to calculate the transfer coefficient α. Since the reduction process proved to be a catalytic one, only high-frequency measurements were used to calculate k_s, a frequency region where $k_c \gg \omega$ does not apply. Looking on the heterogeneous rate constant data (Table II), there are two phenomena to notice. k_s increases with decreasing number of p-Br-bzac ligands, within a single n value, when the complex is less sterically hindered.

Decreasing the number of p-Br-bzac ligands in a complex causes less steric hindrance, when a molecule is reduced at the mercury solution interface. This also reduces the quasiaromatic stabilization of the β-diketonate–metal ring and thus leads to a higher k_s value. However, there is an exception to this general trend, since the trans isomer (A) when $n = 3$ has a larger k_s value than all of the isomers with $n = 2$. As was true for the separation of the compounds, the number of p-Br-bzac ligands is not the only major factor influencing separation but also is important in the relative position of the phenyl rings. The k_s values of the trans isomer (A, $n = 3$) and the trans-cis isomer (B, $n = 2$) are similar, 0.0703 ± 0.0130 and 0.0674 ± 0.0215 cm/s, respectively. They are the only two isomes which have two phenyl rings in trans positions and thus allow the molecule being reduced to come closer to the mercury electrode, resulting in a higher k_s value. Within a single value of n, the variations in k_s are in accordance with the predicted behavior of these complexes, based on steric effects. When $n = 3$, the trans isomer has higher k_s than has the cis, 0.0703 ± 0.0130 and 0.0220 ± 0.0580 cm/s, respectively. From Figure 1 it can be seen that the trans isomer (A) has an open site between the trans phenyl rings, which does not exist in the symmetrical cis isomer (C), and this allows closer access to the electrode surface, resulting in a larger k_s value for isomer A. For $n = 2$ the largest

k_s is for the trans-cis isomer (B) again for the same reason of having two phenyl rings at a trans position. According to these results the isomers which have two phenyl rings in a trans position have a larger k_s value than those who do not. Even though isomer D (cis-trans isomer $n = 2$) appears to be less sterically hindered, it does not have phenyl rings in a trans position and it has a lower k_s value than the trans,cis isomer (B). This strongly implies that the relative trans position has more influence than only the steric hindrance. This phenomenon is under investigation.

Of significant importance is an inductive effect which clearly shows in the $E_{1/2}$ values for the various complexes (Table II). A replacement of one acac ligand by one p-Br-bzac ligand results in a positive shift of $E_{1/2}$ by 72–118 mV on an average. We believe that this positive shift is due to the presence of the bromine in the phenyl ring. This assumption is currently being investigated in a similar series of complexes where the p-Br-bzac ligand is replaced by 1-phenyl-1,3-butanedione (benzoylacetone, bzac). The relative trans position of two phenyl rings has an effect also on the $E_{1/2}$ values. It is clear from the data presented that complex B which has two phenyl groups in a trans position has an $E_{1/2}$ value of 0.247 mV which is much closer to that of complex A [trans-Co(p-Br-bzac)$_3$], 0.267 mV, than to that of the other complexes with $n = 2$, which are reduced at 0.201 and 0.183 mV.

We have shown here a good correlation between the structure of the specific isomers, their behavior in separation, and heterogeneous rate constants for electron transfer. We were able to get a more detailed picture for the reduction mechanism than what was obtained previously.

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On the Concept of Local Hardness in Chemistry

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Abstract: Density functional theory is shown to provide a natural definition for a local atomic or molecular property called the local hardness,

$$\bar{\eta}(r) = \frac{1}{2N} \int \frac{\delta^2 F[\rho]}{\delta\rho(\bar{r})\delta\rho(\bar{r}')} \rho(\bar{r}') \, d\bar{r}'$$

Weighted by the Fukui function $f(\bar{r})$ of Parr and Yang and integrated over all space this gives the global absolute hardness $\eta = {}^1/_2 \, (d^2E/dN^2)_v$ of Parr and Pearson

$$\eta = \int f(\bar{r})\bar{\eta}(\bar{r}) \, d\bar{r}$$

The corresponding integral over a portion of a molecule gives a regional or group hardness. Various properties and identities involving local hardness are discussed, and it is shown that local hardness constitutes a generalization of the classical electrostatic potential due to an electron distribution.

