The mechanism of the ethane hydrogenolysis–a reconsideration of some kinetic data

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In order to justify the deduction made previously from isokinetic effects of ethane hydrogenolysis, i.e., that the rate determining step of this reaction on Pt and Ni is the C–C bond breaking of the chemisorbed C_2H_5 unit, some kinetic data from literature are scrutinized. It turns out that the variation of the observed rate with ethane and/or hydrogen pressure is such as predicted by the simple mechanism $C_2H_5^* + H^* + n^* \rightarrow CH_3^* + CH_3^* + n^*$, where n means the number of free sites (*) involved. From an analysis of the kinetic data it is shown that $n = 1$.

Keywords: Hydrogenolysis; ethane; platinum; nickel; mechanism

1. Introduction

The precise mechanism of hydrogenolysis of alkanes on metals has been under constant debate for many decades. Ever since it was shown by Kemball and coworkers [1] that methane and ethane–following Le Chatelier's principle–dissociated on metal surfaces it has been customary to assume some kind of C_2H_x intermediate in hydrogenolysis. The value of x is supposed to vary from metal to metal. For nickel, e.g., it has been suggested [2] that a complete dehydrogenation takes place even in the presence of a non-negligible partial pressure of hydrogen. The rate determining step is assumed to be the C–C splitting of the C_2H_x unit or possibly the rehydrogenation of the carbonic species formed via this mechanism.

Recent observations on the isokinetic effects for some hydrogenolysis reactions [3] have indicated that it is the C_2H_5 group that is of real importance for the reaction. The vibration frequency characteristic of the reactant [4] corresponded closely to that found for M–C_2H_5 species and not to those of M–C_2H_4–M or M=C–CH_3 or similar species. This observation made it necessary to go back to the original reports to try to reconcile the differing views. It turns out that very few papers actually report detailed tables of the kinetic original data. From only a few experimental points it is indeed very difficult to tell if one or the other of the suggested models are correct. This is also obvious from the rather varying views that are found in literature [5,6].

Some of the best papers in respect of original raw data are that of Gudkov, Guczi and Tetenyi [7] and that of Kemball and Taylor [8]. We will concentrate on these reports in trying to substantiate the proposal [3] that the C–C scission of ethyl groups is the rate determining step for metals like Pt, Ni and Ir. Especially important when trying to distinguish between different models of mechanisms is to describe the position and magnitude of the maximum of the reaction rate found by Gudkov et al. [7] for constant hydrogen and varying ethane concentrations.

For other metals, such as Fe and Co, it is suggested [9,10] that the C–C scission is so fast that the metal-carbon breaking (desorption, reductive elimination) becomes the slowest step. This mechanism will, however, not be exemplified in the present paper.

2. Model of the mechanism

The basic assumption of this presentation is that one should try to keep the model as simple as possible.

The starting reactants and the products in this case are given by the formula

$$C_2H_6 + H_2 = 2CH_4.$$

As the hydrogenolysis thus involves a further addition of hydrogen to already heavily hydrogenated species at a relatively high pressure of hydrogen, we will consider only such dehydrogenated species that might be formed in the first dissociative adsorption, i.e., without an excessive dehydrogenation. As said above there is an indication from the analysis of the isokinetic effect [3] that the chemisorbed ethyl group is the most important species.

The following steps are assumed:

$$C_2H_6 + 2^* = C_2H_5^* + H^* \tag{1}$$

equilibrium constant K_1

$$H_2 + 2^* = 2\,H^* \tag{2}$$

equilibrium constant K_2

$$K_1 = [C_2H_5^*][H^*]/[C_2H_6][^*]^2 \tag{3}$$

$$K_2 = [H^*]^2/[H_2][^*]^2. \tag{4}$$

The symbol $[C_2H_5^*]$ means the surface concentration of adsorbed C_2H_5 units,

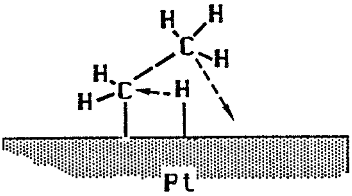

Fig. 1. Schematic description of the species involved in the reaction.

[H*] means the surface concentration of adsorbed H atoms and [*] means the corresponding surface concentration of free sites.

These equilibria are expressing the experimental observation, cf. Guzci et al. [9], that isotope exchange reactions proceed much easier than the (irreversible) hydrogenolysis reaction. From the equations above it follows that we can express these surface concentrations in terms of hydrogen and ethane partial pressures, $[H_2]$ and $[C_2H_6]$, respectively.

$$[C_2H_5{*}] = K_1/\sqrt{K_2}\,[C_2H_6]/\sqrt{[H_2]}\,[*] \tag{5}$$

$$[H{*}] = \sqrt{K_2}\sqrt{[H_2]}\,[*] \tag{6}$$

$$1 = [*] + [C_2H_5{*}] + [H{*}]. \tag{7}$$

Furthermore it is assumed that the equilibrium constants are expressed in appropriate units so that the surface concentrations can be expressed as fractions of the total available surface.

