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Nonequilibrium Effects in Kinetics of Cycloaddition Reactions under High Pressure

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A Diels–Alder condensation reaction in liquid phase under varying pressure conditions is modeled as a pair of coordinates, one associated with a chemical reactive motion and the other describing the accompanying contraction of the medium cavity which surrounds the chemical subsystem. A two-dimensional enthalpy surface with a pressure-dependent activation barrier is constructed. The dynamical problem involves the friction and random forces applied to the medium (i.e., the cavity contraction) coordinate. It reduces to the rate constant expression investigated earlier. The corresponding kinetics covers both equilibrium (obeying the transition-state theory) and nonequilibrium behavior. The hypothesis is suggested that the latter can be revealed in the experiment as a systematic deviation from the linear relationship between the logarithm of the pressure-dependent rate constant and universal El'yanov–Vasilvitskaya scaled-pressure function. Illustrative calculations confirm this idea. The role of nonlocal medium relaxation forces with memory is discussed.

1. Introduction

The theoretical kinetics of elementary chemical processes in condensed media is an extensively developing domain of modern chemical research. Various kinetical experiments are frequently interpreted in terms of stochastic models which treat medium relaxation characteristics, such as viscosity, diffusion coefficient, etc., as dynamical parameters entering the underlying equation of motion. The strong (exponential) pressure dependence of relaxation parameters means that by systematically performing experiments in a wide pressure range one could test efficiently the validity of stochastic theories.

The isomerization of organic molecules in their ground^{1–3} and excited^{4–6} electronic states has been thoroughly studied recently in the framework of these concepts. In particular, the photoisomerization of stilbene and 1,4-diphenylbutadiene studied both in gas and liquid phases under varying pressure conditions was interpreted by means of simple stochastic approaches, such as Kramers theory^{4–6} and the generalized transition-state (TS) theory.⁷

It is expedient to mention here that the theoretical treatments of the observable kinetic effects in condensed phase are faced with certain difficulties. Two forces, namely the dissipative (associated with friction) and random ones, are needed to introduce fluctuations in a chemical subsystem arising due to its interactions with the environment. These forces are commonly accepted to be a distinctive feature of processes proceeding in condensed media. However, interactions of the chemical subsystem with its environment also produce regular forces which can by no means be ignored. The corresponding potential changes, associated with a chemical conversion, appear as uncertainties in a potential barrier height. For isomerizations even in the absence of polar forces the influence of this nonstochastic effect on a rate constant is comparable in magnitude with friction effects calculated by the Kramers method.^{2,4} For other types of chemical reactions the relative importance of medium-induced regular forces is expected to be considerably greater.

Under high-pressure conditions a chemical conversion is described by an enthalpy rather than potential energy surface.^{8,9} So

a regular contribution $p\Delta V^{\ddagger}_0$ in the potential barrier height arises. We denote by p the external pressure. The quantity ΔV^{\ddagger}_0 , having the dimension of volume, can be interpreted as the intrinsic (geometrical) volume change when a chemical subsystem changes from its initial (the reactant minimum on the enthalpy surface) to transition (the saddle point) state. According to simple versions of the quasithermodynamic theory^{8,10,11} the observed activation volume ΔV^{\ddagger} is interpreted geometrically and is identical with ΔV^{\ddagger}_0 . This seems to be an oversimplification, although both the quantities may have the same order of magnitude. So, rough estimates suggest that $\Delta V^{\ddagger}_0 = -1$ to -2 cm³/mol for the cyclohexane isomerization reaction,² which is approximately twice as small as the total activation volume ΔV^{\ddagger} .

The problem of separation of regular and fluctuational effects in observable kinetics is very serious. As a matter of fact, it is the lack of knowledge on the true barrier height which makes the theoretical interpretation of isomerization kinetics not at all definite.

2. Diels–Alder Reaction: A Preliminary Discussion of Its Stochastic Modeling

The kinetics of cycloaddition reactions has not yet been considered in the context of stochastic theories, despite the large experimental material on their pressure dependence.^{12,13} Their main distinction from isomerization reactions is large absolute values of volume changes. Both experimentally observed activation volumes ΔV^{\ddagger} and estimates of geometrical volume variations ΔV^{\ddagger}_0 usually constitute -30 to -40 cm³/mol. The remarkable difference as compared to isomerizations is easily understandable. Let us imagine the medium as a continuum with a cavity in which a chemical subsystem is inserted. Isomerizations mainly change the shape of the cavity whereas a cycloaddition is accompanied by a contraction of the volume. This notion suffices to explain, in terms of an intuitive geometrical reasoning, why typical volume changes are many times as large in the latter case.

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Therefore, the influence of external pressure on cycloaddition reactions is strong and its main part arises evidently due to the lowering of a potential barrier by the volume contraction term $p\Delta V^\ddagger$.⁸ There is no need in stochastic theories to describe this effect. However, more fine pressure effects are hardly understandable in terms of a purely geometrical model. Some of them may be interpreted by considering pressure changes of the thermal expansion contribution to activation volumes in the framework of the TS theory.⁹ Our intention in the present work is to bypass the restrictions of the TS treatment by introducing a simple dynamical picture fit for investigation of nonequilibrium effects, at least in principle.

Among various cycloaddition processes, the Diels–Alder reaction is the most thoroughly studied. In many cases the solvent does not influence its kinetics. This is illustrated in Table I where experimental values of the Arrhenius parameters measured in a gas phase and in nonpolar liquids are compared. Within an experimental error they are solvent independent and even the same in gas and liquid phases. The data of Table I refer to normal pressure (1 atm) but elevation of pressure usually does not modify the picture. This has been demonstrated^{20,21} in a precise treatment of earlier reported measurements for 56 Diels–Alder systems in which both a chemical subsystem and a solvent were varied. This empirical approach was based on the following equation for the rate constant $k(p)$ at temperature T

$$\ln \frac{k(p)}{k_0} = -\frac{\Delta V^\ddagger_r}{RT} \Phi_r(p) \quad (2.1)$$

where $\Phi_r(p)$ with empirically estimated constants $\alpha = 0.17$ and $\beta = 4.94 \text{ kbar}^{-1}$ is a universal function for the whole reaction series:

$$\Phi_r(p) = (1 + \alpha)p - (\alpha/\beta)(1 + \beta p) \ln(1 + \beta p) \quad (2.2)$$

In (2.1) R is the gas constant and k_0 represents the rate constant at normal pressure. Formulas 2.1 and 2.2 work with a high precision for a majority of systems, so that the activation volume ΔV^\ddagger_r proved to be the single quantity needed to account for their specific features associated with both chemical and solvent nature. It has been also shown that ΔV^\ddagger_r became solvent independent after recalculations eliminating polar interactions by a standard prescription. Only in a few cases were systematic deviations from dependence (2.1) observed. So the conclusion can be inferred that for typical Diels–Alder systems the experiment registered no signs of a viscosity dependence of activation volumes.