By now it is clear that the density functional description[1] of many-electron systems provides a highly useful framework for rigorous quantitative definition of important concepts in chemistry and schemes for their calculation as well. In the present paper

we show how this language includes the idea that different particular places in an atom or molecule can be "hard" or "soft"—the concept of local or site hardness.

Two properties of a molecule as a whole, global rather than local, are its electronegativity χ and hardness η. These may be

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defined as the first and second derivatives of the total electronic energy E with respect to the number of electrons N,

$$\chi = -(\partial E/\partial N)_v \tag{1}$$

$$\eta = \frac{1}{2}(d^2E/dN^2)_v \tag{2}$$

where v is the external (nuclear) potential. These formulas are due to Iczkowski and Margrave[2] and Parr and Pearson,[3] respectively. Density functional theory also identifies electronegativity with the negative of the chemical potential μ of the electronic cloud[4]

$$\mu = -\chi = (\partial E/\partial N)_v \tag{3}$$

and the thermodynamic-like attributes of the electronegativity concept are thereby rigorously confirmed. The hardness concept of eq 2 explains the widely used but otherwise empirical fact that for acids and bases "hard likes hard" and "soft likes soft".[3,5,6] For the hardness we have

$$2\eta = (\partial\mu/\partial N)_v \tag{4}$$

Hardness measures the sensitivity of the electronegativity to change in the number of electrons. Here and throughout this paper the discussion is confined to ground states.

The characterization of a molecule solely by a set of global quantities excludes the possibility of predicting the preferential site for a chemical reaction, and so the description of chemical reactivity by density functional theory demands the introduction of local quantities. One important such quantity is the frontier or Fukui function,[7,8] given by

$$f(\bar{r}) = \left[\frac{\delta\mu}{\delta v(\bar{r})}\right]_N = \left[\frac{\partial\rho(\bar{r})}{\partial N}\right]_v \tag{5}$$

where $\rho(\bar{r})$ is the electron density. From the successes of the frontier electron theories of chemical reactivity,[9] it follows that $f(\bar{r})$ is a useful reactivity index for early stages of a chemical reaction. Below we examine another quantitative local concept in density functional theory, the local hardness $\bar{\eta}(\bar{r})$, and we show how this concept validates describing a molecule as a collection of hard or soft functional groups.

Local Hardness

We begin with the fundamental equations of density functional theory. All molecular properties are functionals of ρ; in particular, the energy is given by

$$E[\rho] = \int v(\bar{r})\rho(\bar{r})\,d\bar{r} + F[\rho] \tag{6}$$

with

$$F[\rho] = T[\rho] + V_{ee}[\rho] \tag{7}$$

in which $T[\rho]$ is the electronic kinetic energy and $V_{ee}[\rho]$ is the electron–electron repulsion energy. Furthermore, minimization of $E[\rho]$ subject to the condition that the number of electrons is a given N value

$$N = N[\rho] = \int \rho(\bar{r})\,d\bar{r} \tag{8}$$

gives the density and energy for the ground state, for a system defined by N and v. This minimization is tantamount to solving the Euler equation

$$\mu = v(\bar{r}) + \frac{\delta F[\rho]}{\delta\rho(\bar{r})} \tag{9}$$

The chemical potential μ is constant through the whole system, a molecular property $\mu[N,v]$.

