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The mechanism of ethane hydrogenolysis over ruthenium catalysts and the isokinetic effect

Ragnar Larsson

Group of Catalysis Research, Inorganic Chemistry 1, Chemical Center, University of Lund,
PO Box 124, S-221 00 Lund, Sweden

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An analysis has been made of the compensation effect observed for literature data on ethane hydrogenolysis over ruthenium catalysts. Using a previously derived expression for the isokinetic temperature it is concluded that the rate determining step is the breaking of the Ru–C bond. This is in accordance with recent views of Sinfelt. In order to substantiate this conclusion a recently published kinetics investigation is reconsidered. The results show two mechanisms, one for ethane/hydrogen pressures < 2, the other one for ethane/hydrogen pressures > 3. In both cases the rate determining step seems to be the Ru–C bond breaking.

Keywords: Ethane hydrogenolysis; isokinetic effect; mechanism; ruthenium

1. Introduction

In some previous papers [1,2] it has been shown that the isokinetic effect [3] can be used to indicate the rate determining step in catalytic reactions. Especially, concerning ethane hydrogenolysis, it was shown [4] that the C–C stretching mode was essential in the case of catalysts such as platinum and probably nickel. On the other hand, the metal–methyl bond stretching mode was crucial for the rate determining step for metals such as cobalt and iron. These findings agree well with the recent generalisation by Sinfelt [5] related to the maximum in rate versus position in the periodic table (e.g., fig 1 in the review by Sinfelt [6]). The metals to the right-hand side of the maximum exert a rather strong influence on the C–C bond so that the cleavage of this bond appears as the rate determining step. For each move to the left in the periodic system this step becomes faster. The metals on the left-hand side of the maximum affect the C atoms so strongly that the C–C bond is split very fast. Thus the metal–carbon bond splitting becomes rate determining in the sense that it is most difficult to activate. This difficulty increases when one moves towards the metals on the far left side of the periodic system, hence the rate constant is decreased [5].

Ruthenium is a metal that is just barely over the top of the maximum [6] and it should therefore be of some interest to test the above-mentioned rules on investigations of this metal. In the first part of this paper we will look for the possible appearance of an isokinetic effect for hydrogenolysis of ethane over ruthenium and what such an effect can tell about the rate determining reaction step. In the second part we will test if kinetic data can be treated assuming the Ru–CH_3 bond breaking as the rate determining step. Luckily enough, investigations appropriate for both these tasks have appeared recently, by Galvagno et al. [7] and by Shang and Kenney [8], respectively. The results of ref. [7] will be used in section 2 and the results of ref. [8] will be used in section 3.

2. The isokinetic effect

For some nearly related systems it may occur in the description of the kinetics that the Arrhenius lines

$$\ln k = \ln A - E_a/RT \tag{1a}$$

cut each other in one single point. (E_a is the energy of activation and R and T keep their conventional meaning.) The temperature of this intersection is called the isokinetic temperature, designated here as Θ.

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

It is easily deduced that such an effect can be described by the linear relation

$$\ln A = b'E_a + c', \tag{2}$$

where

$$b' = 1/R\Theta, \tag{3a}$$

$$c' = \ln Z. \tag{3b}$$

The linear relation (2) is often referred to as "the compensation effect", for obvious reasons. Linert has pointed out [9] that an uncritical use of such linear relations can be misguiding and he strongly recommended the point of intersection as the most reliable criterion for the isokinetic temperature. Hence we use in the present context the data given by Galvagno et al. [7] in their table 3. Activities for four Ru/Au catalysts with different Ru/Au ratios were given as reported here in table 1. Unfortunately, measurements were made [7] at only two different temperatures. Assuming that all reactions were measured at the same ethane and hydrogen pressures the activity will be proportional to the rate constant of the reaction. Hence we have plotted in fig. 1 ln(activity) versus $1/T$

Table 1
The data of Galvagno et al. [7] for the hydrogenolysis of ethane over Ru–Au/SiO_2 catalysts. (Activities in ethane molecules s^{-1} Ru_s^{-1})

