



SELECTIVE ACTIVATION OF HETEROGENEOUS SYSTEMS: A CONSEQUENCE OF THE JAHN-TELLER EFFECT

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A general selective activation mechanism based on the vibrational energy transfer is suggested. The proposed mechanism provides a simple and rational interpretation of the concept of activation energy used in case of reactions in heterogeneous or solid systems. The bonds in the solid state are assimilated to a system of Morse oscillators. The main advantage of this model is the possibility of identification of the bond responsible for the evolution toward the transition state. For this identification, a relationship between a structural and a kinetic parameter was presented. Our model shows that the discrete variation of activation energy for a set of similar reactions is more rational than the assumption of continuous variations.

INTRODUCTION

The question of activation in solid state reaction is far from a satisfactory explanation. In many reactions taking place in gas phase on a gas/solid surface the activated state is attained by the redistribution of the free energy.¹ But it is well known that in condensed phases the process of dissipation proceed rapidly.² So, in fields like heterogeneous catalysis, respectively thermal decomposition of solids, the question how a molecule stay excited in order to react is actual and of an obvious importance.

In two previous paper^{3,4} we analyzed the possibility of a specific activation of molecules in a homogeny and isotropic heat field. The possibility of identification of that part of a molecule responsible for early of a thermal degradation was underlined.

The topic of the present work is to suggest a general selective activation mechanism based on the vibrational energy transfer and to prove an adequate data processing strategy based on the concept of supersymmetry (SUSY).⁵ We started from an attractive hypothesis suggested by Bersuker:⁶ the

vibronic interactions due to the Jahn-Teller effect generate a labile state, a dynamic instability, *i. e.* an increased reactivity. This hypothesis is in agreement with the general opinion regarding the necessity of energetic exchanges by the specific activation of solid states reactants.

More specifically, we will approach the problem of activation energy by solid state reactions, in connection with the step-by-step variation of the vibrational transferred energy.

In the Appendix of our work we propose a theoretical treatment of the Morse potential, using the concept of SUSY shape invariance.

MECHANISM OF SELECTIVE ACTIVATION OF A SOLID STATE REACTANT

Hypotheses

The bonds in the molecular architecture are assimilated to a system of Morse oscillators. The energy levels of the Morse oscillators, growing up

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due to vibrational energy, can be described as an energy spectrum (see Appendix):

$$E_v = -D_e \left[1 - \frac{\alpha \hbar}{\sqrt{2mD_e}} \left(v + \frac{1}{2} \right) \right]^2 \quad (1)$$

in which α is the range factor and D_e is the dissociation energy.

The oscillator's energy is quantified by means of the vibrational number v . In spectral terms, eq. (1) is rewritten:

$$G_v = \omega \cdot v - \chi \cdot v^2 \quad (2)$$

where ω – the wave number of the oscillator, χ – anharmonicity constant and $G_v = E_v/hc$, c – is the light velocity.

The energy necessary for the selective activation of the molecular architecture depends on the vibrational number v needed to attain the transition state.

For “one mole” of bonds this energy is even the activation energy, *i. e.*

$$E_a = N_A \cdot G_v \quad (3)$$

with N_A the Avogadro's number.

After attaining the transition state, the selective activated bond will be broken and the molecular architecture will be evolve to the reaction products.

Consequences

According to eqs. (2) and (3), by reactions involving reactants in solid state the activation energy is discreet. It means that the selective activation takes place by a step-by-step energy accumulation.

Eqs. (2) and (3) allow the identification of the activated bond and the corresponding vibrational

mode. Indeed, considering, in a first approximation, $\chi \ll \omega$, we obtain

$$\omega_c = \frac{1}{a} \cdot \frac{E_a}{v} \quad (4)$$

where $a = hcN_A$ with a value of $11.9 \text{ J}\cdot\text{cm}\cdot\text{mol}^{-1}$ or $a = 2.85 \text{ cal}\cdot\text{cm}\cdot\text{mol}^{-1}$.

By means of constant a , the activation energy values are converted into calculated wave numbers ω_c , and by comparison with accepted IR wave numbers, the activated bond and the vibrational mode will be identified.

In a series of similar reactions, where the selective activated bond is expected to be the same, the variations in the values of the activation energy will be a multiple of (E_a/v) . This suggests a data processing strategy presented and discussed below.

RESULTS AND DISCUSSION

In a series of similar reactions, the difference ΔE_a between two nearest values of activation energy has made. The ΔE_a values suggest a scale of E_i values which divided by an integer v_i (not too great) lead to near E_i/v_i number. By means of eq. (4), the ω_c will be calculated and then it will be compared with accepted values in IR spectrometry.

