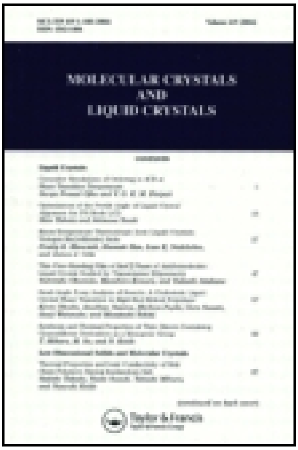

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Lattice Mediation in Thermo-and Photo-Induced Reactions; Co-Operative Activation

Tadeusz Luty [a]

[a] Instytut Chemii Fizycznej i Teoretycznej, Politechnika Wroclawska, PL50-370 Wroclaw Laboratoire de Dynamique et Structures des Materiaux Moleculaires, Universite de Lille 1, F59655, Villeneuve d'Ascq

To cite this article: Tadeusz Luty (2001): Lattice Mediation in Thermo-and Photo-Induced Reactions; Co-Operative Activation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 539-548

To link to this article: http://dx.doi.org/10.1080/10587250108023732

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp.539-548
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Lattice Mediation in Thermo- and Photo-Induced Reactions; Co-Operative Activation

TADEUSZ LUTY

Instytut Chemii Fizycznej i Teoretycznej, Politechnika Wroclawska, PL50–370 Wroclaw Laboratoire de Dynamique et Structures des Materiaux Moleculaires, Universite de Lille 1, F59655 Villeneuve d'Ascq

Thermo- and photo-induced reactions are discussed from a point of view of a competition between local and global structures. A role of lattice mediation is focused on elastic aspect of the competition; a cavity as a local stress and their interaction. In particular the problem how an interplay between cooperative and competitive role of the lattice mediation influences a kinetics of a solid state reaction has been addressed. It is shown that thermal activation is highly cooperative and its energy is a quadratic function of transformed cavities. In a competition with photo-induced transformation, the cooperative activation may cause homogeneous/heterogeneous reaction when induced by weakly/strongly absorbed light.

Keywords: solid state reactions; cooperative activation

INTRODUCTION

For a reaction in the solid state, the lattice plays a role of a "solvent" at an initial stage of reaction, but also becomes a reactant itself in the course of the reaction ("active solvent"). Thus, a solid state transformation must be considered as a self-consistent and highly correlated process of creation of chemically induced perturbations (the product molecules). In an attempt to understand such processes, basic questions arise, such as what is a "component" and what is a "phase", as addressed by J.D. Dunitz,[1] in the context of solid state reactions. The problem of polymorphs and components has been recently elaborated within the concept of broken ergodicity and kinetics of a transformation.[2] For chemical reactions in solids, where various kinds of structural symmetries are strongly coupled to extended modification in electronic configurations, one may even use a term "chemical states of matter"[3] and ask ... "a solid of what ?".

An unreactive molecular crystal is not a set of independent molecules, nor it is an electric and elastic continuum. It is rather a set of molecules embedded in electric/elastic continuum. This picture takes an advantage of the fact that there is a significant difference between intra- and inter-molecular forces and that "a molecule" can be defined. Many physical properties of molecular solids can be related to, and predicted from, molecular properties (for example electric susceptibilities[4]).

Let us consider transformation in a molecular crystal, photo- or thermally induced. An initiation is a local process, which results in a local structure and equilibrium. It is convenient to analyze the process within (diabatic, adiabatic) energy curves for product (P) and reactant (R) molecules, with the chemical potential difference, $\Delta\mu^0$. At the initiation step, a crystal lattice assists the reaction statically by forming a cage for a reacting site and the effect is expressed as topochemical and least motion principles. The principles determine molecular and crystal structure of a product at this stage. The solid state chemistry exploits the concept of "reaction cavity", for a description of a region of material where a reaction is initiated (see ref. [5] for an excellent review of the concept). A cavity is an effective reacting site, with the chemical potential difference modified by short-range interactions of a reacting molecule with its neighbours, $\Delta\mu = \Delta\mu^0$ - (short-range interaction within a cavity) . Strong, often of a chemical nature, the short-range effects are different and competing with long-range effects of the crystal lattice. By the very nature of a chemical transformation, a product molecule/structure (a "component") is different from the parent phase, a reactant crystal, leading to geometrical and/or energetical frustration. When a reaction proceeds, the local structure expands and often competes with global one. (In the convention of analogies to human society, drawn in ref. [5], it reminds the slogan „think globally, act locally"). In thes competion, a dynamical role of the lattice becomes more and more important, as the reaction proceeds. A global equilibrium is a result of a compromise between competition and cooperativity due to lattice mediation. The lattice contributes to both, thermodynamical stability of a system and kinetics. Some of thermodynamical consequences of the lattice mediation have been discussed recently,[6],[7] and here I shall discuss mainly kinetic aspects.

