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# LETTERS

## Activation Energies and Softness Additivity

**José L. Gázquez**

*Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, México, D.F. 09340, Mexico*

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It is shown that the activation energy of a chemical reaction depends mainly on the difference between the hardness of the initial state of a reaction and the hardness of the transition state, that these two quantities may be estimated from the softnesses of the reacting molecules and the softnesses of the molecular fragments that characterize the transition state, by making use of the additive properties of the softness, and that the proportionality constant that characterizes the softness of the transition state may provide information about the structure and the looseness of the latter. In addition, it is shown, through the sign of the reaction energy, that reactions tend to go in the direction that produces the hardest possible species. Finally, it is demonstrated that the gap between the eigenvalues of the highest occupied and the lowest unoccupied molecular orbitals takes its minimum value at the transition state.

The mechanism of barrier and transition state formation is of fundamental importance in the description of a chemical reaction, and it is the object of many experimental and theoretical studies.[1,2] In the present work, it will be shown that the activation energy depends mainly on the difference between the hardness[3,4] of the initial state of a reaction and the hardness of the transition state and that these two quantities may be estimated from the softnesses[5] of the reacting molecules and the softnesses of the molecular fragments that characterize the transition state, by making use of the additive properties of the softness.[6−10] The implications of the present approach with respect to reaction energies will also be analyzed.

Consider a system that is composed of several molecules that react with each other. To determine the activation energy, one needs to calculate the total energy difference between the initial state, when the interacting molecules are very far apart from each other, and the transition state, when all molecules are close to each other, and some bonds are being broken, while some new bonds are being formed. According to density functional theory this energy difference is given by[4]

$$\Delta E_{act} = E_{ts}[\rho_{ts}] - E_i[\rho_i] + V_{NN}^{ts} - V_{NN}^{i} \qquad (1)$$

where the transition state is characterized by the electronic energy $E_{ts}$, the external potential $v_{ts}(\mathbf{r})$, the electronic density $\rho_{ts}(\mathbf{r})$, and the chemical potential $\mu_{ts}$, while the initial state is characterized by $E_i$, $v_i(\mathbf{r})$, $\rho_i(\mathbf{r})$, and $\mu_i$. The external potential $v_{ts}(\mathbf{r})$ is the potential generated by the nuclei in the configuration corresponding to that of the transition state, while $v_i(\mathbf{r})$ is the potential generated by the nuclei when all the reacting molecules are very far away from each other. The quantities $V_{NN}^{ts}$ and $V_{NN}^{i}$ represent the nuclear−nuclear repulsion energy in the transition and in the initial states, respectively.

To evaluate the electronic energy difference, one can make use of the expression[9−12]

$$E[\rho] = N_e\mu - {}^{1}/_{2}N_e^2\,\eta + E_{core}[\rho] \qquad (2)$$

where $\eta = (\partial^2 E/\partial N^2)_v = (\partial\mu/\partial N)_v$ is the hardness[3] (the factor of ${}^{1}/_{2}$ in the original definition of the global hardness has been omitted here for convenience), $N_e = N - N_c$ represents an effective number of valence electrons, and

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$$E_{\mathrm{core}}[\rho] = \int \mathrm{d}\mathbf{r}\, \rho_{\mathrm{c}}(\mathbf{r})\, \mathrm{v}(\mathbf{r}) + {}^{1}\!/_{2} \int\!\!\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \frac{\rho_{\mathrm{c}}(\mathbf{r})\, \rho_{\mathrm{c}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + {}^{1}\!/_{2} \int\!\!\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \rho_{\mathrm{c}}(\mathbf{r})\, \rho_{\mathrm{c}}(\mathbf{r}')\, \frac{\delta^{2}\, (T[\rho] + E_{\mathrm{xc}}[\rho])}{\delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} \quad (3)$$

represents the core contribution to the total electronic energy. In the latter expression $T[\rho]$ and $E_{\mathrm{xc}}[\rho]$ are the kinetic and the exchange-correlation energy density functionals,[4] the second functional derivative of the classical Coulomb interaction energy density functional,[4] $J[\rho]$, has been replaced by $1/|\mathbf{r} - \mathbf{r}'|$, $\rho_{\mathrm{c}}(\mathbf{r}) = \rho(\mathbf{r}) - N_{\mathrm{e}}f(\mathbf{r})$, $f(\mathbf{r}) = (\partial\rho(\mathbf{r})/\partial N)_{v}$ is the fukui function,[13] and $\rho_{\mathrm{c}}(\mathbf{r})$ integrates to $N_{\mathrm{c}}$. Equation 2 is an exact, up to second-order, expression for the total electronic energy of a system, and substituting it in eq 1 one finds that

$$\Delta E_{\mathrm{act}} = N_{\mathrm{e}}(\mu_{\mathrm{ts}} - \mu_{\mathrm{i}}) - {}^{1}\!/_{2}\, N_{\mathrm{e}}^{2}\, (\eta_{\mathrm{ts}} - \eta_{\mathrm{i}}) + E_{\mathrm{core}}[\rho_{\mathrm{ts}}] - E_{\mathrm{core}}[\varrho_{\mathrm{i}}] + \Delta V_{\mathrm{NN}} \quad (4)$$