For the change of one ground state to another,

$$dE = \mu\,dN + \int \rho(\bar{r})\,dv(\bar{r})\,d\bar{r} \tag{10}$$

and

$$d\mu = 2\eta\,dN + \int f(\bar{r})\,dv(\bar{r})\,d\bar{r} \tag{11}$$

where μ, η, and $f(\bar{r})$ are given by eq 3, 4, and 5. The quantities μ and η, like E, are global quantities (numbers); $f(\bar{r})$, like $\rho(\bar{r})$, is a local quantity (function of position).

Also, as already was pointed out some time ago,[4]

$$d(E - N\mu) = d\left[F - \int \frac{\partial F[\rho]}{\delta\rho(\bar{r}')}\rho(\bar{r}')\,d\bar{r}'\right] =$$
$$-\int\int \frac{\partial^2 F[\rho]}{\delta\rho(\bar{r})\delta\rho(\bar{r}')}\,d\rho(\bar{r})\rho(\bar{r}')\,d\bar{r}\,d\bar{r}' \tag{12}$$

Here is where local hardness comes in. Following Ghosh and Berkowitz,[10] we define

$$\bar{\eta}(r) = \frac{1}{2N}\int \frac{\delta^2 F[\rho]}{\delta\rho(\bar{r})\delta\rho(\bar{r}')}\rho(\bar{r}')\,d\bar{r}' \tag{13}$$

and find

$$d(E - N\mu) = -2N\int \bar{\eta}(\bar{r})\,d\rho(\bar{r})\,d\bar{r} \tag{14}$$

$\bar{\eta}(\bar{r})$ is the local hardness, a function of position. Eliminating dE from eq 10 and 14, we obtain

$$d\mu = 2\int \bar{\eta}(\bar{r})\,d\rho(\bar{r})\,d\bar{r} + \frac{1}{N}\int \rho(\bar{r})\,dv(\bar{r})\,d\bar{r} \tag{15}$$

This is the "local" counterpart of eq 11 in the sense of Nalewajski,[11] in which there now appears the local hardness in place of the global hardness. Similarly, eq 10 has the counterpart

$$dE = \int \mu\,d\rho(\bar{r})\,d\bar{r} + \int \rho(\bar{r})\,dv(\bar{r})\,d\bar{r} \tag{16}$$

but this is not so interesting as eq 15.

From eq 15 we find another formula for $\bar{\eta}(\bar{r})$,

$$\bar{\eta}(\bar{r}) = \frac{1}{2}\left[\frac{\delta\mu}{\delta\rho(\bar{r})}\right]_v \tag{17}$$

Also, from eq 15 and eq 5 we obtain

$$\eta = \int \bar{\eta}(\bar{r})\,f(\bar{r})\,d\bar{r} \tag{18}$$

These equations show how hardness can be computed by density functional theory. Finite difference approximations to eq 17 and 18 are easily constructed.

Identities Involving Local Hardness

Taking the gradient of eq 9, multiplying by $\rho(\bar{r})$, and integrating over all space gives

$$2N\int \bar{\eta}(\bar{r})\nabla\rho(\bar{r})\,d\bar{r} + \int \rho(\bar{r})\nabla v(\bar{r})\,d\bar{r} = 0 \tag{19}$$

But Levy and Perdew[12] have shown that $\int\rho(\bar{r})\nabla v(\bar{r})\,d\bar{r} = 0$. Hence

$$\int \bar{\eta}(\bar{r})\nabla\rho(\bar{r})\,d\bar{r} = 0 \tag{20}$$

This is a simple but important condition on $\bar{\eta}$, which would be sensible to impose on approximations to $\bar{\eta}$. For example, one might

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try imposing a local version of eq 19,

$$2N\bar{\eta}(\bar{r})\nabla\rho(\bar{r}) + \rho(\bar{r})\nabla v(\bar{r}) = 0 \tag{21}$$

Note, however, that this condition is not satisfied by Thomas–Fermi theory.

