DISSOCIATIVE ADSORPTION OF METHANE AND ETHANE ON EVAPORATED METAL FILMS

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The adsorption of methane and ethane on evaporated metal films has been investigated. Observations were made at 0-100°C for both gases on tungsten and for ethane on nickel; for these systems the initial adsorption required no activation energy. Higher temperatures were necessary to adsorb methane on nickel (140°) and iron (170°) and ethane on iron (70°), because the initial adsorptions required activation.

The adsorption of the hydrocarbons usually led to the formation of gaseous hydrogen especially at the higher temperatures. Analysis of the gas phase by means of a Pirani gauge enabled the gross composition of the adsorbed phase to be determined as CH_n or C_2H_n . In some cases remarkably low values of *n* were observed after about 3 h. Typical compositions were CH_2 at 100°C and C_2H_2 at 90°C on tungsten, CH_{0-1} on nickel and CH_2 on iron at 200°C.

The rate of liberation of hydrogen to the gas phase was followed and activation energies for this process determined. The rate-determining step appeared to be the breakdown of the adsorbed radicals and not the desorption of hydrogen.

There have been a number of observations on the chemisorption of methane and ethane on metals but there has been a need for careful and detailed work particularly on the kinetics of the processes involved. Kubokawa¹ showed that the adsorption of methane occurred on a reduced nickel oxide catalyst at 140°C requiring an activation energy of 7 kcal/mole. The gas obtained on desorbing was at first almost pure methane but it contained increasing amounts of hydrogen up to nearly 100 % as the desorption was continued. Troesch^{2, 3} followed the adsorption of methane on a commercial-type catalyst Ni: Mn: Al: kieselguhr, 16:3:1:12. Adsorption began at 100°C and the activation energy was 17 kcal/ mole. Analysis of the gas phase by means of a Pirani gauge showed that between 140° and 200°C the partial pressures ³ of hydrogen and methane attained after 2-3 days corresponded to the establishment of the equilibrium

$$CH_{4(g)} \rightleftharpoons C_{graphite} + 2H_{2(g)}$$

The catalyst adsorbed much less methane than it would hydrogen.

Since the present work was completed, Trapnell ⁴ has reported on the adsorption of methane and ethane on evaporated films of a large number of metals at temperatures between -78° and 70° C. Although he did not make detailed analyses of the gas phase nor study the kinetics of the process, he was able to estimate the hydrogen liberated from ethane by freezing out the latter. This method was not possible with methane but the quantity of hydrogen liberated was thought to be small because the total pressure did not rise. An estimate of the fraction of the surface left bare after the hydrocarbon had been adsorbed was found by measuring the amount of oxygen or hydrogen which could still be adsorbed at -195° C.

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Trapnell found a liberation of hydrogen from ethane on tungsten, molybdenum and tantalum. There was a considerable non-activated adsorption of methane on tungsten and except on the ferromagnetic metals the initial activation energy of chemisorption for both gases was low.

It was clear that more information was required about the kinetics of the adsorption of these simple hydrocarbons on clean metals and in particular about the kinetics of the liberation of hydrogen resulting from the adsorption. It was decided, therefore, to measure the composition of the gas phase with time at a series of temperatures and thereby to obtain information about the changes in the nature of the adsorbed hydrocarbon on the three metals tungsten, nickel and A further reason for endeavouring to learn more about the adsorbed iron. radicals formed by the hydrocarbons was to check the conclusions which have been drawn from observations on the catalytic exchange of the hydrocarbons with deuterium. The methane-deuterium exchange 5, 6, 7 has been shown to occur by two reactions-the first, forming CH3D and believed to involve adsorbed methyl radicals and the second, forming mainly CD₄ and probably involving adsorbed methylene, methine or carbon. Deuterium exchange occurs at much lower temperatures for ethane ⁴ than for methane and is believed to involve adsorbed ethyl radicals and adsorbed ethylene molecules. Iron was included in the present investigation in order to see if there were obvious differences between the adsorption of the gases on it and on tungsten or nickel which might account for the inactivity of iron as a catalyst for the deuterium-hydrocarbon exchange reactions.

