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F. Zaera and G.A. Somorjai

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The Reaction of Ethane with Deuterium over Platinum (111) Single Crystal Surfaces.

by F. Zaera and G.A. Somorjai

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ABSTRACT

Deuterium exchange and hydrogenolysis of ethane were studied over (111) platinum surfaces under atmospheric pressures and a temperature range of 475-625K. Activation energies of 19 Kcal/mole for exchange and 34 Kcal/mole for hydrogenolysis were obtained. The exchange reaction rates displayed kinetic orders with respect to deuterium and ethane partial pressures of -0.55 and 1.2, respectively. The exchange product distribution was U-shaped, peaking at one and six deuterium atoms per ethane molecule, similar to results reported for other forms of platinum, e.g., supported, films, and foils. The presence of ethylidyne moieties on the surface was inferred from low energy electron diffraction and thermal desorption spectroscopy. A mechanism is proposed to explain the experimental results, in which ethylidyne constitutes an intermediate in one of two competitive pathways.
INTRODUCTION

The development of apparatuses in which samples can be transferred from Ultra High Vacuum (UHV) to high pressure reactors and back without exposure to air, together with the powerful tools of surface science, allows a more detailed examination of the mechanism of catalytic surface reactions. We have recently reported a study of ethylene hydrogenation over Pt (111) single crystal surfaces [1], where it was concluded that ethylidyne (a hydrocarbon fragment which forms under UHV when ethylene is adsorbed at room temperature) is also present during high pressure reactions, covering the metallic surface. Since ethylidyne is stable in the presence of high pressure of H$_2$ below 350K, the hydrogenation of gas phase ethylene takes place on top of this first chemisorbed layer.

In this paper we report a similar study of the ethane deuterium exchange reaction. An activation energy of 19 Kcal/mole was obtained, consistent with values reported previously on supported platinum, platinum films or foils [2-6]. Furthermore, a U-shaped product distribution was obtained, with maxima at one and six D atoms per ethane molecule, indicating the existence of two competitive exchange reactions. Low energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS) suggest the presence of ethylidyne fragments on the surface after these reactions. Since the initial step for exchange is the dissociative adsorption of ethane, the reaction requires temperatures above about 400K. Under these conditions ethylidyne moieties present during the high pressure reaction are readily rehydrogenated. We propose a mechanism for the exchange reaction in which initially adsorbed ethane either
desorbs immediately, yielding monodeuterated ethane, or undergo through sequential hydrogen exchange reactions involving ethylidyne as an intermediate, to finally produce fully deuterated ethane.

**EXPERIMENTAL**

All the experiments were carried out in a UHV/high pressure apparatus designed for combined UHV surface analysis and high pressure studies using small area catalyst samples, as described in detail in previous publications [7]. The system is equipped with standard instrumentation for performing LEED, Auger electron spectroscopy (AES), and TDS; and with a retractable cell that allows the catalyst sample to be isolated from UHV and inserted into a high pressure recirculation loop that can be operated up to 10 atm. for kinetic studies. Most of the experimental details have been described extensively in a previous paper [1]. A platinum single crystal, cut and polished in a (111) orientation, was used as the catalyst. The total area was about 1.5 cm², with less than 30% polycrystalline surface. Research purity ethane (Matheson, 99.96%), and deuterium (Matheson, >99.5% atomic purity) were used as supplied.

To carry out a reaction, the crystal was first cleaned until no impurities were detectable by AES. It was then inserted into the high pressure loop, and cooled to near room temperature in the presence of about 150 torr of D₂. The D₂ was evacuated, ethane and deuterium were introduced in that order to the desired pressures and circulated for 2-3 minutes to ensure adequate mixing, and finally the crystal was heated to the reaction temperature.
Methane formation was followed by gas chromatography, using a 6'xl/8" Chromosorb 104 column. The deuterium exchange was followed mass spectrometrically by leaking a small amount of the reactant mixture into the vacuum chamber. The product distribution was obtained by deconvoluting the data using the mass spectrum of each pure deuterated ethane, as reported in the literature [8]. These calculations proved to be fairly accurate [1], although the errors accumulate in the light alkane region of the distribution.

After reactions, the crystal was returned to UHV, where LEED patterns were photographed, and AES and H₂ and D₂ thermal desorption spectra were obtained in the usual manner.