We now suggest the following rate determining step

$$C_2H_5{*} + H{*} + n{*} \rightarrow CH_3{*} + CH_3{*} + n{*}. \tag{8}$$

As is illustrated in fig. 1 it is not the same free sites (*) that are involved on the two sides of the formula (8). *A priori* we do not know how many sites that are needed for the reaction to proceed. (It has been suggested [2] that a large number, e.g. 12, is needed.) Therefore we use the formal number n for the number of sites. As will be seen below it is possible to estimate this number from the experimental data of [7] and [8]. Another tacit assumption is that $[CH_3{*}]$ is small and negligible.

Hence we can write, following eq. (8):

$$\begin{aligned}\text{Rate} &= k[C_2H_5{*}][H{*}][*]^n = kK_1[C_2H_6][*]^{n+2}\\ &= kK_1[C_2H_6]\left\{1 + K_1/\sqrt{K_2}\,[C_2H_6]/\sqrt{[H_2]} + \sqrt{K_2}\sqrt{[H_2]}\right\}^{-(n+2)}.\end{aligned} \tag{9}$$

This relation can obviously explain the maxima observed by Gudkov et al. [7] for $n+2>1$. To simplify notations we write:

$$kK_1 = a \tag{10a}$$

$$K_1/\sqrt{K_2} = b \tag{10b}$$

$$\sqrt{K_2} = c \tag{10c}$$

$$[C_2H_6] = E \tag{10d}$$

$$[H_2] = T \tag{10e}$$

$$m = n + 2.$$

Introducing these notations and also making the assumption (to be verified below) that we can neglect $[*]$ besides $[C_2H_5{}^*]$ and $[H^*]$ we obtain the rate, R as follows:

$$R = aET^{m/2}\{bE + cT\}^{-m}. \tag{11}$$

We can now treat this equation for two different cases. In the first one the hydrogen pressure is kept constant (i.e. $T=$ const.), in the other one the ethane pressure is kept constant (i.e. $E=$ const.).

These two cases correspond, e.g., to the two important illustrations in the paper of Gudkov et al. (fig. 1 and fig. 2 of [7], respectively).

CASE 1. CONSTANT HYDROGEN PRESSURE

By forming $\{\mathrm{d}R/\mathrm{d}E\}_T$ and putting it equal to zero one obtains the condition for a maximum of rate

$$E_{\max} = cT/(m-1)b. \tag{12}$$

Introducing expression (12) into the expression for rate (11) one obtains the maximum value of R_T that we will call "Peak" here

$$\mathrm{Peak}_T = ab^{-1}c^{-(m-1)}(m-1)^{(m-1)}m^{-m_T(1-m/2)}. \tag{13}$$

It thus follows from the model of the mechanism that, given that the rate can be measured as a function of E for a series of constant values of T, the abscissa value of the observed maxima should increase with increasing T (eq. (12)) and that also the magnitude of these rate maxima should increase as T approaches zero (eq. (13)). The latter relation holds for $m>2$.

$$\mathrm{Log\ Peak}_T = \mathrm{const} + (1 - m/2)\log T. \tag{14}$$

From this relation it should be possible to determine the magnitude of m. Both these criteria, eqs. (12) and (14), must be fulfilled to make the suggested mechanism trustworthy.

Introducing the relations (10) and (4) into (12) one gets

$$(E_{\max})_T = cT/(m-1)b = K_2T/(m-1)K_1 = [H^*]^2/[*]^2 1/K_1. \tag{15}$$

Thus the expression for this maximum contains the dimensionless ratio [H *]/[*]. Obviously this ratio should increase with the hydrogen pressure.

CASE 2. CONSTANT ETHANE PRESSURE

By forming $\{\mathrm{d}R/\mathrm{d}T\}_E$ and putting it equal to zero one obtains the condition for a maximum of rate

$$T_{\max} = bE/c \tag{16}$$

and in analogy to the first case we can obtain the expression for the maximum value of rate in this case

$$\mathrm{Peak}_E = 2^m ab^{-m/2}c^{-m/2}E^{-m/2}. \tag{17}$$

This equation, however, will not be explicitly used in this paper.

