Reactions and Properties of Organic Compounds Chemisorbed on a Supported Nickel Cracking Catalyst

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An investigation has been made of the reactions occurring when the species formed by the adsorption of each of the following compounds, methyl alcohol, ethyl alcohol, acetone, diethyl-ether, ethylamine, ethyl chloride and ethyl iodide, on a nickel-silica cracking catalyst at 0°C were heated, both *in vacuo* and in a hydrogen stream. On heating such adsorbed radicals *in vacuo* to 230°C a considerable fraction of the constituent hydrogen was dissociated and could be pumped out of the catalyst vessel; quantitative measurements showed that the behaviour of acetone and of ethylamine was slightly different from the other compounds. The apparent surface area occupied by each adsorbed molecule, as measured by the change in adsorption capacity of the catalyst for hydrogen at 0°C, was comparatively small for the oxygen-containing compounds and ethylamine adsorbed at 0°C but increased markedly if such radicals were heated to around 230°C prior to admission of hydrogen. The apparent area occupied by the ethyl halides after adsorption at 0°C was comparable to the areas occupied by the other substances after heating to 230°C.

On heating adsorbed radicals, of each of the substances studied, at 230°C in a stream of hydrogen, methane was formed in almost quantitative yield, from the constituent carbon of the molecules adsorbed, by the second-order kinetic equation,

$$d[CH_4]/dt = kp_{H_2}[C],$$

where p_{H_2} was the gaseous pressure of hydrogen and $[C]$ the total quantity of adsorbed carbon. A single value of k was observed for both alcohols and diethylether, a rather smaller value for both acetone and ethylamine and a much smaller value for the ethyl halides. The temperature coefficient of k corresponded to an *apparent* energy of activation of about -1 kcal/mole for all substances studied. Reaction schemes are proposed to account for these observations.

A recent study [1] of the properties of the radicals formed by the dissociative adsorption of small quantities of a number of hydrocarbons on a high-area supported nickel cracking catalyst has shown that adsorption may be accompanied by considerable dissociation with the formation of species which are strongly bonded to the surface. From the experimental observations it was concluded that chemisorbed n-pentane, 2, 2-dimethylbutane and cyclohexane readily formed the same surface species as are given by the dissociative adsorption of methane, but the surface radicals resulting from the adsorption of the unsaturated compounds studied, cyclohexene and benzene, were different. Quantitative removal of adsorbed carbon by reaction of the surface radicals, formed on the dissociative adsorption of all the hydrocarbons mentioned, with excess hydrogen, yielded methane as the almost exclusive product by a second-order reaction in which the rate was directly proportional to hydrogen pressure and to the amount of carbon remaining bonded to the catalyst. The rate constants for methane formation from all saturated substances (including adsorbed methane) were equal, but differed from those found for the unsaturated compounds though the same kinetic laws were obeyed.

The present work was undertaken to investigate the influence of various substituents in the adsorbed molecule on the nature of the species formed on the catalyst surface and to study the reactions which occurred when such adsorbed species were heated *in vacuo* or in a hydrogen stream. The compounds selected for study were

methyl alcohol, ethyl alcohol, diethylether, acetone (compounds in which oxygen is bonded in a number of different structures), ethylamine, ethyl chloride and ethyl iodide (to study the effect of substituents other than oxygen).

EXPERIMENTAL

The vacuum apparatus and the experimental methods have been described previously.[1, 2] In the present study greater attention was directed to the characterization of trace condensable products formed in hydrogenation experiments.   These were condensed in a liquid-nitrogen trap until completion of kinetic readings and subsequently analyzed by gas chromatography over 120 cm dinonylphthalate, supported on celite, column.   In a series of experiments with diethylether the desorption kinetics of products, other than methane, were investigated by direct withdrawal of samples and analysis over the same chromatographic column.

The same sample of nickel-silica as used previously [1] was used under identical conditions as described.   Measurements of the apparent surface area of the catalyst, as determined by hydrogen adsorption and the activity for cracking adsorbed radicals, measured for cyclohexane cracking under standard conditions, were repeated at intervals between the study of other compounds.   No appreciable change in these characteristics occurred in the course of the work, except for a reduction in adsorption capacity during work with the halides which will be discussed below.

Methyl alcohol, ethyl alcohol and acetone were A.R. grade, anhydrous diethylether was supplied by May & Baker Ltd. ; ethylamine, ethyl chloride and ethyl iodide were Chemicals for Laboratory Use supplied by B.D.H. Ltd.   Gas-chromatographic analysis of each of these substances, after fractional distillation with rejection of initial and final fractions, showed that they contained no appreciable impurities.   These were outgassed by alternately pumping while frozen in liquid nitrogen and melting after isolation from the pumps, and were stored frozen in liquid nitrogen.