Now, by assuming that the core density of the system remains unchanged at any distance during the interaction and that there is practically no overlap between the core densities of all the atoms that form part of the molecules that interact with each other, one can show that if $N_{\mathrm{e}} \ll N$, the sum of the terms in $(E_{\mathrm{core}}[\rho_{\mathrm{ts}}] - E_{\mathrm{core}}[\rho_{\mathrm{i}}])$ associated with the first two terms in the right-hand side of eq 3 is approximately equal to $-\Delta V_{\mathrm{NN}}$. If it is further assumed that the core difference terms related with the second functional derivatives of the kinetic and the exchange correlation energies cancel each other, one finds, from eq 4, if the chemical potential remains constant along the reaction coordinate, that

$$\Delta E_{\mathrm{act}} \approx -\, {}^{1}\!/_{2}\, N_{\mathrm{e}}^{2}\, (\eta_{\mathrm{ts}} - \eta_{\mathrm{i}}) = -\, {}^{1}\!/_{2}\, N_{\mathrm{e}}^{2} \left(\frac{1}{S_{\mathrm{ts}}} - \frac{1}{S_{\mathrm{i}}}\right) \quad (5)$$

where $S = 1/\eta = (\partial N/\partial\mu)_{v}$ is the softness.[5]

The set of assumptions that lead to eq 5 have already been used[10] to derive an expression for the bond energy, and according to the results that have been obtained with $N_{\mathrm{e}} \approx 1$, they seem to be reasonable. On the other hand, in relation with the constant chemical potential constraint, it is important to note that, in the present case, the initial state corresponds to the situation in which all the reacting molecules are very far away from each other, but where all of them have the same chemical potential; therefore, the changes in $\mu$ could arise only from the changes in the external potential along the reaction coordinate. However, the numerical evidence[14−21] has shown that these changes in $\mu$ are, in general, very small in comparison with the changes in $\eta$. Thus, one may assume that for many cases the change in the chemical potential is negligible with respect to the change in the hardness, and therefore eq 5 may be used as an approximate expression for the activation energy.

It is important to note that since $\Delta E_{\mathrm{act}} \geq 0$ and $E_{\mathrm{ts}}$ is a maximum at the transition state, one can see that eq 5 implies that the softness of the system is also a maximum in the transition state, while the hardness is a minimum. This result is in agreement with theoretical calculations[15,18,22] that show that the transition state is softer than any other state of a system.

Now, to calculate the global softness of the initial state ($S_{\mathrm{i}}$) and the global softness of the transition state ($S_{\mathrm{ts}}$), it is important to note that $S = (\partial N/\partial\mu)_{v}$. Thus, it has been found that the global softness of a system is approximately equal to the sum of the softness of its components when there is practically no overlap among them[6,8,10] and that the arithmetic average of the softness of the constituent atoms of a molecule provides a rather good representation of the molecular global softness in the equilibrium position.[7] This situation implies that, in general, the softness of a system in terms of its constitutive parts is proportional to the sum of the softness of the constitutive parts, that the proportionality constant is equal to one when the constitutive parts are very far away from each other, and that it is approximately equal to one over the number of atoms when the chemical bonds between the atoms have been formed. Therefore, it seems reasonable to assume that $S_{\mathrm{i}}$ is proportional to the sum of the softnesses of all the reactants and that $S_{\mathrm{ts}}$ is proportional to the sum of the softnesses of all the molecular fragments that participate in the bond-breaking and bond-forming processes. In the first case, the proportionality constant may be assumed to be equal to one, because in the initial state all the reacting molecules are very far away from each other, while in the second case, the proportionality constant may be assumed to be equal to or slightly lower than one, because in the transition state the molecular fragments are weakly bonded to each other, and therefore it represents a different situation to the one corresponding to the arithmetic average principle that describes the molecular softness in terms of the constituent parts in the equilibrium position, when strong bonds have been formed. Thus, in general, the activation energy given by eq 5 may be written in the form

$$\Delta E_{\mathrm{act}} \approx -\, {}^{1}\!/_{2}\, N_{\mathrm{e}}^{\,2} \left(\frac{1}{\alpha \sum S_{\mathrm{mf}}^{\mathrm{ts}}} - \frac{1}{\sum S_{\mathrm{r}}^{\mathrm{i}}}\right) \quad (6)$$

where $S_{\mathrm{r}}^{\mathrm{i}}$ is the softness of a given reactant and the sum is to be taken over all the reactant molecules in the initial state, and $S_{\mathrm{mf}}^{\mathrm{ts}}$ is the softness of a given molecular fragment and the sum is to be taken over all the molecular fragments in the transition state. The proportionality constant $\alpha$ is expected to have a value that lies between one and one over the number of molecular fragments in the transition state. A value of $\alpha$ around one is interpreted as if there were practically no bonding between the molecular fragments, while a value of $\alpha$ lower than one is interpreted as if there were a weak bonding between the molecular fragments. Thus, the proportionality constant provides a measure of the looseness of the transition state.

