

On the catalytic decomposition of formic acid. I. The activation energies for oxide catalysis

Ragnar Larsson^{a,*}, Michal H. Jamróz^b, Marek A. Borowiak^b

^a *Group of Catalysis Research, Chemical Engineering II, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden*

^b *Industrial Chemistry Research Institute, 8, Rydygiera Street, PL 01-793 Warsaw, Poland*

Received 1 February 1997; accepted 18 June 1997

Abstract

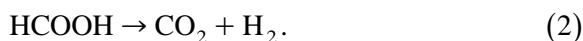
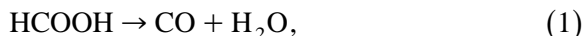
Literature data of the activation energies for the dehydration and the dehydrogenation reactions of formic acid over a series of oxide catalysts are treated to exemplify the idea of a stepwise variation of activation energies. By applying the formalism for the energy of an anharmonic vibrator, one can derive that very vibrational mode of the reacting intermediate (formate ion) that must be excited for the two reactions to occur. For the dehydration this is mainly the anharmonic O–C–O stretch and for the dehydrogenation reaction it is mainly the O–C–O in plane bending mode. An algorithm SETOS is presented that facilitates the analysis of the data. © 1998 Elsevier Science B.V.

Keywords: Formic acid; Catalytic decomposition; Activation energy; Vibrational energy transfer

1. Introduction

The decomposition of formic acid over solid phase catalysts is a classical reaction in heterogeneous catalysis. Many problems concerning this reaction have been highlighted through the years, among which the following three can be mentioned here:

(a) What factor determines the specificity of a catalyst, i.e., the direction of the reaction towards dehydration (Eq. (1)) and towards dehydrogenation (Eq. (2))?



(b) Why does the latter reaction, at least, show [1] an isokinetic effect?

(c) Why does the activation energy, at least of Eq. (2), change from system to system [2,3] in a seemingly stepwise manner?

It is the last-mentioned question that we want to address in the present paper. It must be emphasized that we will treat only oxide catalysts. The effects observed over metal catalysts may be quite different as regards the mechanism; the HCOOH decomposition over metals will be discussed in a following paper [4].

To illustrate the problem of the stepwise change of activation energies, we take the liberty of restating the presentation of Trillo et al. [2] by reploting only the data for the dehydrogenation (Eq. (2)) from the very illustrative figure 6 of their review [2]. The resulting graph

* Corresponding author. Tel.: +46-46-108113; fax: +46-46-104439; e-mail: Ragnar.Larsson@inorg.lu.se

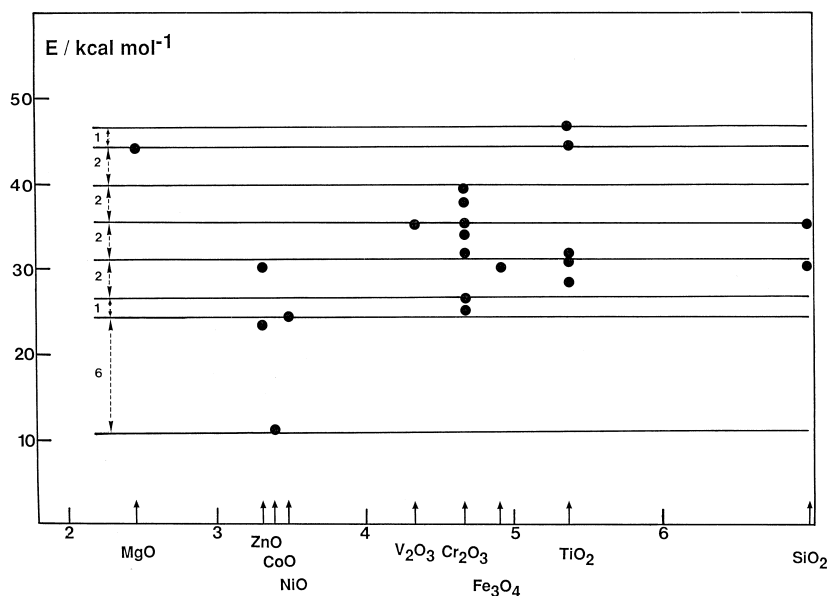


Fig. 1. A reproduction of the figure 6 of the review of Trillo et al. [2] including only the data of the dehydrogenation reaction (1 kcal = 4.184 kJ). The horizontal lines are drawn to fit the proposed separation of the data by some constant increment. The figures on the left hand side measures the number of the common factor that must be used to obtain the separation observed. The abscissa scale relates to the argumentation of [2] and is of no importance here.

(Fig. 1) indicates that there is a stepwise change of the values of the activation energies with an increment of some factor of about 2.3 kcal/mol.

In the present paper some of the results [5–8] reported in the paper of Trillo et al. [2] are used for a closer examination. Although these measurements were made some decades ago, they were supposedly registered with as great care as that of present-day investigations. Therefore, unless some obvious error of experimentation can be indicated, one has to accept also these older data. Activation energies have the advantage of not being related to absolute rate measurements as long as all measurements are made with the same technique.

