

Kinetics, Thermochemistry and Mechanism of Hydrogenolysis of Aliphatic Aldehydes on Ni-SiO₂

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An investigation of the kinetics of the hydrogenolysis reaction of aliphatic aldehydes on Ni-SiO₂ by stopped-flow chromatography is described and the rate plots fitted to theoretical equations which reveal that the reaction proceeds in two kinetically discernible stages, one apparently by a Langmuir-Hinshelwood mechanism and the other by a Rideal-Eley mechanism. These conclusions are supported by the dependences of the rates on the hydrogen pressure. Thermochemical measurements using a microcalorimetric device, have enabled the determination of the thermochemistry of a reaction leading to a surface species. A discussion of the prevailing mechanism is presented.

The hydrogenolysis reaction on Ni-SiO₂ and other supported metal catalysts has received wide attention in the literature, particularly in the case of the reaction of hydrocarbons,^{1, 2} where on nickel, the reaction has shown considerable selectivity toward cleavage of terminal C—C bonds of hydrocarbon chains and in some cases almost exclusive terminal cleavage.² Investigation of this reaction while operating the catalyst in a "chromatographic" regime provided new mechanistic information and this paper describes an extension of this work wherein the functionality of the terminal carbon atom is altered to a carbonyl group.

Molecules with functionality other than simple alkanes have received scant attention with respect to the hydrogenolysis reaction; in particular the reaction of aldehydes on metal catalysts does not appear to have been widely reported, although investigations of aldehyde and alcohol adsorptions on Ni have been studied using i.r. spectrophotometry.³ The results of this present work indicate that a study of the hydrogenolysis reaction using molecules of different functionality may throw important new light on the chemical mechanism involved. Investigations reported here were of two kinds: a kinetic investigation in which the reaction was observed by stopped-flow chromatography in a chromatographic system, using Ni-SiO₂ as a catalyst and as a stationary phase to effect the separation of the products, and thermochemical investigations where a microcalorimetric method was employed to measure the enthalpies of reactions occurring on the catalyst.

EXPERIMENTAL

Kinetic studies were carried out using a Varian model 920 gas chromatograph fitted with an integral katharometer detector, and an external flame ionization detector, constructed in the laboratory. The chromatograph was fitted with 1 and 3 m stainless steel columns 4.5 mm i.d., 6.7 mm o.d., checked for catalytic inactivity by blank experiments, and packed with catalyst material. A stop-tap was inserted in the carrier gas supply directly before the injection port, to allow stopped-flow chromatography to be carried out. The catalyst was prepared as described previously,² from a chromatographic grade of silica gel (Silica Gel for Adsorption Chromatography 60-120 mesh, B.D.H.) and nickel nitrate (Analytical Grade, Riedel De Haan AG, Seelze, Hannover). The resulting catalyst was a uniform

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black colour and contained 2.3 % w/w nickel metal. After packing, the catalyst was activated at 350°C using a hydrogen carrier gas (30 cm³ min⁻¹) for 1 h; this procedure was repeated before each new kinetic experiment.

Hydrogen carrier gas was purified catalytically to remove traces of oxygen by passing through Ni-SiO₂ catalyst at 250°C, and dried using liquid nitrogen traps and freshly activated silica gel. Reagents were introduced by means of syringe injections; in most experiments aliquots of 4-5 mg were employed. The flux of product hydrocarbon issuing from the catalyst column was measured by interrupting the carrier-gas flow for periods of 1 min at intervals during the development of the reaction chromatogram, a procedure which generated a chromatogram of the products from which the molar flux of each component could be calculated.⁴ The detectors were calibrated by introduction of measured amounts of alkanes and the catalyst was calibrated for its retention of alkanes so that retention times could be used for product identification.

Thermochemical measurements were carried out using a microcalorimeter system which was a modification of the design of Jones *et al.*⁵ Principally, the modification involved replacing the bed of the calorimeter with a packing of the supported metal catalyst, around a filament, being chosen of the same metal as on the catalyst support. The calorimeter consisted of a Pyrex tube nominally 6 mm o.d., and 4 mm i.d. which contained a coil of nickel wire of total length 40 cm, of diameter 0.33 mm, wound in a helix 1.9 mm in diameter. Copper connecting wires were brazed to each end, and the coil surrounded by a packing of the supported Ni-SiO₂. The packing material was retained by plugs of glass wool, and glass capillary tubing was used to connect the calorimeter to the chromatographic column which followed it. A chromatographic grade of silica gel was used as a stationary phase in the latter, and the column effluent fed directly to a flame ionization detector.

The temperature of the filament was controlled by a self-balancing bridge circuit used by Jones *et al.*⁵ and by Wolstenholme,⁶ which achieved the balance of a bridge (of which one arm was the filament) by varying the bridge current. The nickel filament and other bridge resistors were calibrated using a Wayne Kerr autobalancing bridge (Type B642). A coil of resistance 0.363 Ω at 20°C, and of temperature coefficient 0.0064°C⁻¹, could be heated to 600°C, using currents of up to 2.4 A, while dissipating up to 10 W. A certain degree of lagging (using glass wool) around the calorimeter was advantageous in reducing noise caused by draughts, although excessive lagging was undesirable since for quantitative measurements of exothermic reactions, a reasonable standing power dissipation was required.