Catalyst	% Ru	Activity at 160°C	Activity at 245°C
RS100	100	0.00268	0.787
RS091	91	0.00092	0.268
RS048	48	0.00036	0.081
RS014	14	0.00014	0.015

for the four different catalysts. One observes that two of the curves run parallel but that three converge and seem to intersect in a common region of

$$1/T \approx (3.2 \pm 0.3) \times 10^{-3}\ \mathrm{K}^{-1}.$$

This corresponds according to eq. (1b) to $\Theta = 315 \pm 30$ K. The extra parallel line may correspond to the effect of parallel compensation lines, discussed by Bond [10]. This means that Θ is the same, Z may differ.

The result above can now be treated further with a model by the present author [1]. This model uses a simple semi-classical concept, viz. the damped coupling between the vibration of frequency ω, characteristic of the heat bath, and the vibration of frequency ν, that turns the molecule into the activated state of the rate determining step. By summing over all possible ways of energy dissipation (the damping) one can deduce a relation between Θ, ω and ν such that

$$\Theta = NhcR^{-1}(\nu^2 - \omega^2)\omega^{-1}\left\{\pm\pi/2 - \mathrm{arctg}\left(0.5\,\nu\omega(\nu^2-\omega^2)^{-1}\right)\right\}^{-1}. \quad (4)$$

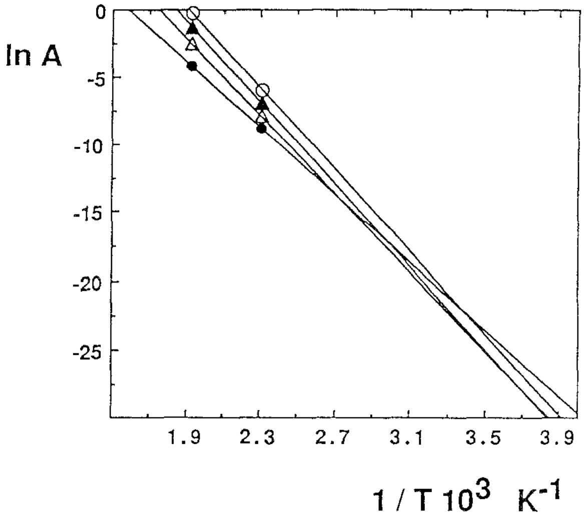

Fig. 1. The Arrhenius lines describing the results of ethane hydrogenolysis over Ru–Au/SiO_2 catalysts [7]. (○) = 100% Ru; (▲) = 91% Ru; (△) = 48% Ru; (●) = 14% Ru. The abscissa values of the crossing points are 2.79, 3.02 and 3.69×10^{-3}, respectively.

Especially if $\omega = \nu$, in which case one has maximum efficiency of resonance energy transfer, it holds [1] that

$$\Theta = (Nhc/2R)\nu = 0.715\ \nu \tag{5}$$

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

Let us, e.g., assume that resonance is fulfilled in the present case: That assumption and eq. (5) will give a value for the frequency of the activating vibration, $\nu = 440 \pm 40\ \text{cm}^{-1}$. One immediately observes that this value is in the range of what is expected for a metal–carbon vibration. One may quote data from organometallic chemistry, e.g., $\nu(\text{Ni-CH}_3) = 507\ \text{cm}^{-1}$ in $(\text{CH}_3)_2\text{Ni}(\text{P}(\text{CH}_3)_3)_2$, $\nu(\text{Ni-CH}_3) = 487\ \text{cm}^{-1}$ in $(\text{CH}_3)_2\text{Ni}(\text{P}(\text{CH}_3)_3)_3$ and $\nu(\text{Ni-CH}_3) = 526\ \text{cm}^{-1}$ in $(\text{CH}_3)\text{Ni}(\text{P}(\text{CH}_3)_3)_2\text{Cl}$ [11]. Also for non-transitional elements ν(M–C) appears in this range, e.g., $\text{Pb}(\text{CH}_3)_4$ has $\nu_{\text{sym}}(\text{Pb–C}) \approx 462\ \text{cm}^{-1}$ and $\nu_{\text{as}}(\text{Pb–C}) \approx 475\ \text{cm}^{-1}$ [12].

