Comment on Mechanism of Ethane Hydrogenolysis

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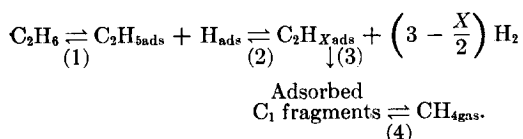*30, Av. Renaissance, B-1040 Brussels, Belgium*

Interpretation of ethane hydrogenolysis results, considering that the carbon-carbon bond breaking is rate determining on almost all studied metallic catalysts, is criticized. Comparison with methane deuterium exchange results and interpretations suggest the hydrogenating desorption of adsorbed C_1 fragments to be rate controlling on several metals such as W, Ru, Rh.

In the last few years, much experimental work has been devoted to the catalytic hydrogenolysis of ethane (1–8). In this respect, particular attention must be given to the valuable and extensive study by Sinfelt and co-workers, who systematically investigated the catalytic activity of various transition metals. In the interpretation of the latter results (1, 9), use is made of the kinetic analysis proposed 20 yr ago by Cimino, Boudart and Taylor (10) for iron catalysts, and the rate determining step is assumed to be identical on all metals where the experimental order with respect to hydrogen is negative, i.e., on all studied metals except Fe and Re.

Our aim here is to suggest a plausible alternative to this commonly accepted interpretation that, in our opinion, is not justified and that is too widely applied to almost every metal catalyst. Our interpretation takes account of unusual hypotheses put forward by some of us when studying CH_4–D_2 exchange (11–14).

The mechanism of hydrogenolysis may be written:

$$C_2H_6 \rightleftharpoons C_2H_{5ads} + H_{ads} \rightleftharpoons C_2H_{Xads} + \left(3 - \frac{X}{2}\right) H_2$$
$$\quad (1) \qquad\qquad\qquad (2) \qquad \downarrow(3)$$

$$\text{Adsorbed}$$
$$C_1 \text{ fragments} \rightleftharpoons CH_{4gas}.$$
$$(4)$$

where there may be distinguished: (1) a dissociative adsorption step, (2) one or more surface dehydrogenation steps with

formation of an adsorbed C_2H_X species whose dissociation (3) lead to adsorbed C_1 fragments ultimately hydrogenated (4) into gaseous methane. Steps (1) and (2) are considered as equilibrium steps, except in the case of cobalt catalyst in the high temperature range, where these steps are considered as irreversible (9). On the other metals, the possible occurrence of irreversible steps (1) and (2) at high temperature is also considered, but is not supported by experimental evidence, the range of temperature where the experimental studies were performed being narrow ($\cong 40°C$). Sinfelt, like most other authors, assumes that dissociation step (3) is rate determining on all metals, except for Fe and Re where the possibility of step (4) being rate determining is suggested.

Arguments supporting the assumption of a carbon–carbon bond breaking rate controlling step may be summarized as follows:

a. C_2H_6–D_2 exchange whose rate determining step is usually assumed to be the dehydrogenating adsorption (15), is known to proceed with a much higher rate than hydrogenolysis. It is then concluded (1, 8) that the adsorption steps (1) or (2) cannot be rate determining in the hydrogenolysis;

b. The rate determining step of the CH_4–D_2 exchange is usually assumed, mainly from Kemball's work (16, 17), to be the CH_4 adsorption. Methane desorption is then considered as a fast step, so

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step (4) cannot be rate determining in the hydrogenolysis (*7, 8*);

c. Dissociation of C_2H_x (step 3) must then be rate determining. This assumption is supported by thermochemical calculations showing that this step must be highly endothermic (*8*).

The fact that Sinfelt did not consider the possibility of the hydrogenating desorption of an adsorbed C_1 radical (step 4) being rate determining on most metals, seems very questionable to us. Indeed Anderson and Baker (*7*) concluded that on Ni, W, Rh, methane desorption was rate controlling. This same hypothesis, though considered as unlikely, was not excluded in recent work on Pt (*18*) and Cu/Ni (*2*) alloys. Furthermore, studies by some of us of the interaction of the CH_4–H_2 system with metal films suggest the step leading to gaseous methane formation to be rate determining for CH_4–D_2 multiple exchange (*11*). Therefore, we consider methane formation as a possible rate controlling step of ethane hydrogenolysis.

In order to test this hypothesis, the respective rates of ethane hydrogenolysis and of methane–deuterium exchange on the same metal are to be compared. In every case where the CH_4–D_2 exchange rate is lower or nearly equal to the hydrogenolysis rate, our hypothesis is plausible.