Cylinder methane and palladium-diffused hydrogen were used to calibrate the gas chromatograph at intervals as before.[1, 2]

RESULTS

DESORPTION OF HYDROGEN ON HEATING ADSORBED RADICALS

Measurements were made of the total volume of the products which were desorbed at 230°C, from a series of known volumes of each substance in turn which had been previously chemisorbed on the catalyst at 0°C, by continued use of the Toepler pump until gas-chromatographic analysis showed desorption to be complete. Hydrogen, the main desorption product, was invariably accompanied by methane and the latter was formed in larger quantities in those experiments where greater volumes of material had been originally adsorbed or with decreased rate of removal of products from the catalyst surface.   The result showed that for all the substances studied there was a linear relation between *total* volume of hydrogen desorbed (i.e., the volume of hydrogen added to twice the volume of methane found on completion of desorption) and the volume of organic compound which had been adsorbed at 0°C.   At high coverages, deviation from linearity became apparent when desorption of unchanged material (detected by gas-chromatographic analysis) became appreciable.

Two types of characteristic behaviour were distinguished :

(a) quantitative desorption of hydrogen from a definite volume of irreversibly adsorbed material; this was observed for methyl alcohol, ethyl alcohol, diethylether and ethyl chloride and has previously been observed with methane and cyclohexane ;

(b) desorption of a definite fraction of the hydrogen of the adsorbed material so that the composition of the surface phase was constant at low coverages where desorption of unchanged material was not appreciable. Behaviour of this type was observed for acetone and ethylamine and has previously been reported [1] for cyclohexene. The stoichiometric compositions of the adsorbed phase, after hydrogen desorption at 230°C was complete, were acetone $C_{2.6}H_{1.4}O$ and ethylamine $C_{1.55}H_{2.66}N$ after due allowance had been made for the volume of methane desorbed which was almost linear over the range of coverages of interest. After adsorption at 0°C the composition of these phases had been C_3H_6O and C_2H_7N respectively. Similarly, the composition of the adsorbed phase after desorption of hydrogen at 100°C from diethylether ($C_4H_{10}O$ when adsorbed at 0°C) was $C_{3.5}H_{7.2}O$.

ADSORPTION OF HYDROGEN AFTER ADSORPTION OF ORGANIC COMPOUND

For all the substances a series of hydrogen adsorption measurements were made following adsorption of organic compound where each measured volume was adsorbed on the catalyst after the standard pretreatment. The volume of hydrogen subsequently adsorbed was measured for constant equilibrium pressure when the catalyst was held at 0 and at 100°C. Two series of experiments were made: (a) following adsorption of the compound at 0°C and (b) following removal of hydrogen from the adsorbed material at 230°C, as described in the previous section. The volume of hydrogen adsorbed in experiments of type (b) was corrected by subtraction of the volume of hydrogen previously evacuated from the system at 230°C. The quantity of carbon remaining adsorbed in experiments of type (b) was determined by subtraction of the volume of adsorbed material which had been cracked to methane at 230°C from the volume originally adsorbed. Plots of volume of hydrogen adsorbed against volume of previously adsorbed organic compound were found to be linear, a typical example (ethyl alcohol) is shown in fig. 1 where crosses are results for ethyl alcohol adsorbed at 0°C and closed circles for experiments where hydrogen had previously been removed at 230°C. Such measurements enabled the average number of sites occupied by each adsorbed molecule to be calculated, where a site is defined (as previously [1]) as the area of surface which may be occupied by a single adsorbed hydrogen atom. The results obtained are summarized in table 1.

TABLE 1.—NUMBER OF " SITES " OCCUPIED/ADSORBED MOLECULE
(i) AFTER ADSORPTION AT 0°C AND (ii) AFTER HEATING TO 230°C WITH EVACUATION

compound	number of sites (as defined in text) occupied/adsorbed molecule	
	after adsorption 0°C	after previous hydrogen removal at 230°C
methyl alcohol	2·26	2·40
ethyl alcohol	2·15	6·88
diethylether	2·12	(>2·12)
acetone	0·91	6·22
ethylamine	1·90	6·63
ethyl chloride	7·90	7·90
ethyl iodide	6∓1	—

Measurements made of hydrogen adsorption following adsorption of ethyl chloride and ethyl iodide showed greater scatter than those for the other substances. Hydrogen adsorption on the catalyst, after standard reduction, during the period of work with halides showed a progressive decrease in apparent surface area.