As argued before [4], the close correspondence between the frequency of ν, i.e. the vibration of the molecule that achieves the activation for reaction, and the frequency of metal–carbon vibrations of M–CH_3 species makes it probable that it is actually the stretching of the M–C bond that is involved in the rate determining step.

It is also interesting to note that the isokinetic temperature for this Ru reaction is close to those observed [4] for Fe- and Co-catalyzed hydrogenolysis, viz. 330 and 320 K, respectively. Using the same assumption of resonance these latter temperatures correspond to the frequencies $\nu(\text{Fe–CH}_3) = 465\ \text{cm}^{-1}$ and $\nu(\text{Co–CH}_3) = 450\ \text{cm}^{-1}$. As Ru is heavier than Fe and Co the frequency should be somewhat lower in the Ru case, assuming the same M–C binding strength. This binding strength, however, is related to the difference in electronegativities between carbon and the metal atom in question. The Pauling (or rather Allred–Rochow) electronegativities [13] represent essentially bond strength data. In Allred–Rochow terms the electronegativities are: $\chi(\text{C}) = 2.50$; $\chi(\text{Co}) = 1.70$; $\chi(\text{Fe}) = 1.64$; $\chi(\text{Ru}) = 1.42$. Thus the C–Ru bond strength will be larger than that of C–Fe and C–Co.

The fine details of the balance between these two factors, mass and binding strength, are outside the scope of this paper, especially so as the errors in the estimated isokinetic temperatures are considerable.

Before closing this section it is necessary to validify the statement that there might be a case of resonance in the Ru catalyzed reaction. Actually, the catalysts are Ru/SiO_2 systems treated in slightly different ways [7]. The common factor is the silica carrier and the frequency found by IR photoacoustic spectroscopy [14] for various silica specimen, 460–468 cm^{-1}, agrees quite well with the frequency deduced above ($440 \pm 40\ \text{cm}^{-1}$). Furthermore, as stated many times, the form of function (4) is such that the minimum is rather flat and a slight deviation from the complete resonance will affect Θ very little.

3. Model of the reaction mechanism

The basic assumption of this presentation is that the C_2H_5 group will be present in very small concentrations on the catalyst surface. It is, however, probably adsorbed as the primary product in analogy with what was found for, e.g., platinum [15]. As the M–CH_3 bond-breaking is supposed to be the process that must be activated, the methyl groups will be present in high concentration on the surface. The following steps are assumed:

$$C_2H_6 + 2* = CH_3* + CH_3*, \tag{6}$$

equilibrium constant K_1. The assumption of an equilibrium implies that the $CH_3 + CH_3$ recombination is much faster than the $CH_3 + H$ reaction,

$$H_2 + 2* = 2H*, \tag{7}$$

equilibrium constant K_2.

$$K_1 = [CH_3*]^2/[C_2H_6][*]^2, \tag{8}$$

$$K_2 = [H*]^2/[H_2][*]^2. \tag{9}$$

The symbol $[CH_3*]$ means the surface concentration of adsorbed CH_3 units, $[H*]$ means the surface concentration of adsorbed H atoms and $[*]$ means the corresponding surface concentration of free sites.

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,

$$[CH_3*] = \sqrt{K_1}\sqrt{[C_2H_6]}[*], \tag{10}$$

$$[H*] = \sqrt{K_2}\sqrt{[H_2]}[*], \tag{11}$$

$$1 = [*] + [CH_3*] + [H*]. \tag{12}$$

In eq. (12) 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 must now suggest a number of models for the rate determining step and apply the resulting formula for the rate to the data presented by Shang and Kenney [8]. From the results one can then select the model that is physically most appropriate. The general model may be formulated as