RESULTS

Deuterium exchange and hydrogenolysis (to produce methane) of ethane were investigated over the close packed (111) platinum crystal surfaces at temperatures between 473 and 623K. The standard reaction conditions utilized pressures of 100 torr deuterium and 10 torr ethane, unless otherwise indicated. Typical product accumulation curves are shown in fig. 1 for both reactions. These curves are plotted using the total number of ethane molecules that underwent reaction as a function of time. As expected, deuterium exchange is more than three orders of magnitude faster than hydrogenolysis over the temperature range studied.

For hydrogenolysis, the initial reaction rates were determined from the slope at zero time from plots like the one shown in fig. 1. Due to the high conversions for exchange, the rates for those reactions were calculated
using first order kinetics for the disappearance of the light alkane \( (d_0) \). The reverse reactions, namely, the production of light alkane from deuterated ones, were neglected, since the equilibrium concentration of \( d_0 \) under our conditions is less than 0.02% of the total ethane (as calculated using the method described by Kemball [9]). The corresponding semilogarithmic plots are linear up to very high conversions, as can be seen in fig. 2, where the data from figure 1 has been replotted to obtain the reaction rate constant. The rates estimated using this procedure were within 20% of the values obtained in a similar way as for the hydrogenolysis (by taking the slope at \( t=0 \) from fig. 1). The first order kinetics is justified by the first order dependence of the reaction rates on ethane pressure, as will be reported later.

Arrhenius plots of the initial rates for both reactions are shown in fig. 3; they give activation energies of 19±2 Kcal/mole for deuterium exchange, and 34±1 Kcal/mole for hydrogenolysis. The dependence of exchange rates on reactant pressures was also studied; the data is summarized in table I. The rate is almost linearly dependent on the ethane partial pressure, and inversely proportional to the square root of the deuterium pressure. All the kinetic parameters obtained for the two reactions are displayed in table II.

The product distribution of the resulting ethane from deuterium exchange was followed mass spectrometrically. A typical distribution is shown in fig. 4. This distribution has an "U" shape, with maxima at one \( (d_1) \) and six \( (d_6) \), and a minimum at 3 \( (d_3) \), deuterium atoms per ethane molecule.
This distribution changes as a function of time of reaction and temperature, as can be seen from figs. 5 and 6. As the time of the reaction increases, $d_1$ increases while $d_2$ decreases, the other ethanes remaining approximately constant. This may be explained by exchange with the scrambled HD and H$_2$ formed and accumulated during reactions as byproducts. The effect of temperature is to decrease the production of totally deuterated ethane, and to increase $d_1$, $d_4$ and $d_5$ products, while $d_2$ and $d_3$ remain almost unchanged. The distribution is also slightly affected by changes in reactant pressures, as shown in table III.

LEED pictures of the platinum (111) surface were taken after each reaction. A very diffuse (2x2) pattern was obtained, the half order extra spots being sharper for reactions performed at lower temperatures. An example of these diffraction patterns is shown in fig. 7, together with one obtained after ethylidyne formation on platinum [10], for comparison.

The Auger spectra taken after reactions always indicated the presence of carbon on the surface. About half of these carbonaceous deposits were reversibly adsorbed, since they could be removed by flashing to high temperature in UHV. The ratio of carbon to platinum atoms, calculated from the Auger spectra taken after flashing, increases as a function of reaction temperature, from about 0.25 at 500K to 0.6 at 620K (fig. 8).

Hydrogen (2 amu) and deuterium (4 amu) TDS were also taken after reactions. Examples are shown in fig. 9. Both TDS exhibit three main peaks: the first one around 470K (A), due to hydrogen coadsorbed with
carbonaceous deposits produced during reactions, and two others at 530-550K (B) and above 640K (C). The shape and relative contribution of each peak to the total desorption does not change appreciably as a function of reaction temperature. However, total area and the hydrogen (or deuterium) to carbon ratio on the surface decrease when the reactions are performed at higher temperature. The (H+D)/C ratio changes from about 1.5 at T<500K, to 0.9 at 575K, where ethylidyne is used as a standard (H/C=1.5). The fact that the mass spectrometer is 1.7 times more sensitive to H₂ than to D₂ was also taken into account for the D/C calculations. A summary of the thermal desorption data is presented in table IV.