Quantitative measurements of the area occupied by diethylether, after high-temperature desorption experiments, were not made. On heating the species formed by adsorption at 0-100°C, in the absence of hydrogen, an increase in the number of sites occupied by each molecule was observed and the plot of volume of hydrogen adsorbed against volume of ether previously adsorbed was not linear.
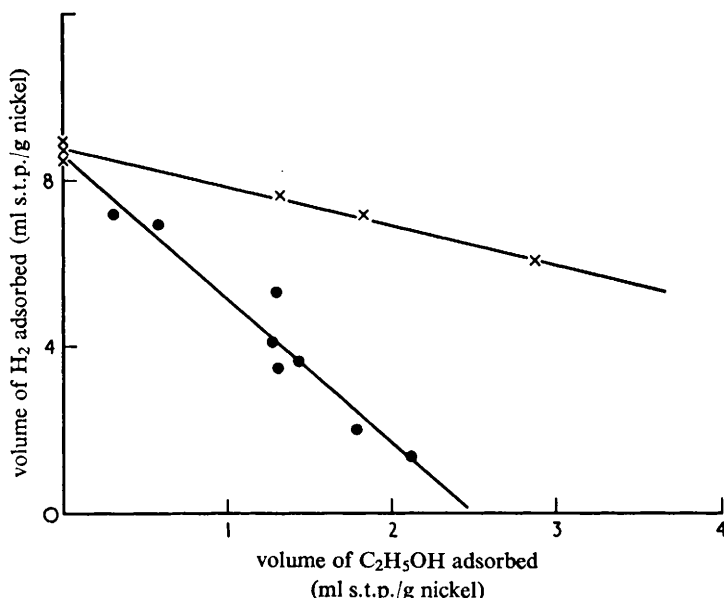
FIG. 1.—Plot of volume of hydrogen adsorbed after previous adsorption of various volumes of ethyl alcohol, (a) alcohol adsorbed at 0°C (×); (b) alcohol previously heated to 230°C, with evacuation of hydrogen (●). Hydrogen desorbed subtracted from apparent adsorption and allowance made for methane formed.

KINETICS OF METHANE FORMATION

All the substances studied, except ethyl alcohol and diethylether, when adsorbed in small amounts at 0°C and subsequently heated to 230°C in a stream of hydrogen, gave methane as the almost exclusive product and the total volume formed corresponded closely to that expected from quantitative formation of methane from the total carbon in the measured volume of compound adsorbed. Appreciable amounts of diethylether and of ethyl alcohol were desorbed unchanged.

The kinetics of the methane formation reaction accurately obeyed first-order kinetics in concentration of adsorbed carbon for reaction in a constant rate of flow of hydrogen. This first-order rate constant was directly proportional to the rate of flow of hydrogen through the reaction vessel. Previous work [1] on the kinetics of hydrogen adsorption on the catalyst under reaction conditions showed that equilibrium between gaseous and adsorbed hydrogen was established in 20-30 min. During kinetic studies of the cracking reaction, however, the gases over the catalyst were changed every 4 (or 8) min, hence it is concluded that the change in volume of gas adsorbed during each reading is small. The concentration of surface hydrogen is therefore almost constant and is controlled by the pressure of hydrogen present in each dose which, for reaction in the constant volume system, is directly proportional to the rate of hydrogen flow. The rate of reaction is therefore first-order in hydrogen pressure. A typical result, for methyl alcohol, is shown in fig. 2 as a

plot of first-order rate constants, determined at 230 and 280°C, against volume of hydrogen withdrawn in each reading for analyses at 4-min intervals; open circles represent reaction following adsorption at 0°C, closed circles after previous desorption of hydrogen at 230°C.
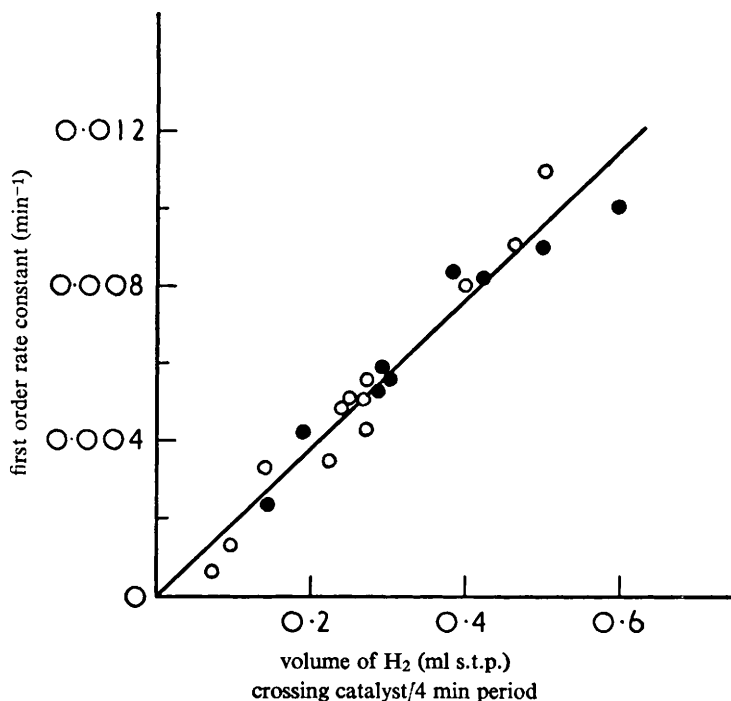

FIG. 2.—Plot of first-order rate constants for methane formation at 230 and 280°C against rate of flow of hydrogen across chemisorbed methyl alcohol. (O) following adsorption at 0°C, (●) with previous hydrogen removal at 230°C.