3. Testing of the derived relations

1. THE WORK OF GUDKOV, GUCZI AND TETENYI

Gudkov et al. [7] found it necessary to introduce two curves for the rate as function of E. They propose that a second intermediate of the classical type C_2H_x (with low x) is formed when the ethane to hydrogen ratio gets large. This is, however, not necessary. We attempt to explore another assumption, i.e., the presence of two different sets of active sites, one for the early curve, one for the second one.

To do this, one can reformulate the expression (11) but, for convenience, one can first determine the value of n that is appropriate for the experiments reported by Gudkov et al. [7]. To do this, in turn, we observe that by multiplication of eqs. (12) and (16) one obtains

$$E_{\max} * T_{\max} = cT'/(m-1)b^* bE'/c = T'E'(m-1)^{-1} \tag{18}$$

where T' means the constant value of T in fig. 1 of [6] (i.e. 1.2 kPa) and E' means, correspondingly, the constant value of E in fig. 2 of [6] (i.e. 1.3 kPa).

One can read from these figures that $E_{\max} \approx 2.3$ kPa and $T_{\max} \approx 0.35$ kPa. We thus obtain from formula (18)

$$2.3 * 0.35 = 1.2 * 1.3(m-1)^{-1} \tag{19}$$

or

$$m = 2.94.$$

This result must mean that $m = 3$ and consequently $n = 1$, i.e., only one free site is involved in the rate determining step of formula (8).

Table 1
The data of fig. 1 of [7] as read from the figure and recalculated according to eq. (21), $Z = T^{1/2} \cdot E^{1/3} R^{-1/3}$ and using $T = 1.2$ kPa as the assumed constant value of the hydrogen pressure

E/kPa	$R/\mu\mathrm{mol}\ \mathrm{g}_{\mathrm{cat}}^{-1}\ \mathrm{s}^{-1}$	Z_T
0.7	0.0069	5.11
1.2	0.0087	5.66
2.0	0.0089	6.66
3.3	0.0075	8.33
3.3	0.0086	7.96
4.7	0.00725	9.48
6.0	0.0076	11.09
9.9	0.00695	12.33
10.3	0.0069	12.52
13.1	0.0064	13.91
19.3	0.0051	17.07

Knowing that $m = 3$ we can reformulate relation (11) as

$$bE + cT = a^{1/3}T^{1/2}E^{1/3}R^{-1/3}. \qquad (20)$$

Then by formally denoting the quantity

$$Z = T^{1/2}E^{1/3}R^{-1/3} \qquad (21)$$

we can write

$$Z = ba^{-1/3}E + ca^{-1/3}T. \qquad (22)$$

Following this formalism we give in tables 1 and 2 the data of Gudkov et al. [7] as read from enlargements of their figs. 1 and 2. The resulting graphs are presented in figs. 2 and 3. From fig. 2 representing Z as a function of E we can learn that the data given by Gudkov et al. [7] do indeed represent two sets of constants. However in contrast to these authors we find that one has not to change the mechanism of reaction to describe the sudden shift. All points are well described by eq. (22), i.e. by eq. (11) and hence by the mechanism suggested

Table 2
The data of fig. 2 of [7] as read from the figure and recalculated according to eq. (21), $Z = T^{1/2} \cdot E^{1/3} R^{-1/3}$ and using $E = 1.3$ kPa as the assumed constant value of the ethane pressure

T/kPa	$R/\mu\mathrm{mol}\ \mathrm{g}_{\mathrm{cat}}^{-1}\ \mathrm{s}^{-1}$	Z_E
0.2	0.0044	2.98
1.3	0.0087	6.05
2.7	0.0040	11.30
3.7	0.0034	13.63
5.7	0.0017	21.8
10.3	0.0006	41.6

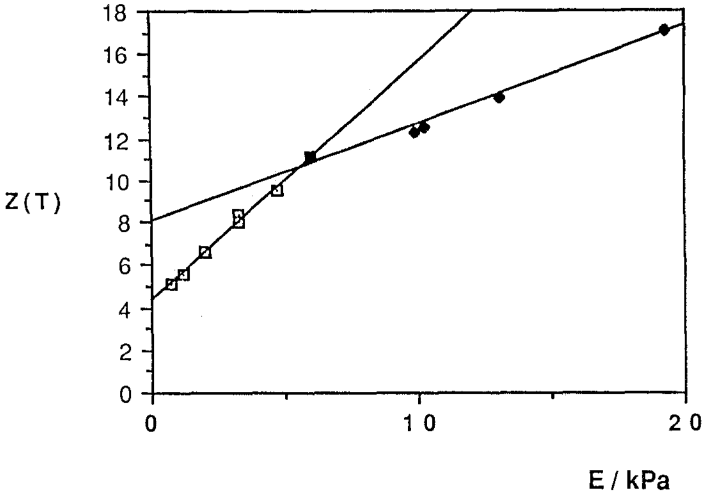

Fig. 2. Graphical representation of the function $Z(T)$, i.e. Z at a constant T value, eq. (22) plotted against E. The parameters of the two resulting straight lines are given by relations $Z = 4.334 + 1.126\ E$ (corr. coeff. = 0.997) and $Z = 7.974 + 0.462\ E$ (corr. coeff. = 0.994).

in eq. (8). One has only to assume that there is another set of sites with other characteristic parameters a', b' and c' in our notation.

