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Isokinetic effects in ethane hydrogenolysis and their relation to the mechanism of the reaction

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Literature data on the kinetics of ethane hydrogenolysis over metal catalysts are used to indicate the existence of isokinetic temperatures, Θ. For platinum $\Theta = 725$ K, for Ni Θ is probably in the same temperature range. For Fe and Co on the other hand Θ is found at much lower values, about 330 K for Fe and 320 K for Co. From an analysis of the model of selective energy transfer, these values support the proposition of Sinfelt that the elements of high atomic number in one and the same transition metal series favour the splitting of the carbon-carbon bond as rate determining step, whereas those elements that have lower atomic numbers cause the splitting of the metal-carbon bond to be the rate determining step.

Keywords: Ethane hydrogenolysis; mechanism; activation energies; isokinetic effects; platinum, iridium, iron and cobalt

1. Introduction

The hydrogenolysis of ethane over metal catalysts has been studied extensively for many years [1–3]. Especially the investigations of Sinfelt and coworkers [2,4] have covered a large number of metal catalyst systems. Although a completely coherent description of the mechanism or mechanisms of this seemingly simple reaction has not yet reached a general consensus, some patterns are appearing. E.g., a comparison of the relative rates of reaction under standardized conditions (fig. 7 of [2]) indicates a maximum rate for Ni, Ru and Os, for the respective series of transition metals. In a recent comment, Sinfelt [4] has proposed that these maxima result from a superposition of two different types of rate determining steps:
For the elements on the right hand side of the maximum (representing elements with higher atomic numbers), the rate determining step is the splitting of the C-C bond in a C_2H_x group adsorbed on the surface. As one proceeds from right

to left one meets elements with progressively lower atomic numbers and decreasing electronegativities. The carbon-metal interaction is increasing, resulting in a continued weakening in the C-C bond, but also making it more and more difficult for the CH_3 groups that result from the splitting to desorb from the surface as CH_4. Thus, for the elements on the left hand side of the maximum one may envisage the C-C splitting to proceed very fast and the combination of methyl groups and hydrogen atoms as forming the rate determining step.

2. Isokinetic effects

The present note will discuss the possible use of any isokinetic effects that may be discovered among this family of reactions to substantiate the general pattern of the mechanisms described above. The isokinetic effect is defined [5,6] as the intersection in a common point of the Arrhenius lines for a series of closely related systems. Under the conditions of such an effect it holds that

$$\ln k = \ln Z + E/R(1/\Theta - 1/T). \tag{1}$$

Consequently at $T = \Theta$ (the isokinetic temperature), $\ln k = \ln Z$ for all of the systems concerned.

An example of this effect for hydrogenolysis reactions is given in fig. 1. The data quoted are from two recent investigations by Shpiro, Joyner and coworkers [7,8] on ethane hydrogenolysis over Pt and Pt-Cr metal particles dispersed in or on the zeolite ZSM-5. The relevant data are given in table 1. One notes that three of the four lines in fig. 1 intersect at $1/T = 1.38\ 10^{-3}\ K^{-1}$, corresponding

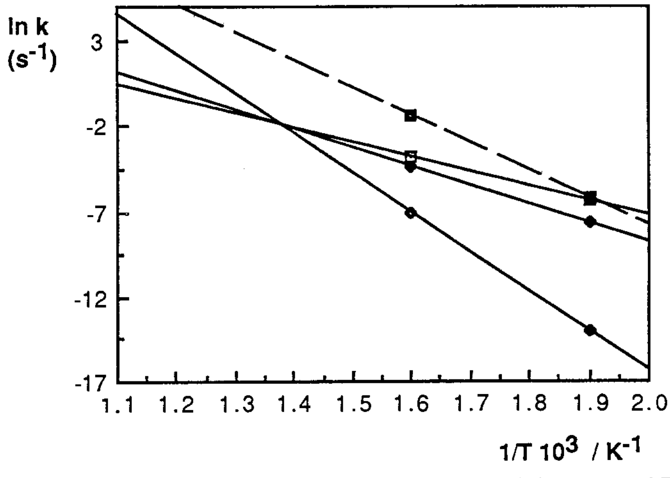

Fig. 1. Isokinetic effect for the hydrogenolysis of ethane over ZSM-5 supported Pt/Pt-Cr catalysts [7,8]. (The points are calculated from the data of table 1 and the lines drawn accordingly.)