The isokinetic temperature (T_{iso}) is another quantity that is not dependent on the absolute values of surface area. But certainly accurate measurements of a relative surface area are needed for the correct formulation of the effect. This quantity (T_{iso}) is used in a model [9] put forward by the present author, called the selective energy transfer (SET). The kernel of this model is that energy is transferred from vibra-

tional modes of the surrounding ('heat bath' such as catalyst, solvent, etc.) to the reacting molecule via a state of resonance with that vibrational mode of the reacting molecule that tends to distort the molecule towards its structure in the 'activated state'. A consequence of this view is that the energy of activation should change in a stepwise manner with the increment being the quantum of energy of the just mentioned vibrational mode [10].

2. Analysis

To proceed to the main problem, i.e., whether it is possible to use the activation energies to differentiate between the two reactions (1) and (2), we have collected, from some of the sources of Trillo et al. [2], activation energies of the dehydration reaction (Table 1) and for the dehydrogenation reaction (Table 2), respectively. As mentioned above various magnitudes of E_a should correspond to different levels of vibrational excitation [9,10]. When anharmonicity is

Table 1

Activation energies for the decomposition of formic acid to carbon monoxide and water. Subsequent treatment according to Eqs. (8) and (12)

Catalyst	Ref.	E_a (kJ/mol)	$E_a - RT$ (kJ/mol)	$(E_a - RT)/18.4$	$n(18.4)$	$(E_a - RT)/17.6$	$n(17.6)$
ZnO	[5]	98.3	92.9	5.05	5	5.29	5
Cr ₂ O ₃		113.0	107.9	5.86	6	6.14	6
Cr ₂ O ₃		125.5	120.1	6.52	7	6.83	7
Cr ₂ O ₃		159.0	154.0	8.36	8	8.76	9
γ-Al ₂ O ₃		100.4	95.4	5.18	5	5.43	5
Al ₂ O ₃		113.0	107.9	5.86	6	6.14	6
α-Al ₂ O ₃		100.4	94.6	5.14	5	5.38	5
Al ₂ O ₃		106.7	101.3	5.50	6	5.76	6
Al ₂ O ₃		100.4	95.4	5.18	5	5.43	5
CaF ₂		87.9	82.8	4.50	4	4.71	5
CaF ₂		100.4	95.4	5.18	5	5.43	5
CaF ₂		87.9	82.8	4.50	5	4.71	5
C		80.3	75.3	4.09	4	4.29	4
SiO ₂		96.2	91.6	4.98	5	5.21	5
SiO ₂		92.0	86.6	4.70	5	4.93	5
TiO ₂	[6]	69.9	65.3	3.55	4	3.71	4
TiO ₂		69.0	63.6	3.45	3	3.62	4
TiO ₂		69.0	63.6	3.45	3	3.62	4
TiO ₂ /0.5% Cr ₂ O ₃		96.2	90.8	4.93	5	5.17	5
TiO ₂ /1% Cr ₂ O ₃		105.4	100.0	5.43	5	5.69	6
TiO ₂ /2% Cr ₂ O ₃		104.6	99.2	5.39	5	5.64	6
TiO ₂	[7]	104.6	98.7	5.36	5	5.62	6
V ₂ O ₃		81.6	75.7	4.11	4	4.31	4
Cr ₂ O ₃		71.1	65.3	3.55	4	3.71	4
MnO		138.1	132.2	7.18	7	7.52	8
Fe ₃ O ₄		118.4	112.5	6.11	6	6.40	6
Cr ₂ O ₃	[8]	74.1	68.6	3.73	4	3.90	4
Cr ₂ O ₃		73.2	67.8	3.68	4	3.86	4
Cr ₂ O ₃		77.0	71.5	3.89	4	4.07	4
Cr ₂ O ₃ /0.5 TiO ₂		63.6	58.2	3.16	3	3.31	3
Cr ₂ O ₃ /1.0 TiO ₂		65.7	60.2	3.27	3	3.43	3
Cr ₂ O ₃ /2.0 TiO ₂		68.2	62.8	3.41	3	3.57	4
Cr ₂ O ₃ /5.0 TiO ₂		72.0	66.5	3.61	4	3.79	4
Cr ₂ O ₃ /0.1 K ₂ O		85.8	80.3	4.36	4	4.57	5
Cr ₂ O ₃ /0.5 K ₂ O		97.5	92.0	5.00	5	5.24	5
Cr ₂ O ₃ /1.0 K ₂ O		98.3	92.9	5.05	5	5.29	5
Cr ₂ O ₃ /2.0 K ₂ O		102.5	97.1	5.27	5	5.52	6

The designations of the catalyst systems are those of the original references and further detail are found in those papers. The original data, presented as kcal/mol, have been recalculated to kJ/mol.

strong, however, one should expect the various increments of activation energy to differ somewhat.