On the other hand, the viscosity and, especially, its pressure dependence is a very specific solvent property. We shall use the equation of the type (2.1)²² derived basing on experimental data, to treat the pressure dependence of solvent viscosity η :

$$\ln \frac{\eta(p)}{\eta_0} = -\frac{\Delta V_\eta}{RT} \Phi_\eta(p) \quad (2.3)$$

Here $\Phi_\eta(p)$ is given by

$$\Phi_\eta(p) = (1 - c)p + \frac{cp}{1 + bp} \quad (2.4)$$

where c and b are constants which, as a first approximation, will be considered to be solvent independent. The quantity $-\Delta V_\eta$ represents the viscosity activation volume.

The simple Kramers theory introduces viscosity in a chemical kinetics as a single-medium parameter and predicts that the rate constant k in the diffusion regime is inversely proportional to η^{23}

$$k \sim (1/\eta)k_e \quad (2.5)$$

Here the equilibrium rate constant k_e is supposed to be calculated

TABLE I: Experimental Values of the Arrhenius Parameters [Preexponential Factor A ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) and Activation Energy E ($\text{kcal}\cdot\text{mol}^{-1}$)] for the Cyclopentadiene Dimerization Reaction

	T, K	$\log A$	E	ref
gas phase	353–423	6.11	16.7	14
	393–467	4.93	14.9	15, 16
	405–455	6.77	16.9	17
nonpolar solvents				
C_6H_6	258–328	6.10	16.4	18
CCl_4	273–328	6.70	17.1	18
CCl_4	273–295	5.90	16.2	19
paraffin	273–445	7.10	17.4	18
CS_2	273–308	6.20	16.9	18
CS_2	273–295	5.57	17.7	19
cyclopentadiene	271–308	5.80	16.2	18
cyclopentadiene	273–331	5.57	16.8	19

by the naive version of the TS theory neglecting all medium effects. The combination of (2.1) and (2.3) in (2.5) results in

$$\ln \frac{k(p)}{k_0} = \frac{\Delta V_\eta}{RT} \Phi_\eta(p) - \frac{\Delta V^\ddagger_r}{RT} \Phi_r(p) \quad (2.6)$$

The quantity ΔV_η varies within the range -10 to $-30 \text{ cm}^3/\text{mol}^{22}$ which is comparable with the magnitude of observed activation volumes of Diels–Alder reactions. So, following from (2.6), strong and regular viscosity dependence, which cannot be overlooked, has no confirmation in experiments.

Our conclusion is that the simple Kramers theory is hardly suitable as a basis of a dynamical model of Diels–Alder reactions in condensed media. The alternative theory that we apply below is based on a two-variable reaction model treating on equal grounds the reaction coordinate of a chemical subsystem as well as a medium coordinate.^{24,25} This development of a dynamical theory has several merits. First, it involves friction effects only in the equation of motion for a medium variable. By this means the interpretation of the friction constant as a self-characteristic of a pure solvent and taking it proportional to the hydrodynamic shear viscosity η has much better motivation than in the one-dimensional Kramers model which deals only with a single chemical coordinate. Second, the interaction between the chemical and medium coordinates can be explicitly involved in the two-dimensional model which underlies the elimination of dissipative and random forces from the equation treating the chemical coordinate. Finally, the two-dimensional theory has the advantage, most important for the present treatment, of being able to describe nonequilibrium kinetic effects operating when friction effects are so strong that the slow medium coordinate lags behind the fast motion of a chemical coordinate. This effect, often referred to as a nonequilibrium TS solvation, is completely missing in any one-dimensional model ignoring explicit consideration of medium variables. It is well established now^{26–28} that a one-dimensional non-Markovian model of a chemical reaction in the condensed phase, combined with the Grote–Hynes approximation²⁹ for the rate constant (the Kramers model proves to be the simplest version of such a theory), is completely equivalent to the equilibrium TS theory as applied to the combined “chemical subsystem + medium”. This states rigorously the absence of nonequilibrium effects in the Kramers treatment.

The theory considered below attains equilibrium limit in which the rate constant becomes friction independent. As the friction grows, the dependence is recovered in a nonequilibrium kinetic regime. It appears that the whole diversity of kinetic regimes is mainly governed by two parameters. One of them, measuring the ratio of characteristic time scales for chemical and medium variables, facilitates nonequilibrium behavior in the case of highly reactive systems with relatively low barriers. However, another

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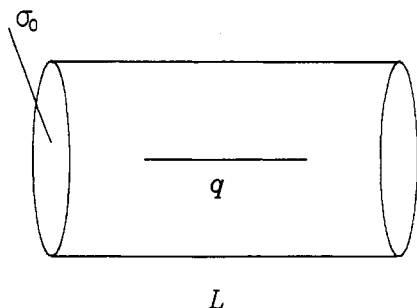


Figure 1. The model scheme of the reacting system.

parameter having the dimension of energy, which should be large enough in order to ensure the nonequilibrium kinetic regime, is bounded from above by the potential barrier height. The event that both parameters fall into a proper range seems to be rather unusual at least until pressure is very high. It follows then that the majority of Diels-Alder reactions, for which the viscosity influence cannot be revealed, proceed as equilibrium ones and only a small number of exceptions are rationalized in terms of a nonequilibrium behavior.

3. Model Enthalpy Surface for a Cycloaddition Reaction in the Condensed Phase

Let us consider as a medium a nonpolar continuum with a cylindrical cavity inside it. The cylinder length is L and its cross section is σ_0 , as shown in Figure 1. The chemical coordinate is modeled as a segment of length q placed at the center of the cavity. A reaction process inside the chemical subsystem is imitated by the contraction of coordinate q . The cavity length L is a medium coordinate. The enthalpy surface for such a model is

$$H(q, L; p) = U_1(q) + U_2(L - q) + p\sigma_0 L \quad (3.1)$$

where $U_1(q)$ is a gas-phase potential attributed to the pure chemical subsystem (a double-well curve), $U_2(L - q)$ is the interaction potential between the terminal points of the segment and the cavity walls and $p\sigma_0 L$ is the work of the cavity expansion.