In Table 1 the data on thermal decomposition of some low carboxilates under non-isothermal conditions^{7,8} are processed as presented before. The activation energies were determined for the first step of the decomposition process, *i. e.* the dehydration. Accepted values of crystallization water in IR spectrometry are between 3400 and 3500 cm^{-1} .¹²

Table 1

Thermal decomposition of: Mn, Ni, Co, Cu, Zn, Cd, La, Eu, Sm carboxilates under non-isothermal conditions

E kJ/mol	$\Delta E = E_{n+1} - E_n$	v	E_i/v_i	$\omega_{\text{spectr.}} = 3400 - 3500 \text{ cm}^{-1}$ for crystallization water
FORMATES				
75		2	37.5	$\left(\frac{\bar{E}_i}{v_i} \right) = 38.825$ $\omega_c = 3262.6 \text{ cm}^{-1}$ $\omega_{\text{calc.}+\text{anharmonicity}} = 3435.1 \text{ cm}^{-1}$
103	28	3	34.3	
115	12	3	38.3	
181	66	4	45.2	
	106			
	$\bar{\Delta E} = 53$			

Table 1 (continued)

ACETATES				
100		3	33	$\left(\frac{\bar{E}_i}{\nu_i}\right) = 42.14$ $\omega_c = 3541.4 \text{ cm}^{-1}$ $\omega_{\text{calc.}+\text{anharmonicity}} = 3596.6 \text{ cm}^{-1}$
114	14	3	38	
172	58	4	43	
205	33	5	.41	
270	65	6	45	
280	10	6	47	
288	8	6	48	
	188 $\bar{\Delta E} = 53$			
PROPIONATES				
51.2		1	51.2	$\left(\frac{\bar{E}_i}{\nu_i}\right) = 43.9$ $\omega_c = 3690 \text{ cm}^{-1}$ $\omega_{\text{calc.}+\text{anharmonicity}} = 3706 \text{ cm}^{-1}$
51.6	0.4	1	51.6	
65	13.4	2	32.5	
86.3	21.3	2	43.1	
124	37.7	3	41	
131	7	3	44	
	80 $\bar{\Delta E} = 26.6$			

According to the data in Table 1, there is a rather good agreement between the calculated data and the assigned values. Obviously, by taking into account the anharmonicity (eq. 2), the agreement became very good.

In Table 2 the values of activation energy by decomposition of some catalyst precursors^{9,10} are processed. The data were obtained for decomposition (under non-isothermal conditions) of anhydrous Copper formate and acetate, supported on carborundum, respective SiO₂.

Table 2

Thermal decomposition of Copper formate and acetate supported on carborundum and SiO₂

<i>E</i> kJ/mol	ΔE	ν	E_i/ν_i	E_a kJ/mol	ΔE	ν	E_i/ν_i
Mixture of Copper acetate							
Carborundum				SiO ₂			
146.8		5	29.36	116.8		4	29.20
155.3	8.5	6	25.88	178.3	10.3	6	29.72
159	3.7	6	26.5	195.4	17.1	7	27.91
171.8	12.8	6	28.63	226.7	31.3	8	28.34
220.9	49.1	8	27.61	452.5	22.58	15	30.17
	74.1 $\bar{\Delta E} = 30$		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 27.60$		284.5 $\bar{\Delta E} = 113.8$		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 29.07$
Supported							
281.2		10	28.12	180.7		7	25.81
314	32.8	11	28.55	189.4	8.7	7	27.06
352.8	0.388	12	29.40	195.8	6.4	7	27.97
356.6	0.038	12	29.72	214.7	18.9	8	26.84
653.4	2.968	22	29.70	243.7	29	9	27.08
	3.722 $\bar{\Delta E} = 1.5$		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 29.10$		63 $\bar{\Delta E} = 25.20$		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 27$
							$\left(\frac{\bar{E}_i}{\nu_i}\right)_m = 28.1$ $\omega_c = 2361,3 \text{ cm}^{-1}$.

Table 2 (continued)

Mixture of Copper acetate							
Carborundum				SiO ₂			
306.5		11	27.86	193.4		7	27.63
317	10.5	11	28.82	247.5	54.1	9	27.5
327.5	10.5	11	29.77	250.2	2.7	9	27.8
340	12.5	12	28.33	262.1	11.9	9	29.12
	33.5		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 28.70$		68.7		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 28.01$
	$\bar{\Delta E} = 16.75$				$\bar{\Delta E} = 34.35$		
Supported							
152.5		6	25.42	128.5		5	25.70
162.7	10.2	6	27.12	141.3	13	5	28.26
219.6	56.9	8	27.45	151.8	10.3	6	25.30
236.6	17	8	29.58	167.7	15.9	6	27.95
	84.1		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 27.39$		39.2		$\left(\frac{\bar{E}_i}{\nu_i}\right) = 26.80$
	$\bar{\Delta E} = 42.05$				$\bar{\Delta E} = 19.60$		
							$\left(\frac{\bar{E}_i}{\nu_i}\right)_m = 28.96$
							$\omega_C = 2319,3 \text{ cm}^{-1}$

The very narrow range of ω_C supports the hypothesis that in all cases the reaction was started by the selective activation of the same vibration.