Table 1
Experimental data [7,8] of the activation energies E_a and ln A for the hydrogenolysis of ethane over Pt and Pt/Cr catalysts supported on ZSM-5.

No	Catalyst system	E_a /kcal mol^{-1}	ln A (s^{-1})	Ref.
1	0.5% Pt/H-ZSM-5	16.92	9.86	[7]
2	0.5% Pt, 0.75% Cr/ H-ZSM-5	22.10	13.45	[7]
3	0.5–1.0% Pt/ H-ZSM-5 (calcined and reduced at 790 K) *	32.03	24.51	[8]
4	0.5–1.0% Pt/ H-ZSM-5 (reduced at 790 K without calcination) *	46.25	30.16	[8]

* mean values of 0.5 and 1.0% Pt preparations are used here.

to an isokinetic temperature of Θ = 725 K, whereas the fourth one is differing in this respect. This means that ln Z is equal for the three first but somewhat larger for the fourth one. Fig. 2 represents these data in the conventional plot of ln A versus E_a. This graph is very similar to those given in an analysis of Bond [9].

The problem that the present paper wants to probe is if the observation of such an isokinetic temperature ("IKT" [6] or Θ) can assist in deciding about the mechanism of the reaction. In a model developed by the present author the IKT has been related to molecular parameters of importance to the dynamics of the reaction. Therefore IKT may be a guide towards an understanding of the mechanism. In this model [10] the isokinetic temperature is derived by considering the selective excitation of the bond breaking vibrational mode (frequency ν).

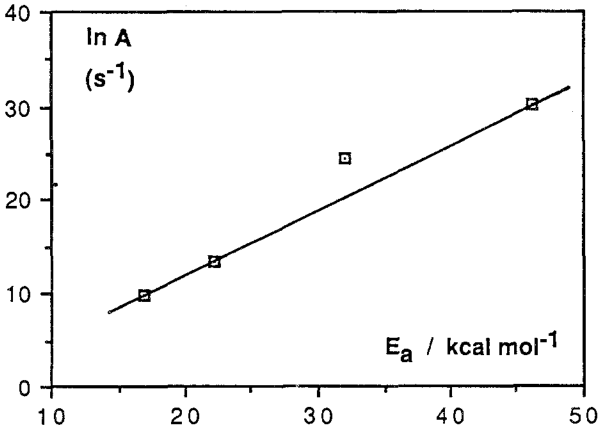

Fig. 2. Reformulation of the data of fig. 1 in terms of the classical compensation relation, ln A versus E_a.

It is assumed that the energy necessary for exciting this vibration is obtained from vibrators of the catalyst system, the frequency of these vibrators being denoted ω.

$$\Theta = NhcR - 1(\nu^2 - \omega^2)\omega^{-1}\left\{\pm\pi/2 - \mathrm{arctg}\; 0.5\nu\omega(\nu^2 - \omega^2)^{-1}\right\}^{-1} \tag{2a}$$

Especially if $\omega = \nu$, in which case one has maximum efficiency of resonance energy transfer, it holds [10] that

$$\Theta = Nhc/2R\nu = 0.715\nu \tag{2b}$$

if Θ is expressed in K and ν and ω is expressed in cm^{-1}. If $\omega \neq \nu$, Θ will be gradually larger, more so the farther from resonance conditions the system is.

Now, assuming that we have an ideal case of full resonance for the reactions of fig. 1, then from formula (2b) we have $\nu = 1014\ \mathrm{cm}^{-1}$. This frequency should correspond to the vibration mode of the bond breaking required for reaction. At this stage one needs some independent means of checking the analysis made above as, after all, only three lines are used. Is there, possibly, any other way from which we can derive the critical frequency of the bond breaking vibration?