A brief report on this work was presented to the 2nd International Congress of Surface Activity.⁴

EXPERIMENTAL

The final form of the apparatus is shown in fig. 1a and 1b. The trap C, maintained at -78° C, prevented mercury and stopcock grease from reaching the reaction vessel RV. Between experiments, the reaction vessel was cut off at L, cleaned and re-assembled. Part of the experimental work was carried out using an adsorption vessel attached by a water-cooled ground joint at L but in each of the systems examined in this apparatus a blank run was carried out to check that no decomposition of the stopcock grease was occurring on the metal.⁹ The leads W were made of 1-mm diam. tungsten wire and the filament S of the metal to be evaporated was joined to the leads by the iron connectors J. Samples amounting to about half the total gas present were compressed into the micro-Pirani gauge ¹⁰, ¹¹ P (fig. 1b) to a fixed pressure in the range of 20 to 50 mm. After analysis, the sample was returned to the system through the tap T and mixing was achieved by raising and lowering the mercury in the McLeod gauge with the tap T open. The resistance of the Pirani was measured by a normal bridge circuit to which a potential of $2\cdot 500 \pm 0\cdot 005 \ V$ was applied. At pressures above 10 mm the resistance varied little with pressure especially for the two hydrocarbons. Typical values for the resistances with the three gases were 19 (H₂), 21 (CH₄) and 22 ohms (C_2H_6). Calibration curves for methane + hydrogen and ethane + hydrogen mixtures were obtained and these were used for analyses of the gas phase in the adsorption experiments. An attempt to operate the gauge at 10^{-2} to 10^{-1} mm failed because identical resistances were found for methane and hydrogen.

Methane and ethane were obtained from cylinders and further purified by distillation between liquid nitrogen traps. Hydrogen was purified by diffusion through palladium.

The volumes of the various parts of the apparatus were found by expanding hydrogen from a standard volume attached to the vacuum line. Evaporated films of the metals were prepared by the methods of Beeck, Smith and Wheeler,¹² and Kemball ¹³ with the reaction vessel maintained at 0°C. In each experiment a known quantity of methane or ethane was admitted to the adsorption system shortly after the film had been prepared and the system was then isolated from the rest of the apparatus. The reaction vessel was heated by a furnace and by appropriate calibrations it was possible to convert all measured pressures to equivalent pressures corresponding to the reaction vessel at 0°C. It was usual to analyze the composition of the gas phase at 15-min intervals for 1 h and then at 30-min intervals for a further 2 h.

At each stage it was possible to find the total number of carbon atoms adsorbed on

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the surface and the gross composition of the surface phase. For methane the latter was expressed as CH_n where n is given by

$$n = 4 - \frac{2p_{\rm H_2}}{p_{\rm CH_4}^\circ - p_{\rm CH_4}},\tag{1}$$

 $p_{CH_4}^{\circ}$ representing the methane introduced initially and the other pressures corresponding to the amounts of the gases in the gas phase at any time during a run. For the adsorption of ethane the composition of the adsorbed phase was determined as C_2H_n .



FIG. 1*a*.—The reaction vessel.

FIG. 1b.—The micro-Pirani and McLeod gauges for following decomposition of the adsorbed gases.

RESULTS

THE ADSORPTION AND DECOMPOSITION OF METHANE

It was found that methane was adsorbed without decomposition on tungsten at 0°C. Adsorption did not occur on nickel and iron until higher temperatures at which decomposition also began.

TUNGSTEN FILMS

(a) ADSORPTION BETWEEN 0° AND 43°C.—The results with a number of films showed that 4.9 to 5.0×10^{18} molecules/100 mg were adsorbed at 0°C at 5×10^{-2} mm. Some 3.0×10^{18} molecules/100 mg were taken up in 2 min leaving a negligible pressure (~ 10⁻⁶ mm) in the gas phase. When sufficient methane was introduced some 4.0 $\times 10^{18}$ molecules/100 mg were taken up rapidly and further adsorption occurred giving the type of result shown in fig. 2. Owing to the way in which the amount adsorbed varies with the logarithm of the time it is not possible to assert that the maximum adsorption observed of $4.97 \times 10^{18}/100$ mg after 210 min at 5.9×10^{-2} mm represents equilibrium.

A tungsten film on which methane had been adsorbed was capable of adsorbing hydrogen. A film holding 3.7×10^{18} molecules/100 mg of methane at less than 10^{-5} mm took up 4.8×10^{18} molecules/100 mg of hydrogen at 7×10^{-2} mm. However, a film after adsorbing 4.8×10^{18} molecules/100 mg of methane only took up 2.7×10^{18} molecules/100 mg of hydrogen, before preparing the film and adsorbing methane, it was possible to show that hydrogen did not displace methane from the tungsten surface.