While all the substances studied obeyed the same kinetic laws there were quantitative differences between the reaction rates of different compounds and it is convenient to make comparisons by use of the second-order rate constant k defined by

$$d[CH_4]/dt = kp_{H_2}[C],$$

where p_{H_2} is the pressure of hydrogen over the catalyst and [C] is the total quantity of carbon, which can be converted to methane, remaining adsorbed on the catalyst. Average values of k determined from measurements made over the whole range of flow rates investigated are summarized in table 2. No change in reaction rate of any substance studied resulted from removal of hydrogen by evacuation at 230°C prior to kinetic experiments. The apparent energy of activation of the methane formation reaction from all the substances studied was between 0 and small negative values (-2 kcal/mole) between 230 and 280°C.

DESORPTION OF SUBSTANCES OTHER THAN METHANE ON HEATING

UNCHANGED ORGANIC COMPOUND

When adsorbed radicals were heated to 230°C in hydrogen, *small* traces of the original compound were invariably desorbed unchanged but the quantities varied

considerably with the different substances. Up to 2·7 ml s.t.p. methyl alcohol, 3·5 ml ethylamine and 1·2 ml ethyl chloride adsorbed per gram of nickel were almost quantitatively retained by the catalyst on heating to 230°C, only traces of material being desorbed unchanged and carbon was only removed from the surface subsequently as methane by reaction with excess hydrogen. Small amounts (some 5 %) of the adsorbed ethylamine were desorbed unchanged at a coverage of 4·0 ml s.t.p./g Ni and about 10-15 % of the total adsorbed ethyl alcohol, diethylether or acetone was desorbed at 4·0 ml s.t.p. adsorbed/g Ni.

TABLE 2.—AVERAGE VALUES OF SECOND-ORDER RATE CONSTANTS FOR THE METHANE FORMATION REACTION AT 230°C

compound	second-order rate constant for methane formation for reaction at 230°C	
	compound adsorbed 0°C k (min^{-1} mm^{-1})	compound adsorbed on adsorbed hydrogen k (min^{-1} mm^{-1})
methyl alcohol	0·0072	—
ethyl alcohol	0·0080	—
diethylether	0·0072	—
acetone	0·0040	0·0040
ethylamine	0·0044	0·0072
ethyl chloride	0·0010	0·001 *
ethyl iodide	0·0005	—

* volume of ethyl chloride adsorbed too small to allow adequate kinetic studies of desorption reaction.

The desorption of unchanged diethylether was studied by estimation in the gas chromatograph and in the latter stages of reaction first-order kinetics were obeyed between 100 and 190°C with an Arrhenius energy of activation 7 kcal/mole for an initial coverage of 1·5 ml adsorbed/g Ni.

FORMATION OF OTHER PRODUCTS

Carbon monoxide was invariably formed in small amounts when adsorbed oxygen-containing compounds were heated to 230°C alone or in the presence of excess hydrogen. This material was, however, only detected immediately after heating in amounts which rapidly decreased in successive samples withdrawn from the reaction vessel and no satisfactory kinetic measurements of its rate of formation could be made.