$$CH_3* + mH* + n* \rightarrow CH_4 + (m-1)H* + (n+2)*. \tag{13}$$

A priori we do not know how many sites are needed for the reaction to proceed. In a previous paper [15] it was possible to estimate this number from the experimental position of the maximum of rate versus $[H_2]$. Such a procedure is not possible here as will be evident from the following treatment:

$$\begin{aligned}\text{rate} = r &= k[\mathrm{CH_3} *][\mathrm{H} *]^m[*]^n \\ &= k\sqrt{K_1}\sqrt{[\mathrm{C_2H_6}]}\left(\sqrt{K_2}\sqrt{[\mathrm{H_2}]}\right)^m \\ &\quad\times\left\{1 + \sqrt{K_1}\sqrt{[\mathrm{C_2H_6}]} + \sqrt{K_2}\sqrt{[\mathrm{H_2}]}\right\}^{-(m+n+1)}. \end{aligned} \tag{14}$$

This relation can obviously explain the maxima observed by Shang and Kenney [8] for $n + 1 > 0$ (which is always the case). To simplify notations we write:

$$a = \left(kK_1^{1/2}K_2^{m/2}\right)^{-1/(m+n+1)}, \tag{15a}$$

$$b = \sqrt{K_1}\left(kK_1^{1/2}K_2^{m/2}\right)^{-1/(m+n+1)}, \tag{15b}$$

$$c = \sqrt{K_2}\left(kK_1^{1/2}K_2^{m/2}\right)^{-1/(m+n+1)}, \tag{15c}$$

$$[\mathrm{C_2H_6}] = E, \tag{15d}$$

$$[\mathrm{H_2}] = B. \tag{15e}$$

Introducing these notations we obtain the rate r as follows:

$$r = E^{1/2}B^{m/2}\{a + b\sqrt{E} + c\sqrt{B}\}^{-(m+n+1)}. \tag{16}$$

4. The reaction model if $E/B \leqslant 2$

In the following we will try to interprete the data given by Shang and Kenney [8] in their fig. 2. In table 2 these data are reproduced as read directly from the

Table 2
The data of fig. 2 of ref. [8] as read from the figure

E (atm)	B (atm)	r (μmol g_{cat}^{-1} s^{-1})	E (atm)	B (atm)	r (μmol g_{cat}^{-1} s^{-1})
0.02	0.0515	2.40	0.04	0.0355	4.70
0.02	0.0445	2.60	0.04	0.0285	4.90
0.02	0.0375	2.85	0.04	0.0215	4.95
0.02	0.0305	3.05	0.04	0.0185	4.80
0.02	0.0235	3.30	0.04	0.0155	4.65
0.02	0.0170	3.40	0.04	0.0100	3.65
0.02	0.0135	3.30	0.04	0.0075	2.60
0.02	0.0105	3.05	0.04	0.0050	1.65
0.03	0.0435	3.55			
0.03	0.0365	3.80			
0.03	0.0295	4.00			
0.03	0.0225	4.10			
0.03	0.0160	4.05			
0.03	0.0100	3.30			
0.03	0.0050	1.60			

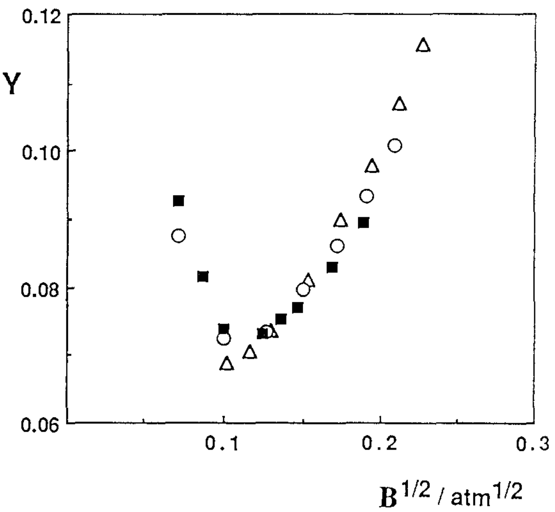

Fig. 2. Y at a constant E value, plotted against $\sqrt{B}$. The parameters of the model are $m = 1$ and $n = 0$ (17a). (△) $E = 0.02$ atm, (○) $E = 0.03$ atm, (■) $E = 0.04$ atm.