A CAVITY AS A LOCAL STRESS.

Following the picture of a molecular crystal as molecules embedded in an electric and elastic continuum, a reacting crystal is viewed as "cavities" embedded in a continuum. The lattice mediates between the cavities via elementary excitations of the electric and elastic fields, e.g., excitons and phonons. The role of electric screening and exciton mediation might be important for solid state transformations based on charge-transfer processes and, although it has not been extensively discussed and elaborated, the theory of dielectric function allows for a quantitative analysis of the effect.[8] However, the nature of a molecular solid suggests that the elastic field of the environment is much more important and...less understood. We shall concentrate on an elastic mediation of the lattice. In this context, the model of reacting crystal raises a question of competition between shapes and energetics of the cavities (local structures) and their long-range, elastic interaction which tends to cooperative construction of a global structure.

First, we shall describe mechanical properties of a cavity. It has been shown[6],[7] that he most convenient way to characterize a reaction cavity is to treat it as a distribution of excess forces. The forces, $\{V_i(R)= [\partial(\Delta\mu)/\partial R_i]\}$, acting on neighbouring molecules at positions, **R**, arise when a local transformation driven by the chemical potential difference, $\Delta\mu$, takes place at a center of the cavity. Then, elastic dipole is defined, $P_{ij}=1/2\Sigma_R[V_i(R)R_j + V_j(R)R_i]$, analogously to an electric dipole for a charge distribution. The elastic dipole can be interpreted as a local stress created at a cavity as a result of a transformation. It is clear that the elastic dipole is a convenient description of both, shape and energetics of a cavity and accounts for redistribution of electron densities and steric effects at "in cavity" transformation. Keeping the analogy to electric properties, one may ask what is an "elastic polarizability" of a cavity and define corresponding (molecular/cavity) compressibility, **K**.[9] This property has to reflect mechanics of a molecular cavity and it can be related to molecular anisotropic displacement parameters (ADP).[6],[7] An exact interpretation of molecular Debye-Waller factors in terms of the local compressibility needs further elaboration.

Now, we shall analyze the system of cavities, the local stresses and compressibilities which characterize local structure (P), embedded in the elastic continuum of reacting crystal (R). Let us define probability density of an elastic dipole, $\rho(x)$, being equivalent to a degree of transformation in a cavity located at $\mathbf{x}$. If a transformation leads to equivalent structures (structural domains), the density is a sum over the domain densities, $\rho(\mathbf{x}) = \sum_\alpha \rho_\alpha(\mathbf{x})$. The probability density is, in general, inhomogeneous within a crystal and can be partitioned into homogeneous and inhomogeneous parts, $\rho(\mathbf{x}) = \rho + \delta\rho(\mathbf{x})$. ρ stands for uniform degree of a transformation and defines so called "virtual crystal", e.g., a crystal composed of sites, $R_{1-\rho}P_\rho$. Such "molecules" can be determined from X-ray crystal analysis,[10],[11] which averages a reacting crystal over space. The inhomogeneous part of the probability density, however, may play an important role and lead to heterogeneous transformation (demixing).

In terms of the elasticity theory, the reacting crystal is considered as a diaelastic medium; an elastic medium with embedded cavities which respond to an external stress by inducing internal strains. An unreacting crystal responds to an external stress, σ, by the strain, $\varepsilon_{ij}=S_{ijkl}\sigma_{kl}$. Tensor components, S_{ijkl} stand for elastic compliance of the reactant crystal. When a reaction proceeds, there are internal strains, $\varepsilon_{ij}(\mathbf{P})$, generated at the cavities by the local stress – elastic dipole, $\mathbf{P}$, and the response is, $\varepsilon_{ij}=S_{ijkl}\sigma_{kl} + \varepsilon_{ij}(\mathbf{P})$. The mediation of a lattice via its elastic field brings interaction between the local stresses, strictly speaking between the elastic dipole densities, $p_{ij}(\mathbf{x})=P_{ij}\rho(\mathbf{x})$. The homogeneous part of the elastic dipole density causes homogeneous strain, $\varepsilon_{ij}(\mathbf{P}) = S_{ijkl}P_{kl}\rho$, known as Vegard's law. The strain is observed experimentally when lattice parameters change in a course of reaction for a homogeneous transformation. It is important to notice that there are only few examples of such studies[12],[13] for molecular systems, and that it is most direct way to learn about local stresses induced by a transformation. Detailed intrepretation, however, requires an extra care concerning symmetry relation between molecules in a primitive unit cell.