In Table 3 data by propene hydrogenolysis on different catalysts are presented. In the approximation of $\chi \ll \omega$ (see eq. 4), a value of $\omega_C = 717,5 \text{ cm}^{-1}$ was obtained. If the anharmonicity is not neglected, by plotting (E_i/ν_i) vs. ν (see eq. 2), the intercept gives a value of $8.74 \text{ kJ}\cdot\text{mol}^{-1}$ or $\omega_C = 730 \text{ cm}^{-1}$.

In IR spectrometry a value of $\omega_C = 717,5 \text{ cm}^{-1}$ is assigned to the "twist" vibration of the C-C-C

bond.¹² Probably the activation of this bond is an explanation for the absence of ethane in the reaction product (only C₁ and C₃ hydrocarbons are present).

The data in Table 4, regarding the catalytic hydrogenation of propene¹¹ suggest a value of $\omega_C = 910 \text{ cm}^{-1}$. By the hydrogenation of propene, a transition from a sp² C atom to a sp³ hybridization is necessary. This transition corresponds to the activation of the $\delta(\text{CH}_2)$ vibration, having an assigned value of 919 cm^{-1} .¹²

Table 3

Propene hydrogenolysis on Copper chromite

Composition %		E_a kJ/mol	ΔE	ν_i	E_i/ν_i		
CuO	Cr ₂ O ₃						
99	1	34.3		4	8.57	$\left(\frac{\bar{E}_i}{\nu_i}\right) = 8.6$ $\omega_C = 717,5 \text{ cm}^{-1}$	$\left(\frac{\bar{E}_i}{\nu_i}\right)_{\text{anharm.}} = 8.74$ $\omega_{\text{Calc. + anharm.}} = 730 \text{ cm}^{-1}$
95	5	42.2	7.9	5	8.44		
80	20	59	16.8	7	8.43		
65	35	52.7	6.3	6	8.78		
50	50	43.9	8.8	5	8.78		

Table 4

Propene hydrogenolysis

Catalyst	E_a kJ/mol	ν_i	E_i/ν_i	
Ni	54.4	5	10.88	$\left(\frac{\bar{E}_i}{\nu_i}\right) = 10.66 \text{ kJ/mol}$ $\omega_C = 910 \text{ cm}^{-1}$
Fe	41.8	4	10.45	
Co	33.9	3	11.3	
Pt	66.9	6	11.15	

Table 4 (continued)

Pd	46.0	4	11.5	
Rh	54.4	5	10.88	
Ir	62.7	6	10.45	
Ru	27.2	3	9.06	
Os	31.0	3	10.33	

CONCLUSIONS

The presented activation model is based on a selective accumulation of vibrational energy in that vibration mode of a molecular architecture where it is best needed. The reactant in solid state and the reaction considered are in the field of heterogeneous catalysis, respectively thermal decomposition. Acceptable consequence of discrete variation of activation energy for a set of similar reactions is more rational than the assumption of continuous variations.

In the next section of this work the energy spectrum of a Morse oscillator was pointed out using the concept of supersymmetry. For a realistic application of our suggested model, the anharmonicity cannot be neglected.

Appendix

Determination of energy spectrum for Morse oscillator using the supersymmetry (SUSY) concept

In comparison with the well-known Schrödinger way, this method provides a very elegant and synthetic way of presenting the operational method⁵ to handle several problems in quantum mechanics. So, given a SUSY hamiltonian, we can generate from it a chain of SUSY hamiltonians in such a way that two consecutive ones have the same spectrum except for the lowest ground state. We use partner potentials V_{\pm} defined by:

$$V_{\pm} = W^2 \pm \frac{\hbar}{2\pi m} W' \quad (\text{A1})$$

Let us start, for Morse potential with the following form for the superpotential W :⁵

$$W(x) = A - Be^{-\alpha x} \quad (\text{A2})$$

It is easily shown that the two supersymmetric partner potentials V_{\pm} are

$$V_{-}(x, A) = A^2 + B^2 e^{-2\alpha x} - 2B \left[A + \frac{\alpha \hbar}{2(2m)^{1/2}} \right] e^{-\alpha x} \quad (\text{A3})$$

$$V_{+}(x, A - \frac{\alpha \hbar}{(2m)^{1/2}}) = [A - \frac{\alpha \hbar}{(2m)^{1/2}}]^2 + B^2 e^{-2\alpha x} - 2BA e^{-\alpha x} \quad (\text{A4})$$

The complete bound state spectrum of $V_{-}(x, A)$, using the shape invariance,⁵ is given by ($n=0, 1, 2, \dots$):

$$E_n^{(-)}(A) = A^2 - (A - \frac{n\alpha \hbar}{\sqrt{2m}})^2, \quad E_0^{(-)}(A) = 0 \quad (\text{A5})$$

with

$$A = \frac{1}{\alpha} \sqrt{\frac{m}{2}} \left(\omega - \frac{\hbar \alpha^2}{2m} \right) \quad (\text{A6})$$

By the reparametrization the spectrum from Eq. (A5) we obtain Eq. (1), for Morse potential.

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