Let us, therefore, consider the anharmonic vibrator with its unequal spacing of the energy levels. The vibrational energy of a molecule, measured relative to its zero level energy, is

described (in the present treatment excluding any higher terms) by Herzberg [11] as:

$$G_0(n) = n\omega_0 + \omega_0 x_0 n^2, \quad (3)$$

where G_0 stands for the vibrational energy of the molecule in excess of the zero energy vibrational level, n is the vibrational quantum num-

Table 2

Activation energies for the decomposition of formic acid to carbon dioxide and hydrogen. Subsequent treatment according to Eqs. (8) and (12)

Catalyst	Ref.	E_a (kJ/mol)	$E_a - RT$ (kJ/mol)	$(E_a - RT)/9.20$	$n(9.20)$	$(E_a - RT)/10.88$	$n(10.88)$
ZnO	[5]	125.5	120.1	13.05	13	11.04	11
Cr ₂ O ₃		142.3	137.2	14.91	15	12.62	13
Cr ₂ O ₃		157.3	151.9	16.50	17	13.96	14
Cr ₂ O ₃		142.3	137.2	14.91	15	12.62	13
γ-Al ₂ O ₃		142.3	137.2	14.91	15	12.62	13
Al ₂ O ₃		188.3	183.3	19.91	20	16.85	17
α-Al ₂ O ₃		150.6	144.8	15.73	16	13.31	13
Al ₂ O ₃		171.5	166.1	18.05	18	15.27	15
Al ₂ O ₃		146.4	141.4	15.36	15	13.00	13
CaF ₂		163.2	158.2	17.18	17	14.54	15
CaF ₂		154.8	149.8	16.27	16	13.77	14
CaF ₂		142.3	137.2	14.91	15	12.62	13
C		148.5	143.5	15.59	16	13.19	13
SiO ₂		146.4	141.8	15.41	15	13.04	13
SiO ₂		125.5	120.1	13.05	13	11.04	11
TiO ₂	[6]	–	–	–	–	–	–
TiO ₂		127.6	122.2	13.27	13	11.23	11
TiO ₂		129.7	124.3	13.50	14	11.42	11
TiO ₂ /0.5% Cr ₂ O ₃		125.1	119.7	13.00	13	11.00	11
TiO ₂ /1% Cr ₂ O ₃		105.4	100.0	10.86	11	9.19	9
TiO ₂ /2% Cr ₂ O ₃		104.6	99.2	10.77	11	9.12	9
TiO ₂	[7]	194.6	188.7	20.50	21	17.35	17
V ₂ O ₃		146.4	140.6	15.27	15	12.92	13
Cr ₂ O ₃		154.8	149.0	16.18	16	13.69	14
MnO		–	–	–	–	–	–
Fe ₃ O ₄		125.5	119.7	13.00	13	11.00	11
Cr ₂ O ₃	[8]	105.9	100.4	10.91	11	9.23	9
Cr ₂ O ₃		110.5	105.0	11.41	11	9.65	10
Cr ₂ O ₃		132.6	127.2	13.82	14	11.69	12
Cr ₂ O ₃ /0.5 TiO ₂		119.2	113.8	12.36	12	10.46	10
Cr ₂ O ₃ /1.0 TiO ₂		123.8	118.4	12.86	13	10.88	11
Cr ₂ O ₃ /2.0 TiO ₂		122.2	116.7	12.68	13	10.73	11
Cr ₂ O ₃ /5.0 TiO ₂		124.7	119.2	12.95	13	10.96	11
Cr ₂ O ₃ /0.1 K ₂ O		85.8	80.3	8.73	9	7.38	7
Cr ₂ O ₃ /0.5 K ₂ O		60.7	55.2	6.00	6	5.08	5
Cr ₂ O ₃ /1.0 K ₂ O		46.0	40.6	4.41	4	3.73	4
Cr ₂ O ₃ /2.0 K ₂ O		25.1	19.7	2.14	2	1.81	2

The designations of the catalyst systems are those of the original references and further detail are found in those papers. The original data, presented as kcal/mol, have been recalculated to kJ/mol.

ber, x_0 is the anharmonicity constant (with negative sign) and ω_0 for small values of x_0 is twice the vibration energy of the zero state. It is our proposal here, that this vibrational energy, $G_0(n)$, can be equalized to the activation energy of the reaction and that the almost constant increment of a series of activation energies can

be identified with the spacing of the energy levels in Eq. (3). In order not to create any confusion with the vibration of the heat bath in our model [9] that we have denoted ω , we take the liberty to change the term notation of Herzberg[11] to Ω instead of ω . From what is said above we suggest that Ω should be equal

to the vibrational energy of the critical vibrational mode, ν , of the reacting molecule. With this formalism, Eq. (3) will read

$$G_0(n) = n\Omega_0 + \Omega_0 x_0 n^2. \quad (4)$$

The frequency of the IR absorption most commonly observed (the $n = 0$ to $n = 1$ transition), following these notations, is

$$\nu(1 - 0) = \Omega + \Omega x. \quad (5)$$

In this formula and further ones below we have deleted the zero suffices of Ω and x for shortness as there can be no reason for misunderstanding. Ω is expressed in the same unit as the energy of activation.

From the model of selective energy transfer [9] which makes the activation energy E the sum of all the quantum steps of the vibrational mode ν , it follows that

$$E = G_0(n), \quad (6)$$

and, thus from Eq. (4)

$$E = n\Omega + \Omega x n^2. \quad (7)$$

This means that the activation energy, E , is quantized. In order to express E from experimental data one must subtract the term RT that represents the influence of a factor proportional to T in the preexponential factor (e.g. kT/h in the theory of absolute rates).