The elastic coupling between reaction cavities, $p_{ij}(\mathbf{x})K_{ijkl}(\mathbf{x},\mathbf{x}')p_{kl}(\mathbf{x}')$, where $K_{ijkl}(\mathbf{x},\mathbf{x}')$ is a non-local compliance tensor (varying as R^{-3} with a distance and expressed in terms of elastic constants) is separated into two contributions; the self-deformation energy (term $\mathbf{x}=\mathbf{x}'$) and cooperative deformation energy (terms $\mathbf{x}\neq\mathbf{x}'$). The self-deformation energy renormalizes the chemical potential difference of a cavity, $\Delta = \Delta\mu$ - (self-deformation energy). This brings a linear decrease of the energy difference with a degree of transformation, $\Delta = \Delta_0 - a\rho$ $(a>0)$. The self-deformation energy plays exactly the same role in a solid state reaction as the solvation energy (the solvent reorganization energy) does in a liquid state reaction. The cooperative elastic coupling, which depends on relative distance and orientation of the reaction cavities, may catalyze or inhibit the transformation, depending on details of the interaction. The elastic coupling between cavities decides how "non-ideal" is the solution of product molecules within the reactant "solvent". It might even bring a spinodal decomposition of the solid solution in a course of the reaction. The competion between cooperative elastic coupling and local structures is reflected in mechanism of transformation (nucleation and growth versus homogeneous cooperativity), its kinetics and activation of the process.

KINETICS AND CO-OPERATIVE ACTIVATION.

Let us discuss a transformation, which will be characterized by structural changes measured by a homogeneous strain, as described above. The strain serves as the reaction path. We consider kinetics of the homogeneous part of the elastic dipole densities, ρ. The transformation is induced by an external field, I, which directly induces a local stress. The rate of the process is given by the equation,

$$d\rho/dt = I(\rho) + W_{R\to P}(1-\rho) - W_{P\to R}(\rho), \qquad (1)$$

where $I(\rho)$ is a function indicating "a power" of the field to initiate the reaction, and is related to effective cross-section and possible field-induced cooperativity. W's stands for probabilities of the corresponding relaxation processes. We shall assume that the transitions are thermally-induced. The probabilities are expressed in terms of an attempt frequency, ν_0, and actiavtion energies, as for example, $W_{R\to P} = \nu_0 \exp[-E_{R\to P}(\rho)/kT]$. $E_{R\to P}(\rho)$ is the cooperative activation energy, dependent on the degree of transformation in the system. A general formula for a time evolution of the elastic dipole densities can be written as a decay function,

$$\rho(t) = \rho(t\to\infty)[1 - \exp\{R(\rho)t\}], \qquad (2)$$

where the decay factor, $R(\rho)$, is strongly dependent on the degree of transformation. It is responsible for very complicated kinetics, from autocatalytic behaviour to inhibition. The factor is determined by the cooperative activation, due to competition between local and coperative elastic effects, which we shall analyze in details. The decay equation (2) describes also a time relaxation of local stress/strain, induced at a cavity in a course of the transformation.

In order to calculate cooperative activation energy we shall analyze relative stability of a cavity in "ground" (R) and "excited" (P) states, being embedded in a virtual crystal, $R_{1-\rho}P_\rho$. For a cavity in "ground" state, the strain (reaction path coordinate) is, $\varepsilon_R = [\mathbf{S}\text{-}\mathbf{K}]\mathbf{P}\rho$, and it is expressed in terms of the difference between compressibility of a crystal and local one. Observe, that for non-interacting cavities the strain is zero. For a cavity in "excited" state the average strain is, $\varepsilon_P = [\mathbf{S}\text{-}\mathbf{K}]\mathbf{P}\rho + \mathbf{KP}$. The energy surfaces for the cavity in "ground" and "excited" states, spanned in the strain component coordinates, are,

$$E_R(\varepsilon) = 1/2\delta\varepsilon_R \mathbf{K}^{-1}\delta\varepsilon_R + 1/2\varepsilon_R \mathbf{K}^{-1}\varepsilon_R, \qquad (3)$$

$$E_P(\varepsilon) = 1/2\delta\varepsilon_P \mathbf{K}^{-1}\delta\varepsilon_P + \Delta, \qquad (4)$$

where $\delta\varepsilon_i = (\varepsilon-\varepsilon_i)$. One sees that the defromation energies depend quadratically on the concentration of the transformed sites. For the calculations of activation energies it is convenient to define hypothetical concentrations, ρ_{max} and ρ_{min}, at which transitions, R→P and P→R are activation-less, respectively. Then, the corresponding activation energies can be expressed as,

$$E_{R\rightarrow P}(\rho) = 1/2[\mathbf{S}\text{-}\mathbf{K}]E_{def}(\rho-\rho_{max})^2. \qquad (5)$$

$$E_{P\rightarrow R}(\rho) = 1/2[\mathbf{S}\text{-}\mathbf{K}]E_{def}(\rho-\rho_{min})^2. \qquad (6)$$