3. Step wise change of activation energies

It follows from the model alluded to that the activation energies for reactions occurring under comparable but somewhat different conditions should change in a stepwise manner with an almost constant increment equal to the vibrational quantum of the bond breaking vibration. (Anharmonicity will give a slight variation of the size of the increment but the data are not accurate enough to make this distinction meaningful.) This stepwise change of the activation energy, E_a, has been demonstrated in the case of ethane hydrogenolysis over iridium [11,12] where the increment is found [12] to be 2.97 kcal mol^{-1}, corresponding to 1038 cm^{-1}. (1 kcal = 4.184 kJ in SI units.) Similar stepwise changes can be found also for Pt catalysts. An analysis corresponding to the one used in [11,12] is indicated in table 2. From an iterative process one finds that also in this case the increment should be nearly equal to 3 kcal mol^{-1}. This figure is used in the last column of table 2. The more precise figure results from the ratio $\Sigma\Delta(\Delta H^\dagger)/\Sigma\Delta n$. (The symbols are implicitely defined in table 2.) The increment is thus also in this case 2.97 kcal mol^{-1}, corresponding to 1038 cm^{-1}. If this latter wave number is used to calculate Θ from eq. (2b) one gets a value of $\Theta = 742$ K or $1/\Theta = 1.35 \cdot 10^{-3}\ \mathrm{K}^{-1}$. Within the experimental errors, this value is the same as that one derived from fig. 1, $1.38 \cdot 10^{-3}\ \mathrm{K}^{-1}$.

It is now important to point out that the C-C vibration of ethyl groups bonded to a metal atom is known from organometallic chemistry to appear at about 1014 cm^{-1} for $C_2H_5\ SnCl_3$ [19] or 959 cm^{-1} and 1013 cm^{-1} for $Pb(C_2H_5)_4$ [20].

Table 2
Collection of data of the activation energy of ethane hydrogenolysis over Pt catalysts.

Ref. (mol^{-1})	E_a (kcal mol^{-1})	RT (kcal mol^{-1})	$\Delta H^{\dagger}$ (kcal mol^{-1})	$\Delta(\Delta H^{\dagger})$ (kcal mol^{-1})	$\Delta n \times 3$ (kcal)
13	34.4	1.1	33.3		
				17.7	6×3
7	16.9	1.3	15.6		
				5.2	2×3
7	22.1	1.3	20.8		
				9.9	3×3
8	32.0	1.3	30.7		
				14.3	5×3
8	46.3	1.3	45.0		
				25.7	9×3
14	20.3	1.0	19.3		
				36.5	12×3
15	57	1.2	55.8		
				3.1	1×3
16	54	1.3	52.7		
				–	
17	54 *	1.4	52.6		
				7.3	2×3
18	46.4	1.1	45.3		
				23.0	8×3
18	23.4	1.1	22.3		
			$\Sigma\Delta(\Delta H^{\dagger}) = 142.7$, $\Sigma\Delta n = 48$ $\Sigma\Delta(\Delta H^{\dagger})/\Sigma\Delta n = 2.97$ kcal mol^{-1}		

* Read from the graph of ref. [17].

These examples are quoted because the study of molecular compounds makes it easier to record high resolution vibration spectra than does studies on surfaces. From these figures it is tempting to identify the reactive intermediate in the case of Pt and Ir catalyzed ethane hydrogenolysis as an ethyl group that is adsorbed on one atom of the metal surface. The C-C stretch of a di σ-bonded M-C-C-M species will be much higher, around 1200 cm^{-1} [21]. Other species of the type C_2H_x, e.g. ethylidyne, might also be suspected to be present on the surface. It has been shown by Wieckowski et al. [21a], however, that the C-C stretch of ethylidyne on Pt(111) is as high as 1121 cm^{-1}. It therefore seems likely that the rate determining step is the splitting of the C-C bond of the C_2H_5 group bonded at just one C to the metal surface, see fig. 3.