graph. We will treat eq. (6) for four different cases:

$$m = 1; \quad n = 0, \tag{17a}$$

$$m = 2; \quad n = 0, \tag{17b}$$

$$m = 1; \quad n = 1, \tag{17c}$$

$$m = 2; \quad n = 1. \tag{17d}$$

We first exemplify using the first combination. It then turns out that eq. (16) can be transformed to

$$Y = E^{1/4} B^{1/4} r^{-1/2} = a + b\sqrt{E} + c\sqrt{B}, \tag{18}$$

where Y is just a designation of the left-hand side expression. One should expect from (18) a linear relation between Y and $\sqrt{B}$ for each of the three sets of constant values of E in table 2.

A plot of Y versus $\sqrt{B}$ is given in fig. 2. One notes immediately that, at least for the sets of data where $E = 0.03$ and 0.04 atm, there are some points drastically falling out of any relationship, linear or not, that seems to hold for the rest of the points. These points clearly correspond to the highest values of E/B. In the next attempt we have therefore excluded the three last points of $E = 0.04$ atm (i.e those with low B), the two last points of $E = 0.03$ atm, and to be on the safe side, the last point of $E = 0.02$ atm.

With this restriction we have repeated the plotting of the appropriate Y functions for each of the combinations (17a)–(17d). The results are reproduced in tables 3 and 4. One notes that in the first two cases the term a of eq. (18) comes out with a negative sign. As the term a represents the concentration on

Table 3
The primary data from the plot of Y versus $\sqrt{B}$

m	n	E	Y	$a+b\sqrt{E}$	c	Corr. coeff.
1	0	0.02	$E^{1/4}B^{1/4}r^{-1/2}$	0.02029	0.4096	0.993
		0.03		0.03055	0.3312	0.995
		0.04		0.04036	0.2567	0.991
2	0	0.02	$E^{1/6}B^{1/3}r^{-1/3}$	0.01656	0.5565	0.997
		0.03		0.02526	0.4904	0.998
		0.04		0.03337	0.4286	0.998
1	1	0.02	$E^{1/6}B^{1/6}r^{-1/3}$	0.09678	0.6075	0.995
		0.03		0.11100	0.4993	0.996
		0.04		0.12848	0.3787	0.969
2	1	0.02	$E^{1/8}B^{1/4}r^{-1/4}$	0.06904	0.7223	0.993
		0.03		0.07964	0.6425	0.999
		0.04		0.08894	0.5706	0.998

the surface of free sites, such a result is obviously not physically realistic. The third and fourth combinations yield positive but small (as it should) values of a. The combination (17d) gives the best correlation coefficient. Therefore we have selected this model as the best one of those considered for the rate determining step under the conditions chosen, viz., $E/B \leqslant 2$. The three lines describing Y of alternative (17d) are shown in fig. 3.

One curious observation must be reported. In all four cases, (17a)–(17d), it is found that the coefficient c is decreasing with increasing E. This must mean that the equilibrium constants involved in this factor are changing with E. Essentially the adsorption coefficient of H_2 adsorption must be decreasing with increasing E, i.e. with increasing population on the surface of CH_3 species. Such an effect is not unknown; indeed it is often observed that the heat of adsorption of a certain species is varying with coverage.