$E_{def} = \mathbf{P}[\mathbf{S}\text{-}\mathbf{K}]\mathbf{P}$ is the deformation energy, which a crystal gains when a transformation goes into complition. The activation energy can be written in a form similar to that known from electron transfer reaction theory, $E_{R\rightarrow P}(\rho) = [\ \Delta E(\rho) + \lambda]^2/4\lambda$. $\lambda = 1/2\mathbf{PKP}$, is the cavity self-deformation energy and the energy difference, $\Delta E = E_P(\varepsilon_P) - E_R(\varepsilon_R)$ is a linear function of ρ. The cooperative activation, resulting in rather complicated dependence of the activation energies on the degree of transformation, is a result of competition between elasticity of a cavity and cooperativity due to elastic interaction between the cavities. It is higly self-consistent process between a reaction cavity and environment, acting as an "active solvent". The cooperative multi-cavity transformation, in which cavities are no longer transformed independently but are dependent on each other may be understood with a help of a sequence of energy curves, as shown in the Figure 1. An initiating transformation event at a cavity triggers subsequent ones by producing "positive friction" loops. If this feedback is adequatly strong, the cavities will be transformed in a cooperative way. It is the essense of self-organization.

As an example, let us consider a steady state, field-induced reaction, R→P. We assume that cooperativity is due to elastic interaction only, and the field induces the transformation linearly. The example corresponds to a typical photo-induced reaction, where a continuous illumination of a system is applied as initiation. The equation,

$$d\rho/dt = I_0(1-\rho) - W_{P\rightarrow R}(\rho)\rho = 0. \qquad (7)$$

indicates that the quadratic dependence of the activation energy for the

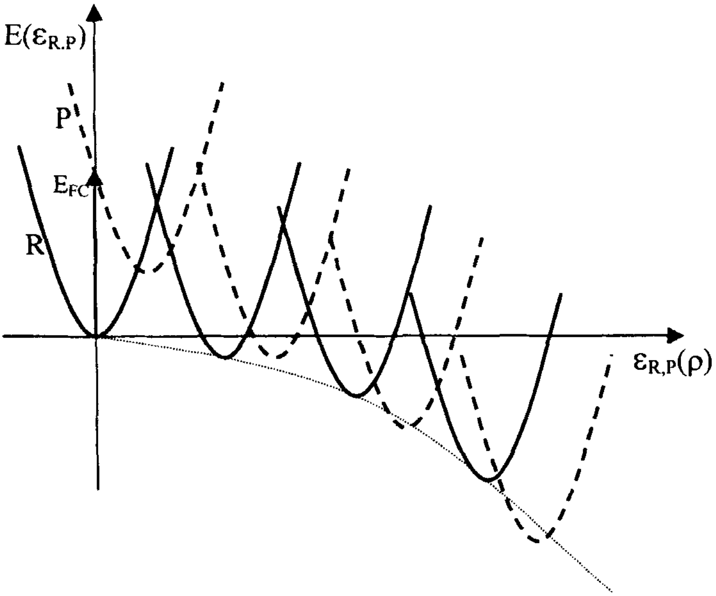

FIGURE 1

Cooperative activation shown as a sequence of diabatic energy curves, eqs. (3) and (4), representing bi-stable cavity embedded in a virtual crystal $R_{1-\rho}P_{\rho}$. A reaction path is chosen to be homogenous lattice strain, $\varepsilon(\rho) = \mathbf{S}\cdot\mathbf{P}\cdot\rho$. E_{FC} indicates the minimum energy required to initiate the reaction by a field.