DISCUSSION

Ethane deuterium exchange on Pt (111) single crystal surfaces was found to have an activation energy of 19 Kcal/mole, and kinetic orders of -0.55 and 1.2 with respect to deuterium and ethane pressures, respectively. These values compare favorably with those obtained on films and supported catalysts (table V). In the case of hydrogenolysis, on the other hand, activation energies between 53 and 55 Kcal/mole have been reported (see, for instance, refs. 12-14), as compared to the value of 34 Kcal/mole obtained here on Pt (111). Still, since hydrogenolysis was about three orders of magnitude slower than exchange, it appears that the limiting step for carbon-carbon bond breaking is not the initial chemisorption of the saturated hydrocarbon [14]. Deuterium pressure dependences of -0.3 to -0.6 for ethane deuterium exchange were obtained on silica and cab-o-sil supported platinum [6], and are also consistent with our value of -0.55.
Where the product distribution has been studied, U-shaped curves similar to fig. 4 were obtained [2,3,5]. Anderson and Kemball [2] studied this reaction using different metal catalysts, obtaining three different product distribution shapes: a) predominantly ethane with one deuterium atom (d1) (Mo, Ta); b) mostly fully deuterated ethane (d6) (Pd, Rh); and c) maxima in the ethane distribution at both d1 and d6 (W, Zr, Cr, V, Pt). In order to explain these results, they propose the following mechanism for exchange:

\[
CH_3CH_3 (g) \overset{k_1}{\rightarrow} CH_2CH_3 \overset{k_2}{\rightarrow} CH_2CH_2
\]

where the asterisks identifies adsorption sites. They then propose the parameter P, defined as the probability for adsorbed C2H5 species to undergo through a C2H5 (ads) + C2H4 (ads) + C2H5 (ads) cycle, rather than directly desorbing and forming ethane (P=k2/k_1, if k_2 is fast). Using this scheme, a value of P<1 reproduces the type a product distribution, namely, a maximum at d1. P>1, on the other hand, accounts for the results for the second group (mainly production of d6). Finally, to obtain the U-shaped distribution characteristic of the third group, they postulate that two different mechanisms occur on different crystal faces with different values for P. To explain the distribution obtained for platinum it was necessary to propose that 54% of the products form via a reaction path with P1=2.0, and the other 46% from a second branch with P2=20.0.

The fact that a similar U-shaped product distribution was obtained on a flat hexagonal close packed platinum (111) crystal surface mediates.
against this argument. The partially ordered (2x2) overlayer observed by LEED after reactions indicates the presence of a short range periodicity, strongly suggesting the presence of only one main moiety on the surface (or at least a common intermediate) which leads to the formation of both d₁ and d₆ ethanes. If this hypothesis is valid, it is kinetically necessary to propose more than one dehydrogenated surface intermediate to reproduce the experimental product distribution. Miyahara [15] has offered an alternative kinetic model to account for the results by Anderson and Kemball, in which intermediates with 5,4 and 3 hydrogen atoms per surface moiety were postulated. The full kinetic treatment of this system successfully reproduced the U-shaped curve, but it was later questioned because the existence of adsorbed C₂H₃ fragments was thought unlikely [16].

However, recent surface studies have shown that such highly dehydrogenated intermediates are, in fact, stable and easy to obtain. Ethyldyne formation, for instance, is now well established. LEED [17,18], UPS, TDS [19], and HREELS [20] studies of chemisorbed ethylene on Pt and Rh (111) indicate the presence of a fragment of C₂H₃ stoichiometry, in which one carbon atom sits on a hollow site, bonding to three metal atoms, and the carbon-carbon bond is perpendicular to the surface so that the terminal carbon constitutes a methyl group. A schematic representation of this ethyldyne is shown in fig. 10. We also reported recently clear evidence showing the presence of this moiety during ethylene hydrogenation [1]. In such reactions the ethyldyne layer formed is too stable to be rehydrogenated, so that the gas phase ethylene hydrogenates on top of an ethyldyne covered platinum surface.
In the present case, the (2x2) LEED pattern obtained after reactions, together with the thermal desorption results, lead us to propose ethylidyne as a reaction intermediate for exchange as well. Unlike room temperature ethylene hydrogenation, H/D exchange reaction temperatures are much higher, around 500K, and $^{14}$C radiotracer experiments have shown that under these conditions those CCH$_3$ fragments can be easily rehydrogenated and removed from the surface [21]. However, the diffuse nature of the extra spots in the LEED pictures indicates some disorder, probably due to the presence of other species. For that reason, the TDS are not of unambiguous interpretation. Although the peaks in both H$_2$ and D$_2$ TDS are in the expected temperature ranges for ethylidyne [11], the relative areas are different. For instance, the high temperature peak in the D$_2$ trace is considerably bigger than expected. This could be explained by the presence of CD fragments on the platinum surface, product of some ethylidyne decomposition at the high reaction temperatures, as obtained in UHV chemisorption studies [11]. These fragments would then account for the production of methane, the end product of hydrogenolysis.