Furthermore by comparing the results of fig. 3, for which E is relatively low, with the parameters of the steep line of fig. 2 (representing the first set of points with not too high E values) it is obvious that the intercept for the function in terms of T should be identifiable with the slope of the function in terms of E and vice versa.

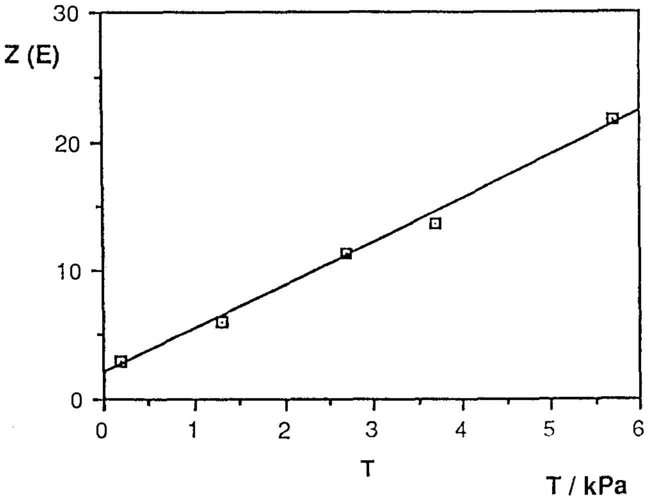

Fig. 3. The function $Z(E)$, i.e. Z at a constant E value, plotted against T. The parameters of the straight line are given by the relation $Z = 1.885 + 3.409\ T$ (corr. coeff. = 0.997).

The following relations are found

$$ca^{-1.3}1.2 = 4.334 \text{ i.e. } ca^{-1/3} = 3.61 \quad \text{(from fig.2)} \tag{23}$$

$$ca^{-1/3} = 3.41 \quad \text{(from fig.3)} \tag{24}$$

and

$$ba^{-1.3}1.3 = 1.885 \text{ i.e. } ba^{-1/3} = 1.45 \quad \text{(from fig.3)} \tag{25}$$

$$ba^{-1.3} = 1.13. \quad \text{(from fig.2).} \tag{26}$$

Although the agreement is not perfect in the case of parameter b, it is much more so for parameter c and one may be allowed to conclude that the same set of parameters are obtained as long as E is not too high ($E \leqslant 5$ kPa). Thus, over a large range of concentrations, it holds that the mechanism can be formulated as involving C_2H_5 only.

By forming the means of the relations between b and a one obtains $b = \beta a^{1/3}$, where $\beta = 1.3 \equiv 0.2$ has the dimension that contains the factor time$^{1/3}$.

Similarily one obtains $c = \gamma a^{1/3}$ with $\gamma = 3.5 \pm 0.1$ having also the dimension containing the factor time$^{1/3}$.

If, however, $E \geqslant 5$ kPa we find (fig. 2) another straight line *following from the same presumptions*. Thus it holds that the mechanism in this range of concentrations is also governed by the splitting of the C_2H_5 unit. For this range it appears that other sites with other parameters are used.

For the line representing the high values of E in fig. 2 one obtains correspondingly

$$b' = \beta' a'^{1/3}, \text{ where } \beta' = 0.46 \tag{27}$$

and

$$c' = \gamma' a^{1/3} \text{ with } \gamma' = 7.974/1.2 = 6.65. \tag{28}$$

From these data it is possible to calculate R (or R') by inserting the expressions for b and c (or b' and c') and the relevant values for E and T into eq. (11). This results in

$$R_{\text{calc}} = ET^{3/2}(\beta E + \gamma T)^{-3}. \tag{29}$$

From the comment above, it is obvious that R thus has the dimension containing {time^{-1}} as it should for a rate expression.

The calculated values are represented in fig. 4, indicating a good agreement with the experimental points.

By forming RT ln bc'/cb' we find that there is a difference in free energy of about 7.9 kJ mol^{-1} (= 2 kcal/mol, see below) between the two sets of sites for the reaction $C_2H_6 + H^* = C_2H_5^* + H_2$. This observation may possibly be quantitatively verified if different crystallographic surfaces are identified with the different sites.