Essential for the following is the shape of potential $U_1(q)$ in the vicinity of its two extrema, namely, the reactant minimum q_0 and the top of the barrier q^* . We apply a quadratic approximation with force constants $\lambda_1 > 0$ and $\lambda_1^* < 0$:

$$U_1(q) = \frac{1}{2}\lambda_1(q - q_0)^2; \quad \lambda_1 > 0 \text{ (in the vicinity of } q_0)$$

$$U_1(q) =$$

$$U^*_0 + \frac{1}{2}\lambda_1^*(q - q^*)^2; \quad \lambda_1^* < 0 \text{ (in the vicinity of } q^*) \quad (3.2)$$

Here U^*_0 denotes the barrier height. The potential $U_2(L - q)$ is composed as a pair of identical terms, each attributed to the interaction of terminal points of q with the closest to it cavity wall. Approximately, they are quadratic potentials with minima at l_0

$$U(L - q) = 2 \left[\frac{1}{2}\lambda_2 \left(\frac{L - q}{2} - l_0 \right)^2 \right] = \frac{1}{2}\lambda_2(L - q - 2l_0)^2 \quad (3.3)$$

where λ_2 is the corresponding force constant and $\lambda_2 = \frac{1}{2}\lambda$.

The stationary conditions $\partial H / \partial q = \partial H / \partial L = 0$ provide us with the coordinates of the reactant minimum (\bar{q} , L) and the saddle point (q^* , L^*) as functions of p :

$$\begin{aligned} \bar{q} &= q_0 - \frac{p\sigma_0}{\lambda_1}; \quad L - \bar{q} = 2l_0 - \frac{p\sigma_0}{\lambda_2} \\ q^* &= q^* - \frac{p\sigma_0}{\lambda_1^*}; \quad L^* - q^* = 2l_0 - \frac{p\sigma_0}{\lambda_2} \end{aligned} \quad (3.4)$$

Next we shift the scales of variables q and L according to

$$\begin{aligned} x &= q - q \\ y &= L - L \end{aligned} \quad (3.5)$$

So we come out with the explicit expressions of the enthalpy surface in the reactant region (the valley) and around the saddle point (the ridge)

close to the bottom of the reactant valley

$$H(x, y; p) = \frac{1}{2}\lambda_1 x^2 + \frac{1}{2}\lambda_2(y - x)^2 + p\sigma_0 L + \frac{1}{2}p^2\sigma_0^2 \left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right)$$

close to the ridge

$$H(x, y; p) = U^*_0 + \frac{1}{2}\lambda_1^*(x - x^*)^2 + \frac{1}{2}\lambda_2(y - x)^2 + p\sigma_0 L^* + \frac{1}{2}p^2\sigma_0^2 \left(\frac{1}{\lambda_1^*} + \frac{1}{\lambda_2} \right) \quad (3.6)$$

The new notations are

$$\begin{aligned} x^* &= \bar{q} - q^* = x^*(p) \\ y^* &= L - L^* = y^*(p) \end{aligned} \quad (3.7)$$

and from the geometry of the model according to (3.4) we obtain the relation

$$y^* = x^* \quad (3.8)$$

Finally, we shift the energy scale by the quantity $p\sigma_0 L + \frac{1}{2}p^2\sigma_0^2(1/\lambda + 1/\lambda_2)$ and introduce the effective force constants

$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}; \quad \frac{1}{\mu} = \frac{1}{\lambda_1^*} + \frac{1}{\lambda_2} \quad (3.9)$$

So the expression for the enthalpy surface becomes

close to the bottom of the reactant valley

$$H(x, y; p) = \frac{1}{2}\lambda_1 x^2 + \frac{1}{2}\lambda_2(y - x)^2$$

close to the ridge

$$H(x, y; p) = U^*(p) + \frac{1}{2}\lambda_1^*(x - x^*)^2 + \frac{1}{2}\lambda_2(y - x)^2 \quad (3.10)$$

The quantity

$$U^*(p) = U^*_0 - p\sigma_0 y^* - \frac{1}{2}p^2\sigma_0^2 \left(\frac{1}{\lambda} - \frac{1}{\mu} \right) \quad (3.11)$$

represents the enthalpy value at the saddle point.

What we need next are a pair of one-dimensional quadratic potentials, the profiles of enthalpy function (3.10) along the bottom of the valley $W(y)$ and along the ridge $W_1(y)$. They are derived by applying the condition $\partial H / \partial x = 0$ to the first and second expressions of (3.10), respectively:

$$W(y) = \frac{1}{2}\lambda y^2$$

$$W_1(y) = U^*(p) + \frac{1}{2}\mu(y - y^*)^2 \quad (3.12)$$

The cross sections of (3.10) along x at fixed y are modifications of the gas-phase double-well curve $U_1(x)$ by the interaction with medium. We expect them to retain the double-well shape for every y under consideration. This obvious condition restricts the parameters of the model and results in the inequality

$$\lambda_1^* + \lambda_2 < 0 \quad (3.13)$$

Differentiation of the pressure-dependent saddle point energy U^* and coordinates $x^* = y^*$ gives as a result

$$\begin{aligned} \partial U^* / \partial p &= -\sigma_0 y^* \\ \frac{\partial y^*}{\partial p} &= -\sigma_0 \left(\frac{1}{\lambda} - \frac{1}{\mu} \right) \end{aligned} \quad (3.14)$$

The explicit expression for y^* is

$$y^*(p) = y^*(0) - p\sigma_0 \left(\frac{1}{\lambda} - \frac{1}{\mu} \right) \quad (3.15)$$

Concluding this section it is expedient to discuss the validity of the enthalpy expression 3.1. The pressure-dependent term in the form $p\sigma_0 q$ was introduced earlier in the framework of the cell model^{8,9} by consideration of changes of chemical coordinates q in the mean field created by the medium environment. The cell model does not consider explicitly medium coordinates. Contrary to that, in the present approach the pressure dependence enters via the medium coordinate, the corresponding term in (3.1) being $p\sigma_0 L$. A more careful consideration shows, however, that this is only a part of the cavity self-enthalpy. The total enthalpy change accompanying the variation of L by ΔL is

$$\Delta H_{\text{cav}} = p\sigma_0 \Delta L + \Delta U_0 + \Delta H_{\text{rel}} \quad (3.16)$$

This change of the cavity formation enthalpy involves two extra contributions. ΔU_0 represents the change of the internal energy due to mutual interactions between all cavity walls whereas ΔH_{rel} appears as a result of a medium reorganization proceeding in the regions well remote from the cavity and accompanying its contractions or expansions. The latter contribution will be referred to as the medium relaxation enthalpy.

By noting that all interactions between the cavity walls, being of van der Waals nature, are short-range ones, we conclude that for large values $L > 10 \text{ \AA}$, which can be accepted in the present case, the internal energy contribution becomes L independent, that is to say

$$\Delta U_0 = 0 \quad (3.17)$$

So, the enthalpy effects neglected in (3.1) can be attributed only to the medium relaxation apart of the place of the cavity location. The corresponding corrections are discussed in more detail in section 6.

