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THE EXCHANGE REACTION BETWEEN ETHANE AND DEUTERIUM ON EVAPORATED METAL FILMS

Comments on MIYAHARA's Theory

By

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Introduction

MIYAHARA¹⁾ 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 KEMBALL²⁾ 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 C_2H_5 radicals and adsorbed C_2H_4 molecules as suggested by ANDERSON and KEMBALL, but also to adsorbed C_2H_3 radicals and to adsorbed C_2H_2 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 C_2H_3 Radicals and Adsorbed C_2H_2 Molecules in the Presence of Gaseous C_2H_6 and 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

$$2C_2H_4 \rightleftharpoons C_2H_6 + C_2H_2 \qquad (1)$$

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$$C_2H_4 \rightleftharpoons C_2H_2 + H_2 \tag{2}$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \tag{3}$$

and the equilibrium constants can be calculated from available data.[3)] We shall consider figures for the temperature 300°K which is in the middle of the temperature range used in the catalytic experiments. At this temperature the equilibrium constants are 1.05×10^{-7}, 2.3×10^{-22} mm and 2.2×10^{-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

$$\begin{array}{ccccc} C_2H_6 & : & C_2H_4 & : & C_2H_2 \\ 1 & : & 10^{15} & : & 10^{30} \end{array}$$

corresponding to differences in the free energy of adsorption of $RT \ln 10^{15} = 20.6$ kcal/mole at 300°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°K

	Initial mixture	Equilibria established	Gas pressures (mm) resulting			
			C_2H_6	C_2H_4	C_2H_2	H_2
Case I (a)	10 mm C_2H_4	(1)	3.2×10^{-3}	10.0	3.2×10^{-3}	—
" I (b)	"	(1), (2) & (3)	3.2×10^{-3}	10.0	3.2×10^{-3}	7×10^{-19}
" II (a)	10 mm C_2H_4 +	(2)	—	10.0	2.3×10^{-22}	10.0
" II (b)	10 mm H_2	(1), (2), & (3)	10.0	1.5×10^{-7}	2.3×10^{-22}	1.5×10^{-7}
" III (a)	3 mm C_2H_6 +	(3)	3.0	2.5×10^{-16}	—	24.0
" III (b)	24 mm H_2	(1), (2), & (3)	3.0	2.5×10^{-16}	2.4×10^{-39}	24.0

experimental observations of the formation of "acetylenic complexes" on catalyst surfaces obtained by BEECK[4)] and more recently by JENKINS and RIDEAL[5)] 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^{23} times as great as the adsorption of ethylene and 10^{39} times as great as the adsorption of ethane.

It is not possible to make detailed calculations about the possibility of existence of adsorbed C_2H_3 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 C_2 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 C_2H_3 Radicals and Adsorbed C_2H_2 Molecules

JENKINS and RIDEAL[5)] have shown that the rete at which "acetylenic comlexes" 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 C_2H_3 radicals and adsorbed C_2H_2 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 C_2H_4 and C_2H_5 are present on the surface. In this connection, it is important to note that KEH[6)] assumed that no part was played by any adsorbed species of lower state of hydrogenation than C_2H_4 in the deutertion 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 C_2H_3 and C_2H_2 takes place is so rapid that the relative amounts of C_2H_3, C_2H_2D, C_2HD_2 and C_2D_3 can be assumed to be in isotopic equilibrium. Admittedly, there is no evidece against this assumption but it should be realised that the success of MEYAHARA's theory for explaining distributions rich in both d_1-ethane and d_6-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 replacement 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 parameters but than a single parameter was sufficient to account for the observed distributions on metals such as molyddenum, tantalum, rhodium 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 between 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[1)] and ANDERSON and KEMBALL[2)] to account for the initial relative abundances of deutero-ethanes in the catalytic exchange of ethane with deuterium are examined. Evidence is given to show that it is unlikely that adsorbed C_2H_3 radials or adsorbed C_2H_2 molecules play any part in this reaction. Other arguments against MIYAHARA's theory are also discussed.

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