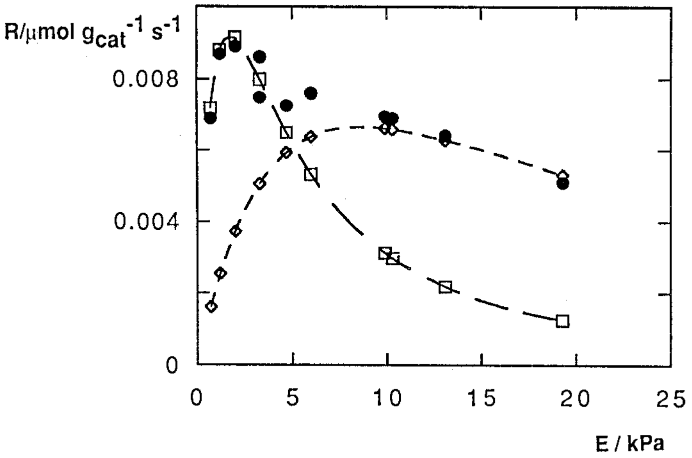

Fig. 4. The rate calculated as a function of E for the constant value of $T = 1.2$ kPa. The two curves are calculated from eq. (29) using the parameters $\beta = 1.2$ and $\gamma = 3.5$ and $\beta' = 0.46$ and $\gamma = 6.65$, respectively. The experimental points [7] are given by •, calculated by □ and ◇, respectively. The left curve was found to be very sensitive to the value of β and the value indicated (1.2) was used to give more weight to the result derived from fig. 2 than to that derived from fig. 3 which latter relies on the somewhat uncertain maximum of fig. 2 of [7].

Furthermore, if the model is adequate and the analysis is correct one should be able to describe the experimental points in table 2 (i.e. fig. 2 of [7]) from eq. (29) using the appropriate parameters β' and γ'. The result is given in fig. 5 and one observes a perfect agreement.

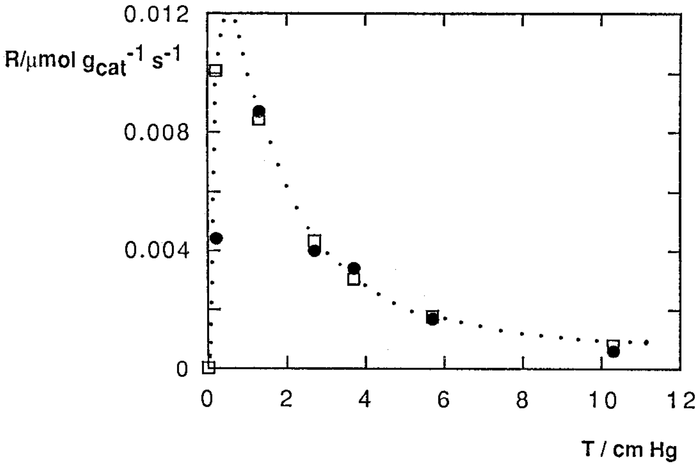

Fig. 5. The rate calculated as a function of T for the constant value of $E = 1.3$ kPa. The two curves are calculated from eq. (29) using the parameters $\beta = 1.2$ and $\gamma = 3.5$. The experimental points [6] are given by •, calculated by □.

Table 3
Selection of experimental rates for some constant values of hydrogen pressure from Kemball and Taylor [8]

Original data [8]		Rate (cm Hg/hr)	Rate 1		Rate 2		Rate 3		Rate 4		Rate 5	
E (cm Hg)	T (cm Hg)		$T \approx 1.6 \pm 0.3$		$T \approx 3.1 \pm 0.3$		$T \approx 4.6 \pm 0.4$		$T \approx 10 \pm 1$		$T \approx 12.5 \pm 0.3$	
			E	Rate	E	Rate	E	Rate	E	Rate	E	Rate
From table 1 [8]												
1.88	4.57	0.147					1.88	0.147				
2.09	15.27	0.032										
9.25	14.13	0.104										
1.95	2.94	0.224			1.95	0.224						
4.79	7.20	0.122										
3.75	10.92	0.082							3.75	0.082		
1.51	4.51	0.109					1.51	0.109				
5.42	10.57	0.114							5.42	0.114		
1.75	3.55	0.176			1.75	0.176						
9.96	9.75	0.135							9.96	0.135		
2.87	2.91	0.279			2.87	0.279						
From table 3 [8]												
12.25	12.23	0.181									12.25	0.181
4.09	4.12	0.333					4.09	0.333				
1.70	1.86	0.743	1.70	0.743								
7.91	3.99	1.30										
1.53	1.26	2.58	1.53	2.58								
24.30 *	11.75	1.74 *										
18.31 *	8.73	2.25 *										
11.21 *	5.11	3.90 *										
9.61	4.61	1.00					9.61	1.00				
6.58	3.11	1.28			6.58	1.28						
25.98	12.78	0.51									25.98	0.51
19.96	9.80	0.51							19.96	0.51		
14.93	7.28	0.62										
10.72	5.26	0.66										
10.44	4.97	0.57					10.44	0.57				

* Disqualified by Kemball and Taylor [8] because of experimental inadeqacy.