Traces of hydrocarbons were detected by gas-chromatographic analysis of the material condensed in the cold trap after kinetic experiments. The quantity of these products, detected after adsorption at low initial coverages, was insignificant compared with the volume of methane detected and it was estimated that they only account for about 0·01 to 0·001 % of the total volume of carbon originally adsorbed. Ethane, and traces of a second substance, almost certainly butane, were identified at concentrations within the range mentioned for all the substances investigated with the exception of methyl alcohol. This reaction was investigated in detail for diethylether since, for this starting material, the range of products separated was greatest and the volume of products was largest of all the substances studied. Approximate kinetic readings during the course of the reaction by direct withdrawal of samples and analysis over the dinonylphthalate column (where it was assumed that the area of the gas-chromatograph response peak was directly proportional to the volume of product) showed that at least 6 products could be detected, formed in a zero-order reaction lasting some 60 min after heating. The results of three sets
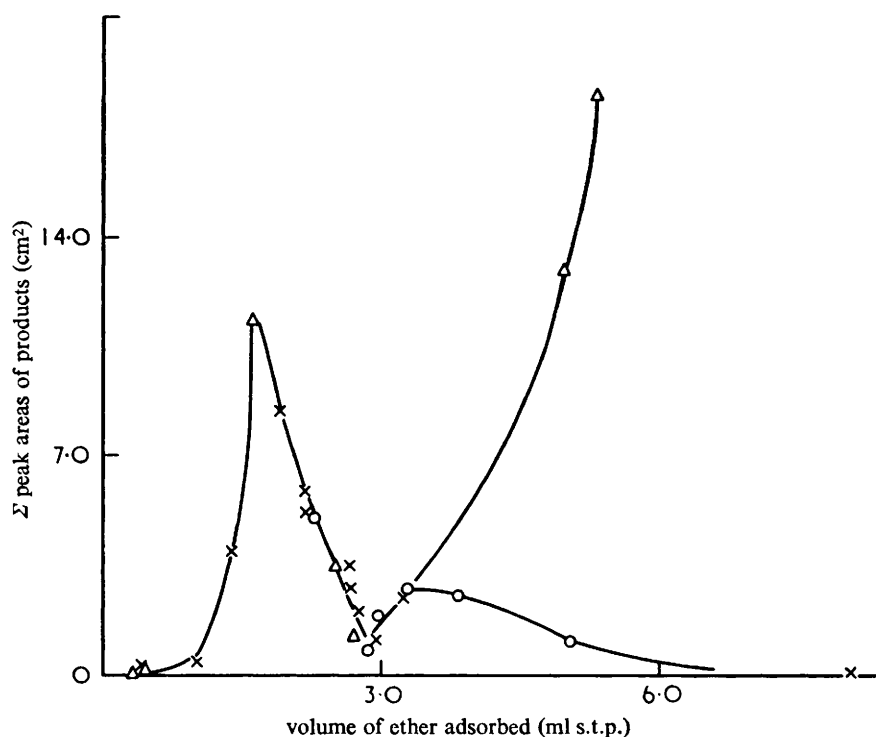
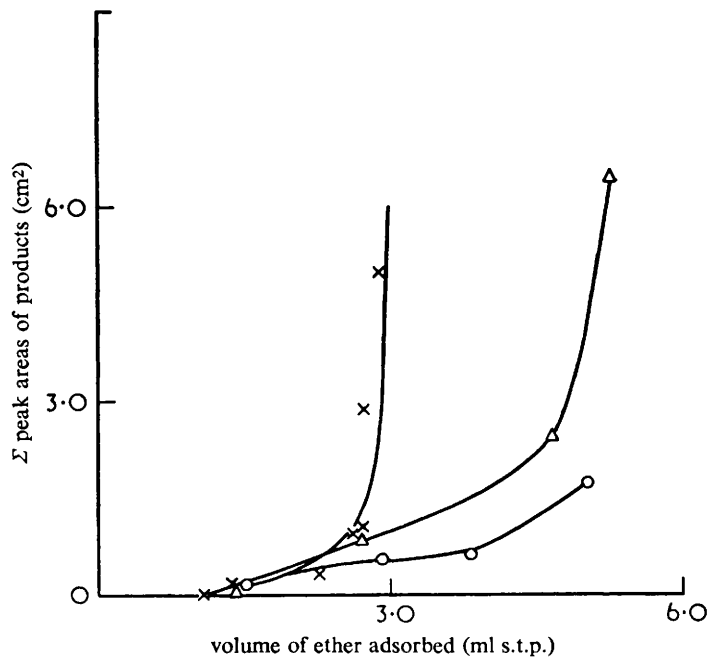FIG. 3a.—Total area of peaks eluted before diethylether peak.

FIG. 3b.—Total area of peaks eluted after diethylether peak.

FIG. 3a and b.—Measurement of products other than diethylether found in cracking reaction plotted as total area of chromatographic recorder response (cm²) against volume of ether initially adsorbed (ml s.t.p.).

$\times$ ether adsorbed 0°C heated to 100°C in absence of hydrogen ;
$\triangle$,,   ,,   250°C   ,,   ,,
$\bigcirc$,,   ,.   100°C in excess hydrogen.

of experiments, (*a*) desorption at 250°C in absence of added hydrogen (triangles); (*b*) as (*a*) but at 100°C (crosses); and (*c*) at 100°C in the presence of hydrogen (circles), are reported as (i) the sum of the areas of those four peaks eluted before diethylether (almost certainly ethane, propane, butane and pentane) and (ii) the sum of the areas of the two peaks eluted after diethylether (probably hexane and ethyl alcohol) plotted against volume of ether originally adsorbed on fig. 3*a* and 3*b* respectively.

DISCUSSION

DESORPTION EXPERIMENTS

On heating chemisorbed radicals to 230°C considerable dissociation occurred, as has been shown by the large fraction of constituent hydrogen which could be evacuated from the reaction vessel. Hydrogen was usually accompanied by smaller amounts of methane as in observations made previously [1] for hydrocarbons and the results here are explained by the same model.