Comparison between rates is quite difficult. Indeed, specific surface areas of catalysts—particularly when metal films are used—are not well known, catalyst activity may be different from sample to sample (*8*), hydrogenolysis and exchange are generally studied in very different pressure ranges and reaction orders are not always determined. Thus, the best we can do is to compare the temperature ranges where the experimental studies are conducted, admitting that a temperature range defines the catalytic activity. This comparison, also including ethane-deuterium exchange results, is given in Table 1. Nevertheless, it is possible, in a few particular cases, to compare directly the C_2H_6 hydrogenolysis and CH_4–D_2 exchange rates at a given temperature and at the same hydrogen and hydrocarbon pressures. This

can be done, using the values of activation energies, of preexponential terms and of reaction orders indicated in the author's papers, whenever the calculation of the rate, at the comparison conditions of temperature and pressure, do not involve a too large extrapolation with respect to the original standard operating conditions. Furthermore, comparison is limited to the same type of catalyst, i.e., results on films are not compared with results on powder catalysts; see Table 2. Examination of both Tables 1 and 2 lead to the following remarks:

a. Ethane-deuterium exchange always takes place at temperatures far lower than hydrogenolysis, except in presence of Fe and Co;

b. Rates of methane-deuterium exchange and of hydrogenolysis are very similar in the presence of W, Ni, Rh, Ru, Re and Pd, hydrogenolysis being slightly slower on Ni, Re, Pd, and slightly faster on W, Rh and Ru;

c. Methane-deuterium exchange is much slower than hydrogenolysis on Fe, Co, Cu, where methane chemisorption is very slow (*19, 20*) or even is not observed at all (Cu) (*12*);

d. On platinum, hydrogenolysis is much slower than methane-deuterium exchange.

As a first conclusion, the formation of gaseous methane is a plausible rate determining step of hydrogenolysis on Rh, W, Ru, Ni, Pd, Re, and more particularly on the three first cited metals. Contrary to Sinfelt's assumption, we think that the rate controlling step is not identical on all metals on which the dependence of hydrogenolysis rate with respect to hydrogen is negative, since the chemical properties of these metals are known to be very different.

Several other arguments support our hypothesis of gaseous methane formation being the rate controlling step of the hydrogenolysis. As already suggested by Anderson (*21*), this hypothesis allows for an easy explanation of the following experimental observations: the slowing down of the rate of C_2H_6–D_2 exchange on Ni, under conditions where hydrogenolysis is effectively taking place (*8*) and the fact

TABLE 1

TEMPERATURE RANGES WHERE EXPERIMENTAL STUDIES OF ETHANE HYDROGENOLYSIS, ETHANE- AND METHANE-DEUTERIUM EXCHANGES ARE PERFORMED

Nature of the metal: —ᵃ		C_2H_6 hydrogenolysis on:				C_2H_6/D_2 exchange on metal^c			CH_4/D_2 exchange on:					
		Powdered metals		Metal films					Metal films			Powdered metals		
		Temp range (°C)	Ref.	Temp range (°C)	Ref.	—^{b}	Temp range (°C)	Ref.	b	Temp range (°C)	Ref.	—^{a,b}	Temp range (°C)	Ref.
Ni	P	174–328	(8)			M	174–328 (4)	(8)	M	230–310	(2)			
	S	177–219	(1)	254–273	(7)	M ≅ S	162–195 (5)	(15)		260–290	(12)	P	208–260	(8)
	K	181–214	(6)	315–340	(2)	S	0–75 (6)	(15)	S	206–255	(28)	P	221–256	(27)
Ru	S	160–190	(25)											
	S	177–210	(1)				0–50	(15)	M	120–190	(12, 13)	P M	119–203	(29, 30)
Rh	S	190–224	(1)	152–162	(7)	M	0–70	(15)	M	138–217	(16)	P M	27–156	(32, 33)
Co	C	272–317	(5)				>300 (7)	(15)						
	S	219–259	(1)				183 (8)	(26)				T S	183	(26)

Metal	Support	Hydrogenolysis T-range (ref)	Exchange (ref)	Exchange (ref)	Exchange (ref)
Re	S	229–265 (1)	>370 (9)	S M 130–212 (12)	
Fe	S	239–376 (1)		>420 (16)	
Cu	S	288–330 (1)		>700 (12)	
Pt	S	313–343 (7) 274–343 (4) 330–360 (3)	M S 134–192 (15)	S M 159–275 (16) M ≅200 (12)	P S 83–139 (32)(33)
Pd	S	273–358 (1)	M 145–207 (15)	S 243–308 (16)	P S 96–189 (29–32)
W		173–183 (7)	S (−80)–(−29) (15)	S 92–174 (16) S 150–200 (12)	

[a] P: Pure metal powder; S: silica supported; C: carbon supported; K: kieselguhr supported; T: thoria supported.

[b] Type of exchange: M: multiple exchange (main product C_2D_6 or CD_4); S: single exchange (main product C_2H_5D or CH_3D).

[c] Except when indicated by a note, all results on metal films.

[d] Pure metal powder.

[e] High temperature film.

[f] Low temperature film.

[g] Simultaneous cracking and exchange.

[h] Thoria supported.

[i] Only cracking is observed.