2. THE WORK OF TAYLOR AND KEMBALL

Let us now take another example, the classical investigation on Ni catalysts by Taylor and Kemball [8].

In our table 3 we quote columns 5, 6 and 7 from tables 1 and 3 of [8] *in extenso* in order to show the unavoidably subjective selection of data we make when representing five different sets of data with constant hydrogen pressure. The results from table 3 are given graphically in fig. 6 and it is seen that the predictions made above on the dependence of position and magnitude of the

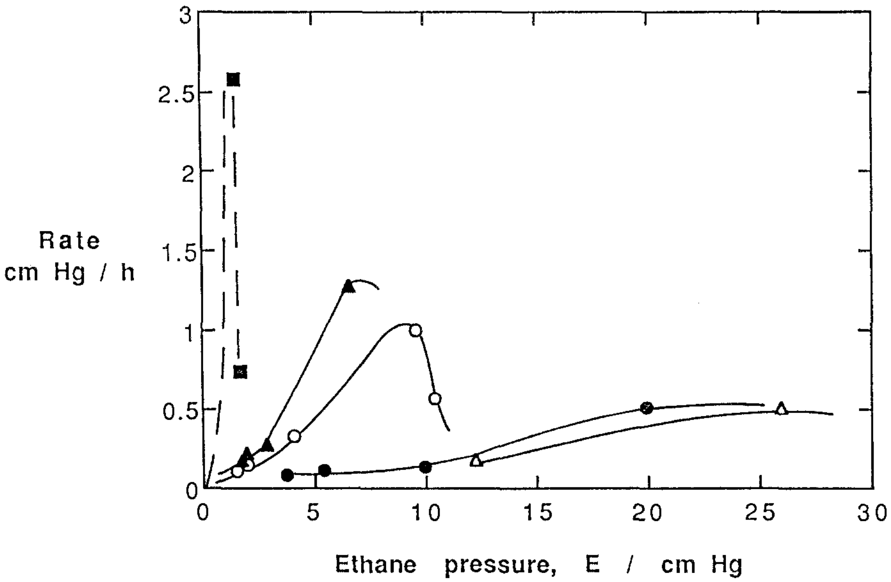

Fig. 6. The experimental data reported by Taylor and Kemball [8] represented in a graphical form. The symbols ■, ▲, ○, ● and △ related to the values of $T = 1.6$, 3.1, 4.6, 10 and 12.5 cm Hg, respectively (compare table 3). The lines are drawn quite subjectively with the aim of trying to fit the data (as grouped together in table 3) to a series of curves, each of which should exhibit a maximum.

observed (or estimated) maxima are fulfilled. One should observe that these data all relate to one and the same catalyst and one and the same temperature of measurement.

One observation that follows from the patterns of fig. 6 is that the abscissa value of the maxima that can be conceived are increasing with the value of the hydrogen pressure, T. This is in accordance with eq. (12) which predicts a direct proportionality of E_{max} with T, and such a relation is verified in fig. 7. This is actually a test for the approximation made when neglecting the term [*] in eq. (7) when forming eq. (11). The lowest point seems to fall outside the general trend; perhaps this approximation is not quite valid for such low pressures. The major reason is, however, probably that we have only two points for this "curve" in fig. 6.

Another observation that can be made is that the maximum value of the peak height seems to increase when T is approaching zero. This is in agreement with the predictions of eq. (14). The relevant data of fig. 6 are collected in table 4.

Actually, by plotting log Peak against log {T we obtain a straight line (fig. 8) From the slope of this line we get the quantity $(1 - m/2)$ following eq. (14). With the actual value of the slope, -0.66, we can estimate m. It follows that $m \approx 3.3$. This means that $n = 1$ and that the reaction proceeds with the assistance of one free site also on nickel surfaces.

