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Entropy oscillations and an isokinetic ratio

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An examination of transition states in organic liquid-phase reactions including reactant and solvent molecules as Prigogine dissipative structures allowed us to derive a mathematical expression for a so-called linear isokinetic correlation between activation parameters.

Linear correlations between activation parameters are frequently observed in studies of the reactivity of organic substances in a liquid phase. These empirical correlations are termed isokinetic, and the corresponding phenomenon is called a compensating effect (CEF).[1] First, such a correlation was discovered by Constable[2] who studied catalytic oxidation. Hinshelwood[3] characterised CEF as ‘one of the basic, although obscure regularity of chemical kinetics.’ The prevalence of this phenomenon suggests that ‘its reason is common but the manifestations sometimes are not always anomalous’.[1]

In order to recognise CEF as a natural phenomenon of chemical kinetics, a physical model should be developed for the elementary act in a liquid phase, which would lead to a linear correlation between activation parameters. Undoubtedly, CEF has a cooperative character and is related to the motion of reactant molecules and solvent molecules in the solvation sphere during an elementary act in the condensed phase. The difficulties of choosing the group, which would include reactant and solvent molecules, create a problem, which is not solved by means of quantum or classical mechanics, as well as statistical physics, which usually consider system energy.

It seems promising to consider entropy, which is of methodological significance for the solution of the CEF problem.

The enormous quantity of organic reactions proceeding through a π-complex or a charge-transfer complex is known for the liquid phase. These are electrophilic substitution, addition[4], and diene condensation[5] reactions. The characteristic peculiarities of the complexes are the structure conservation of reactant molecules and the presence of an electric charge distribution in the complex and the solvation sphere.[6] Molecular complexes and transition states are ordered molecular systems in solution; the formation of them is accompanied by a decrease in the entropy.[7] This allows us to consider the supramolecular structure of a molecular complex and a solvation sphere as Prigogine dissipative structures.[8]

By definition given in ref. 9, the structure is a stable order in space and time made of some elements and their interconnections. This means that, first, due to the order, the given structure formation process is connected with a decrease in entropy and hence $\Delta S < 0$. Second, the structure stability means that it is in a stationary state and

$$\mathrm{d}S_i/\mathrm{d}t = \mathrm{d}S_e/\mathrm{d}t, \tag{1}$$

where *i* is entropy production (entropy appeared inside the system and entered the environment); *e* is the entropy flow (entropy entered the system from the environment).

Prigogine dissipative structures are open systems with the permanent entropy exchange with the environment. A structure occurs in the stationary state until it is unable to equalise the flow of entropy from the environment by its internal properties. If the entropy flow due to internal or external circumstances starts to overwhelm the entropy production, then equation (1) takes the form

$$\mathrm{d}S_i/\mathrm{d}t < \mathrm{d}S_e/\mathrm{d}t, \tag{2}$$

Let us assume that $\mathrm{d}_eS/\mathrm{d}t = x$. Then, in the time interval Δt, the value of x gets the positive increment Δx. The change of the entropy flow can be characterised by the expression $\Delta x/\Delta t$, which characterises the rate of entropy flow change. Let us substitute the finite increments by differentials and the expression $\Delta x/\Delta t$ by $\mathrm{d}x/\mathrm{d}t$. The positive value of the derivative obtained means an increase in the entropy flow in the system up to a positive value $\Delta S > 0$. This means that the structure is destroyed and a chaotic system arises. The entropy production increases during the transformation into the chaotic state, and the system will start to actively affect the environment. If the entropy production is denoted as y, analogously to x, the rate of entropy production can be characterised by $\mathrm{d}y/\mathrm{d}t$. The entropy production will increase until the entropy flow and entropy production balance again and the system gets back into the stationary state, which corresponds to an entropy maximum at this time:

$$\mathrm{d}S_i/\mathrm{d}t = \mathrm{d}S_e/\mathrm{d}t, \tag{3}$$

After that, the entropy flow from the environment can decrease and then the entropy production, and, conformably, the entropy flow from the dissipative structure starts to overwhelm the flow of entropy from outside:

$$\mathrm{d}S_i/\mathrm{d}t > \mathrm{d}S_e/\mathrm{d}t, \tag{4}$$

Accordingly, the system entropy will start do decrease and again the state will arise, when $\Delta S < 0$, which means the structure formation. The entropy flow can decrease up to the equilibrium of the entropy flow and production until attaining a stationary state, which corresponds to the minimum of entropy or to a stable structure. The cycle of entropy changes from a maximum to a minimum and back can continue; this means the transition from the order to chaos, an average statistical distribution of molecules by energy in the restricted volume and back. The derivative $\mathrm{d}y/\mathrm{d}t$ varies from its maximal (positive) value to zero and from zero to its minimal negative value. Next, it changed from the minimal negative value through zero to the maximal positive. This derivative corresponds to the entropy production rate introduced by Prigogine for characterising dissipative structures.[8] This value is the time derivative of entropy production and, accordingly, has the character of second derivative. For the second derivative, according to ref. 10, we can write the equation of harmonic oscillator vibrations

$$\frac{\mathrm{d}^2y}{\mathrm{d}t^2} + 2\lambda\frac{\mathrm{d}y}{\mathrm{d}t} + \omega_0^2y = F_{\mathrm{inf}}\cos(\omega t + \varphi) \tag{5}$$

where y is the vibrating physical quantity; ω_0 is the eigenfrequency of the oscillator vibrations; λ is the attenuation constant; ω is the frequency of disturbing force oscillations; φ is the phase of disturbing force oscillations.

Equation (5) shows the balance of forces under the condition of full system energy conservation. The first item characterises the inertial force and, correspondingly, the kinetic energy; the second is the returning force connected with the potential energy. If energy exchange with the environment occurs, one should add two components to the equation of a harmonic oscillator $2\lambda\mathrm{d}S/\mathrm{d}t$, $F_{\mathrm{inf}}\cos(\omega t + \varphi)$. The item in the left-hand side characterises the dispersion (dissipation) of energy into the environment, which is proportional to the first time derivative of a physical quantity. The item in the right-hand side is a so-called disturbing force F_{inf}, which characterises the periodical influence of the environment on the oscillating system. Taking into account these two components, equation (5) takes the form

$$\frac{d^2\Delta S}{dt^2} + 2\lambda\frac{d\Delta S}{dt} + \omega_0^2\Delta S = F_{\mathrm{inf}}\cos(\omega t + \varphi) \tag{6}$$

The state corresponds to a resonance when the frequency of disturbing force oscillations aims at the eigenfrequency of entropy oscillation ω_0.[10] Under conditions of resonance, the amplitude of an oscillating physical quantity and, accordingly, energy consumption reach a maximum. There is a special formula[11] for the maximum amplitude ΔS_{max}. In our case, the maximum in the resonant curve has to correspond to the maximum of a potential barrier, and the amplitude of entropy has to be equal to the experimentally measured activation entropy ΔS_{a}. Then, according to ref. 11, we can write the following expression for the activation entropy $\Delta S_{\mathrm{max}} = \Delta S_{\mathrm{a}}$:

$$\Delta S_{\mathrm{a}} = \frac{F_{\mathrm{inf}}}{2m\lambda\sqrt{\omega_0^2 - \lambda^2}}, \tag{7}$$

where m is the characteristic of oscillating system sluggishness.

As long as the outer disturbing force carries energy required for overcoming the potential barrier, whose height is equal to the activation energy, the outer disturbing force has to be proportional to the activation energy E_{a}:

$$F_{\mathrm{inf}} = k_{\mathrm{F}}E_{\mathrm{a}} \tag{8}$$

where: k_{F} is a proportionality factor.

Using the value of F_{inf} from equation (8) in (7), we obtain

$$\Delta S_{\mathrm{a}} = \frac{k_{\mathrm{F}}E_{\mathrm{a}}}{2m\lambda\sqrt{\omega_0^2 - \lambda^2}}, \tag{9}$$

For a narrow reaction series in the same solvent, we can neglect changes in the denominator of equation (9). Then, the coefficient in the right-hand side becomes constant K_1:

$$\Delta S_{\mathrm{a}} = K_1 E_{\mathrm{a}} \tag{10}$$

Let us transform expression (10) with regard to E_{a}:

$$E_{\mathrm{a}} = \Delta S_{\mathrm{a}}/K_1 \tag{11}$$

Equation (11) corresponds to an isokinetic correlation,[1] where the reciprocal of K_1, is isokinetic temperature.[12,13] Equation (11) is evidence for the advantage of the proposed approach to consider transition states in organic liquid-phase reactions as oscillating Prigogine dissipative structures, as well as a resonant mechanism of obtaining energy for molecules to overcome a potential barrier in the solvation sphere from electromagnetic radiation (activation of chemical reaction). Deviations from (11) should be considered as exclusions from a common correlation having some real reasons. The Prigogine dissipative structures can be useful for studying the nature of these reasons in the test reactions.

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