There is a close agreement between the isokinetic temperature derived from the stepwise change of a series of activation energies using the formula for perfect resonance, eq. (2b), and the value observed experimentally. This indicates that under the conditions used by Joyner et al. [7,8] a state of perfect resonance must exist. Then, what constitutes the energy supply, i.e., the energy

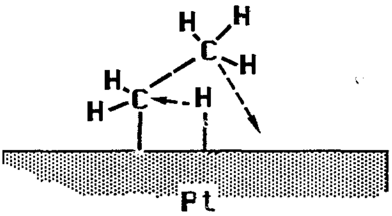

Fig. 3. Schematic representation of a possible mechanism for the attack of hydrogen atoms on the adsorbed ethyl group to give two methyl groups adsorbed on the surface.

of the vibration ω in the formula (2a)? This question is not easy to answer if one confines the search to the metal particle itself. If one enlarges the scene somewhat, however, the most likely energy source is the skeletal vibrations of the H ZSM-5 carrier. One can compare the IR spectra with a pronounced band reaching considerable strength already below 1000 cm^{-1} and centering at 1093 cm^{-1} [22]. Obviously these particles are not in direct contact with the reacting ethane molecule. Therefore one must conclude that the energy transfer occurs via radiative transfer from the zeolite to the reactant. At the frequencies required for full resonance 1017–1038 cm^{-1} there must be a strong IR emission, corresponding to the observed strong absorption, and consequently a good possibility of energy transfer.

The change of $\nu_{C\text{-}C}$ from the value of gaseous ethane ($\nu = 995$ cm^{-1} [23]) to that of an $M\text{-}C_2H_5$ unit depends on two factors. First of all, there is an increase due to the *mechanical* coupling of the M-C movement to that of the C-C one. In other words, we can not approximate the C-C motion as that of a two-atomic molecule $(H_3C)\text{-}(CH_3)$ but we have to consider a quasi-three-atom molecule $M\text{-}(CH_2)\text{-}(CH_3)$. Superimposed on this effect is the other one, arising from the *chemical* interaction of M on the electron distribution in the C-C bond. This effect is more difficult to estimate, but a starting point may be that there will be an increase of electron density of the carbon atoms for a decrease in the electronegativity of the metal. With this simple picture one can suppose that the C-C bond will be weakend when one passes from right to left meeting lower and lower electronegativity on the metals (Ti 1.5 ... Cu 1.9; C 2.5 [24]). This is indeed the basis for the argument of Sinfelt [4]. Obviously, the two effects counteract each other, making it difficult without a detailed calculation to make any definite statements on the expected value in a specific case.

The above considerations support the view that the metals that are to the right hand side of the maxima in Sinfelt's plots [2], would show isokinetic temperatures at about the range found in fig. 1. In order to substantiate this statement somewhat, the relevant data for Ni [25,26] has been put together in a common graph, fig. 4. With 'relevant' in this case we mean that the rate constants must be expressed in the same units, preferably determined in the same way. Otherwise, even a small inaccuracy will shift the lines away from a

