



ON THE VALIDITY OF LINEAR FREE ENERGY RELATIONSHIPS IN CHEMICAL KINETICS

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Linear free energy relationships (LFER) have been used extensively in chemical kinetics (1). However such correlations, which have a strong empirical basis, should be contained in any theoretical model which relates activation energy and molecular structure. We have recently developed such a model (2, 3) which is quite general, because it encompasses, as particular cases, the well known BEBO and Marcus theories. Thus it is useful to investigate under what conditions LFER are valid. For a reaction $A + BC \rightarrow AB + C$ the free energy of activation can be given by

$$\Delta G^\ddagger = (\Delta G^0 + \frac{1}{2} f d^2)^2 / 2 f d^2 \quad (1)$$

under the assumption that the bonds BC and AB have a harmonic behaviour with an average force constant f ; ΔG^0 is the reaction free energy and d is the sum of the bond distensions from reactant and product to the transition state. This parameter depends on the sum of the equilibrium bond lengths of BC and AB, $l = l_{AB} + l_{BC}$,

$$d = \eta l \quad (2)$$

where the reduced bond distension η is

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2\lambda^2} (\Delta G^0)^2 \quad (3)$$

n^\ddagger is the bond order of the bonds in the transition state ABC^\ddagger , a' is a constant ($a' = 0.156$) and λ is the so called «mixing entropy», which has the dimensions of energy (2, 3).

LFER (1) can be conveniently expressed by

$$\Delta G_X^\ddagger - \Delta G_R^\ddagger = -2.3 RT \rho \sigma_X \quad (4)$$

where ΔG_R^\ddagger is the activation free energy of a reaction considered as reference, ΔG_X^\ddagger refers to the presence of a substituent (or different medium) and ρ and σ_X are parameters. The constant ρ is a function of the reaction ($\rho = 1$ for the ionization of $ArCO_2H$

at 25°C), and σ_X is a function of the substituent

$$\sigma_X = \log \frac{K_X}{K_R} \quad (5)$$

where K are the equilibrium constants of the reactions under consideration, which have free energies ΔG_X^0 and ΔG_R^0 . Consequently

$$\sigma_X = - \frac{(\Delta G_X^0 - \Delta G_R^0)}{2.3 RT} \quad (6)$$

Let us assume that the presence of a substituent X causes a change in the reaction free energy. Considering that we can neglect the contribution for the energy barrier of all bonds except the bond-breaking bond-forming ones, or that such effect can be expressed in terms of an overall force constant, it is reasonable to assume that changes in ΔG^0 are caused by changes in the potential energies of the reactive bonds, i. e., by changes in f and/or l . Consequently we can consider that

$$(a' l n^2) (f_X l_X^2 - f_R l_R^2) = \alpha (\Delta G_X^0 - \Delta G_R^0) \quad (7)$$

where α is a constant of proportionality. With eq. (7) and under the assumption that the bond orders at the transition state are the same for the two reactions, $n_X^\ddagger = n_R^\ddagger = n^\ddagger$, then we can write

$$\Delta G_X^\ddagger - \Delta G_R^\ddagger = (\Delta G_X^0 - \Delta G_R^0) \frac{(2n^{\ddagger 2} + \alpha)^2}{8 \alpha n^{\ddagger 2}} \quad (8)$$

by neglecting the quadratic dependence of η on ΔG^0 , i. e., $|\Delta G^0| \ll \lambda$. By comparison of eqs. (8) and (4) and (6) we conclude that

$$\rho = \frac{(2n^{\ddagger 2} + \alpha)^2}{8 \alpha n^{\ddagger 2}} \quad (9)$$

which shows that ρ is proportional to the bond order at the transition state.

For the reaction of ionization of benzoic acid which has $n^\ddagger = 0.84$ (5), is $\alpha = 1.41$. With this same α value and for the expected range of

n^\ddagger values we have $\rho = 1.294$ ($n^\ddagger = 0.5$ and $\rho = 1.031$ ($n^\ddagger = 1$)). The parameter α should vary with the nature of the reaction and even negative values can be found, namely for strong exoenergetic reactions. For example with $\alpha = -10$, $\rho = -4.5$ ($n^\ddagger = 0.5$), and $\rho = 5.5$ with $\alpha = 10$ which more than covers the experimental range of the ρ values (1). Substituent effects can cause change in free energies typically of 15 kJ mol^{-1} . With typical values for the ionization of benzoic acid, $f_R = 4 \times 10^3 \text{ kJ mol}^{-1}$ and $l = 2 \text{ \AA}$ (4), eq. (7) reveal that changes in $|\Delta G_X^0 - \Delta G_R^0| = 15 \text{ kJ mol}^{-1}$ correspond to changes in $f l^2$ of ca. 10 % with $\alpha = 1.4$. This is a reasonable change in force constants and/or equilibrium bond lengths for substituent effects. For other reactions even higher f_R and l_R values can be found, and for the set of values $f = 6 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ $l = 4 \text{ \AA}$ the estimated variation in $f l^2$ with $\alpha = \pm 10$ is only 14 %.

We can now discuss briefly under what conditions LFER cannot be verified:

- a — The force constants of the reactive bonds are not equal. This condition however is not restrictive of LFER as long as conditions of eqs. (7) can be verified by the force constant of the reactant and product.
- b — Eq. (7) is not valid. This condition is associated with the additivity rules, which are quite general molecular properties. However this topic can be addressed to the recent work of Murdoch (5).
- c — It is not possible to neglect the linear dependence of η on $(\Delta G^0)^2$. Such a dependence is proportional to the mixing entropy, which has been found to be also related with ΔS^\ddagger (3). Since the effect of substituents or media on ΔS may be different from the one on ΔG , this condition may cause a breakdown of LFER. However this may cause some scatter in the linear relationships, but it is not expected to cause a strong failure of LFER.

d — The bond order at the transition state is not the same for all reactions. This causes the breakdown of LFER. An example will illustrate this point. We have shown that the bond order at the transition state varies continuously from $n^\ddagger = 1/2$ for S_N^2 to $n^\ddagger = 1$ or even higher values for S_N^1 mechanisms (3). In fact, $\log(k_X/k_R)$ versus σ_X for the reactions of substituted benzyl chloride with triethylamine and benzyl bromides with pyridine, (supposedly typical nucleophilic substitutions), are strongly curved (6). Changes in the bond order n^\ddagger are caused by siphoning of electron density mainly from nonbonding and antibonding orbitals into bonding orbitals in the transition state (2, 3).

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ABSTRACT

An intersecting-state-model which relates activation energy and molecular and thermodynamic parameters is used to investigate the validity of LFER in chemical

kinetics. It is shown that such relationships should be verified as long as substituents or media do not alter the bond order of the transition states.

SUMÁRIO

Através de um modelo de intersecção de estados que permite estimar energias de activação em função de parâmetros moleculares e termodinâmicos, mostra-se que a linearidade de relações de energia livre em cinética é verificada desde que a ordem de ligação do estado de transição seja independente da natureza de substituintes e solventes.

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