To obtain another identity, proceed as follows. From eq 10 and 11 one has $d(E - N\mu) = \int [\rho(\bar{r}) - Nf(\bar{r})] \, dv(\bar{r}) \, d\bar{r} - 2N\eta \, dN$, which one may equate to eq 14:

$$\int [\rho(\bar{r}) - Nf(\bar{r})] \, dv(\bar{r}) \, d\bar{r} = -2N\int \bar{\eta}(\bar{r}) \, d\rho(\bar{r}) \, d\bar{r} + 2\eta N \, dN \tag{22}$$

Now write

$$d\rho(\bar{r}) = f(\bar{r}) \, dN + \int \left(\frac{\delta\rho(\bar{r})}{\delta v(\bar{r}')} \right)_N dv(\bar{r}') \, d\bar{r}' \tag{23}$$

substitute in eq 22, and use eq 18. There follows

$$\int \rho(\bar{r}) \, dv(\bar{r}) \, d\bar{r} =$$
$$N \int f(\bar{r}) \, dv(\bar{r}) \, d\bar{r} - 2N \int \bar{\eta}(\bar{r}) \left(\frac{\delta\rho(\bar{r})}{\delta v(\bar{r}')} \right)_N dv(\bar{r}') \, d\bar{r} \, d\bar{r}' \tag{24}$$

In more detail, from the perturbation formula

$$\left(\frac{\delta\rho(\bar{r})}{\delta v(\bar{r}')} \right)_N = \left(\frac{\delta\rho(\bar{r}')}{\delta v(\bar{r})} \right)_N = 2 \, \text{Re} \sum_k{}' \frac{\rho_{k0}{}^*(\bar{r})\rho_{0k}(\bar{r}')}{E_k - E_0} \tag{25}$$

one finds

$$\int \rho(\bar{r}) \, dv(\bar{r}) \, d\bar{r} = dE|_N =$$
$$N \int f(\bar{r}) \, dv(\bar{r}) \, d\bar{r} - 4N \, \text{Re} \left\{ \sum_k{}' \frac{\langle\psi_0|dv|\psi_k\rangle \langle\psi_0|\bar{\eta}|\psi_k\rangle}{E_k - E_0} \right\} \tag{26}$$

This fascinating formula expresses the Hellman–Feynman force in terms of a force acting on $f(\bar{r})$ plus terms, often small, involving products of matrix elements of a perturbation dv with matrix elements of the local hardness $\bar{\eta}$.

Calculation of Local Hardness. Relationship to Classical Electrostatic Potential

We here do not go into full detail as to how $\bar{\eta}(\bar{r})$ can be calculated for particular species (though that is of much interest). It can be done, though since no exact method is yet known to calculate $F[\rho]$, approximations are necessary.

If in eq 7 we break $V_{ee}[\rho]$ into its classical and nonclassical parts, and write

$$F[\rho] = T[\rho] + J[\rho] - K[\rho] \tag{27}$$

where

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\bar{r})\rho(\bar{r}')}{|\bar{r} - \bar{r}'|} \, d\bar{r} \, d\bar{r}' \tag{28}$$

and $K[\rho]$ is the rest of V_{ee}, then the local hardness becomes the sum of three terms,

$$\bar{\eta}(\bar{r}) = \bar{\eta}_T(\bar{r}) + \bar{\eta}_J(\bar{r}) + \bar{\eta}_K(\bar{r}) \tag{29}$$

Here

$$\bar{\eta}_J(\bar{r}) = \frac{1}{2N} \int \frac{\delta^2 J[\rho]}{\delta\rho(\bar{r})\delta\rho(\bar{r}')} \rho(\bar{r}') \, d\bar{r}' =$$
$$\frac{1}{2N} \int \frac{1}{|\bar{r} - \bar{r}'|} \rho(\bar{r}') \, d\bar{r}' = \frac{1}{2N}\phi(\bar{r}) \tag{30}$$

where $\phi(\bar{r})$ is the classical electrostatic potential at $\bar{r}$ due to the entire electron density.