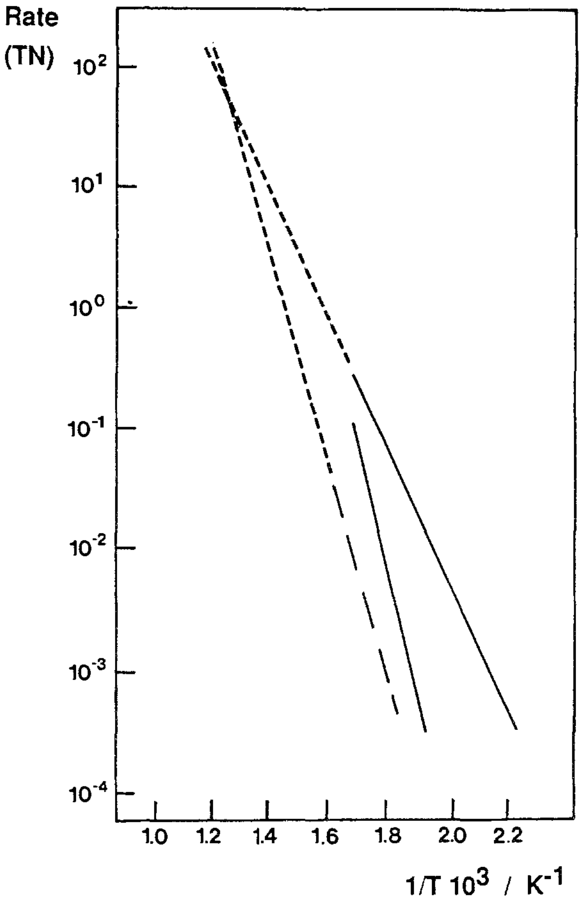

Fig. 4. Arrhenius lines for ethane hydrogenolysis over Ni surfaces, redrawn from the data of Goodman [25]. The lines from left to right represent: Ni/SiO_2 [26]; Ni(111); Ni(100).

supposedly common (ln Z; $1/\Theta$) point. Fig. 4 is constructed by merely fusing together the two figures presented by Goodman [25] which includes a recalculation of data from Martin [26]. For the worth it may have, one recognizes that the lines cut in the temperature range 1.4 ± 0.2 10^{-3} K^{-1} covering the crossing point of the Shpiro-Joyner data. Nickel, platinum and iridium are all metals that belong to the right hand side class of catalysts in the sense used above. It is therefore to expect that isokinetic temperatures of the same order should be observed.

Before leaving this matter, it must be emphasized that the spectroscopic data arrived at here indicate that C_2H_5 is the reactive intermediate. This is in sharp contrast to most other interpretations [2] in which one assumes a highly dehydrogenated species C_2H_x with x close to zero. This dilemma will be treated in another paper [27], but one should point out here that investigations reporting a large number of original data point [18,28] support interpretations in terms of kinetic schemes where C_2H_5 is the only form required.

4. Isokinetic effects of cobalt and iron

Now turning to the other side of the Sinfelt plots, comprising elements like Fe, Co, Os and Re we can present some data showing isokinetic effects from the work of Taylor and coworkers [29,30]. The data for Fe are shown in fig. 5 and 6 and are taken from tables I–V of the paper by Cimino, Boudart and Taylor [29]. Almost all points are used in the representation. Only those points are left out that clearly fall outside an Arrhenius line (cf., fig. 5). The experimental data discarded are recorded in fig. 6.

One notes that the lines intersect in almost the same point, with $1/T = 3.0 \pm 0.3 \cdot 10^{-3}$ K^{-1}. Θ thus corresponds to 330 ± 30 K. In this case measurements are on the high temperature side of the point of intersection, in contrast to the pattern for Pt and Ni. From an investigation on Co by Taylor and Taylor [30] we report in table 3 and fig. 7 the relevant data. Unfortunately only two temperatures of measurement are available here, decreasing the accuracy of the lines. The catalyst and the pressure of hydrogen during experiment are varied. One notes that the Arrhenius lines cut each other pairwise at the same abscissa value (ca $3.15 \cdot 10^{-3}$ K^{-1}). One of the lines runs parallel to another one but in a slightly different position. The common abscissa value indicates an isokinetic temperature of about $\Theta = 320$ K.

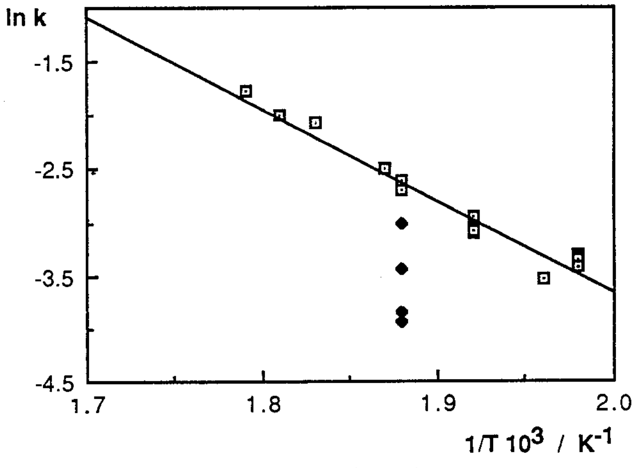

Fig. 5. Typical Arrhenius graph of the data for ethane hydrogenolysis over Fe (from table I of Cimino, Boudart and Taylor [29]). Those points that are marked ◆ are omitted in the following treatment.