4. Dynamical Equations and Reaction Rate

4.1. The Kinetic Background. The equations of motion following from the model of section 3 are

$$m \frac{d^2 x}{dt^2} + \frac{\partial H}{\partial x} = 0$$

$$\gamma \frac{dy}{dt} + \frac{\partial H}{\partial y} = \delta - \text{correlated random force} \quad (4.1)$$

Here m and γ are the reduced mass of the chemical subsystem and the friction coefficient; H is the enthalpy surface as given by (3.10). Being interested in revealing nonequilibrium kinetic effects we shall concentrate on the case of anisotropy of characteristic time scales associated with chemical x and medium y dynamical variables.^{24,25} When the time scales greatly differ, a nonequilibrium situation arises and the reaction flow bypasses the TS region of the enthalpy surface violating the equilibrium rate constant expression as calculated according to the Kramers-Grote-Hynes approximation.²⁹ This extreme case reduces the dynamical system (4.1) to a single diffusion equation with a sink for a slow medium variable y . The corresponding diffusion problem generates the rate constant as the lowest eigenvalue k of the following eigenvalue equation with eigenfunction $\varphi(z)$:

$$\left[H + \frac{K(z)}{\omega} \right] \varphi(z) = \frac{k}{\omega} \varphi(z) \quad (4.2)$$

The variable z in (4.2) is the scaled medium coordinate

$$z = (\lambda/RT)^{1/2} y \quad (4.3)$$

The inverse time of z (or y) relaxation in the effective potential $V(y)$ (3.12) is denoted as ω

$$\omega = \lambda/\gamma \quad (4.4)$$

By its variation the degree of anisotropy of time scales, which essentially directs the dynamics, can be varied in a wide range. The operator H is identical with the oscillatory Hamiltonian

$$H = -\frac{d^2}{dz^2} + \frac{1}{4}z^2 - \frac{1}{2} \quad (4.5)$$

and the sink term $K(z)/\omega$ has the meaning of a perturbation potential of the "Schroedinger equation" (4.2). In terms of the original medium variable y the explicit expression for $K(z)$ is

$$K(y) = \frac{\omega_e}{2\pi} \exp\left[-\frac{1}{RT}\Delta W\right]$$

where

$$\Delta W = W_1(y) - W(y)$$

$$\omega_e = \left(\frac{\lambda_1 + \lambda_2}{m} \right)^{1/2}$$

The transformation to z yields

$$\frac{K(z)}{\omega} = \rho^{1/2} \frac{k_e}{\omega} \exp\{-\rho[z - (2\epsilon)^{1/2}]^2 + z^2\} \quad (4.6)$$

The following contractions are used

$$k_e = \frac{\omega_e}{2\pi} \rho^{-1/2} \exp\left(-\frac{U^*}{RT}\right) \quad (4.7)$$

for the equilibrium rate constant, the limit of k when the medium relaxation time is short (large ω);

$$\rho = \mu/\lambda \quad (4.8)$$

for the ratio of force constants appearing in the effective potential cross sections $W(y)$ and $W_1(y)$ (3.12);

$$\epsilon = \frac{1}{2}(z^*)^2 = \frac{\lambda}{2RT}(y^*)^2 \quad (4.9)$$

for the dimensionless parameter which characterizes the energetics of medium reorganization and displays how sharp the enthalpy surface relief is along the valley associated with the y (or z) motion.

According to (4.7)–(4.9) we obtain three dimensionless parameters, namely, k_e/ω , ϵ , and ρ , which govern the rate expression. The first of them, obtained by dividing (4.7) by (4.4), measures the ratio of time scales associated with x and y . The rate constant k can be calculated numerically²⁵ by solving eq 4.2. Calculations in a wide range of parameters ($10^{-8} \leq k_e/\omega \leq 10^3$; $5 \leq \epsilon \leq 50$; $0.5 \leq \rho \leq 6$) confirmed the prediction²⁴ on the existence of the nonequilibrium regime with $k/k_e \ll 1$. This kind of behavior dominates at large ϵ values ($\epsilon > 10$), which corresponds to a sharp potential relief for the medium motion.

4.2. Analytical Representation of the Rate Constant $k(k_e/\omega, \epsilon, \rho)$. By considering the dependence of rate constant k on the parameter ϵ two extremes can be revealed:²⁵

$$-\ln(k/k_e) = A\epsilon + B \quad (\epsilon \gg 1) \quad (4.10)$$

$$k/k_e = 1 \quad (\epsilon \ll 1) \quad (4.11)$$

We took these expressions as a basis for analytical approximation of the numerical data²⁵ over the whole parameter range according to

$$\frac{k}{k_e} = \frac{1}{1 + \exp(A\epsilon + B)} \quad (4.12)$$

where A and B are treated as functions of k_e/ω and ρ . For different fixed values $\rho = 1.5, 3.0$, and 6.0 we accepted

$$A(k_e/\omega) = A_1[\ln(k_e/\omega) - A_2]^2 + A_3$$

$$B(k_e/\omega) = B_1[\ln(k_e/\omega) - B_2]^2 + B_3 \quad (4.13)$$

The constants A_1, A_2, A_3 and B_1, B_2, B_3 are listed in Table II for

TABLE II: Parameters of Formulas 4.13

	$\rho = 1.5$	$\rho = 3.0$	$\rho = 6.0$
A_1	-0.143×10^{-3}	-0.134×10^{-3}	-0.103×10^{-3}
A_2	-0.595	0.239	0.385×10^1
A_3	0.298	0.394	0.493
B_1	0.110×10^{-1}	0.096×10^{-1}	0.638×10^{-2}
B_2	-0.251×10^2	-0.326×10^2	-0.496×10^2
B_3	-0.577×10^1	-0.915×10^1	-0.159×10^2

different ρ . The function (4.12) has a deficiency of having an incorrect limit at $\epsilon \rightarrow 0$. So it cannot reproduce (4.11) exactly; however, after $B(k_e/\omega)$ was properly adjusted, the limit (4.11) was obtained within 3–5%. In the whole parameter range this interpolation provides the quantity k/k_e within 10–15% accuracy or even better.