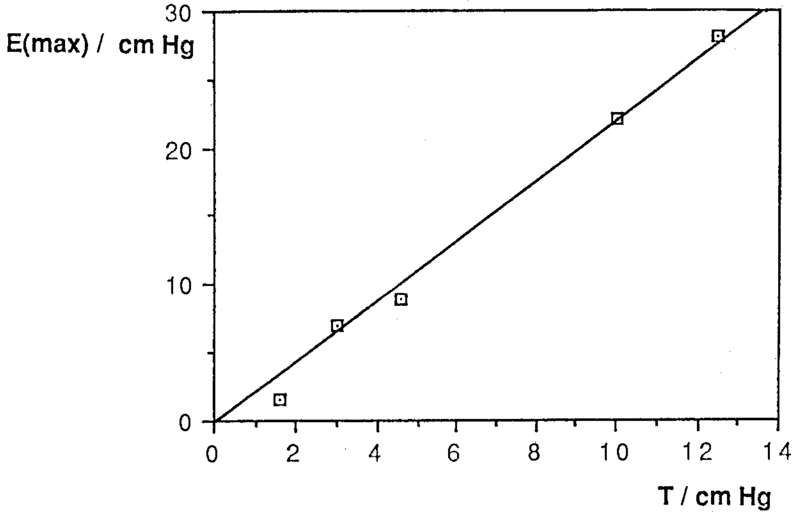

Fig. 7. The position of the maxima estimated roughly from the curves drawn in fig. 6 plotted against T in accordance with the relation (12). The lowest point seems to fall outside the general pattern and has not been used in fig. 8.

This is as far as we can use the data of ref. [8]. The analysis represented by the application of eqs. (12) and (14) does not contradict a mechanism that involves only the ethyl group on the surface.

3. The temperature dependence of some parameters derived from the work of Gudkov, Guczi and Tetenyi

Let us return to the work discussed above, by Gudkov et al. [7]. In their table 2 these authors report measurements at three different temperatures. In order to extract physical parameters from these data one can make use of eq. (22) as has been done above. From the table 2 [7] some values have been selected with fairly constant E values. These are: 523 K; 1.59, 1.67, 1.62, 1.69 (mean = 1.64) and 3.41, 3.41 (mean = 3.41) 573 K; 0.68, 0.68, 0.58 (mean = 0.65) and 2.36, 2.21,

Table 4
Collation of roughly estimated characteristics of the curves in fig. 6

T/cm Hg	E_{max}/cm Hg	Peak/cm Hg h^{-1}
1.6 ± 0.3	1.5	3
3.1 ± 0.3	7	1.3
4.6 ± 0.4	9	1
10 ± 1	22	0.6
12.5 ± 0.3	28	0.5

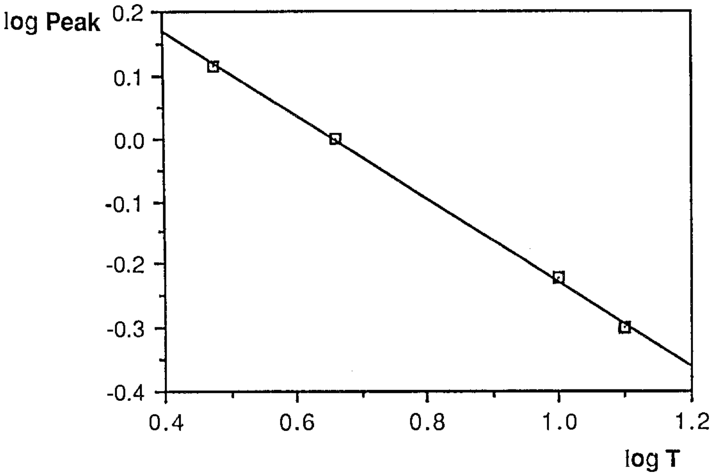

Fig. 8. A test of eq. (14) from the data presented in table 4 and originating from the interpretation (fig. 6) of the data of table 3. The line is described by log Peak = 0.436 − 0.664 log T (corr. coeff.. = 0.999).

2.36 (mean = 2.31) 623 K; 0.41, 0.65, 0.76 (mean = 0.61).

The data that result from the application of eq. (20) are given in table 5.

It now holds that

$$\begin{aligned}\ln K_2/K_1 &= -\Delta \mathrm{H}_2/RT + A_2 - (-\Delta \mathrm{H}_1/RT + A_1)\\ &= (\Delta \mathrm{H}_1 - \Delta \mathrm{H}_2)/RT + A_2 - A_1.\end{aligned}$$

By plotting ln c/b ($c/b = K_2/K_1$) versus $1/T$ we thus obtain the slope as the ratio $(\Delta \mathrm{H}_1 - \Delta \mathrm{H}_2)/R$. The data of table 5 are plotted in fig. 9. From the slope we derive $\Delta \mathrm{H}_1 - \Delta \mathrm{H}_2 = 48 \pm 2$ kcal/mol.