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An attempt was made to determine what fraction of the hydrogen atoms of the adsorbed methane was readily exchangeable with deuterium by carrying out a similar experiment with the Pirani gauge pre-filled with deuterium. Unfortunately the accuracy of the experiment was not great owing to the small difference in Pirani resistance of only 0.205 ohms between hydrogen and deuterium and to the relatively large amount of deuterium which had to be used to give a measurable pressure in the gas phase. A value of 3 ± 1 was found for the number of hydrogen atoms per carbon atom adsorbed not readily exchangeable.

The adsorption at 43° C, as at 0° C, consisted of a fast process followed by a slow process. Values of 5.42×10^{18} and 5.72×10^{18} molecules/100 mg were found at pressures of 7×10^{-4} and 3.3×10^{-2} mm. It is clear that the initial adsorption on tungsten must occur without activation and that the adsorption becomes an activated process only after the surface is fairly well covered. Attempts to determine initial rates of adsorption by using the linear relationship between amount adsorbed and the logarithm of the time (fig. 2) were worthless owing to the extent of the extrapolation required.



FIG. 2.—Increase of adsorptions with time. CH₄ on tungsten at 0° C, \triangle ; C₂H₆ on nickel at 0° and 22·5°C, O.

(b) LIBERATION OF HYDROGEN FROM THE ADSORBED LAYER.—Liberation of hydrogen occurred slowly at 60° C and more rapidly at higher temperatures. Little methane beyond that adsorbed at the beginning of each experiment was taken up during the reaction. At each temperature studied there was a rapid evolution of hydrogen followed by a slower rate, decreasing steadily with time. The volume of *n* fell smoothly with time at any temperature although the value attained after 3 h depended on the temperature, e.g. 3.15 at 76°C and 2.2 at 98°C.

Activation energies were found for the initial rates of decomposition expressed either as rate of formation of hydrogen (6.7×10^{16} molecules/100 mg min at 86°C) or as rate of decrease of *n* (0.030/min at 86°C) and are shown in table 1. The initial pressures of methane varied somewhat and thus the experiments at different temperatures were not performed under strictly comparable conditions.

TABLE 1.—ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR THE INITIAL RATE OF DECOMPOSITION OF METHANE

W	Ni
314	97
33	23.5
$8 imes 10^{30}$	$4 imes 10^{22}$
31	22
$4 imes 10^{15}$	$2 imes10^8$

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Apart from the rapid fall in n for the first 15 min at any temperature, it was found that the rate of decrease of *n* followed the second-order kinetic expression

$$- dn/dt = k_2(n - n_{\infty})^2, \qquad (2)$$

where n_{∞} was obtained by extrapolation. The activation energy associated with the second-order constant k_2 in eqn. (2) was 16 kcal/mole compared with 31 kcal/mole for the initial rate during the first 15 min.

Nickel films.—Adsorption of methane was negligible at 0°C but became rapid at 140°C and slow liberation of hydrogen began at the same temperature. A typical experiment is shown in fig. 3. Breakdown of the adsorbed methane was extensive and increased with



FIG. 3.—Decomposition of CH₄ on 20.8 mg nickel at 156°C; total pressure, ●; p_{CH_4} , \triangle ; p_{H_2} , \bigcirc ; n, \Box .



FIG. 4.—Decomposition of CH₄ on 11·1 mg iron at 211°C; symbols as in fig. 3.

temperature. After 3 h the composition of the surface corresponded to CH2 at 150°C and CH at 200°C. The amount of methane adsorbed was about 1.1×10^{18} molecules/ 100 mg. Initial rates of adsorption at various temperatures indicated that the activation energy for adsorption was about 10 kcal/mole. Activation energies for the initial rate of decomposition are shown in table 1. The fall of n with time could be fitted to the firstorder kinetic expression

$$- dn/dt = k_1(n - n_{\infty}) \tag{3}$$

and the activation energy associated with k_1 was the same as the value given in table 1 for the initial rate of reaction.

Iron films .- Adsorption and decomposition occurred at temperatures about 170°C. The reproducibility of the results was less satisfactory than with the other metals probably

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on account of the difficulty in preparing clean films. The number of methane molecules adsorbed varied from 1×10^{18} to $4 \times 10^{18}/100$ mg. The value of *n* fell smoothly to about 2. The rate of decrease of *n* with time followed the second-order eqn. (2) but it was not possible to obtain a reliable activation energy for the decomposition.

THE ADSORPTION AND DECOMPOSITION OF ETHANE

On all three metals the adsorption of ethane occurred much more readily than that of methane. Rapid decomposition was observed at temperatures above those at which adsorption took place.