To make use of eq 6, one may assume[10] that $N_{\mathrm{e}} = 1$, and the softness values for the reactant molecules and for the molecular fragments in the transition state may be determined from the experimental values of the hardness provided by the finite differences approximation to the second derivative of the energy with respect to the total number of electrons at constant external potential,[3,23] $S = 1/\eta = 1/(\partial^{2}E/\partial N^{2})_{v} = 1/(I - A)$, where $I$ is the first ionization potential and $A$ is the electron affinity of the reference system. As an example, consider the reaction $\mathrm{Y}^{-} + \mathrm{CH_3{-}X} \rightarrow \mathrm{Y{-}CH_3} + \mathrm{X}^{-}$. In this case, the reactants are $\mathrm{Y}^{-}$ and $\mathrm{CH_3{-}X}$ and the molecular fragments in the transition state are $\mathrm{Y}^{-}$, $\mathrm{CH_3}$, and $\mathrm{X}^{-}$. Thus, one can determine the softnesses required in eq 6 to calculate the activation energy for this particular reaction. In the case of the anions, one can make use of the values $I$ and $A$ of the corresponding radicals, as suggested by Pearson.[23] In Table 1, one can see that this approach provides the correct trends of the activation energies when $\alpha = 1$ and that the values of $\alpha$ that are required to reproduce the experimental activation energies lie, in general, within the range expected (between 1 and $^{1}\!/_{3}$ in this case[7]). It is interesting to note, in Table 1, that the values of $\alpha$ agree rather well with the calculated looseness of the transition state, when the latter is determined from the formula[1]

$$L \approx [(d_{\mathrm{CY}}^{\mathrm{ts}} - d_{\mathrm{CY}}^{\mathrm{gs}})/d_{\mathrm{CY}}^{\mathrm{gs}}] + [(d_{\mathrm{CX}}^{\mathrm{ts}} - d_{\mathrm{CX}}^{\mathrm{gs}})/d_{\mathrm{CX}}^{\mathrm{gs}}] \quad (7)$$

**TABLE 1: Hardness Values ($\eta$), Activation Energies ($\Delta E_{\text{act}}$), and Looseness ($L$) of the Transition State for the Reaction $Y^- + CH_3{-}X \rightarrow Y{-}CH_3 + X^-$**

| | | | | | $\Delta E_{\text{act}}$ | | | |
|---|---|---|---|---|---|---|---|---|
| $Y^-$ | $X^-$ | $\eta_Y$[a] | $\eta_X$[a] | $\eta_{CH_3X}$[a] | eq 6[b] | exptl[c] | α[d] | $L$[e] |
| F | F | 14.02 | 14.02 | 18.80 | 45.6 | 26.2 | 0.71 | 0.50 |
| Cl | Cl | 9.40 | 9.40 | 15.00 | 30.1 | 10.2 | 0.65 | 0.42 |
| Br | Br | 8.48 | 8.48 | 12.22[f] | 23.7 | 11.2 | 0.73 | |
| I | I | 7.40 | 7.40 | 9.400 | 16.8 | 5.5 | 0.73 | |
| CN | CN | 10.20 | 10.20 | 15.00 | 31.4 | 24.0 | 0.84 | 0.90 |
| OH | OH | 11.34 | 11.34 | 15.05[f] | 33.3 | 21.2[g] | 0.77 | 0.60 |
| H | H | 12.86 | 12.86 | 20.60 | 46.6 | 52.0[g] | 1.14 | 1.16 |
| H | F | 12.86 | 14.02 | 18.80 | 42.3 | 16.0 | 0.64 | 0.80 |
| OH | F | 11.34 | 14.02 | 18.80 | 37.6 | 9.1[g] | 0.61 | 0.56 |
| H | CN | 12.86 | 10.20 | 15.00 | 38.4 | 23.5[g] | 0.74 | 1.13 |
| F | Cl | 14.02 | 9.400 | 15.00 | 42.4 | 6.9 | 0.54 | |
| CN | Br | 10.20 | 8.480 | 12.22 | 27.9 | 8.9 | 0.66 | |
| CN | F | 10.20 | 14.02 | 18.80 | 33.9 | 26.6[g] | 0.85 | 0.70 |
| H | OH | 12.86 | 11.34 | 15.05 | 37.0 | 18.5[g] | 0.70 | 0.96 |
| OH | CN | 11.34 | 10.20 | 15.00 | 34.6 | 26.6[g] | 0.83 | 0.74 |
| CN | Cl | 10.20 | 9.400 | 15.00 | 32.5 | 9.4 | 0.62 | |