Furthermore, one must correct for the influence of the adsorption pre-equilibrium. It is well known [12] that for surface reactions preceded by adsorption, the apparent activation energy is equal to the true activation energy, E_t , decreased by the heat of adsorption, Q ($Q > 0$). Thus:

$$E_t = E_a - RT + Q. \quad (8)$$

According to the quantization postulate of the selective energy transfer model we can equalize Eqs. (7) and (8):

$$E_t = E, \quad (9)$$

and thus

$$E_a - RT + Q = n\Omega + \Omega x n^2, \quad (10)$$

or

$$(E_a - RT + Q)/\Omega = n + x n^2. \quad (11)$$

Thus we find that in a general form $(E_a - RT + Q)/\Omega$ should be a second order function of n :

$$(E_a - RT + Q)/\Omega = M_0 + M_1 n + M_2 n^2. \quad (12)$$

It can be noted from Eq. (12) that the coefficient of the first order term must be equal to 1 if Eq. (12) shall be physically significant and that the coefficient of the second order term gives the anharmonicity constant. The zero order term is added to correct for any inadvertently introduced error.

In the present paper the analysis is performed under the assumption that Q is constant and small. The basis for this assumption has recently been presented [13]. It was deduced that if the reactive species is loosely adsorbed contrary to what may be the case for non reacting species, the resulting Q is small and can be positive or negative.

In the calculations of this paper we put $Q = 0$. Consequently, the value M_0 that results from Eq. (12) may express this rest value of Q ($M_0 = -Q/\Omega$) or anyway be related to error introduced by this supposedly small neglect.

3. Results for $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$

In Table 1 we have presented and treated the data of E_a obtained from literature [5–8] of Eq. (1) in the following way: For an arbitrarily chosen value of Ω , viz. $\Omega = 18.4$ kJ/mol corresponding to about 1540 cm^{-1} , and $Q = 0$, we have formed the ratio $(E_a - RT)/\Omega$. For the so resulting set of $(E_a - RT)/\Omega$ we have printed out the nearest whole number, $n(\Omega)$, assumed

to represent 'n' in Eqs. (7) and (10). The resulting values $n(18.4)$ are represented in the following column of Table 1.

It is easily seen that those values $n(18.4)$ fit Eq. (12) as

$$(E_a - RT)/\Omega = 1.32 + 0.52n + 0.04n^2. \quad (13)$$

Notice that in the above expression the M_1 and M_2 parameters have no physical meaning since M_1 is far from 1 and M_2 is not negative.

But this is only one single example; for another arbitrarily chosen value of Ω , viz. $\Omega = 17.6$ kJ/mol corresponding to 1469 cm⁻¹, and $Q = 0$, we obtain the data also included in Table 1 and the relation

$$(E_a - RT)/\Omega = 0.04 + 1.04n - 0.009n^2. \quad (14)$$

However, even if the M_1 value of Eq. (14) seems to be close to 1 and the M_2 value is negative, such a trial and error calculation can never give a well-founded result. There might always be some doubt about the choice of parameters.

Therefore, in order to find that value of Ω that most closely gives $M_1 = 1$ we have used the following procedure (Program SETOS [14]):

4. Description of the program SETOS

The program SETOS calculates the coefficients M_0 , M_1 , M_2 by a least squares procedure for a chosen value of Q and for Ω values in the range $\langle \Omega_{\text{start}}, \Omega_{\text{end}} \rangle$. The Ω scale is digitized by the parameter Ω_{step} such as $\Omega_i = \Omega_{\text{start}} + (i - 1)\Omega_{\text{step}}$, ($i = 1, 2, \dots$).

The function $F(\Omega, Q) = 1/(1 - M_1)^2$ is formed and calculated for Ω_i and plotted versus the Ω scale.

This computing was tested in the Ω range from 4 to 20 kJ/mol on the 37 data pairs $\{E_a, T\}$ from Table 1. These introductory calculations showed that a value $\Omega_{\text{step}} = 0.42$ kJ/mol was definitely too large as one obtained two completely different graphs for two different

values of Ω_{start} . Further work showed that Ω_{step} must be as small as 0.01 kJ/mol in order to get satisfactory results in the sense that the plots were independent on Ω_{start} .

As these plots were extremely noisy we averaged the F -function over the following intervals:

$$\langle \Omega_j - 0.5\Omega_{\text{step}}, \Omega_j + 0.5\Omega_{\text{step}} \rangle,$$

where

$$\Omega_j = \Omega_{\text{start}} + j\Omega_{\text{step}}, \quad j = 0, 1, 2, \dots$$

Each interval was divided into N subintervals and the F -function was calculated in the $N + 1$ points defining these intervals. Next, the standard deviations SD_j of the F -function were calculated using the weight linear functions as $W = 0.5$ on the two ends of the interval, and $W = 1$ in the middle. Based on Student's t -test at the confidence level = 0.95, some F -function values were eliminated. This filtering routine was repeated a few times. The procedure yielded a very sharp response on the Ω scale and a simultaneous filtering of undesirable, enormously intense maxima.