By using the parameters thus deduced for the alternative (17d) one can calculate the rate from eq. (16). The results are given in fig. 4. One notes a fair agreement with the experimental points. Actually, excluding the last three points of $E = 0.04$ atm, the two last ones of $E = 0.03$ and the last one of $E = 0.02$ atm, the spread measured as the root mean square of the relative

Table 4
The resulting parameters from an analysis of the E dependence of parameters $(a+b\sqrt{E})$ and c from table 3

m	n	a	b	c
1	0	−0.02826	0.3420	$0.5619 - 7.647E$
2	0	−0.02410	0.2866	$0.6837 - 6.394E$
1	1	0.01976	0.5382	$0.8385 - 11.443E$
2	1	0.02098	0.3394	$0.8727 - 7.586E$

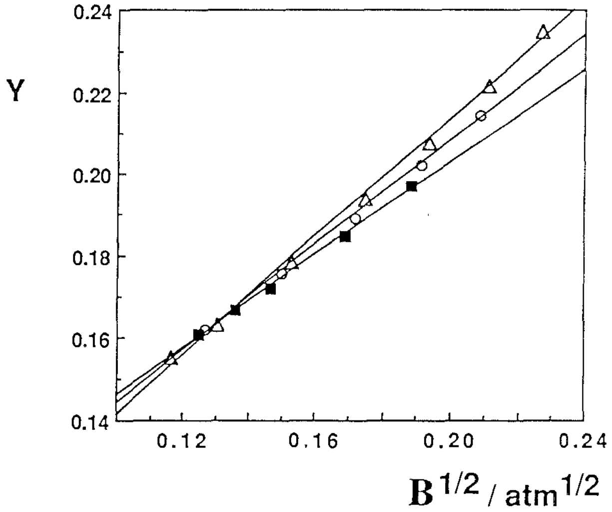

Fig. 3. The function Y plotted against $\sqrt{B}$ for the three series $E = 0.02$ (△), 0.03 (○) and 0.04 (■) atm. The model (17d) is used, i.e. $m = 2$, $n = 1$. One, two and three points for the different series are omitted for reasons described in the text.

deviation is only 2.5% as compared to 9% suggested by Shang and Kenney [8] for their best model. Hence we can conclude that the rate determining step for $E/B \leqslant 2$ is described by

$$CH_3 * + 2H * + * \rightarrow CH_4 + H * + * . \tag{19}$$

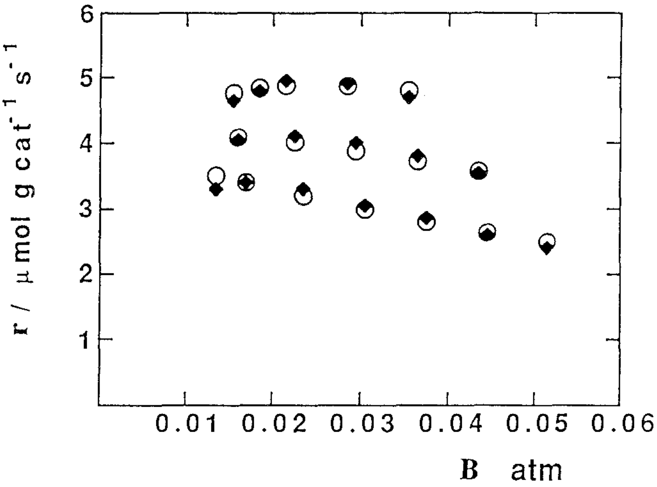

Fig. 4. The rate calculated as a function of B for the constant values of $E = 0.02$, 0.03 and 0.04 atm (from the low to the high set of points). The curves are calculated from eq. (16) using the parameters $a = 0.02098$, $b = 0.3394$ and $c = 0.8727 - 7.586E$. The experimental points [8] are given by (♦), calculated by (○).

It should be remarked that for the other alternative (17c) the analogous root mean square estimate is 3.0% and the fit of the calculated points to the experimental ones is not as good as that in fig. 4. This indicates that (17d) is the most likely mechanism alternative but that both are much better than those of the original work [8]. The kinetics analysis might be improved in a more detailed investigation by considering the rates of ethane associative desorption as comparable to that of methane desorption.