4.3. *The Pressure Dependence of Parameters.* According to (4.12) the rate constant dependence on pressure appears implicitly via parameters k_e/ω and ϵ . We neglected the pressure dependence of parameter ρ and fixed it by the following reasoning. In terms of force constants entering (3.2), (3.3), and (3.9)

$$\rho = \frac{\lambda_1^*}{\lambda_2} \frac{\lambda_1 + \lambda_2}{\lambda_1^* + \lambda_2}$$

Here λ_1 represents the interaction of reactants at initial minimum and λ_2 is one half of the force constant of the interaction between the reactants and the cavity walls. They both correspond to weak van der Waals interactions. So we assume $\lambda_1 \approx 2\lambda_2$ and simplify the ρ expression as

$$\rho \approx \frac{3}{2} \left(1 + \frac{\lambda_1}{2|\lambda_1^*| - \lambda_1} \right) \quad (4.14)$$

The force constant λ_1^* is negative and its absolute value significantly exceeds λ_1 . This allows one to assume $\rho \approx 3/2$.

To obtain the pressure dependence of ϵ and k_e/ω we need some results following from the microscopic definition of the enthalpy surface according to section 3 in combination with the empirical expressions 2.1–2.3. Under the assumption that all force constants are pressure independent we derive from (4.8) and (4.9)

$$\frac{d\epsilon}{dp} = \frac{1}{RT} \left(1 - \frac{1}{\rho} \right) \frac{dU^*}{dp} \quad (4.15)$$

The basic expressions 4.14 and 4.15 accumulate all the model-induced information, as extracted from an explicit operation with the enthalpy surface, which is needed for the further application.

The value of dU^*/dp in (4.15) can be obtained from (3.14). We prefer, however, to minimize the errors introduced by the model assumptions and estimate this key quantity empirically. The way to perform this follows from the fact that, according to the model, the prefactor in (4.7) can be considered as a p -independent quantity. So from (4.7) we obtain the empirical estimate

$$\frac{dU^*}{dp} = RT \frac{d}{dp} \ln k_e \quad (4.16)$$

What we finally need to complete the expressions for k_e/ω and ϵ as functions of p are the pressure dependences of the TS rate constant k_e and the friction coefficient γ related to ω according to (4.4). The first expression is identified with (2.1) and (2.2):

$$\ln k_e(p) = \ln k_e(0) - (\Delta V^*_e/RT)\Phi_e(p) \quad (4.17)$$

Here ΔV^*_e is the equilibrium activation volume:

$$\Delta V^*_e = \left(-RT \frac{d}{dp} \ln k_e \right)_{p=0}$$

For equilibrium reactions

$$\Delta V^*_e = \Delta V^*_{r,e}, \quad \Phi_e(p) = \Phi_r(p) \quad (4.18)$$

Our main hypothesis is that the majority of reactions obeying empirical linear relationships 2.1 and 2.2 proceed in the equilibrium

kinetic regime which allows one to apply (4.17) and (4.18) when estimating k_e .

Dealing with the friction coefficient γ we assume it to be proportional to the shear viscosity η for which the empirical formula 2.3 will be taken. Then, combining (4.4), (4.17), and (2.3) we obtain

$$\ln(k_e/\omega) = \ln(k_e/\omega)_0 - \frac{\Delta V^*_e}{RT} \Phi_e(p) - \frac{\Delta V^*_e}{RT} \Phi_r(p) \quad (4.19)$$

The working expression for ϵ is obtained by integration of (4.15) and (4.16):

$$\epsilon(p) = \epsilon_0 + (1 - 1/\rho)(\Delta V^*_e/RT)\Phi_r(p) \quad (4.20)$$

The notations $\ln(k_e/\omega)_0$ and ϵ_0 are attributed to the normal pressure values. These last quantities, as well as ρ , may be either estimated from the model microscopic reasoning or considered as free adjustable parameters. The second way is preferable when the correlation of experiments is the main goal. The first way may supply us with tentative estimates which, after a comparison with their empirical counterparts, would allow one to judge on the consistency of the whole treatment.

If (4.18) is true, we may identify ΔV^*_e with the experimental activation volume. This implies that at normal pressure a reaction proceeds as an equilibrium one. A special estimate of ΔV^*_e is necessary when evidence exists that it is not so. Finally, $\Phi_r(p)$, $\Phi_e(p)$, and ΔV^*_e are known from the experiment.^{20–22}

5. Evaluation of Possible Nonequilibrium Effects

5.1. *Deviation from Equilibrium Kinetics.* According to the above treatment, two nonequilibrium phenomena are expected in pressure-dependent kinetic measurements. First, the activation volume, the quantity obtained by the zero pressure extrapolation, can be violated and, second, one can expect a systematic deviation from the linear relation between $\ln[k(p)/k_0]$ and $\Phi_r(p)$ which we have postulated to manifest the normal equilibrium proceeding of a reaction. Let us consider how the choice of the parameters of the kinetic model can affect these changes.

We represent the rate constant expression 4.12 in the form

$$\ln k(p) = \ln k_e(p) - f(p) \quad (5.1)$$

with

$$f(p) = \ln[1 + \exp(\Omega(p))]; \quad \Omega(p) = A\epsilon + B \quad (5.2)$$

The equilibrium rate constant $k_e(p)$ can be found from the empirical formula 4.17. The nonequilibrium effects are condensed in $f(p)$, the quantity that depends on pressure via parameter ϵ and also via coefficients A and B (4.13). The latter kind of dependence appears by means of the entering A and B parameter k_e/ω , which varies with pressure according to (4.19).

The corresponding nonequilibrium correction to activation volume ΔV^* is

$$\Delta V^* - \Delta V^*_e = RT \frac{\exp \Omega}{1 + \exp \Omega} \frac{d\Omega}{dp} \bigg|_{p=0} \quad (5.3)$$

We infer from (5.1)–(5.3) that the quantity $\Omega(p)$ can be interpreted as a measure of a nonequilibrium effect. The equilibrium limit of $k(p)$, that is, the TS rate constant k_e , is revealed when $\Omega \ll -1$. When $\Omega = 0$ one obtains $k/k_e = 1/2$. We assume the value $\Omega = 0$ as a natural boundary between equilibrium and nonequilibrium kinetic regimes. When the degree of nonequilibrium behaviour is high, we obtain

$$f(p) \approx \Omega \gg 1 \quad (5.4)$$

The sign of the derivative $d\Omega/dp$ determines the direction of nonequilibrium effects. If, for instance,

$$\frac{d\Omega}{dp} \bigg|_{p=0} > 0 \quad (5.5)$$

one will observe a decrease of absolute values of activation volumes relative to their equilibrium predictions. The function $\ln[k(p)/k_0]$