Since the input experimental data $\{E_a, T\}$ are usually given with 3 significant digits, it determines the M_1 accuracy to 0.001 when M_1 approaches 1. As the consequence, in the calculations, the F -function is truncated at 1 000 000 for $\text{abs}(M_1 - 1) < 0.001$.

Furthermore, as experimental data errors can cause accidental F -function values to be enormously large for M_1 close to 1, an additional linear weight function WF was applied for large F -function values:

$$\text{WF} = 1 \quad \text{for } F \leq 250\,000$$

$$(\text{corresponding to } \text{abs}(M_1 - 1) \leq 0.002),$$

$$\text{WF} = 0.25 \quad \text{for } F = 1\,000\,000$$

$$(\text{corresponding to } M_1 - 1 = \pm 0.001).$$

In the final stage of calculations, a smoothing procedure on the discrete representation of the F -function averaged in subintervals was applied. The smoothing procedure consists in in-

terpolating the F -function by second order polynomials based on K -points intervals using a weight function dependent on SD_j and WF. The polynomials are mutually overlapping. The F -function value in each point was calculated on the basis of K values obtained from the polynomials. Next, the smoothing procedure was repeated for polynomials based on $(K - 2)$ - and $(K - 4)$ -points. For the reactions under discussion we used $K = 13$.

The thus described filtering routines of averaging and smoothing of the $F(\Omega, Q)$ -function included in the SETOS program, enable the selection of different ranges of: Ω_{scale} , Ω_{step} parameter, number of subintervals over which the F -function is averaged, confidence level, number of points for smoothing procedure and number of smoothing circuits.

5. SETOS results for $\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$

Using the above described procedures for filtration and smoothing, starting from two different Ω_{start} , qualitatively the same graphs were obtained (Figs. 2 and 3) with the main maximum at ca. 1505 cm^{-1} ($\approx 18.0 \text{ kJ/mol}$).

It is now of great interest that the position of this major component of the graphs correspond to a frequency not far from the value of the asymmetric mode of the carboxylate group of the free formate ion. Nakamoto [15] gives 1567 cm^{-1} for this stretching mode. Hence one might conclude that the decomposition of the formic acid to CO and H_2O is caused by the selective vibrational excitation of the stretching mode of the CO bonds so that one of them is broken. The geometry of the oxide catalyst might deter-

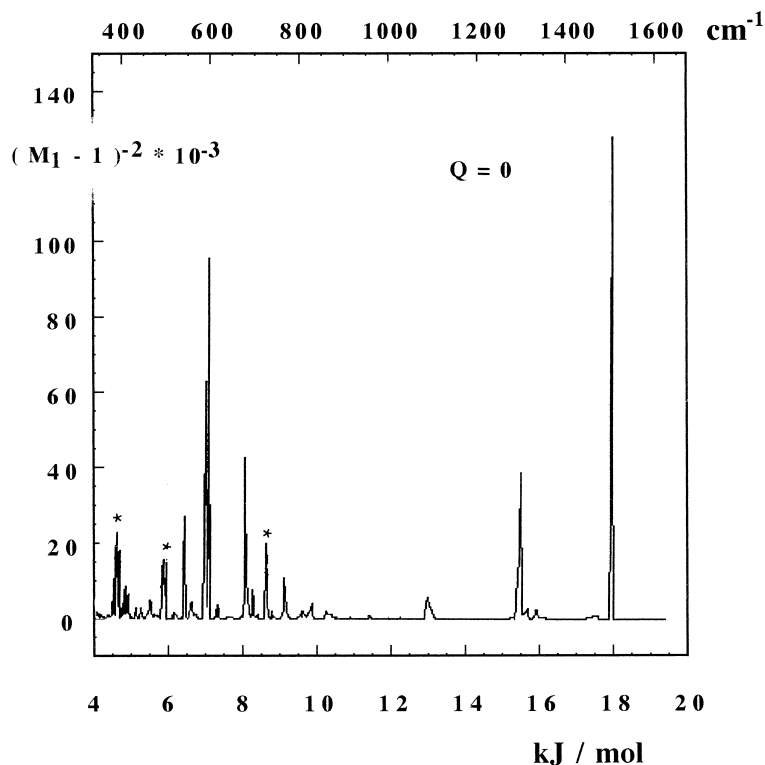


Fig. 2. The graph of $F(W, Q) = (M_1 - 1)^{-2}$ for the dehydration reaction (Eq. (1)). The Ω parameters are: $\Omega_{\text{start}} = 3.8 \text{ kJ/mol}$, $\Omega_{\text{step}} = 0.01 \text{ kJ/mol}$. The F -function is averaged over 20 subintervals (21 points). The F -function is smoothed triply based subsequently on 13, 11 and 9 point. Peaks marked with an asterisk represent positive values of M_2 and should be disregarded.