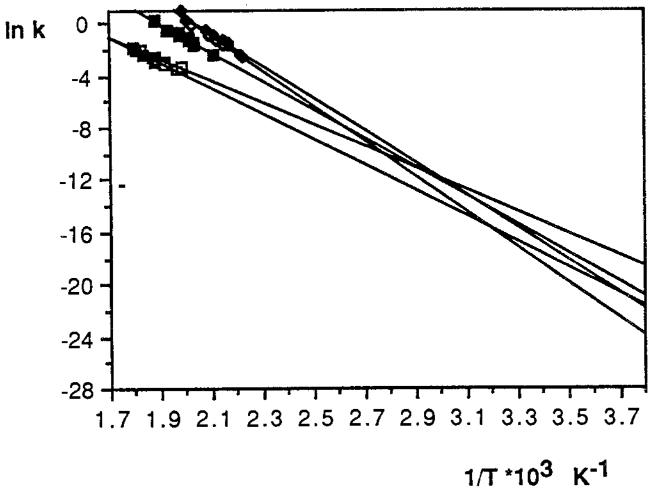

Fig. 6. Arrhenius graphs for all the tables of [29] but with omission of those points that are considered to fall outside the Arrhenius line ((cf. fig. 5). The data omitted are: in Table 1 (b1–b5; e1, e2); in Table II (a11–a15; b2, b5–b7, b10–b12); in Table III (a27–a29, a31); in Table IV (none) and in Table V (a7, a8). The designations of the authors [29] are used.

Now assuming, as before, that we by chance have conditions of perfect resonance, we can deduce a value for the appropriate vibration frequency $\nu = \nu_0$. $\nu_0 = 330/0.715 = 465$ cm^{-1} for Fe and $320/0.715 = 450$ cm^{-1} for Co, respectively. If we do not have perfect resonance, however, the vibrating molecule interacts with heat bath vibrations with frequencies on both sides of ν, where ν is a frequency $< \nu_0$ (cf., eq (2a) and fig. 8). This means, from the proposed model, that if conditions are not of perfect resonance, the data $\nu = 465$ cm^{-1} resp. 450 cm^{-1} are maximum values, cf., fig. 8. Of course, the

Table 3
Hydrogenolysis of ethane over Co catalysts from Taylor and Taylor [30]

Catalyst No	Temperature (°C)	$1/T$ ($K^{-1} \cdot 10^3$)	Initial hydrogen pressure (mm Hg)	initial rate (r) (% h^{-1} gCo^{-1})	ln r
2	255	1.894	147	48	3.871
2	280	1.808	147	167	5.118
2	255	1.894	220	40	3.689
2	280	1.808	220	130	4.868
4A	184	2.188	147	15	2.708
4A	218	2.037	147	173	5.153
4A	184	2.188	220	8.6 *	2.150
4A	218	2.037	220	99	4.595
4E	218	2.037	147	35	3.555
4E	255	1.894	147	350	5.858

* Calculated from $r = k[p(H_2)]^n$; assuming that n is the same at 184 °C as it is for 218 °C.

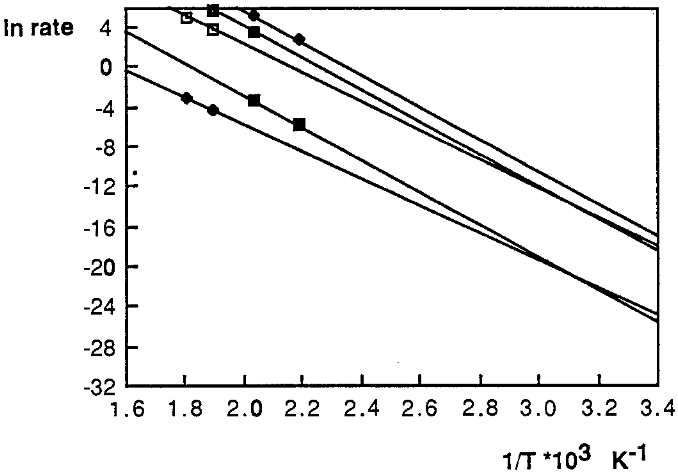

Fig. 7. The data of ethane hydrogenolysis over Co catalysts reported by Taylor and Taylor [30] (cf., data in table 3).

experimental uncertainties of the original data most probably give errors of about ±40 cm^{-1} in the wave numbers, a fact that must be taken into consideration when making comparisons like the following ones.

