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THE EXCHANGE REACTION BETWEEN ETHANE AND DEUTERIUM ON EVAPORATED METAL FILMS

Comments on MIYAHARA’s Theory

By

Charles KEMBALL. (*)

(Received February 11, 1957)

Introduction

MIYAHARA has recently suggested a new explanation to account for the experimental observations of the initial relative abundances of different deutero-ethanes obtained by ANDERSON and KEMBALL in investigating the exchange reaction between ethane and deuterium on various metallic catalysts. He postulated that the dissociation of ethane leads not only to adsorbed $\text{C}_2\text{H}_4$ radicals and adsorbed $\text{C}_2\text{H}_2$ molecules as suggested by ANDERSON and KEMBALL, but also to adsorbed $\text{C}_2\text{H}_6$ radicals and to adsorbed $\text{C}_2\text{H}_4$ molecules. While MIYAHARA’s theory gives excellent agreement with the experimental observations, there are reasons to doubt some of the assumptions on which it is based and this may mean that the theory is not valid. The purpose of this note is to discuss some of the concepts assumed by MIYAHARA.

1. The Likelihood of Existence of Adsorbed $\text{C}_2\text{H}_6$ Radicals and Adsorbed $\text{C}_2\text{H}_4$ Molecules in the Presence of Gaseous $\text{C}_2\text{H}_4$ and $\text{H}_2$

Although there is not sufficient evidence about the strengths of adsorption of ethane, ethylene and acetylene, particularly under the conditions used in catalytic experiments, to make accurate assessments of the surface covered by these molecules, valuable information can be derived from the equilibrium constants for reactions involving these molecules. The important equilibria are

$$2\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_6 + \text{C}_2\text{H}_2 \quad (1)$$

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The Exchange Reaction Between Ethane and Deuterium on Evaporated Metal Films

\[ \text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2 \]  \hspace{1cm} (2)  

\[ \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2 \]  \hspace{1cm} (3)  

and the equilibrium constants can be calculated from available data.\(^3\)

We shall consider figures for the temperature 300\(^\circ\)K which is in the middle of the temperature range used in the catalytic experiments. At this temperature the equilibrium constants are \(1.05 \times 10^{-7}\), \(2.3 \times 10^{-22}\) mm and \(2.2 \times 10^{-15}\) mm of Hg, respectively. Only two of these equilibria are independent and consequently once any two of them have been established, the third is automatically established.

The resulting gas pressures after the establishment of one or more of these equilibria are indicated in Table I for different initial mixtures. Using these figures and making assumptions about the relative strengths of the adsorption of the three substances ethane, ethylene and acetylene, it is possible to estimate the relative fractions of the catalytic surface that will be covered by these molecules. Suppose that the relative strengths of adsorption are

\[ \text{C}_2\text{H}_6 : \text{C}_2\text{H}_4 : \text{C}_2\text{H}_2 = 1 : 10^{15} : 10^{10} \]

corresponding to differences in the free energy of adsorption of \(RT \ln 10^{15} = 20.6\) kcal/mole at 300\(^\circ\)K. Consequently the surface would be almost entirely covered with acetylene in Cases I(a) and (b) and with ethylene in Case II(a). For Case II(b) there would be approximately equal coverages of ethylene and acetylene and in Cases III(a) and (b) approximately one-tenth coverage of ethylene compared with the coverage of ethane and negligible coverage of acetylene. The

**Table I.** Examples of equilibria involving ethane, ethylene, acetylene and hydrogen at 300\(^\circ\)K

<table>
<thead>
<tr>
<th>Initial mixture</th>
<th>Equilibria established</th>
<th>Gas pressures (mm) resulting</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{C}_2\text{H}_6)</td>
</tr>
<tr>
<td>Case I (a)</td>
<td>10 mm (\text{C}_2\text{H}_6)</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>(1), (2) &amp; (3)</td>
</tr>
<tr>
<td>II (a)</td>
<td>{10 mm (\text{C}_2\text{H}_4) + }</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>(1), (2), &amp; (3)</td>
</tr>
<tr>
<td>II (b)</td>
<td>{10 mm (\text{H}_2)}</td>
<td>(3)</td>
</tr>
<tr>
<td>III (a)</td>
<td>{3 mm (\text{C}_2\text{H}_6) + }</td>
<td>(3)</td>
</tr>
<tr>
<td>III (b)</td>
<td>{24 mm (\text{H}_2)}</td>
<td>(1), (2), &amp; (3)</td>
</tr>
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</table>

--- 223 ---
experimental observations of the formation of "acetylenic complexes" on catalyst surfaces obtained by BEECK and more recently by JENKINS and RIDEAL were obtained using ethylene alone and would correspond to Cases I (a) and (b). Once hydrogen is added to the initial mixture the likelihood of finding acetylene adsorbed on the surface must decrease substantially (Cases II (a) and (b)) and a further substantial decrease must occur when excess hydrogen is present (Cases III (a) and (b)). These conclusions about the comparative amounts of adsorbed acetylene present in the three cases will be true whatever values for the relative strengths of adsorption are assumed. The mixture specified for Cases III (a) and (b) corresponds closely to that used by ANDERSON and KEMBALL, and it is clear that appreciable amounts of adsorbed acetylene could only be formed under these conditions if the adsorption of acetylene was $10^n$ times as great as the adsorption of ethylene and $10^m$ times as great as the adsorption of ethane.