To check the physical relevance of the model, one can, e.g., estimate the free energy change of the reaction

$$H_2 + 2CH_3* = C_2H_6 + 2H* . \tag{20}$$

By forming the ratio $c(E \to 0)/b$ using the parameters of table 4 one gets from (15c) and (15d) the corresponding ratio $\sqrt{K_2}/\sqrt{K_1} = 2.57$ or $K_2/K_1 = 6.6$. Thus $-RT \ln 6.6$ expresses ΔG of reaction (24), cf. (6)–(9). At the conditions of experiment ($E \to 0$ and temperature $\approx 200°\mathrm{C}$) one finds $\Delta G = -3.4$ kcal/mol. This indicates that hydrogen is adsorbed dissociatively slightly easier than ethane.

5. The reaction model for $E > B > 3$

We may now ask why the last points of $E = 0.03$ and 0.04 atm are falling so significantly out of the pattern. Actually, if one considers only these points in an enlargement of fig. 2 of ref. [8], we observe a beautiful linear relationship between rate and B (fig. 5). Even more noteworthy is that this relation seems to

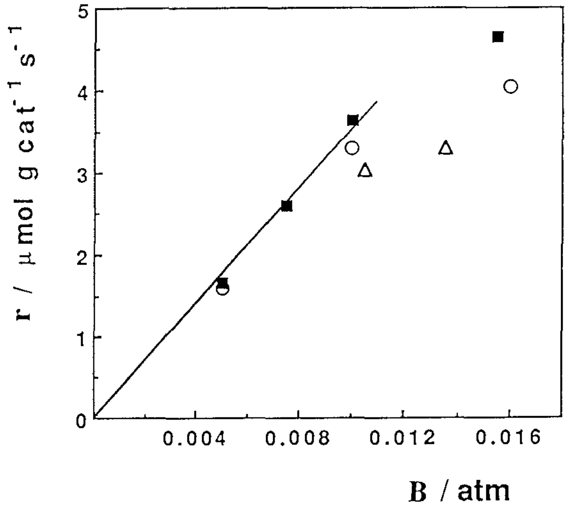

Fig. 5. The experimental points for $E/B > 3$ showing a linear dependence on the hydrogen pressure, independent of the ethane pressure. Designations as in figs. 2 and 3.

be independent of the value of E. This observation forces us to construct the following relation for the rate:

$$r=\sqrt{E}\ B\left(d+e\sqrt{E}\right)^{-1}, \tag{21}$$

where the term d corresponds to a and possibly $c\sqrt{B}$ in the expression (16) that in its turn is related to (12). In order for the experimental observations to be described by (21) it must hold that d is negligible besides the term $e\sqrt{E}$,

$$r\approx(1/e)B. \tag{22}$$

Eq. (22) indicates that for this experimental situation, the following step is the rate determining one:

$$\mathrm{CH_3}*+\mathrm{H_2}\rightarrow\mathrm{CH_4}+\mathrm{H}*, \tag{23}$$

$$r=k'[\mathrm{CH_3}*][\mathrm{H_2}]. \tag{24}$$

This might mean that for very high ratios of ethane to hydrogen, the methyl groups are almost completely covering the surface and the hydrogen is reacting with these surface species in a Rideal–Eley kind of mechanism. (Note, however, that the equilibrium constant of reaction (20) discussed above, i.e. $K_2/K_1=6.6$ would predict a $[\mathrm{H}*]/[\mathrm{CH_3}*]$ ratio of about unity. This discrepancy is mainly caused by the E dependence of the variable c, i.e. of $\sqrt{K_2}$.)

As the two different mechanisms operate independent of each other it follows that the maxima observed (fig. 2 of ref. [8]) are artefacts in the sense that they do not describe the culmination of anyone of the two mechanisms. The true maxima of reaction (19) for the three sets of E values are those indicated in our fig. 4. If these maxima had really been observed they might have served the purpose of indicating the appropriate values of n and/or m by a similar procedure as that used in the previous paper [15].

6. Final comments

In section 5 it was shown that the kinetics as measured by Shang and Kenney [8] is best described in terms of the reaction of methyl groups adsorbed on the catalyst surface as a result of a dissociative adsorption of ethane. The reaction occurs by interaction with adsorbed hydrogen atoms and free sites when hydrogen atoms on the surface are in excess. It occurs by interaction with hydrogen molecules when the surface is almost completely covered by methyl groups. In both cases it must be the stretching of the metal–carbon bond that activates the reaction. In fig. 6 we attempt to sketch the essentials of the two mechanisms.