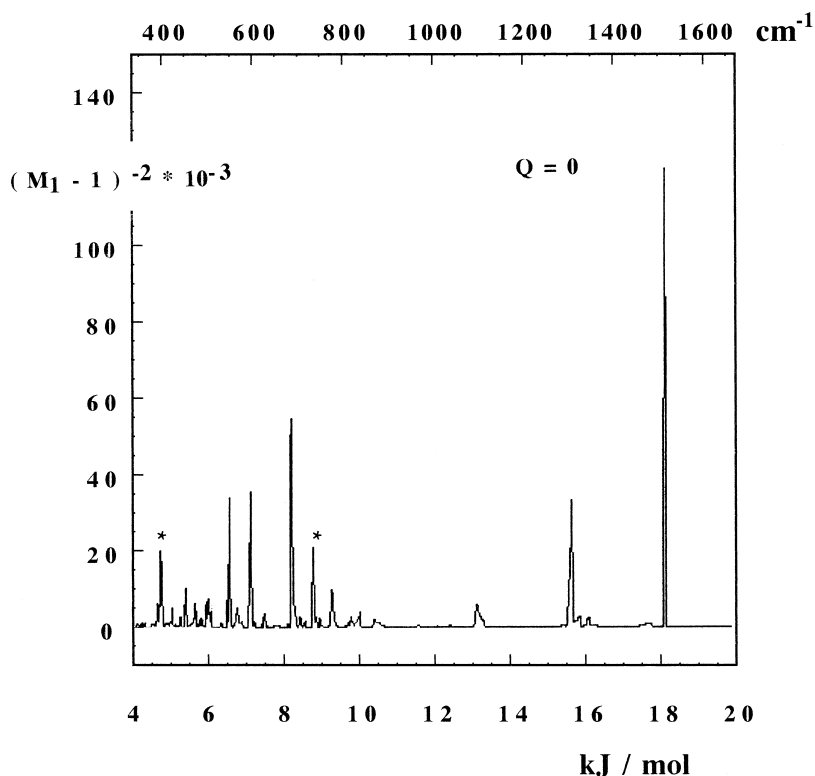


Fig. 3. The graph of $F(W, Q) = (M_1 - 1)^{-2}$ for the dehydration reaction (Eq. (1)). The Ω parameters are: $\Omega_{\text{start}} = 4.0$ kJ/mol, $\Omega_{\text{step}} = 0.01$ kJ/mol. The F -function is averaged over 20 subintervals (21 points). The F -function is smoothed triply based subsequently on 13, 11 and 9 point. Peaks marked with an asterisk represent positive values of M_2 and should be disregarded.

mine how large this bond elongation must be and consequently how large the activation energy must be.

It might be worth observing that the coefficient M_2 gives the anharmonicity constant. For $\Omega = 18.0$ kJ/mol the above calculations give us $M_2 = x = -6.1 \cdot 10^{-3}$, and the product $x\Omega$ is -9.2 cm^{-1} . Actually, experiments on the solid sodium and potassium formates made by Bajdor [16] indicates that the anharmonicity constant is of that order. Such a magnitude will also be expected for bond stretching vibrations.

6. Results for $\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$

Corresponding results for the reaction leading to the formation of H_2 and CO_2 are reported in Table 2, including exemplifications for $\Omega = 9.20$

and 10.88 kJ/mol. The results of the SETOS calculation for all the data reported are given in Figs. 4 and 5.

A preliminary calculation indicated that the function $1/(1 - M_1)^2$ showed a pronounced maximum at about 9.20 kJ/mol (765 cm^{-1}). Figs. 4 and 5 indicate a much more irregular pattern than that of Figs. 2 and 3 that were describing the dehydration reaction. However, the program adopted gives also in this case qualitatively similar graphs for two different starting values, Ω_{start} . The major maximum of the F -function appears at $\Omega = 9.2$ kJ/mol, confirming the preliminary calculation and consequently one might select this value as the critical one for the reaction in question. It corresponds to a wave number of 765 cm^{-1} . This wave number is close to the $\delta(\text{COO})$ given by Nakamoto [15], viz. 772 cm^{-1} . Thus, the forma-