Tungsten films.—About 6.0×10^{18} molecules/100 mg were adsorbed rapidly at 0°C and adsorption appeared to be complete after 15 min. A very slow liberation of hydrogen



FIG. 5.—Variation of the extent of the decomposition of C_2H_6 on the three metals with temperature and time: *n* after 80 min, \triangle ; *n* after 180 min, \bigcirc .

was detected at 0°C. The shape of the curves for the liberation of hydrogen (or fall in n) with time were qualitatively similar to those for methane, i.e. there was a rapid initial reaction followed by a prolonged slow reaction. The values obtained for the composition of the adsorbed phase, measured as C_2H_n , at different temperatures are shown in fig. 5.

In a number of experiments the reaction vessel was cooled, either in the course of the run or at the end of the run, to 0° C. Some hydrogen was readsorbed rapidly with little or no change in the partial pressure of ethane. The maximum increase in *n* observed in this way was 0.4. Replacement of the furnace restored this readsorbed hydrogen to the gas phase.

The effects of temperature on the initial rates of decomposition are shown in fig. 6. Because of the high rate of liberation of hydrogen and the time taken to adjust the reaction vessel to the reaction temperature, it was not possible to obtain reliable values for the



FIG. 6.—Variation of initial rates of decomposition of C_2H_6 on tungsten and nickel with temperature: \log_{10} (mol. of $H_2/\min 100 \text{ mg}$), \Box (W), \bigtriangledown (Ni); \log_{10} (decrease of n/\min), \bigcirc (W), \bigtriangleup (Ni).

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initial rate of decomposition above 50° C. The activation energies are given in table 2. The kinetics of the decomposition appeared to be approximately first-order with respect to n [eqn. (3)] at 20°C but at higher temperatures, even ignoring the early points, the rate of reaction fell off more sharply than would have been expected for either a first or second-order reaction.



	W	Ni
liberation of H ₂ (kcal/mole)	15.8	18.3
frequency factor (mol./cm ² sec)	$5 imes 10^{21}$	$5 imes 10^{21}$
decrease of n (kcal/mole)	16.1	20.7
frequency factor (sec ⁻¹)	$2.5 imes10^9$	$1 imes10^9$



FIG. 7.—Decomposition of C₂H₆ on 31·3 mg nickel at 98°C; total pressure: \bigcirc ; $p_{C_2H_6} \triangle$; $p_{\mathbf{H}_2}, \bigcirc; n, \square.$

Nickel films.—The adsorption of ethane on nickel was similar in character to the adsorption of methane on tungsten. A typical experiment is shown in fig. 2. Some 4×10^{17} molecules/100 mg were taken up in less than 1 min at 0°C and adsorption continued to increase with the logarithm of the time for 2 to 3 h. Increasing the temperature from 0° to 22.5°C gave little change in the slope of the curve and the final adsorption after 3 h was about 1.2×10^{18} molecules/100 mg.

It was shown that hydrogen can displace ethane from a nickel surface. Some 12.5 %of the adsorbed ethane was displaced to the gas after 30 min at 22.5°C and this figure increased to 17.5 % after 45 min at 46°C and to 23 % on cooling back to 0°C. From a measurement using deuterium instead of hydrogen, a value of 4.5 ± 1.5 was obtained for the number of non-exchangeable hydrogen atoms per C_2 unit on the surface, 2 min after the introduction of deuterium.

Liberation of hydrogen was observed in the temperature range 60-100°C and the values of n are shown in fig. 5. A typical run is shown in fig. 7 and it can be seen that most of the liberated hydrogen was re-adsorbed on cooling to 0°C and reliberated on replacing the furnace. The activation energies (fig. 6) associated with the initial rate of liberation of hydrogen are given in table 2. It was not possible to establish kinetics of the decrease of *n* with time.

Iron films.—No detectable adsorption occurred at 0°C. At 77.5°C some 1.1×10^{18} molecules/100 mg were adsorbed but liberation of hydrogen was very slow. No hydrogen was formed after 120 min and only 6×10^{-4} mm (~1 %) after 225 min. At higher temperatures (fig. 5 and 8) more hydrogen was formed but even in these cases the initial adsorption was not accompanied by decomposition. All hydrogen liberated at 98.5°C was re-adsorbed on cooling to 0°C. As the initial rate of liberation of hydrogen was always zero no values for the activation energy were obtainable.