In the section on the isokinetic effect deduced from the data of Galvagno et al. [7], it was shown by using the model of selective energy transfer [1] that the stretching of the Ru–C bond was involved in the rate determining step.

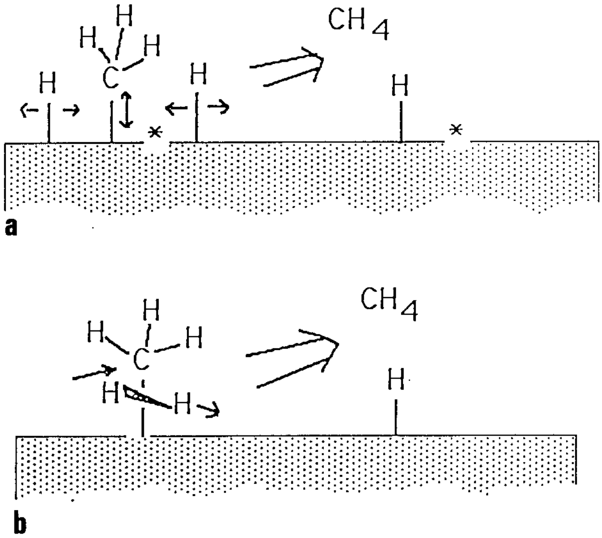

Fig. 6. Schematic description of the species involved in the reaction. (a) $E/B \leqslant 2$. It was found in the analysis that $m=2$, i.e. two hydrogen atoms adsorbed on the surface are engaged in the process. Probably one is needed to force the methyl radical to bend towards the other hydrogen atom, with which it reacts. The forcing hydrogen is then attacking a free site, leaving its previous site of adsorption to be a free site. Cf. eq. (19). (b) $E/B > 3$. For very high values of ethane partial pressure the analysis of the kinetics shows that the surface must be almost saturated with methyl radicals. The only chance for hydrogen to react is then to approach the Ru–C bond as H_2. At this process methane is formed and the hydrogen molecule is split.

As the kinetics data of ref. [8] could be so successfully described by assuming a mechanism that was suggested by the investigation on the isokinetic effect one must conclude that the model of selective energy transfer is a powerful tool for elucidating the mechanism of a complex reaction. The prerequisite for its use is a well developed isokinetic effect.

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References

[1] R. Larsson, J. Mol. Catal. 55 (1989) 70.
[2] R. Larsson, J. Catal. 107 (1987) 568.
[3] E. Cremer, Adv. Catal. 7 (1955) 75.

[4] R. Larsson, Catal. Lett. 11 (1991) 137.
[5] J.H. Sinfelt, Catal. Lett. 9 (1991) 159.
[6] J.H. Sinfelt, Adv. Catal. 23 (1973) 91.
[7] S. Galvagno, J. Schwank, G. Parravano, F. Garbassi, A. Marzi and G.R. Tauszik, J. Catal. 69 (1981) 283.
[8] S.B. Shang and C.N. Kenney, J. Catal. 134 (1992) 134.
[9] W. Linert, Chem. Phys. 129 (1989) 381.
[10] G.C. Bond, Z. Phys. Chemie (NF) 144 (1985) 21.
[11] *Gmelin, Handbuch der Anorganischen Chemie*, Erg. Werk, 8th Ed., Band 16 (Springer, Berlin, 1973) pp. 11, 72.
[12] *Gmelin, Handbuch der Anorganischen Chemie*, 8th Ed., 47, Part 1 (Springer, Berlin, 1987).
[13] J.E. Huheey, *Inorganic Chemistry*, 3rd Ed. (Harper and Row, New York, 1983).
[14] J.B. Benziger, S.J. McGovern and B.S.H. Royce, ACS Symposium Series 288 (1985) 449.
[15] R. Larsson, Catal. Lett. 13 (1992) 71.