It is therefore suggested that in the case of exchange reactions, associative desorption of the C$_2$H$_5$ adsorbate formed during the initial adsorption of ethane with a surface deuterium atom would yield mainly d$_1$ products, while the formation and rehydrogenation of ethylidyne could account for the formation of fully deuterated molecules. The proposed mechanism could be described as follows:
\[ CX_3CX_3 (g) \xrightarrow{k_1} CX_3 \xrightarrow{k_2} CX_3 + X \xrightarrow{k_3} C + 3X \]

\[ CX_3 \xrightarrow{k_4} X \xrightarrow{+5X} 2C + X \xrightarrow{2CX_4 (g)} \]

where X can be either H or D. The limiting step for exchange would be given by \( k_1 \), while the shape of the final distribution would depend on the ratio \( k_2/k_1 \). \( k_3 \), \( k_2 \), and \( k_2 \) are postulated to be fast reactions.

For the \( d_6 \) production, once ethylidyne is formed, hydrogen exchange in the methyl group should be much more rapidly than ethylidyne rehydrogenation. The slow step for hydrogenolysis would be the carbon-carbon bond breaking, \( k_4 \). An energy diagram of the same mechanism is shown in fig. 11. It is analogous to one previously proposed for methane deuterium exchange [22], except that here the limiting step for the formation of both \( d_1 \) and \( d_6 \) is the same, namely, the dissociative adsorption of ethane. This also explains why methane \( d_4 \) and \( d_1 \) production have different activation energies, but ethane \( d_1 \) and \( d_6 \) pathways have the same value.

In the energy diagram presented in fig. 11, the initial dissociative chemisorption of ethane is the proposed limiting step for the exchange [4], and it has therefore an activation energy of 19 Kcal/mole. Also, the resulting \( C_2X_5 \) moiety (an ethyl radical) has to be less stable than ethane gas, since its desorption is faster than the adsorption. Once formed, this initial adsorbed specie can either rehydrogenate and form ethane again, or undergo further dehydrogenation. These are the two competitive pathways responsible for the U-shaped distribution of products, so the activation
barriers have to be of similar height. Using the temperature dependence data of the product distribution shown in fig. 6, it can be seen that the barrier for rehydrogenation should be slightly higher than that for multiple exchange, by about 2 Kcal/mole, because less d_6 is produced at higher temperatures. The relative energies of other adsorbed species can be estimated using values of $D_{298}^0(H-H)=104$ Kcal/mole [23], $E_{act}=17.5$ Kcal/mole for hydrogen desorption from Pt(111) [24], $\Delta H_f^0(C_2H_6)=-20$ Kcal/mole and $\Delta H_f^0(C_2H_2)=54$ Kcal/mole [25], and calculations reported by Gavezotti and Simonetta for the adsorbed hydrocarbons [26], giving:

\[
C_2H_6(g) + CHCH_3(ads) + 2H(ads) \quad \Delta H=29 \text{ Kcal/mole}
\]

and

\[
CHCH_3(ads) + CCH_3(ads) + H(ads) \quad \Delta H=9 \text{ Kcal/mole}
\]

Although the absolute values may not be accurate, the relative stabilities of the species involved have been used in the drawing of our diagram. The equilibrium between different adsorbates may also change as a function of hydrogen pressure. Thus, ethylidyne, which is very stable under UHV conditions, may hydrogenate under an atmosphere of H_2 to yield ethylenedene (CCHX_3), or further to ethyl radical (CX_2CX_3). The deuterium exchange in the methyl group of ethylidyne is assumed to go through an ethyldiene intermediate, as proposed previously by Salmeron et. al. [11], and must be faster than ethylidyne rehydrogenation. If this would not be the case, a large proportion of d_3 would be observed at low conversion, and this was not the case (no maximum in d_3 in fig. 5 was obtained).