Quantitative measurements of hydrogen desorption at 230°C as a function of volume of material previously adsorbed showed that all the saturated compounds of the present study, with the exception of ethylamine, gave quantitative desorption following the irreversible adsorption of a small volume. It is suggested that complete dissociation of the adsorbed species occurred on heating and pumping to give adsorbed hydrogen atoms and surface (or bulk) carbide by reactions summarized in scheme I below. Hydrogen may be pumped out of the system when it is present in sufficient quantity to exert an appreciable equilibrium gas pressure. The hydrogen remaining on the catalyst, when desorption has ceased, is below the point on the hydrogen isotherm where the pressure has become too low for appreciable amounts of the gas to be removed by the Toepler pump. Methane formation is believed to be the same rate process as occurs in the cracking reaction of adsorbed species. Reaction occurs between hydrogen and carbon containing radicals and this accounts for the relatively large quantities of methane desorbed on heating adsorbed diethylether as compared with the negligible quantities observed on heating adsorbed ethyl chloride. In the former case both the large concentration of available hydrogen (in the large volume of material adsorbed) and the relatively large rate constant for methane formation both favour methane formation. In contrast to this both the smaller volume of hydrogen present in the adsorbed ethyl chloride and the smaller rate constant for methane formation (table 2) both tend to reduce the rate of methane formation in accordance with the experimental results.
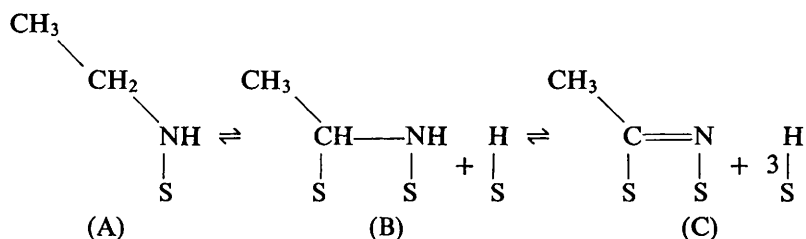
SCHEME I

$$CH_4 \text{ (gas)} \qquad\qquad\qquad H_2 \text{ (gas)} \rightleftharpoons 2H$$

$$CH_3 \quad H \qquad CH_2 \quad H \qquad CH \quad H \qquad C \qquad H$$
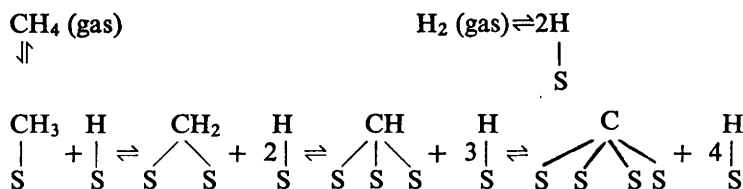
where S is a surface " site " as defined above.

Acetone and ethylamine showed rather different behaviour in that an appreciable *fraction* of the hydrogen remained on the surface (cf. cyclohexene [1]). The similarity between acetone and cyclohexene in this respect may be attributed to the presence of the double bond in both molecules, but the reason for the behaviour of ethylamine is less obvious. Moss and Kemball,[3] in a study of the catalytic fission of the

C—N bond, have obtained evidence that the following surface equilibria may be set up on the adsorption of ethylamine:

$$
\begin{array}{cccc}
CH_3 & & & \\
\backslash & & & \\
CH_2 & CH_3 & & CH_3 \\
\backslash & \backslash & & \backslash \\
NH \rightleftharpoons & CH{-}{-}NH \quad H \rightleftharpoons & C{=\!=\!=}N \quad H \\
| & | \quad\ \, | \ + | & | \quad\ \, | \ + 3| \\
S & S \quad S \quad S & S \quad S \quad S \\
(A) & (B) & (C)
\end{array}
$$

Radical C, which may be envisaged as containing a π bond and therefore could be regarded as a dissociatively adsorbed olefin is expected to be formed readily by adsorption of ethylamine on the unsaturated surface. The observed composition of the adsorbed phase is $C_{1.55} H_{2.66}N$ or a C/H ratio of 2 : 3·4 in good agreement with that of radical C if it is assumed that a fraction of the methyl groups have been hydrogenated to methane during hydrogen desorption reaction.

Measurements of the stoichiometric composition of the adsorbed surface phase formed from diethylether after removal of hydrogen at 100°C were made because Clarke and Kemball [4] observed poisoning of deuterium exchange on nickel films with this compound above 104°C. The results here show that diethylether dissociates an appreciable part of its constituent hydrogen at 100°C to give the surface phase of composition $C_{3.5}H_{7.2}O$ which is clearly more strongly bonded to the surface than the species, which occupies about 2 sites per molecule (table 1), formed on adsorption at 0°C. Adsorption in the absence of hydrogen, however, would tend to favour the formation of a more highly dissociated species than those formed on the deuterium-covered surfaces used in exchange studies.