thermal relaxation, P→R, competes with the linear dependence of the field-induced product molecules. The competition may cause temperature and/or field-induced bistability.[14] It can be related to a homogenoeus or inhomogeneous transformation and may explain well known observations[12],[13] that reactions induced by weakly absorbed light, go into a complition homogeneously, while those initiated by strongly absorbed light, result in strongly heterogenoeus transformations. The competition between cooperativity caused by phonon mediation and the field may become much more complicated when the cooperativity is induced already at the initiation stage. This brings non-linear function for the field-dependent term in the eq. (7). Thermo- and photo-induced, neutral-to-ionic, transformation in quasi-onedimensional charge-transfer systems, exceptionally cooperative transition, illustrates the problem.[15],[16] A formation of charge-transfer strings in the systems is highly cooperative process due to both, cooperativity within an electronic subsystem at the initiation step of the transformation (Coulomb interaction) and structural relaxation (elastic interaction). As a result, highly cooperative charge-transfer process takes place, which may serve as a model for cooperative multielectron transfer in biological systems that have developed self-organization to a perfection.

CONCLUDING REMARKS

Thermo- and photo-induced reactions have been discussed from a point of view of a competition between local and global structures and a role of lattice mediation. We have focused on elastic aspect of the competition. At the initial stage of a reaction, there is static lattice assistance, expressed in terms of topochemical and least motion principles. The local structure is a result of transformation within a reaction cavity and is well characterized as elastic dipole (local stress) and local compressibility. When the reaction proceeds, concentration of transforming cavities increases and the local structures tend to expand, the elastic lattice mediation brings cooperativity and/or competition between the structures and the global one. We discussed how the interplay between competitive and cooperative role of the lattice mediation influences kinetics of the transformation. It has been shown that the activation process is highly cooperative, activation energies are quadratic functions of the degree of transformation as a result of competition between elasticity of a cavity and cooperativity due to elastic interaction between the cavities. The cooperative activation causes multi-cavity transformation, in which cavities are no longer transformed independently but are dependent on each other. As an example, the photo-induced reaction in its steady state has been discussed. The cooperative activation when competing with linear dependence of field-induced product molecules may cause a bistability of a system and explain homogeneous/heterogeneous transformation induced by weakly/strongly absorbed light. Finally, we have discuss of briefly an exceptional, neutral-to-ionic transformation in quasi-onedimensional charge-transfer systems, where the elastically driven cooperativity is enhanced by electronically driven cooperativity at the initiation step of the transformation.

Acknowledgements
The author thanks "Region Nord-Pas de Calais" for supporting the stay at Laboratoire de Dynamique et Structure des Materiaux Moleculaires, Universite de Lille 1.

References

[1] J.D. Dunitz, *Pure Appl. Chem.*, **63**, 177 (1991).
[2] T. Luty, *Phase Trans.*, in press.
[3] J.A. Krumhansl, *Europhys. News*, **10**, 10 (1981).
[4] R.W. Munn, *Mol. Phys.*, **64**, 1 (1988), and references therein.
[5] E.V. Boldyreva, *Solid State Ionics*, **101–103**, 843 (1997).
[6] T. Luty and C.J. Eckhardt, in *Reactivity of Molecular Solids*, V. Boldyrev, E. Boldyreva (eds), *John Wiley & Sons*, in press.
[7] T. Luty and C.J. Eckhardt, *J. Am. Chem. Soc.*, **117**, 2441 (1995).
[8] T. Luty and K.H. Brose *Chem. Phys.*, **161**, 33 (1992).
[9] T. Luty, *J. Phys. Soc. Japan*, **61**, 3636 (1992).
[10] V. Enkelmann, G. Wegner, K. Novak and K.B. Wagener, *J. Am. Chem. Soc.*, **115**, 10390 (1993).
[11] K. Novak, V. Enkelmann, G. Wegener and K.B. Wagener, *Angew. Chem. Int. Ed. Engl.*, **32**, 1614 (1993).
[12] E.V. Boldyreva, D.Yu. Naumov and H. Ahsbahs, *Acta Cryst.*, **B54**,798 (1998).
[13] L. Wiehl, W. Spiering, P. Gutlich and K. Knorr, *J. Appl. Cryst.*, **23**, 151 (1990).
[14] A. Desaix, O. Roubeau, J. Jeftic, J.G. Haasnoot, K. Boukheddaden, E. Codjovi, J. Linares, M. Nogues and F. Varret *Eur Phys, J.*, **B6**, 183 (1998).
[15] M.H. Lemee-Cailleau, M. LeCointe, H. cailleau, T. Luty, F. Moussa, J. Ross, D. Brinkmann, B. Toudic, C. Ayache and N. Karl, *Phys. Rev. Lett.*, **79**, 1690 (1997).
[16] S. Koshihara, Y. Takahashi, H. Sakai, Y. Tokura and T. Luty, *J. Phys.Chem.*, **B103**, 2592 (1999).