From the relations (1) to (4) it follows that the ratio K_2/K_1 describes the equilibrium

$$\mathrm{H}_2 + \mathrm{C}_2\mathrm{H}_5{}^* = \mathrm{H}^* + \mathrm{C}_2\mathrm{H}_6. \tag{30}$$

Table 5

Values of $ba^{-1/3}$ and $ca^{-1/3}$ as obtained from the linear relationship (22) and the data of table 2 of Gudkov et al. [7]

T/K	E_{mean}	Slope	Intercept	$ba^{-1/3}$	$ca^{-1/3}$	$c/b = K_2/K_1$	ln c/b
523	1.64	17.33	−0.56	−0.34	17.33		
	3.41	17.84	1.39	0.41	17.84		
				0.04 ± 0.4	17.6	440	6.09 *
573	0.65	4.50	0.23	0.36	4.50		
	2.31	4.12	2.01	0.87	4.12		
				0.62 ± 0.3	4.31	7.0	1.95
623	0.61	0.58	1.32	2.16	0.58	0.27	−1.31

* A somewhat uncertain value because of the small value of the intercept $ba^{-1/3}$.

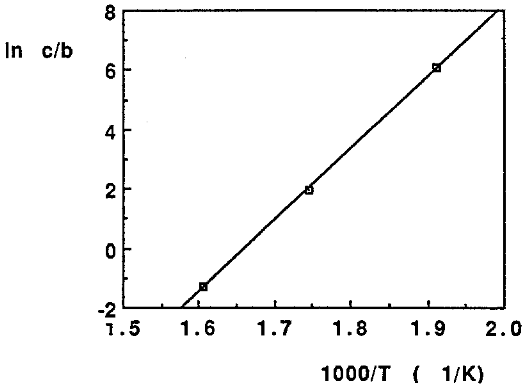

Fig. 9. The Van 't Hoff plot of the data of table 5 ($c/b = K_2/K_1$).

From Hess' law and known values of the enthalpies of formation for the four species we can calculate the entalpy change of reaction (30):

$\Delta H^0(H_2) = 0$ by definition
$\Delta H^0(Pt\text{-}C_2H_5{}^*) = -146 \pm 2$ kcal/mol [11]
$\Delta H^0(Pt\text{-}H^*) = -84 \pm 9$ kcal/mol [11]
$\Delta H^0(C_2H_6) = -84.667$ kJ/mol [12]
$= -20$ kcal/mol.

This gives $\Delta H_{\text{eq. (30)}} = -20 - (84 \pm 9) + (146 \pm 2) = 42 \pm 11$ kcal/mol.

Perhaps one can find better values for the dissociation energy of the Pt–H and Pt–C bonds than those two-atomic (or pseudo two-atomic) ones that are quoted [11] here for simplicity. The agreement with the value obtained from fig. 5, $\Delta H_1 - \Delta H_2 = 48 \pm 2$ kcal/mol, can be considered as a support of the presented scheme of reaction. Parenthetically, one may observe here that the difference in ΔG of the same reaction between the two sets of sites is found to be only 2 kcal/mol.

4. Conclusion

One should like to conclude that the analysis of this paper indicates that new experiments should be constructed in the sense that a series of measurements is performed at well controlled constant values of one of the pressure parameters while varying the other.

The successful analysis in these simple terms, showing the prevailance of the C_2H_5 group reacting on the surface of Pt and Ni, gives support to the treatment of the isokinetic effect presented previously [3]. This in turn might give support to such treatments generally and thus to another conclusion from an analysis of isokinetic effects, viz., the exchange reaction of alkanes (especially hexane) on some different surfaces. In this analysis [13] it was made plausible that the exchange D + C–H = C–D + H occurred as a Walden inversion without the actual formation of an M–C bond. Only an M–H bond was required to produce the attacking hydride group. This is worth recalling as it is so strongly pointed out by Guczi, Frennet and Ponec [9] that there is a distinct difference between "weakly" adsorbed states and "strongly" adsorbed states. The former is responsible for deuterium exchange, the latter for hydrogenolysis or isomerization. If now, as the present analysis indicates, the "strong" adsorption is really the very first step of dissociative adsorption, it follows that the "weak" adsorption should correspond to some kind of physisorbed alkane. This was, as said, the conclusion of a previous investigation [13]. Emphasizing the role of C_2H_5, one must remember, of course, that for very low partial pressures of hydrogen other equilibria will establish themselves on the surface. This has been especially strongly pointed out be Menon [14] and also by Förster and Otto [6].

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