It is important to point out that the intermediates proposed in the preceding paragraph for exchange are 1,1 and 1,1,1 adsorbed species, as
opposed to the 1,2 and 1,1,2 adsorption modes that have been previously reported. In other words, the multiadsorbed fragments bond to the metal through one of the carbon atoms only. These new species are well documented in chemisorption studies under UHV, as discussed earlier. Ethylidyne, that can be formed at room temperature, is triply bonded to the surface through one of the carbon atoms, and only at higher temperatures, above 450K, does it "tip over" and further decomposes to CH fragments [11,27]. These intermediates can also explain the thermal desorption results.

The large peak at 691K in the 4 amu trace corresponds to the CD fragments from ethylidyne decomposition, after having exchanged with D₂. They constitute the intermediates for methane formation, a reaction which is much slower than the exchange. It is worth noticing that the calculated activation energy from the high temperature peak in the TDS is 33 Kcal/mole [11], close to the value for hydrogenolysis over the (111) surface. It is also interesting that, according to our model, the mechanisms for ethane deuterium exchange and ethylene hydrogenation are not directly related, since in the latter case the ethylidyne is stable on the surface, while ethylene hydrogenates on a second layer through a hydrogen transfer process [1]. Finally, recent HREELS work in our group has shown that chemisorption of ethyl iodide over Pt(111) results in the formation of ethylidyne under UHV [28]. This means that once a C₂H₅ ethyl moiety is formed on the surface (product of the C-I bond breaking), further dehydrogenation of the α carbon is a facile process, easier than the formation of adsorbed ethylene over the same surface.

Further testing of the previously proposed ethane H/D exchange me-
chanism is difficult. The identification of adsorbed species on the platinum surface is complicated by the presence of different types of fragments. In addition to HREELS, $^{13}$C-NMR and high resolution mass spectroscopy [29, 30] have been used to attempt to obtain the exact position of the deuterium atoms in the ethane produced during reactions. This information could be related to surface intermediates, but no solid conclusions have been obtained in this respect. It is hoped that further studies will lead to more satisfactory results to give an insight to the details of the reaction mechanism.

In conclusion, we propose that the mechanism of ethane deuterium exchange proceeds through an initial slow step, the dissociative adsorption of ethane, followed by two competitive reaction branches: the immediate desorption of the $C_2H_5$ fragment formed from chemisorption, and the further dehydrogenation to form ethylidyne, $C_2H_3$, followed by hydrogen exchange in the methyl group and then desorption as a fully deuterated ethane molecule. Further experiments are under way in our laboratory to test this model. These two reaction channels explain the predominance of the single ($d_1$) and fully ($d_6$) deuterated ethane formation among the products of the exchange process.

ACKNOWLEDGEMENT

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REFERENCES


28) B. Bent and G.A. Somorjai, private communications.


FIGURE CAPTIONS

Fig. 1. Product accumulation curves as a function of reaction time for ethane deuterium exchange and hydrogenolysis over Pt (111) single crystal surfaces. T=573K, $P_{C_2H_6H} = 10$ torr and $P_D = 100$ torr.

Fig. 2. First order kinetic plot of the product accumulation curve for ethane deuterium exchange over Pt (111). Same conditions as in fig. 1.

Fig. 3. Arrhenius plots for ethane deuterium exchange and hydrogenolysis over Pt (111). $P_{C_2H_6} = 10$ torr and $P_D = 100$ torr.

Fig. 4. Deuterium atom distribution in the resulting ethane from the exchange with deuterium over Pt (111). Same pressures as in fig. 3, T=550K.

Fig. 5. Deuterium atom distribution of ethane as a function of reaction time for deuterium exchange over Pt (111). Same conditions as in fig. 4.

Fig. 6. Temperature dependence of the deuterium atom distribution in ethane deuterium exchange over Pt (111). Same conditions as in fig. 3.

