small η) are of large size and high polarizability (relatively small core charge, well-shielded nucleus). This suggests that for them, $|\upsilon_X|$ and ΔZ_Y (which they effectively produce when approaching their partners) are relatively small. The *hard reactants* (large η) are usually of smaller size and low polarizability (relatively large core charges, less shielded nucleus), thus having large $|\upsilon_X|$ and inducing large ΔZ_Y in their partners.

The expression for the chemical potential $\mu(N,Z)$ of an atom-in-a-molecule (from eq 4) is

$$\mu(N,Z) = \mu^\circ + 2(\eta \Delta N + \alpha \Delta Z) \quad (5)$$

We require the flow of electrons ΔN to equalize the chemical potentials of the reactants:[1,5]

$$\mu_A(N_A,Z_A) = \mu_B(N_B,Z_B)$$

Hence,

$$\Delta N = \frac{1}{2(\eta_A + \eta_B)}\{\mu_B{}^\circ - \mu_A{}^\circ + 2(\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)\} \quad (6)$$

It should be noticed that the coupling term, including α moduli, should be small due to cancellation of contributions from A and B, and it vanishes exactly in a homonuclear diatomic. Therefore, as already indicated by Parr and Pearson, the amount of electron transfer is proportional to the difference in chemical potentials (or electronegativities) and inversely proportional to the sum of hardness parameters. Using this expression in calculating the first-order stabilization energy $\Delta E^{(1)}$ gives

$$\Delta E^{(1)} \equiv (\mu_A{}^\circ - \mu_B{}^\circ)\Delta N + \upsilon_A{}^\circ \Delta Z_A + \upsilon_B{}^\circ \Delta Z_B = -\frac{(\mu_B{}^\circ - \mu_A{}^\circ)^2}{2(\eta_A + \eta_B)} + \frac{(\mu_A{}^\circ - \mu_B{}^\circ)(\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)}{\eta_A + \eta_B} + (\upsilon_A{}^\circ \Delta Z_A + \upsilon_B{}^\circ \Delta Z_B) \quad (7)$$

which is the basic expression in our theoretical justification of the HSAB principle.

We first observe, as already indicated, that the second term should always be small due to expected cancellation of terms in the numerator. This is obvious in the hard–hard and soft–soft interactions, since then α's and ΔZ's are of comparable magnitude for both reactants. In the hard–soft case the hard reactant has larger $|\alpha|$ but its ΔZ is smaller (due to a soft partner), while the opposite is the case for the soft reactant: smaller $|\alpha|$ and larger ΔZ (due to a hard partner). In the case of a soft reactant being of much larger size than its hard partner, a large atom will be perturbed less than a small atom because the core of a small atom appreciably affects only a portion of a large atom's outer electrons, while the perturbation due to a large atom is felt almost equally by all of the small atom's outer electrons. Soft species, however, create a small electrostatic perturbation (small charge and large size of the core) so that again the dominating term $|\alpha_{\text{hard}} \Delta A_{\text{hard}}|$ should be small. Therefore, also in the mixed case the cancellation of terms in the numerator should be substantial, so that, taking into account a large denominator ($\sim\eta_{\text{hard}}$), the stabilization energy is expected to be dominated by the first (electron transfer) and last (external potential) terms in eq 7 (both negative).

If both acid and base are soft the last term is of secondary importance since than both $|\upsilon|$'s and ΔZ's (due to soft partners) are small. As identified by Parr and Pearson,[1] it is the first electron transfer term (small $\eta_A + \eta_B$) that explains the stability of the soft–soft complex.

For hard acid–hard base combinations, the magnitude of the first term becomes small (large $\eta_A + \eta_B$), and the stability originates from the last term in eq 7. Namely, for such a pair of reactants both ΔZ's (due to hard partners) and $|\upsilon|$'s are large, so that the favorable effect from the external field, due to a relatively unshielded nucleus of the partner, becomes dominant.

For a hard–soft combination both the first and the last terms should be small: the first since one of the hardness parameters is large, and the last since a large $|\upsilon|$, of the hard reactant, is multiplied by a small ΔZ (due to a soft partner) and vice versa for the soft reactant (small $|\upsilon|$ and large ΔZ). Therefore, stability is enhanced neither by the electron transfer (first term) nor the change in the external potential (last term). If the soft–hard combination involves a very large atom of a soft reactant and a small atom of a hard reactant, only the perturbation of a small atom by a large one is important (see the above discussion of the coupling terms, $\alpha \Delta Z$). This perturbation (ΔZ_{hard}) is very small, however, as due to a soft partner, so that again the stabilization from the dominating term $\upsilon_{\text{hard}} \Delta Z_{\text{hard}}$ should be negligible.

This completes our theoretic, model explanation of the trends of the HSAB principle. It is gratifying that this simple extension of the original model of Parr and Pearson covers the whole content of the HSAB principle. The electron transfer (predominantly covalent bond) has been shown to be responsible for the stability of the soft–soft interactions, while the external potential perturbation (predominantly ionic bond) assures the stability of hard–hard interactions.

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