HYDROGEN ADSORPTION EXPERIMENTS

The outstanding result summarized in table 1 is the large difference in the number of sites occupied by the oxygen and nitrogen containing molecules at 0°C as compared with the number occupied by the dissociated fragments of the molecule after heating to 230°C. This contrasts with observations [1] on the adsorption of saturated hydrocarbons (with the exception of neohexane) where the number of sites occupied at 0°C was unchanged by heating the adsorbed material to higher temperature. It is reasonable to suppose here that adsorption at 0°C involves linkage to the surface at the oxygen (or nitrogen) atom. This suggestion has been discussed previously by Clarke and Kemball [4] who believe that diethylether is initially adsorbed at the oxygen atom. Furthermore, deuterium exchange studies reported by Galwey and Kemball [5] showed that the species formed by adsorption of methyl alcohol, ethyl alcohol, diethylether and acetone, on a sample of the catalyst used for the present work, in the absence of added hydrogen, did not exchange constituent hydrogen at 0°C, indicating that low-temperature adsorption probably occurs at the oxygen atom only. It is also possible that part of the adsorbed material may be attached to the silica support, but there seems to be little doubt that on heating all the dissociated hydrocarbon radicals are formed on the nickel where they may be subsequently hydrogenated to methane. Considerable dissociation occurred on heating adsorbed oxygen-containing compounds, as was shown by the exchange studies,[5] though quantitative estimations of the number of hydrogen atoms exchangeable were not always reliable owing to the onset of cracking and the present study shows the average number of sites occupied by each adsorbed molecule markedly increases.

Comparison of the adsorption results with previous observations for hydrocarbons is complicated by the presence of oxygen which may (*a*) remain on the surface, (*b*) be desorbed as water, or (*c*) be chemisorbed (as hydroxyl radicals or water) on the silica surface. The results for methyl alcohol and ethyl alcohol favour (*b*) or (*c*) since the number of sites occupied after heating to 230°C is close to 3 and 6 respectively, values expected if water is removed *and* if the same mixture of adsorbed species is formed as has been previously postulated [1] for hydrocarbons where, on average, each atom of the adsorbed species apparently occupies a single site (scheme I, above).

The area occupied by dissociated species from diethylether could not be satisfactorily measured due to considerable methane desorption. Results for acetone are consistent with the conclusion reached [1] from work with hydrocarbons that unsaturated materials apparently occupy a smaller number of sites than a saturated molecule containing the same number of atoms. The surface species may therefore still retain some double-bond character. Results for ethylamine, together with those obtained in exchange studies,[5] show that dissociation occurs on heating, but, since this was the only amine studied, no useful comparisons can be made to enable conclusions to be drawn about the adsorbed species. The observed number of sites occupied on heating (6·63) is somewhat greater than the structure mentioned above (occupation of 5 sites) but the influence of the methyl group close to the surface and the double bond on hydrogen sorption isotherm will both tend to increase the effect of each molecule on the volume of hydrogen adsorbed.

Results obtained for adsorption of ethyl chloride were much more closely comparable to those of hydrocarbons than the other compounds of the present study since the comparatively large number of sites occupied by each molecule on adsorption at 0°C was unchanged on heating to 230°C. Furthermore, each adsorbed molecule contained 2 exchangeable hydrogen atoms after adsorption at 0°C.[5] These results suggest that the adsorbed species is multiple-bonded to the surface and, on heating, is dissociated into the equilibrium given in scheme I. In close agreement with work on hydrocarbons the number of sites occupied is close to the number of atoms in the molecule, if it is assumed also that each adsorbed chlorine atom occupies a single site. Ethyl iodide behaved in a similar manner but little work was undertaken since hydrogen adsorption measurements showed that it rapidly reduced the area of the catalyst.

KINETICS OF METHANE FORMATION

Measurements of the kinetics of the methane formation reaction, summarized in table 2, show striking similarity, and often quantitative agreement of rate constants with values found for hydrocarbons. It is concluded, therefore,[1] that, the reaction which results in desorption of methane is the controlling process in the cracking of all the species studied. Methane desorption kinetics for the hydrogenation of methyl alcohol, ethyl alcohol and diethylether are quantitatively identical to those for the desorption of chemisorbed methane under the same conditions. This is consistent with the conclusions reached above that these substances are dissociated to single carbon units on heating. Oxygen clearly does not influence reaction kinetics, but no conclusion could be reached, on the evidence available, as to whether it was desorbed as water, transferred to the support or incorporated into the bulk of the metal.

Hydrogenation of ethylamine and of acetone to methane followed the same kinetic laws as the other substances but the reaction rate was somewhat slower. This is believed to be due to the reduced rate of reaction of adsorbed hydrogen with a radical retaining double-bond character, or to the formation of a surface

polymer which is only attacked by hydrogen at the edges. Similar behaviour has been observed previously from comparison of cracking kinetics of adsorbed cyclohexane and cyclohexene.[1] Two new experimental results are, however, evident from table 2.