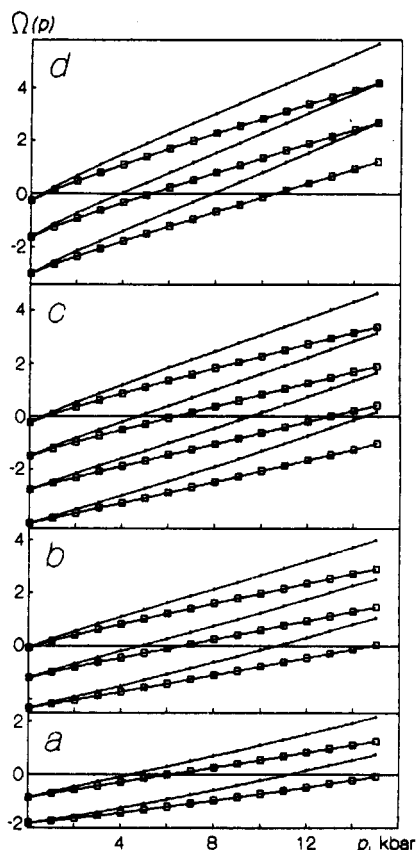


Figure 2. The nonequilibrium parameter Ω versus pressure for different values of governing kinetic parameters $(k_e/\omega)_0$ and ϵ for $\Delta V^\ddagger = -20$ cm³/mol (dots) and -10 cm³/mol (squares). (a) $(k_e/\omega)_0 = 10^{-12}$ and $\epsilon_0 = 20$ and 25; (b) $(k_e/\omega)_0 = 10^{-10}$ and $\epsilon_0 = 15, 20$, and 25; (c) $(k_e/\omega)_0 = 10^{-8}$ and $\epsilon_0 = 5, 10, 15$, and 20; (d) $(k_e/\omega)_0 = 10^{-6}$ and $\epsilon_0 = 5, 10$, and 15. The corresponding ϵ_0 values in panels a–d increase from the bottom upwards.

TABLE III: Dependence of the Differential and Integral (in Parentheses) Reaction Volume Deviations $\Delta V^\ddagger/\Delta V^\ddagger_e$ from the Equilibrium Values on the Parameters $(k_e/\omega)_0$ and ϵ_0 ($\rho = 3/2$) for Typical Cycloaddition Reactions

ϵ_0	$(k_e/\omega)_0$			
	10^{-12}	10^{-10}	10^{-8}	10^{-6}
5	1.0 (1.0)	1.0 (1.0)	1.0 (0.98)	0.99 (0.91)
10	1.0 (1.0)	1.0 (0.99)	0.99 (0.94)	0.95 (0.79)
15	1.0 (0.99)	0.99 (0.95)	0.96 (0.85)	0.84 (0.65)
20	0.99 (0.96)	0.96 (0.88)	0.87 (0.73)	0.70 (0.55)
25	0.96 (0.90)	0.89 (0.78)	0.76 (0.63)	0.61 (0.50)

will go lower than its equilibrium counterpart in this case.

5.2. Calculations. A qualitative impression on the importance of nonequilibrium effects can be got by considering function $\Omega(p)$ in a large range of parameters. As stated before,^{24,25} the degree of a nonequilibrium increases with increase of both k_e/ω and ϵ . As these quantities depend on p , the pressure dependence appears. The explicit calculations additionally involve the values $(k_e/\omega)_0$ and ϵ_0 which were considered below as free parameters. The calculations presented use the following basic constants: $\rho = 3/2$ (according to (4.14)); $\Delta V^\ddagger_e = -40$ cm³/mol (the typical value for the Diels–Alder reactions^{13,20,21}; $\Delta V^\ddagger = -20$ and -10 cm³/mol (the typical values for organic solvents²¹). The results are displayed in Figure 2 only for the cases that we considered as most realistic. The criterion was the fact of taking the function $\Omega(p)$ as reaching the calculated function $\Omega(p)$ the above-mentioned nonequilibrium threshold value $\Omega = 0$ when $0 < p < 15$ kbar. At lower initial values of $(k_e/\omega)_0$ and ϵ_0 the threshold was unattainable within the investigated pressure range. At greater values the nonequilibrium effects are significant ($\Omega > 0$) even at $p = 0$.

As a consequence of increasing Ω we obtain the decreasing absolute value of activation volume ΔV^\ddagger as compared to ΔV^\ddagger_e .

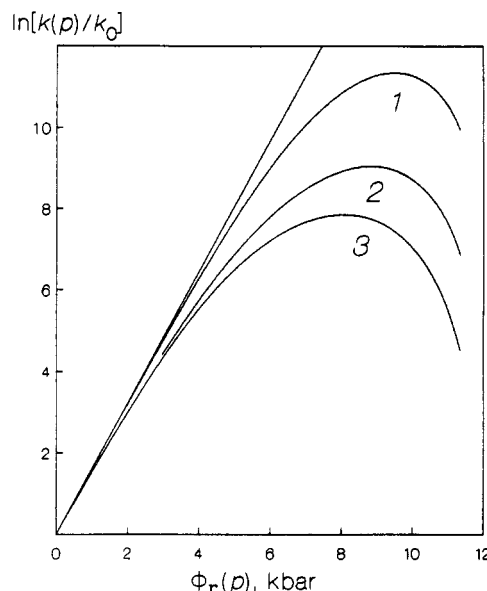


Figure 3. Logarithm of the relative rate constant $\ln [k(p)/k_0]$ versus function $\Phi_T(p)$ in the pressure range 0–50 kbar. (1) $(k_e/\omega)_0 = 10^{-12}$ and $\epsilon_0 = 20$; (2) $(k_e/\omega)_0 = 10^{-10}$ and $\epsilon_0 = 20$; (3) $(k_e/\omega)_0 = 10^{-8}$ and $\epsilon_0 = 15$.

The calculated ratio $\Delta V^\ddagger/\Delta V^\ddagger_e$ is listed in Table III as a function of $(k_e/\omega)_0$ and ϵ_0 . Its differential (at $p \rightarrow 0$) estimate was obtained from (5.3). The alternative calculation using the integral procedure artificially represented the nonlinear plot of $\ln [k(p)/k_0]$ versus $\Phi_T(p)$ as a straight line in the range $0 < p < 10$ kbar. It is seen that the ratio $\Delta V^\ddagger/\Delta V^\ddagger_e$ can become much smaller than unity, the integral estimate being always lower than the true differential one. It is the integral method which is conventionally applied to calculate an activation volume from the experiment (in order to smooth possible experimental errors). So, if a systematic nonequilibrium effect is significant, the integral estimate of the experimental ΔV^\ddagger value can distort its true value significantly. The corresponding error depends on the pressure range used in the integral smoothing procedure.