FIG. 8.—Decomposition of C_2H_6 on 32.6 mg iron at 90°C; symbols as in fig. 7.

DISCUSSION

ADSORPTION MEASUREMENTS

In general, the results obtained in this work are in fair agreement with those of Trapnell.⁴ The amount of methane adsorbed on tungsten at $0^{\circ}C$ of 4.9×10^{18} molecules/100 mg agrees with Trapnell's value of 3.9×10^{18} in the same units, when it is noted that Trapnell's films had a smaller area by 11 % (as measured by hydrogen adsorption), and also with Kemball's ⁵ rough value of 4×10^{18} molecules/100 mg. In our work approximately 60 % of the methane was adsorbed completely and instantaneously at 0° C. We find a substantially greater adsorption of ethane at 0°C on tungsten than Trapnell observed—6.0 as opposed to 2.5×10^{18} molecules/100 mg—but in respect to the liberation of hydrogen at 70°C and the re-adsorption of hydrogen on cooling to 0°C the two sets of results are similar. The discrepancy between the values for the adsorption of ethane on iron films is even greater, Trapnell finding 0.06×10^{18} at 70°C compared with our value of 0.8×10^{18} at 77.5°C, and this probably means that Trapnell's iron films were not His values for the adsorption of ethane on nickel are also somewhat clean. lower than ours, although this discrepancy is partly attributable to the smaller area of his films. The fact that Trappell made no observations above 70°C accounts for his failure to observe chemisorption of methane on nickel or iron, because these only occur at much higher temperatures, or the liberation of hydrogen from methane on tungsten or from ethane on nickel, both of which take place only very slowly at 70°C according to our results.

Three points appear to be clearly established about the adsorption of the two gases on the three metals.

- (i) The adsorption of ethane always occurs much more readily than the adsorption of methane.
- (ii) Tungsten adsorbs the gases much more readily than nickel and iron somewhat less readily than nickel.
- (iii) The amounts of the gases adsorbed on tungsten are substantially greater than on the other two metals but even on tungsten the amount of the hydrocarbon adsorbed is substantially less than the amount of hydrogen adsorbed on the same area of film.

The first of these points probably accounts for the very substantial differences which have been observed in the exchange of ethane and methane with deuterium.

Part of the difference in reactivity may be attributed to the difference ¹⁴ of 5 kcal/mole between the bond dissociation energy of the $H-C_2H_5$ and $H-CH_3$ but there may well be a more fundamental point involved. Although the chemisorption of both molecules involves the dissociation of a carbon-hydrogen bond, the influence of the metal surface on both methyl groups in ethane may be responsible for the greater ease with which a hydrogen atom can be dissociated from one of the groups than from the methane molecule. More experimental evidence on the adsorption of different types of compounds is clearly necessary to establish this concept.

The comparative ease, and greater extent, of the adsorption of the hydrocarbons on tungsten are in line with the fact that strengths of adsorption of other gases are greater on tungsten than on iron or nickel. The general pattern of the results, i.e. the low amounts adsorbed compared with adsorption of hydrogen and also the plots shown in fig. 2 indicate that the heat of adsorption of the hydrocarbons must fall fairly sharply as the surface is covered and also the activation energy for adsorption must rise with coverage. Contributory factors to these effects are certainly steric hindrance to adsorption on sites adjacent to those covered with hydrocarbon radicals and also the additional amounts of the surface covered by the hydrogen atoms dissociated from the hydrocarbon molecules. The technique of distinguishing between exchangeable hydrogen atoms (presumably present as atoms) and non-exchangeable hydrogen atoms (assumed to be held in hydrocarbon radicals) is one which ought to be developed further. Ignoring the uncertainties in the values found for non-exchangeable hydrogen atoms, the results can be interpreted as indicating the adsorption of methane as a methyl radical and a hydrogen atom and the adsorption of ethane as approximately equal parts of ethylene molecules and ethyl radicals and 1.5 hydrogen atoms per molecule adsorbed.

LIBERATION OF HYDROGEN

Five of the systems show features in common in respect to the liberation of hydrogen-the adsorption of methane on all three metals and the adsorption of ethane on tungsten and nickel. The adsorption of ethane on iron will be discussed separately.

Increase of temperature always leads to enhanced liberation of hydrogen and at any temperature the process is at first rapid and then becomes progressively slower with time. Three processes must be considered as possible rate-determining steps:

- (i) further adsorption of hydrocarbon over and above the quantity adsorbed before hydrogen is first liberated;
- (ii) the desorption of hydrogen from the metal surfaces;
- (iii) the breakdown of the hydrocarbon radicals on the metal surfaces.