In spite of these uncertainties, it is of paramount importance to realise that frequencies of this magnitude are characteristic of metal-carbon bonds. From

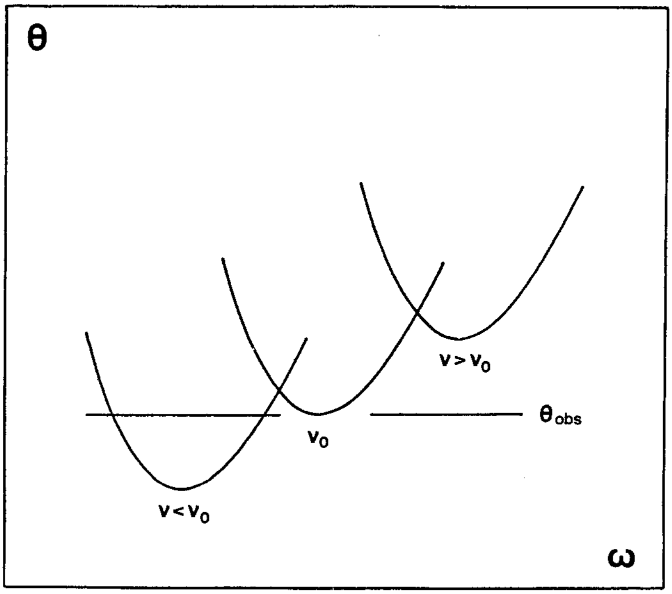

Fig. 8. The function $\Theta(\omega)$, eq. (2), for three different cases of the frequency of the reacting molecule relative to an experimentally observed isokinetic temperature.

surface spectroscopy no definite assignments to M-CH_3 adsorbed species seem to be available, but one can quote the data for C_2H_2 adsorbed (presumably as a di σ-bonded species) on Pt (570 and 340 cm^{-1}) and on Pd (500 cm^{-1}) [31]. Similarly one finds for C_2H_4 on Fe (580 and 450 cm^{-1}) [31]. Also in this case organometallic chemistry can be useful, giving for Ni-CH_3 507 cm^{-1} for $(CH_3)_2Ni(P(CH_3)_3)_2$, 487 cm^{-1} for $(CH_3)_2Ni(P(CH_3)_3)_3$ and 526 cm^{-1} for $(CH_3)Ni(P(CH_3)_3)_2Cl$ [32]. Also for non-transitional elements ν M-C appears in this range, e.g., $Pb(CH_3)_4$ has $(\nu_{Pb\text{-}C})_{sym} \approx 462$ cm^{-1} and $(\nu_{Pb\text{-}C})_{as} \approx 475$ cm^{-1} [33].

Taking all these data together, it seems that the analysis of the isokinetic effects indicates that on Fe and Co the process of hydrogenolysis is governed by the M-C bond stretching and breaking as the rate determining step. The simple electronegativity argument above suggests that the Fe-C bond should be stronger than the Co-C one. This is confirmed so far that the isokinetic temperature of Fe is found to be higher than that of Co. With the assumptions above this observation indicates a somewhat higher frequency of Fe than of Co, and consequently a stronger bond for Fe-C than for Co-C.

5. Conclusion

We can now conclude that the analysis proposed puts Ir, Pt and possibly Ni in the same category, viz, one where the C-C bond breaking determines the rate, and Fe and Co are put in the other category where the M-C bond breaking is important for determining the rate. In this respect our findings completely support the analysis of Sinfelt [4]. With respect to the nature of the reactive intermediate, however, we differ from Sinfelt [2]. The analysis indicates a singly bonded M-C species, probably M-C_2H_5, not a heavily dehydrogenated M-C-C-M species.

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