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TABLE 2
COMPARISON OF THE ETHANE HYDROGENOLYSIS AND METHANE DEUTERIUM
EXCHANGE RATES ON DIFFERENT METALS

Nature and form of the metal:	Hydrocarbon pressure (Torr)	H_2 pressure (Torr)	Temp (°C)	Hydrogenolysis rate (mol cm^{-2} sec^{-1} × 10^{-13})	Exchange rate (molecules cm^{-2} sec^{-1} × 10^{-13})	
					Multiple	Single
Rh (film)	3.7	44.5	158	2.0[a]	0.11[b]	0.04[b]
Rh (powder)	80	40	177	1.36[c]	0.49[d]	0.13[d]
W (film)	3.7	44.5	177	1.23[a]	0.05[b]	0.15[b]
Ru (powder)	80	40	177	5.77[c]	0.17[d]	0.07[d]
Ni (film)	0.75	9	307	1.28[e]	2.82[e]	
Ni (film)	3.7	44.5	257	0.08[a]	0.13[b]	0.05[b]
Pd (film)	3.7	44.5	277	0.11[a]	0.33[b]	5.0[b]
Pt (film)	3.7	44.5	277	0.04[a]	19.9[b]	70.9[b]

[a] From Anderson's work [Refs. (4, 7)]; standard operating conditions: 3.7 Torr hydrocarbon; 44.5 Torr H_2.

[b] From Kemball's work [Ref. (16)]; standard operating conditions: 6.45 Torr hydrocarbon; 6.45 Torr H_2.

[c] From Sinfelt's work [Ref. (1)]; standard operating conditions: 22.8 Torr hydrocarbon; 152 Torr H_2.

[d] From MacKee's work [Refs. (29–33)]; standard operating conditions: 80 Torr hydrocarbon and 40 Torr H_2.

[e] From Clarke and Plunkett's work [Ref. (2)]; type of exchange not indicated; standard operating conditions: 0.75 Torr hydrocarbon; 9 Torr H_2.

that on Fe, when raising temperature, only hydrogenolysis is observed, but no ethane–deuterium exchange (15). Indeed, if it is admitted that methane desorption is rate determining in the hydrogenolysis, the most abundant surface intermediate must be a C_1 adsorbed radical; the concentration of C_2 adsorbed radicals resulting from ethane chemisorption, which constitute the active intermediate in the C_2H_6–D_2 exchange, must then be very weak.

The latter analysis may also explain the independence of the rate of hydrogenolysis upon the methane pressure mentioned in Tetenyi's paper (8). Indeed, the surface coverage in C_1 adsorbed radicals, as resulting from ethane chemisorption, may be so high that it has never been realized during methane chemisorption: it must then correspond, following Kemball, to a methane "virtual" pressure much higher, by a factor that may reach 10^6 (23), than the pressure of reacting ethane. It is then quite normal that a pressure of a few Torr of methane has no influence on the hydrogenolysis rate.

It results also from this concept of "virtual" pressure that a perfect correlation between methane exchange and hydrogenolysis rates is not necessary. The rate

controlling step of hydrogenolysis may be methane desorption even if the hydrogenolysis rate is much higher than the methane exchange rate in the same temperature and pressure conditions.

Another comment concerns the hydrogen content X of the adsorbed intermediate C_2H_X, that must be zero on metals such as Pd, Pt, Rh where the order with respect to hydrogen is highly negative (1, 9). Sinfelt's statement: "this conclusion does not conflict with known facts" (1b) may be questioned. It seems to us very improbable that C_2 adsorbed radicals totally devoid of hydrogen could be in equilibrium with gaseous ethane and that they could act as reaction intermediates. Kemball (24) also argued against the existence of more hydrogenated species such as C_2H_2 and C_2H_3 in fast equilibrium with the gaseous phase. It is interesting to note that the metals for which a very low, sometimes zero, value of X (in C_2H_X) is postulated, are effectively (except for Pt) those for which our assumption of a rate determining step being the gaseous methane formation, is the more likely to hold and consequently Sinfelt's kinetic analysis the more questionable.

In a recent attempt to improve the

Cimino, Boudart and Taylor (10) mechanism, Boudart (22) proposes a new analysis of ethane hydrogenolysis. This analysis takes competition for the surface by hydrogen into account, but in very particular way, by introducing two types of surface sites (22). It then follows that the value of X (in C_2H_X) may reach a maximum value of 2 in the cases of doubtful zero value in the Sinfelt analysis. Furthermore, the formalism remains unchanged whether the most abundant surface intermediate is a C_1 or a C_2 adsorbed radical (34). Making the mechanism more complex, as by introducing two types of sites, will often make the situation more reasonable.

We think that the sole kinetic measurements of the global reaction, even if they are carried out in a very large range of well-defined conditions, cannot provide enough information to elucidate the mechanism. Therefore, our aim here is not to give a new complete treatment of the mechanism of ethane hydrogenolysis. Lack of available experimental data, particularly on the composition of chemisorbed radicals and on elementary steps at the surface under the conditions of catalytic reaction do not allow us to go further than simple comparisons like those made in the present paper.

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