The first of these may be ruled out because in none of the five systems is the amount of additional adsorption of hydrocarbon sufficient to account for the amount of hydrogen liberated even if, as seems unlikely, complete breakdown of the molecules occurred. Process (ii) may also be excluded because of results obtained on cooling the systems $C_2H_6 + W$ and $C_2H_6 + Ni$ to 0°C and then restoring them to the reaction temperature. The comparatively rapid readsorption of hydrogen on cooling and the almost equally rapid restoration of the hydrogen to the gas phase on reheating indicate that the equilibrium distribution of hydrogen between the gas phase and the metal surface is established rapidly on metal surfaces contaminated with hydrocarbon residues just as on Although similar experiments involving cooling and reheating were clean metals. not carried out with the methane systems, the same conclusion must hold because the temperatures for liberation of hydrogen were above those observed for the ethane systems. Consequently, it appears that process (iii) the breakdown of the adsorbed hydrocarbon radicals is the rate-determining step. Now process (iii) is, in fact, complex and may consist of three steps for the breakdown of methane, i.e. $CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C$ and even more steps for ethane. Some or all of these possible dissociations will be contributing in different amounts at different times and temperatures to the liberation of hydrogen and it is doubtful if much meaning can be attached to the apparent values of the order of the decomposition reactions with respect to *n*. However, it may be significant that these orders of reaction appeared to be less well defined for the decomposition of ethane for which there can be more reactions contributing than in the decomposition of methane.

The only case where the desorption of hydrogen might be rate-determining is in the initial part of the decomposition of methane on tungsten where the activation energy of the initial rapid process appeared to be substantially greater than that for the subsequent decomposition, and approximately equal to the expected value of the heat of adsorption of about 30 kcal/mole under the conditions of coverage existing.

The frequency factors derived from the initial rates (whether expressed in terms of liberation of hydrogen or of fall of *n*) are nearly equal for the three systems $CH_4 + Ni$, $C_2H_6 + W$ and $C_2H_6 + Ni$. For the system $CH_4 + W$ the frequency factor is much greater (as also is the activation energy). This difference is further evidence that a different rate-determining step (desorption of hydrogen) is the slow step for the initial liberation of hydrogen from methane on tungsten. In this connection it is interesting that the frequency factor for the slower subsequent part of this reaction (with activation energy 16 kcal/mole) is relatively low, $3 \times 10^5 \text{ sec}^{-1}$.

The process of the liberation of hydrogen from the system C_2H_6 + Fe differs from the other systems in two ways. The initial rate of formation is very small but the rate increases with time whereas the rate decreased with time in the other systems. Furthermore, a substantial quantity of ethane is taken up during the formation of hydrogen. Consequently it is possible in this case that the adsorption of the hydrocarbon may be the rate-determining process in the formation of gaseous hydrogen. Nevertheless, the differences between the behaviour of the hydrocarbons on iron and nickel do not seem to be sufficiently striking to explain why iron should be inactive in the catalytic exchange of the hydrocarbons with deuterium while nickel is active.

An important factor which has been neglected in calculating the values of n for the adsorption of methane on both iron and nickel is the absorption of carbon into the bulk of the metal. Uptake of carbon in the temperature range used to decompose methane on these metals has been reported by Jenkins and Rideal ¹⁵ for nickel and by Kemball and Moss ¹⁶ for both metals. This solution of carbon would mean that the apparent values of n are smaller than the true values for the surface phase and it might account for the slow additional adsorption of methane which occurs during the formation of hydrogen on iron and nickel.

The results obtained in this work show a striking parallel to those found for the exchange reactions of hydrocarbons on metal films. Tungsten is the most active of the three metals both for adsorption, for decomposition and for exchange of the hydrocarbons. Also, on both tungsten and nickel, the adsorption, the decomposition and the exchange of ethane take place at substantially lower temperatures than the simMar phenomena with methane.

The fact that with ethane on nickel hydrogen is liberated readily towards 100° C and not completely re-adsorbed on cooling to 0° C (fig. 7), even although the amount of ethane on the surface is small, indicates that the ethane must be rather highly dissociated. This is evidence for the presence of these highly dissociated (and presumably strongly adsorbed) species which Anderson and Kemball ⁸ postulate to explain the decrease in the rate of the exchange reaction of ethane at temperatures between 0° and 100° C.

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