(a) The behaviour of ethylamine is characteristic of an unsaturated compound. The kinetic results are therefore consistent with the conclusions that the adsorbed ethylamine radicals dissociate on the surface to form a species which may be formally represented as adsorbed methyl cyanide. The rate of methane formation on hydrogenation is slower than found with all other saturated compounds (except the ethyl halides, which will be discussed below), but is, however, close to that observed for the cracking of acetone or cyclohexene which is explained by retention of " double bond character " in the adsorbed species. Adsorption of ethylamine on a surface of reduced activity, for example, through previous saturation with hydrogen, prevents the formation of highly dissociated species which retain the double bond and the subsequent reaction rate was then identical with that observed for saturated compounds.

(b) Adsorption of acetone on a hydrogen-covered surface did not result in subsequent removal of methane at a rate characteristic of a saturated substance. Two factors, both of which may influence the nature of the radical formed on the surface, are : (i) the hydrogenation of acetone on nickel films at 0°C was relatively slow,[6] and (ii) removal of the constituent oxygen as water on heating would remove at least one hydrogen atom from the immediate vicinity of the site on which the acetone was simultaneously adsorbed. It seems clear, therefore, that under the experimental conditions acetone adsorbed on the hydrogen covered surface retained double-bond character and subsequent desorption of methane kinetics were not altered by hydrogenation.

The formation of methane from the constituent carbon of ethyl chloride and ethyl iodide by reaction with hydrogen was much slower than observed for all other substances studied. This is undoubtedly due to adsorbed halogen atoms which must cause a reduction in the total available adsorbed hydrogen. In experiments immediately following the work with ethyl chloride the rate of cyclohexane cracking after standard regeneration of the catalyst was less than that found previously but slowly returned to the original value on continued reduction. This effect is attributed to the difficulty in removing adsorbed halogen atoms from the surface and is suggested by the data given in Mellor [7] on the reduction of nickel chloride which is a slow process at 430°C, the approximate temperature of reduction in the present work. Adsorbed iodine was not removed at this temperature, as shown by a progressive decrease in apparent surface area ; no data on the temperature at which nickel iodide is reduced by hydrogen could be found. Adsorbed chlorine apparently reduces the number of potential methane-forming reactions, presumably through modification of the hydrogen adsorption isotherm, an effect that is not shown by oxygen which may be removed from the surface more easily ; bulk nickel oxide is reduced by hydrogen at around 200°C,[7] which is lower than the temperature at which the kinetic studies were made. The mechanism of removal of water cannot be established from the data available but it is clear that it exerted no appreciable effect on the methane-formation reactions.

CRACKING PRODUCTS OTHER THAN METHANE

Desorption of unchanged material was favoured at the higher coverages than were investigated for hydrocarbons.[1] Furthermore, at low temperatures these substances were not dissociatively adsorbed, hence, when heated, may have reverted

to the gaseous phase on fission of the single co-ordinate link to the surface if it is assumed that the observed occupation of two sites results from a dative link to the surface. It is also possible that a part of the low-temperature adsorption occurs on the support and on heating these molecules are desorbed with lower probability of cracking than for a molecule adsorbed on the metal surface. Since products other than methane have been detected from cracking of all the substances studied, with the exception of the only single carbon atom substance, methyl alcohol, this suggests that at higher coverages linkage between two " ethyl units ", C_2, on the surface may occur in small amounts, and the results for diethylether, summarized in fig. 3, support this. The alternative explanation, that these products result from reactions of an impurity, cannot be discounted on the evidence available but an explanation of their formation by a by-product reaction can be given as follows. With increasing coverage of diethylether greater amounts of the lighter products believed to be the C_2 and C_4 hydrocarbons are given until a point is reached where appreciable surface polymerization of the C_2 units forms detectable amounts of C_6 compound, possibly a hexane isomer. At a lower reaction temperature (100°C) the higher-boiling-point products predominate but at higher temperatures (250°C) these may crack and a second region of increase in production of the lower-boiling-point materials is observed. The presence or absence of gaseous hydrogen seems to exert little influence on the course of these reactions.

It is not intended to discuss this reaction in detail since only preliminary measurements have been made, but it has been reported to show a particular application of gas chromatography as an analytical tool in determining those products which might easily have been missed using a less sensitive analytical tool.

[1] Galwey, *Proc. Roy. Soc. A*, in press.

[2] Galwey, *Chem. and Ind.*, 1960, p. 1417.

[3] Moss and Kemball, *Proc. Roy. Soc. A*, 1958, **244**, 398.

[4] Clarke and Kemball, *Trans. Faraday Soc.*, 1959, **55**, 98.

[5] Galwey and Kemball, *Proc. 2nd Int. Congr. Catalysis*, Paris 1960 (Technip, Paris 1961), p. 1063.

[6] Kemball and Stoddart, *Proc. Roy. Soc. A*, 1957, **241**, 208.

[7] Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. 15 (Longmans, 1936).