Fig. 7. a) (2x2) LEED pattern resulting from the adsorption of ethylene on a Pt (111) surface at room temperature and UHV, b) diffuse (2x2) LEED pattern obtained after ethane reactions with deuterium over Pt (111) surfaces at 500-650K. Electron energy ~ 70 eV.

Fig. 8. Amount of carbon on the Pt (111) surface after ethane deuterium exchange as a function of reaction temperature, measured using Auger electron spectroscopy. Same conditions as in fig. 3.
Fig. 9. 2 amu (H₂, trace a) and 4 amu (D₂, trace b) thermal desorption spectra after ethane reactions with deuterium over Pt (111). Same conditions as in fig. 3. Heating rate 40 K/sec.

Fig. 10. Atomic surface structure for ethylidyne adsorbed over Pt (111) single crystal surfaces.

Fig. 11. Schematic energy diagram for the reaction of ethane with deuterium. X represents either H or D.
Table I

Pressure dependence of the initial reaction rates for ethane deuterium exchange over platinum (111) single crystal surfaces at 550K.

<table>
<thead>
<tr>
<th>$P_{C_2H_6}$ (torr)</th>
<th>$P_D$ (torr)</th>
<th>Rate ($C_2H_6$ molec./Pt atom sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>8.94</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>4.78</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>3.46</td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>10.96</td>
</tr>
</tbody>
</table>
Table II

Kinetic parameters for the reactions of ethane with deuterium over platinum (111) single crystals.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_a$ (Kcal/mole)</th>
<th>$\log A^a$</th>
<th>$a^b$</th>
<th>$b^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$ exchange</td>
<td>19.2</td>
<td>9.8 0.5</td>
<td>-0.55 0.05</td>
<td>1.2 0.2</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>34.1</td>
<td>11.2 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Preexponential factor, in molec/Pt atom sec. (Pressures in atm.).
b) orders in deuterium (a) and ethane (b) partial pressures.
c) includes pressure dependence, $P_{C,H} = 10$ torr, and $P_{D} = 100$ torr.
Table III

Pressure dependence of the deuterium atom distribution for ethane deuterium exchange over Pt (111) single crystal surfaces, T=550K

<table>
<thead>
<tr>
<th>$P_{C_2H_6}$ (torr)</th>
<th>$P_{D_2}$ (torr)</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$d_4$</th>
<th>$d_5$</th>
<th>$d_6$</th>
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</thead>
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<tr>
<td>10</td>
<td>100</td>
<td>29</td>
<td>10</td>
<td>1</td>
<td>4</td>
<td>11</td>
<td>46</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>27</td>
<td>14</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>27</td>
<td>14</td>
<td>4</td>
<td>4</td>
<td>7</td>
<td>44</td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>28</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>9</td>
<td>49</td>
</tr>
</tbody>
</table>
Table IV

Compilation of thermal desorption data obtained after ethane deuterium exchange reactions on Pt (111).

<table>
<thead>
<tr>
<th>m/e (molec.)</th>
<th>Peak A (^a)</th>
<th>Peak B (^a)</th>
<th>Peak C (^a)</th>
<th>Area(^b)</th>
<th>Area(^b)</th>
<th>Area(^b)</th>
<th>(E_a) (^c)</th>
<th>(E_a) (^c)</th>
<th>H or D/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (H(_2))</td>
<td>473</td>
<td>17</td>
<td>60</td>
<td>21.6</td>
<td>23</td>
<td>36.9</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>533</td>
<td>12</td>
<td>64</td>
<td>22.7</td>
<td>24</td>
<td>36.6</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>548</td>
<td>19</td>
<td>56</td>
<td>21.9</td>
<td>25</td>
<td>37.1</td>
<td>0.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>22</td>
<td>54</td>
<td>21.9</td>
<td>24</td>
<td>36.9</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>18</td>
<td>59</td>
<td>22</td>
<td>24</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (D(_2))</td>
<td>513</td>
<td>9</td>
<td>46</td>
<td>22.2</td>
<td>45</td>
<td>39.8</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>548</td>
<td>13</td>
<td>41</td>
<td>22.7</td>
<td>46</td>
<td>40.4</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>9</td>
<td>42</td>
<td>22.2</td>
<td>49</td>
<td>40.4</td>
<td>0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>10</td>
<td>43</td>
<td>22</td>
<td>47</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Peak A at 470K, peak B at 540K, peak C above 640K.
b) Reaction temperature, in K.
c) Activation energy, in Kcal/mole, assuming first order desorption kinetics, and \(=2\times10^9\) for peak B and \(=10^{13}\) for peak C, as for ethylidyne [11].
Table V