The plot of $\ln [k(p)/k_0]$ versus $\Phi_T(p)$ in the pressure range 0–50 kbar is shown in Figure 3 for three typical pairs $[(k_e/\omega)_0, \epsilon_0]$. These plots are practically linear for $p < 5$ kbar. At higher pressures curvature appears and finally nonequilibrium effects dominate so that for $p \geq 20$ kbar the rate constant even begins to decrease with pressure. Note that similar plots having a maximum on the $\ln [k(p)/k_0]$ versus p dependence at high pressures have been registered in several experiments.^{30,31} However, an extrapolation of our harmonic theory onto very high pressure range may be an oversimplification.

5.3. Estimates for Real Diels–Alder Systems. The microscopic values of parameters $(k_e/\omega)_0$ and ϵ_0 can be extracted from (4.4) and (4.9):

$$\omega = \lambda/\gamma$$

$$\epsilon_0 = \frac{\lambda}{2RT} [y^*(0)]^2 \quad (5.6)$$

According to (3.7) and (3.8), $y^*(0) = x^*(0) = q_0 - q^*$. For a typical Diels–Alder reaction this value is $1.1 + 1.2 \text{ \AA}$.⁸ For organic solvents at $T = 300$ K and normal pressure the typical value of γ is $3 \times 10^{-9} \text{ g s}^{-1}$. Hence, we need only the force constant λ to make use of (5.6). Since λ must be associated with nonpolar intermolecular interactions we tried to calculate it from the formula

$$\lambda = m\omega_0^2 \quad (5.7)$$

where m and ω_0 are tentative estimates of the system mass and

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intermolecular frequency. Using $m = 50$ carbon units and $10 \text{ cm}^{-1} < \omega_0 < 100 \text{ cm}^{-1}$ we obtain

$$0.4 \leq \epsilon_0 \leq 40, \quad 10^{11} \text{ s}^{-1} \leq \omega \leq 10^{13} \text{ s}^{-1} \quad (5.8)$$

Finally, we assume at normal pressure

$$k_e \simeq (10^{12} \text{ s}^{-1}) \nu \exp(-U^*/RT)$$

and come out with the following estimate:

$$(k_e/\omega)_0 \simeq \nu \exp(-U^*/RT) \quad (5.9)$$

The multiplier $\nu < 1$ reduces the equilibrium preexponential factor as compared to its typical unimolecular value which constitutes $\approx 10^{12} \text{ s}^{-1}$. In order to estimate its value let us consider the Diels-Alder reaction as a bimolecular one, according to a standard kinetic treatment. Then ν will show how the real prefactor deviates from the typical bimolecular value which constitutes $\approx 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The corresponding ν value is known to be $10^{-3} < \nu < 10^{-1}$,^{32,33} which is usual for concerted reactions with "tight" transition states. By comparison of (5.8) and (5.9) with the calculations displayed in Figure 2 one may conclude that the possibility of finding the nonequilibrium kinetic regime is quite reliable for Diels-Alder reactions with $U^*/RT < 25$ ($U^* < 15 \text{ kcal/mol}$). Some comment is needed, however, since in the above calculations we varied ϵ_0 as a free parameter ignoring the limitation^{24,25}

$$\epsilon < U^*/RT \quad (5.10)$$

which puts an additional restriction on the scope of the nonequilibrium theory.

Finally, we applied our formulas to a pair of Diels-Alder reactions showing systematic deviations³⁹ from linear $\ln[k(p)/k_0] - \Phi_r(p)$ plots, namely, the isoprene dimerization in 1-bromobutane at 50°C (I) and the condensation of cyclopentadiene with dimethyl acetylenedicarboxylate in ethyl acetate at 10°C (II). In calculations we used formulas 4.12, 4.13, and 4.19, and 4.20. The pressure dependence of viscosity in (4.19) was treated more accurately than in section 5.2. Now the parameters b and c entering the function $\Phi_r(p)$ (2.4), as well as ΔV_r , were taken specifically for different solvents.²² We accepted $\Delta V_e = -40 \text{ cm}^3/\text{mol}$ as before. Experimental Arrhenius activation energies were taken as estimates of U^* which constituted 18.9 and 14.2 kcal/mol for reactions I and II, respectively. We tried to reproduce the experimental pressure dependence of rate constants by varying ϵ_0 and $(k_e/\omega)_0$. Tentative estimates (5.8) and (5.9) and the restriction (5.10) were kept in mind.

A satisfactory fit of experimental data was obtained (Figure 4) with the values $\epsilon_0 = 28$ for reaction I and $\epsilon_0 = 20$ for reaction II. The corresponding $(k_e/\omega)_0$ values (2×10^{-12} and 6×10^{-8} for reactions I and II, respectively) are in reasonable agreement with the estimates from formula 5.9 when $\nu = 10^{-2}$. The results from our treatment for activation volumes ΔV^* are $-36.5 \text{ cm}^3/\text{mol}$ (reaction I) and $-33.4 \text{ cm}^3/\text{mol}$ (reaction II).

6. Discussion of the Model

The enthalpy surface expressions 3.10 and 3.11 used in the above investigation were based on several simplifying assumptions. First, the model of section 3 dwells upon a purely geometrical interpretation of volumetric effects accompanying a chemical conversion in condensed media. It neglects the medium reorganization in areas remote from the cavity regions and the respective enthalpy relaxational contribution. Second, the expressions 3.10 and 3.11 are based on harmonic approximation implying all force constants to be pressure independent. This approximation is legitimate only at low pressure ($p < 5 \text{ kbar}^8$).

In trying to cancel the impact of these and other inconsistencies upon the kinetic conclusions we exercised some caution when applying formulas of section 3 with the hope of compensating their deficiencies by introducing additional empirical corrections. So,

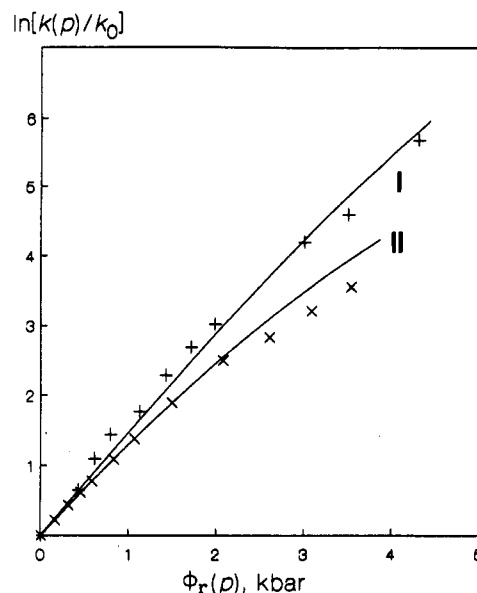


Figure 4. Rate constants of reactions I and II as functions of $\Phi_r(p)$. Experimental points are shown as (+) and (x) for cases I and II.

the idea of using relations 4.16 and 4.17 was to empirically insert in the theory the pressure dependence of the potential barrier, the quantity strongly affecting the kinetics. By this means, in the working rate expressions 5.1 and 5.2 the assumptions underlying the enthalpy surface model appear only via expression 3.14. All other approximations have no contribution to the structure of the theory and work only at the auxiliary stage of connecting parameters k_e/ω , ϵ , and p to real chemical systems.