[a] Experimental values in eV from ref 23, except as indicated; the global hardness of the methyl radical is 9.74 eV. [b] With $N_e = 1$ and α = 1, in kcal/mol. [c] Experimental values in kcal/mol from ref 1, except as indicated. [d] Using eq 6 with $N_e = 1$ to reproduce the experimental activation energy value. [e] Theoretical values calculated with a 4-31G basis set, from ref 1. [f] From ref 28. [g] Theoretical values calculated with a 4-31G basis set, in kcal/mol, from ref 1.

where $d^{gs}_{CY}$ and $d^{gs}_{CX}$ are the equilibrium C−Y and C−X bond lengths in the ground state of the molecules $CH_3{-}Y$ and $CH_3{-}X$, respectively, and $d^{ts}_{CY}$ and $d^{ts}_{CX}$ are the bond lengths between C−Y and C−X in the transition state. The values of $L$ reported in Table 1 correspond to eq 7, with all the parameters determined with a 4-31G calculation,[1] while the α values correspond in some cases to experimental activation energy barriers and in others to 4-31G activation energy barrier calculations. However, the overall agreement seems to indicate that eq 6 may be useful to estimate the trends of the activation energy for a family of molecular reactions, and it may also be useful to understand the nature of the transition state through the knowledge of the experimental activation energy barrier, because through the latter, one can determine the value of α, which allows one to estimate the degree of looseness of the bonds in the transition state.

Now, since the difference between the activation energy corresponding to the reaction in the direction of reactants to products and the activation energy corresponding to the reaction in the direction of products to reactants is equal to the reaction energy, then, if $N_e = 1$, according to eq 6,

$$\Delta E_{\text{reac}} = \Delta E_{\text{act}}^{r\rightarrow p} - \Delta E_{\text{act}}^{p\rightarrow r} \approx 1/\sum S_r - 1/\sum S_p \tag{8}$$

Therefore, $\Delta E_{\text{reac}} < 0$ if the sum of the softnesses of the products is lower than the sum of the softnesses of the reactants, and $\Delta E_{\text{reac}} > 0$ if the opposite occurs. These statement is in complete agreement with the experimental evidence, which shows that the reactions almost always go in the direction that produces the hardest molecule, or the products of highest average hardness.[24,25]

It is important to note that, through the analysis of the difference between the energy of the bonds broken and that of the bonds formed in exchange reactions, it has been shown that $\Delta E_{\text{reac}} < 0$ if the sum of the hardnesses of the products is greater than the sum of the hardnesses of the reactants, and $\Delta E_{\text{reac}} > 0$ if the opposite occurs.[10] Thus, one may conclude that, through a bond energy analysis, the arithmetic average of the hardnesses of the reactants and the products determine the sign of the reaction energy, while from a transition state energy analysis, the harmonic mean of the hardnesses of the reactants and the products (replace the softness of each one of the softnesses of the reactants and each one of the products by the inverse of the corresponding hardness), determine the sign of the reaction energy. In general, both average values will lead to the same results and provide a strong support to the statement that reactions tend to go in the direction that produces the hardest possible species.

An important aspect related to eq 5 is that if the hardness is approximated in terms of the eigenvalues of the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO),[26] $\eta = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$, then eq 5 equals

$$\Delta E_{\text{act}} \approx -\,{}^{1}/_{2}\, N_e^2\, [(\epsilon^{ts}_{\text{LUMO}} - \epsilon^{ts}_{\text{HOMO}}) - (\epsilon^{i}_{\text{LUMO}} - \epsilon^{i}_{\text{HOMO}})] \tag{9}$$

a result that shows, explicitly, that the frontier orbitals[27] play a fundamental role in the description of a chemical event. In addition, eq 9 shows that the lowest value of the HOMO−LUMO gap occurs at the transition state, when the system, as a whole, reaches the state of maximum softness. Such a statement is in agreement with theoretical calculations.[15,18,22]

The overall analysis presented in this work seems to indicate that the hardness difference term provides fundamental information for the description of a chemical event. In addition, the description of the total softness in the transition state, in terms of the molecular fragments associated with the bond-breaking and bond-forming processes, may be useful to describe the reaction mechanism, if the experimental activation energy is known, because one can determine the looseness of the transition state and because, among several possibilities, one may select the molecular fragments that provide the best description.

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