It is not possible to make detailed calculations about the possibility of existence of adsorbed $\text{C}_2\text{H}_2$ radicals but the amount of these must decrease in the order Case I > Case II > Case III because the gas mixture is in hydrogen the more the equilibria on the surface will be shifted towards the more fully hydrogenated $\text{C}_5$ entities.

Increase of temperature would favour the formation of the less stable substances such as ethylene and acetylene in the gas phase but this effect would be largely, if not completely, counterbalanced by the decrease in the relative strength of adsorption of these more strongly adsorbed molecules.

2. The Rate of Reaction of Adsorbed $\text{C}_2\text{H}_2$ Radicals and Adsorbed $\text{C}_2\text{H}_4$ Molecules

JENKINS and RIDEAL have shown that the rate at which "acetylenic complexes" are rehydrogenated is very much slower than the usual rate observed for the hydrogenation of ethylene. It, therefore, seems unlikely that such entities as adsorbed $\text{C}_2\text{H}_2$ radicals and adsorbed $\text{C}_2\text{H}_4$ molecules, even if present on the surface, will play any part in the hydrogenation of ethylene of the exchange of ethane with deuterium where the more reactive entities $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_5$ are present on the surface. In this connection, it is important to note that KEMBALL assumed that no part was played by any adsorbed species of lower state of hydrogenation than $\text{C}_2\text{H}_4$ in the deuteration and exchange of ethylene.
Since there must be substantially lower quantities of these highly
dissociated species under the hydrogen-rich conditions used in the
exchange of ethane it follows that it is most unlikely these entities
can react sufficiently rapidly to play any part in the mechanism of
the exchange reaction.

Miyahara assumes that the rate at which the interconversion of
C₂H₆ and C₂H₅ takes place is so rapid that the relative amounts of
C₂H₅, C₂H₆D, C₂HD₂ and C₂D₃ can be assumed to be in isotopic equi-
librium. Admittedly, there is no evidence against this assumption but
it should be realised that the success of Miyahara's theory for ex-
plaining distributions rich in both d₁-ethane and d₆-ethane is largely
due to this assumption.

3. The Neglect of Differences in Activity of
Different Crystal Faces

The results obtained by Anderson and Kemball on non-oriented
and oriented nickel films showed clearly that substantially different
initial distributions of products were formed by different crystal faces.
It was, therefore, justifiable to assume more than one value for the
single parameter required to evaluate distributions on their theory,
when dealing with results over non-oriented films. This parameter
was a measure of the extent of multiple exchange, i.e. the replace-
ment of two or more hydrogen atoms in one visit of an ethane molecule
to the catalyst, compared with the extent of simple exchange of one
hydrogen atom on each visit. The surprising feature of the results
obtained by Anderson and Kemball was not that it was necessary to
assume that two parts of the catalyst were acting with different para-
meters but than a single parameter was sufficient to account for the
observed distributions on metals such as molybdenum, tantalum, rho-
dium and palladium. Presumably, in these cases either the activity
was mainly confined to one crystal face or different crystal faces
were operating with parameters which were sufficiently close for the
total distributions to be described adequately by a mean value of the
parameter. Miyahara's theory requires the choice of three parameters
in all cases and makes no allowance for the proved differences be-
tween the types of reaction on different crystal faces.
4. The Slowest Step in the Exchange Reaction

MIYAHARA's theory gives results which indicate that the dissociative adsorption of hydrogen is the slowest step in the exchange reaction on tungsten, molybdenum and tantalum. It is well-known that tungsten is an extremely efficient catalyst for the hydrogen-deuterium exchange reaction and consequently the adsorption of hydrogen could only be the slowest step if the ethane were very strongly adsorbed and occupied most of the surface. The kinetic results obtained by ANDERSON and KEMBALL showed that ethane was only adsorbed to a moderate extent and not sufficiently strongly to inhibit the reaction.

Conclusion

The careful examination of initial product distributions obtained in catalytic exchange experiments by the appropriate theoretical treatment can undoubtedly lead to valuable information about the nature and reactivity of adsorbed radicals. It is inevitable that such theoretical treatment should involve a fair degree of mathematical complexity and consequently it is important that the chemical concepts upon which the theory is based should be carefully examined. If this is not done it is possible to obtain good agreement with the experimental observations even although the concepts of the theory are unsound because of the complexity of the mathematics and the number of arbitrary constants which have to be selected. For the reasons given above, there are a number of features of MIYAHARA'S theory which make it less acceptable than that of ANDERSON and KEMBALL.

Summary

The theories of MIYAHARA and ANDERSON and KEMBALL to account for the initial relative abundances of deuterio-ethanes in the catalytic exchange of ethane with deuterium are examined. Evidence is given to show that it is unlikely that adsorbed C_2H_2 radicals or adsorbed C_2H_3 molecules play any part in this reaction. Other arguments against MIYAHARA'S theory are also discussed.
The Exchange Reaction Between Ethane and Deuterium on Evaporated Metal Films

References

1) MIYAHARA, this Journal 4, 148 (1956).
3) American Petroleum Institute, Research Project 44, National Bureau of Standards.
6) KEII, this Journal 3, 36 (1953).