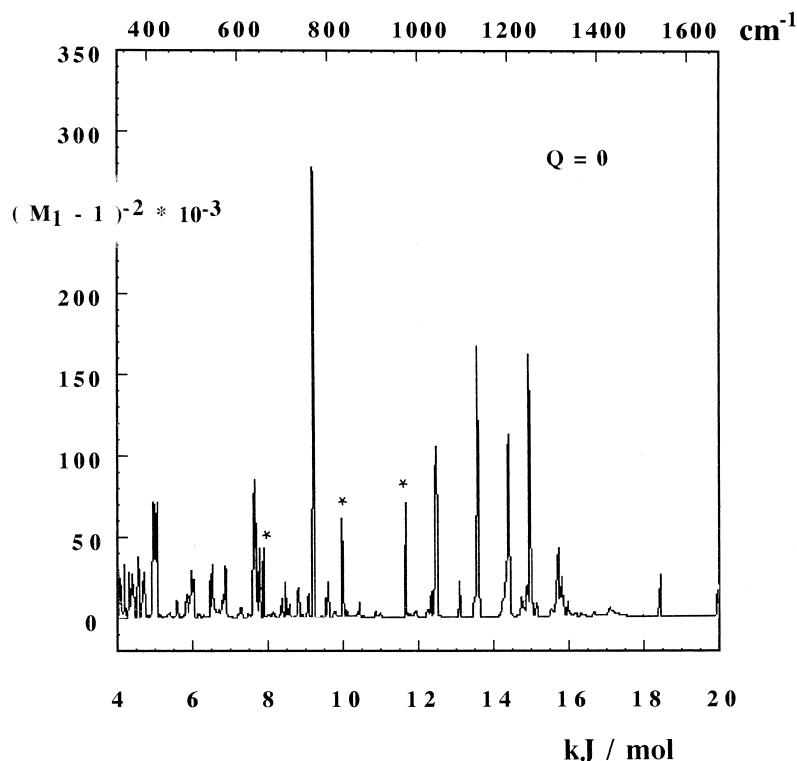


Fig. 4. The graph of $F(W, Q) = (M_1 - 1)^{-2}$ for the dehydrogenation reaction (Eq. (2)). The Ω parameters are: $\Omega_{\text{start}} = 3.8$ kJ/mol, $\Omega_{\text{step}} = 0.01$ kJ/mol. The F -function is averaged over 20 subintervals (21 points). The F -function is smoothed triply based subsequently on 13, 11 and 9 point. Peaks marked with an asterisk represent positive values of M_2 and should be disregarded.

tion of CO_2 might be obtained by deformation of the $\text{O} - \text{C} - \text{O}$ angle to such a degree that the H atom is split off and the CO_2 molecule is formed.

It can also be pointed out that this result agrees well with the values for the isokinetic temperature given by Cremer [1], viz., $T_{\text{iso}} = 690, 652, 610$ and 586 K. The 'ideal resonance' formula proposed by Larsson [9] for the isokinetic effect,

$$T_{\text{iso}} = 0.715\nu \quad (15)$$

will give $T_{\text{iso}} = 547$ K for $\nu = 765 \text{ cm}^{-1}$. For an energy supply from the heat bath somewhat differing from the ideal resonance, one would expect, from [9], T_{iso} values of the range quoted above.

Furthermore, if Ω is 9.20 kJ/mol one finds that $M_2 = x = -6.7 \times 10^{-4}$. Consequently $x\Omega$ is -0.5 cm^{-1} . Generally, a bending mode has

lower anharmonicity than a bond stretching mode, indicating some coherence of the results.

7. Comments on the results

A close agreement between the energy value (Ω), for which Eq. (7) is most precisely fulfilled, and a characteristic vibration of the reacting molecule is observed for both reactions (1) and (2). It is, therefore, tempting to conclude that these vibrational modes are actually of importance for the reactions. It may be worth telling that the data used in this study were sampled in a very arbitrary way. They originate from those references of Trillo et al. [2] that happened to most easily available in our libraries. Obviously the next step to validate the model in question would be to use a much

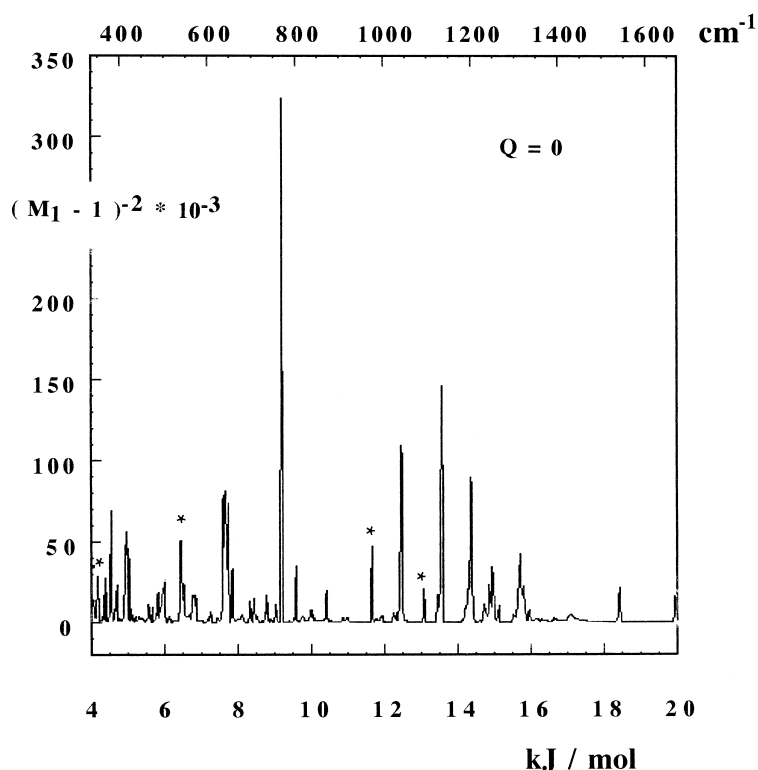


Fig. 5. The graph of $F(W, Q) = (M_1 - 1)^{-2}$ for the dehydrogenation reaction (Eq. (2)). The Ω parameters are: $\Omega_{\text{start}} = 4.0$ kJ/mol, $\Omega_{\text{step}} = 0.01$ kJ/mol. The F -function is averaged over 20 subintervals (21 points). The F -function is smoothed triply based subsequently on 13, 11 and 9 point. Peaks marked with an asterisk represent positive values of M_2 and should be disregarded.

larger experimental material, originating from many sources.