The quantity $\bar{\eta}_T(\bar{r})$ can be examined, for example, using the Thomas–Fermi model. Thus, using

$$T[\rho] = C_K \int \rho(\bar{r})^{5/3} \, d\bar{r}; \quad C_K = \tfrac{3}{10}(3\pi^2)^{2/3} \tag{31}$$

one obtains

$$\bar{\eta}_T(\bar{r}) = \frac{1}{2N}C_K\frac{10}{9}\rho(\bar{r})^{2/3} \tag{32}$$

Similarly the local density approximation to the exchange contribution $K[\rho]$ would yield

$$\bar{\eta}_K(\bar{r}) = \frac{1}{2N}C_X\frac{4}{9}\rho(\bar{r})^{1/3}; \quad C_X = -\frac{3}{4\pi}(3\pi^2)^{1/3} \tag{33}$$

Alternatively, one can use the Kohn–Sham theory[13] where, instead of eq 27, one writes $F[\rho]$ in terms of the noninteracting kinetic energy $T_s[\rho]$ and the exchange-correlation contribution, namely,

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \tag{34}$$

Using the expression of T_s in terms of the orbital densities $\{\rho_i\}$, i.e.,

$$T_s[\rho] = \frac{1}{8}\sum_i \int \frac{\nabla\rho_i \cdot \nabla\rho_i}{\rho_i} \, d\bar{r} \tag{35}$$

we find in Kohn–Sham theory

$$\bar{\eta}_{Ts}(\bar{r}) = \frac{1}{8N}\left(\frac{(\nabla\rho_H \cdot \nabla\rho_H)\rho}{(\rho_H)^3} - \frac{(\nabla\rho_H \cdot \nabla\rho)}{(\rho_H)^2} - \nabla^2\left(\frac{\rho}{\rho_H} \right) \right) \tag{36}$$

where ρ_H denotes the HOMO density. The exchange-correlation contribution can be evaluated by using, e.g., the local density approximation.[1]

It is clear from the Thomas–Fermi result that because of exponential fall-off of the density in the outer regions of an atom or molecule, the principal part of $\bar{\eta}(\bar{r})$ is $\phi(\bar{r})$

$$\bar{\eta}(\bar{r}) \simeq \frac{1}{2N}\phi(\bar{r}) \tag{37}$$

in outer regions. The same conclusion also follows from the local density version of the Kohn–Sham theory if one makes the reasonable assumption that in the outer regions the total density is dominated by the HOMO density.

Thus we have in the local hardness a concept that is a generalization of the concept of classical electrostatic potential.

Final Remarks

We accept the arguments in the literature as to why the global η of eq 2 or eq 4 should be called "hardness".[3,6] But we should ask: how can we be sure that the right name for the local quantity $\bar{\eta}$ of eq 13 or eq 17 is local "hardness"? The answer is in eq 17 itself. For a small element of volume, eq 17 is what eq 2 is for a large volume. A formula from the classical thermodynamics of a one-component homogeneous system may help make this clear, namely,

$$\left(\frac{\partial\mu}{\partial N} \right)_{T,V} = -\frac{V^2}{N^2}\left(\frac{\partial P}{\partial V} \right)_{T,N} \tag{38}$$

or equivalently

$$\rho\left(\frac{\partial\mu}{\partial\rho} \right)_{T,V} = \frac{1}{\rho\kappa} \tag{39}$$

where κ is the compressibility. Local hardness, then, is in effect the reciprocal of a local compressibility. A related concept, local softness, is discussed elsewhere.[14]

A subtlety in the hardness concept exists that has not yet been mentioned but should be; there is a discontinuity in the derivative of a hardness just as there is for a chemical potential[15] or for the Fukui function.[7] When an electron is being added, one has μ^+,

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$f^+(\bar{r})$, η^+, $\bar{\eta}^+(\bar{r})$; when it is being subtracted one has μ^-, $f^-(r)$, η^-, $\bar{\eta}^-(\bar{r})$. One also has the averages μ^0, $f^0(\bar{r})$, η^0, $\bar{\eta}^0(\bar{r})$.