Comparison of ethylene deuterium exchange kinetic parameters for different platinum catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( E_a ) (Kcal/mole)</th>
<th>( \log A^a )</th>
<th>( M^D )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt film</td>
<td>12.5</td>
<td>4.32</td>
<td>3.5 (415K)</td>
<td>2</td>
</tr>
<tr>
<td>Pt black</td>
<td>19.0</td>
<td>7.03</td>
<td>2.6 (373-413K)</td>
<td>3</td>
</tr>
<tr>
<td>Pt powder</td>
<td>18.9</td>
<td>3.18</td>
<td>1.7 (377K)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.7 (551K)</td>
<td></td>
</tr>
<tr>
<td>Pt film</td>
<td>26.2</td>
<td>7.82</td>
<td>2.12 (573K)</td>
<td>5</td>
</tr>
<tr>
<td>1% Pt/SiO(_2)</td>
<td>17.7</td>
<td>7.07</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>1% Pt/Cab-O-Sil</td>
<td>17.1</td>
<td>5.26</td>
<td>—</td>
<td>6</td>
</tr>
<tr>
<td>Pt (111)</td>
<td>19</td>
<td>9.8</td>
<td>3.74 (523K)</td>
<td>our</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.30 (573K)</td>
<td>work</td>
</tr>
</tbody>
</table>

a) Preexponential factor, including pressures, in \( \text{C}_2\text{H}_6 \) molec./Pt atom sec.

b) Average number of deuterium atoms incorporated per ethane molecule.
Pt (III)  
$P_{C_2H_6} = 10$ Torr  
$P_{D_2} = 100$ Torr  
$T = 573$ K  

Deuterium exchange  

Hydrogenolysis  

Fig. 1
Pt(III), Ethane deuterium exchange

\[ P_{C_2H_6} = 10 \text{ Torr} \]
\[ P_{D_2} = 100 \text{ Torr} \]
\[ T = 573 \text{ K} \]

Slope = 0.0329 min\(^{-1}\)

Fig. 2
Deuterium exchange
$E_a = 19 \text{ Kcal/mole}$
($\pm 2$)

Hydrogenolysis
$E_a = 34.4 \text{ Kcal/mole}$
($\pm 0.8$)

Pt(III)
$P_{C_2H_6} = 10 \text{ Torr}$
$P_{D_2} = 100 \text{ Torr}$

Fig. 3
Pt (III) Ethane deuterium exchange

\[ P_{C_2H_6} = 10 \text{ Torr} \]
\[ P_{D_2} = 100 \text{ Torr} \]
\[ T = 550 \text{ K} \]

Composition of Products (%)

57.6% total conversion

Number of Deuterium Atoms / C\textsubscript{2}H\textsubscript{6} molecule

XBL835-5647

Fig. 4
Pt (III) Ethane deuterium exchange

$P_{C_2H_6} = 10$ Torr
$P_{D_2} = 100$ Torr
$T = 550$ K

% Total Conversion
17 32 43 52 58

Composition of Products (%)

Time (min)

Fig. 5
Pt (III)
Ethane deuterium exchange
\( P_{C_2H_6} = 10 \text{ Torr} \)
\( P_{D_2} = 100 \text{ Torr} \)

Composition of Products (%) vs. \( T \) (K)

Fig. 6
Pt (111) Ethane deuterium exchange

$P_{C_2H_6} = 10 \text{ Torr}$

$P_{D_2} = 100 \text{ Torr}$

Fig. 8
Pt (III)
Thermal desorption after ethane deuterium exchange

\[ P_{C_2H_6} = 10 \text{ Torr} \]
\[ P_{D_2} = 100 \text{ Torr} \]
\[ T = 550 \text{ K} \]

Fig. 9
Pt (III) + ethylidyne

Fig. 10
Fig. 11
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