Despite the fact that the catalytic decomposition of formic acid has been investigated for a long time, there is still no agreement about its mechanism. The aim of the present study is to concentrate on a modeling procedure. Nevertheless, the result seem to indicate that the activation of the asymmetric stretching vibration is most important for the dehydration reaction (Eq. (1)). Therefore, the key-element of the reaction mechanism is the approach of the one O-atom to the C-atom with the simultaneous removal of the second O-atom. It is clear that such a situation should favour the HCOOH decomposition into CO and H₂O.

On the other hand, CO₂ formation (Eq. (2)) is found to be favoured by the activation of the $\delta(\text{OCO})$ deformation mode, periodically mak-

ing the O–C–O moiety almost linear. Therefore, the key – element of this reaction should be the distortion of the O–C–O mode so that the formation of the linear CO₂ molecule is facilitated.

Even with the detailed operations of smoothing and filtering described above, some extra lines are found in the graphs of Figs. 2–5, especially in Figs. 4 and 5. Some of these may be due to experimental errors and artifacts following from the assumptions when treating the data. Some are, however, so persistent that one is tempted to allocate a physical meaning to them in the same sense as to, e.g., the 765 cm⁻¹ peak of Figs. 4 and 5. We find some extra peaks at approximately 1040 cm⁻¹, 1130 cm⁻¹, 1200 cm⁻¹ and perhaps at 1245 cm⁻¹.

The first one might be ascribed to the $\pi(\text{CH})$ bending mode that appears at 1073 cm⁻¹ ac-

ording to Nakamoto [15]. The others might possibly be combination bands of the $\delta(\text{COO})$ at 765 cm^{-1} and metal oxygen vibrations of the catalyst systems. How such extra vibrations can be incorporated in the model of selective energy transfer will be discussed forthwhile [17].

The analysis [18] of the same reactions based on the impulse oscillation model [19] predicts the same modes to be crucial for the initiation of the reactions, i.e., the asymmetric stretching vibration mode of the carboxylate group for the dehydration reaction (Eq. (1)) and the $\delta(\text{OCO})$ bending mode for the dehydrogenation reaction (Eq. (2)). For Eq. (2), the model predicts the $\delta(\text{OCO})$ mode to be located in the range $760\text{--}720\text{ cm}^{-1}$. Moreover, it is predicted that the $\pi(\text{C-H})$ bending mode in the range $1050\text{--}1040\text{ cm}^{-1}$ and the C-O(M) stretching vibration mode located in the range $1130\text{--}1120\text{ cm}^{-1}$, are also important for Eq. (2).

Acknowledgements

This work is part of a COST project, D3/007/94 “Modelling of selective energy transfer, spatial and time coherence in catalytic reactions, tested on carbon dioxide reactions”. It is a pleasure to acknowledge the valuable discussions by Drs. K. Bajdor and J. Cz. Dobrowolski, ICRI, Warsaw, taking part in the same project. The work was partially financed by the Polish State Committee for Scientific

Research (KBN) by a Grant 3T09B03309. It is also our pleasure to acknowledge the support of this project from the Royal Swedish Academy of Sciences and the Polish Academy of Sciences.

References

- [1] E. Cremer, *Adv. Catal.* 7 (1955) 75.
- [2] J.M. Trillo, G. Munuera, J.M. Criado, *Catal. Rev.* 7 (1972) 51.
- [3] P. Mars, J.J.F. Scholten, P. Zwietering, *Adv. Catal.* 14 (1963) 35, Fig. 22.
- [4] M.A. Borowiak, J.Cz. Dobrowolski, M.H. Jamroz, R. Larsson, in preparation.
- [5] G.M. Schwab, E. Schwab-Agallidis, *J. Am. Chem. Soc.* 71 (1949) 1806.
- [6] Z.G. Szabo, F. Solymosi, *Acta Chim. Acad. Sci. Hung.* 25 (1960) 145.
- [7] J.M. Criado, F. Gonzalez, J.M. Trillo, *J. Catal.* 23 (1971) 11.
- [8] Z.G. Szabo, F. Solymosi, *Acta Chim. Acad. Sci. Hung.* 25 (1960) 161.
- [9] R. Larsson, *J. Mol. Catal.* 55 (1989) 70.
- [10] R. Larsson, *Z. Physik. Chem. (Leipzig)* 268 (1987) 721.
- [11] G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., Van Nostrand, New York, 1950.
- [12] S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
- [13] R. Larsson, *Catal. Lett.* 36 (1996) 171.
- [14] M.H. Jamroz, Information on request.
- [15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, 1986.
- [16] K. Bajdor, unpublished results.
- [17] R. Larsson, J.Cz. Dobrowolski, M.H. Jamroz, M.A. Borowiak, to be published.
- [18] M.A. Borowiak, M.H. Jamroz, J.Cz. Dobrowolski, R. Larsson, to be published.
- [19] M.A. Borowiak, *Elementary Catalytic System Model for Rational Design of Catalysts at Atomic/Molecular Levels*, Ossolineum, Wroclaw, 1991.