Extension of the local or point hardness to a regional or group hardness is immediate and provides the means for evaluating the hardness of a particular atom in a molecule, some group, or any specified region. We merely break eq 18 into regional components:

$$\eta = \sum_{\Omega} \eta_{\Omega} \qquad (40)$$

$$\eta_{\Omega} = \int_{\Omega} \bar{\eta}(\bar{r}) f(\bar{r}) \, d\bar{r} \qquad (41)$$

Equation 41 admits of calculation as desired.

It may be mentioned that eq 41 is a different definition of regional hardness than the one implied by the approach of Bader and colleagues,[16] who speculate that the hard–soft behavior can

be rationalized from the properties of the Laplacian $\nabla^2\rho$. They characterize a hard site in a molecule by the appearance of a large maximum (minimum) of $\nabla^2\rho$ which is tightly bound (occurs at small r); and they ascribe the soft behavior to a site with opposite characteristics. They then state the hope that chemical reactions can be predicted on the basis of "hard maxima reacting with hard holes and soft maxima with soft holes".

Generally, then, each atom has its own effective hardness in a molecule (whereas electronegativities of all atoms are the same). While a detailed discussion along these lines remains to be given, we may confidently expect, in accordance with the extended HSAB principle,[5] that a hard reactant will generally attack the hardest part of the partner, and similarly soft will prefer soft. Calculated group hardnesses should allow prediction of site selectivity in chemical reactions.

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Radical Cations of Fulvenes: Planar or Twisted?

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Abstract: The reactions of several fulvene derivatives with photoexcited electron acceptors (chloranil, anthraquinone) give rise to strong nuclear spin polarization effects. These results offer insight into the structures of the radical cation intermediates. For all systems studied, the spin density is restricted to the ring carbons. Electron-donating substituents in the exomethylene position affect the delocalization of the positive charge and the strength of the exocyclic bond in the radical cations. For example, the (Z)- and (E)-2-tert-butyl-6-(dimethylamino)fulvene radical cations rearrange readily, whereas the di-tert-butylfulvene
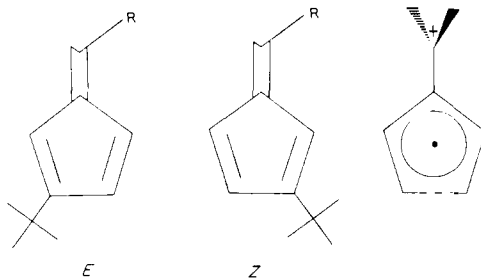
radical cations show no interconversion. The results are compatible with either planar or slightly twisted radical cations and preclude the intermediacy of perpendicular radical cations.

The fulvenes long have been a focus of interest as prototypes of cyclic, cross-conjugated molecules and because of their unique properties.[1] The electronic spectra of most fulvenes show transitions in the visible region as a result of a small HOMO–LUMO gap.[2] The comparatively large dipole moments of the parent molecule (0.42 D)[3] and simple derivatives (1.44 D for 6,6-dimethylfulvene)[4] attest to the importance of zwitterionic character in the ground state. The dipole moment can be understood as

resulting from intramolecular charge transfer from the exocyclic double bond to the five-membered ring thereby acquiring pseudoaromatic cyclopentadienide character. Substituents can affect the degree of zwitterionic character, and such perturbations manifest themselves as shielding effects in NMR spectra.[5] Furthermore, substituents which reinforce the zwitterionic structure, i.e. electron-releasing groups at C6 and/or electron-accepting groups on the ring, stabilize the fulvene and reduce its tendency for dimerization, polymerization, and oxygenation.[1]

We were attracted to the fulvenes as potential precursors of nonvertical radical cations, a concept we have introduced recently.[6]

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