This empirical approach allows one to incorporate implicitly the electrostatic interactions of a chemical subsystem with a solvent. Indeed, formula 2.1 successfully treats the majority of reactions (considered as equilibrium ones) in terms of the universal function $\Phi_r(p)$. The specific influence of solvation is reflected by activation volume ΔV_r^* . So, by use of (2.1) with experimentally found activation volumes in the calculation of k_e/ω according to (4.19), all equilibrium solvent effects are incorporated.

Hence, the only model assumption important at the formal mathematical level is formula 3.14. Both it and its consequence, formula 4.15, are differential relations. As a result, the formal treatment of rate constant does not fix the origin of the pressure scale. The final expressions of section 4.2 are invariant under an arbitrary origin shift Π :

$$p \rightarrow p + \Pi \quad (6.1)$$

The corresponding change of the pressure variable can only modify the particular estimates based on (5.6) when parameters k_e/ω and ϵ for real systems are extrapolated to normal pressure.

It seems expedient to consider the ambiguity in the choice of Π in (6.1) in connection with nonlocal relaxation processes in remote medium regions. Let us express the total volume change in the course of reaction as

$$\begin{aligned} \Delta V &= \Delta V_0 + \Delta V_{\text{rel}} = (\sigma_0 + \sigma_{\text{rel}})\Delta L \\ \Delta V_0 &= \sigma_0 \Delta L \\ \Delta V_{\text{rel}} &= \sigma_{\text{rel}} \Delta L \end{aligned} \quad (6.2)$$

Only the geometrical part ΔV_0 is explicitly treated in (3.1). The quantity ΔV_{rel} is the relaxation contribution to the volume variation, assumed to be proportional to the change ΔL of the cavity length. The proportionality constant σ_{rel} has no clear interpretation (even its sign is indefinite) although its geometrical counterpart σ_0 should be treated as the cavity cross section.

An important conclusion (3.17) states that a geometrical change does not influence the internal energy of the cavity. After addition

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of the relaxation effects the enthalpy of the cavity formation becomes

$$\begin{aligned}\Delta H_{\text{cav}} &= p\Delta V + \Delta U_{\text{rel}} \\ &= p\Delta V_0 + \Delta H_{\text{rel}} \\ \Delta H_{\text{rel}} &= p\Delta V_{\text{rel}} + \Delta U_{\text{rel}}\end{aligned}\quad (6.3)$$

The internal energy change due to relaxation is ΔU_{rel} . The statement (3.17) then means that ΔU_{rel} coincides with ΔU_{cav} , the total energy change. The latter quantity can be estimated in terms of purely thermodynamical reasoning invoking internal pressure Π of a liquid:³⁴

$$\Delta U_{\text{cav}} = \Pi\Delta V = \Delta U_{\text{rel}}\quad (6.4)$$

Hence,

$$\Delta H_{\text{cav}} = (p + \Pi)\Delta V\quad (6.5)$$

Expression 6.5 motivates identification of Π in (6.1) as the internal pressure. It also provides an argument in favor of neglecting the corresponding enthalpy contribution, at least at a preliminary step of the investigation. The reason is that conventional interpretations of activation volumes always deal with the external pressure p , not with the combination $p + \Pi$.¹² Another empirical argument follows from Table I. For instance, the internal pressure of benzene is 4.05 kbar.³⁵ Such a pressure change, as applied to a reacting Diels-Alder system transferred into liquid from the gas phase, should raise the rate constant by an order of magnitude. This effect is, however, not visible in the data of Table I. So, the totality of the experimental evidence draws us to a conclusion that internal pressure is a quantity hardly observable in a kinetic experiment, although its importance in connection with thermodynamical properties of liquids is beyond doubt. Due to this reasoning, the enthalpy expression 3.1 without the relaxation term obtains some experimental foundation.

The underlying physical picture can also be constructed. Suppose that relaxation processes proceed with a time lag τ behind the motion of the cavity environment. According to (6.3)

$$\Delta H_{\text{rel}} = A\Delta L; \quad A = (p + \Pi)\sigma_{\text{rel}} + \Pi\sigma_0\quad (6.6)$$

Treating ΔH_{rel} and ΔL explicitly as temporal functions we obtain

$$\Delta H_{\text{rel}}(t) = A\Delta L(t - \tau)\quad (6.7)$$

By adding this term to (3.1) we ultimately obtain an extra force

applied to the medium coordinate y in the dynamical equations (4.1):

$$-\frac{\partial H_{\text{rel}}}{\partial y(t)} = -A\frac{\dot{y}(t-\tau)}{\dot{y}(\tau)}\quad (6.8)$$

The reaction event in a cavity must be completed within a time $\tau_0 \approx \omega^{-1}$. For a typical reaction trajectory the velocity $\dot{y}(t)$ does not vanish only within a time interval of order τ_0 , because we consider the cavity size as fixed both before and after the reaction. In combination with (6.8) this condition gives

$$\begin{aligned}\frac{\dot{y}(t-\tau)}{\dot{y}(\tau)} &= 1 \quad \text{when } \tau_0 \gg \tau \\ &= 0 \quad \text{when } \tau_0 \ll \tau\end{aligned}\quad (6.9)$$

It immediately follows from (6.8) and (6.9) that the remote medium reorganization does not affect the cavity kinetics when $\tau_0 \ll \tau$. This establishes the legitimacy condition for model 3.1. The derivation can be easily extended onto a more detailed treatment with time lag τ considered as a random variable defined by a given distribution.

As a consequence we conclude that provided $\tau_0 \ll \tau$ the change ΔV_{rel} of relaxation volume does not contribute to activation volume ΔV^* , although its contribution to such equilibrium quantity as the reaction volume is beyond doubt. Since, as mentioned above, the signs of ΔV_0 and ΔV_{rel} may be opposite, this fact may be responsible for the sometimes observed breakdown of a correlation between activation and reaction volumes. This explanation, along with others (invoking secondary orbital interactions^{36,37} or steric effects^{20,38}), is worth keeping in mind.

Acknowledgment. We express our sincere gratitude to B. S. El'yanov and E. M. Gonikberg for providing their interpretations of experimental data and the valuable discussion.

Registry No. Cyclopentadiene, 542-92-7.

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