Under our conditions, a stream of 30 cm³ min⁻¹ of dry hydrogen was used as a carrier gas, and reagents in quantities of 0.2-10 mm³ were introduced into the carrier stream through a septum cap above the calorimeter. The injected material was allowed to fall first on to a plug of glass wool maintained at 200°C by an external heater, before entering the calorimeter since the material then entered as a sharp plug, which led to greater precision in the thermal measurements. The amount of heat abstracted from or supplied to the calorimeter as a result of any reaction occurring was determined by recording continuously the voltage across the filament which, together with a knowledge of the resistance of the filament at its operating temperature, could be used to compute the power dissipation. The integral with respect to time of the change in power dissipation during a reaction was then a measure of the enthalpy of the reaction under the experimental conditions.

The microcalorimeter system was checked for quantitative behaviour by measuring the enthalpies of reactions which could be reacted to completion to gas phase products. Such reactions included: the hydrogenation of benzene, the complete hydrogenolysis of n-hexane to methane, and the complete hydrogenolysis of propanal to methane and water. In all these cases measured enthalpies corresponded within 10 % to the accepted values.

CHROMATOGRAPHIC PROPERTIES OF THE Ni-SiO₂ CATALYST

Since stopped-flow reaction chromatography has been the principal method for determining the kinetics described in this paper, the chromatographic properties of the Ni-SiO₂ catalyst are important and deserve brief description. In cases like those described here where investigations are carried out without a separate analytical chromatographic column

the general requirements are that the catalyst should be able to resolve reactants and products under conditions of reaction, and the chromatographic capacity of the catalyst should be such that the concentrations of products generated by flow-stops under reaction conditions are those which result in linear chromatography (*i.e.*, the relevant range of the adsorption isotherm should be linear). The catalyst used in these studies fulfilled both of these requirements.

Injection of any of the reactant aldehydes onto a three metre catalyst column at temperatures up to 200°C resulted in reaction products only being eluted from the column, the retention of the aldehydes being extremely long. Even after following a reaction for several hours, there was no indication that the reactant had moved any significant distance along the column. This behaviour of the reactants was satisfactory for three reasons: first, the time for which the reaction could be studied was not limited by the retention time of the reactant; second, during the progress of the reaction, the reactant remained effectively in the first section of the column leaving a maximum column length for separation of the products; and third, the number of catalytic sites occupied by the reactant was fixed which results in a simpler theoretical treatment (see below).

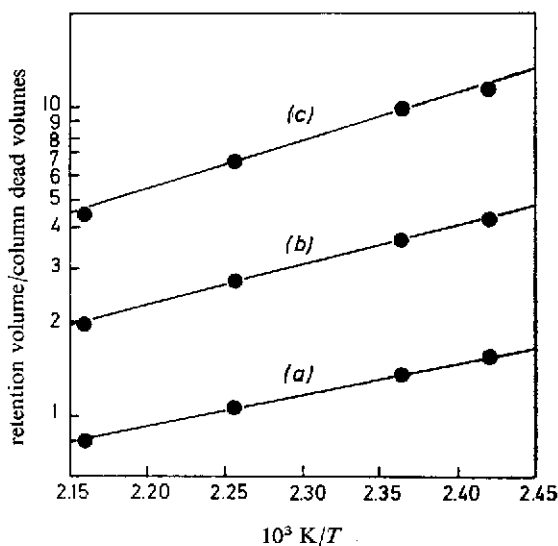


FIG. 1.—Chromatographic retention volumes (in column dead volumes) for n-alkanes on Ni-SiO₂ catalyst: (a) ethane, (b) propane and (c) n-butane.

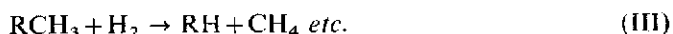
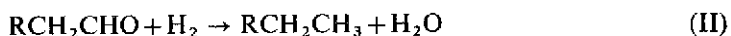
Hydrocarbon products were, however, eluted more rapidly from the catalyst column and could be conveniently separated in periods up to 10 min under reaction conditions. The chromatographic characteristics were determined before investigation of reactions by injecting n-alkanes on to the column at different temperatures; the results are shown in fig. 1 where the corrected retention volumes (expressed in column dead volumes) are plotted against the reciprocal of the absolute temperature. At all temperatures investigated methane was eluted at the column dead volume as an unretained peak, and other hydrocarbons retained up to ten column dead volumes were eluted symmetrically using injection amounts of up to 10⁻⁵ mol.

RESULTS

KINETIC RESULTS AT 2 atm HYDROGEN PRESSURE

The results presented here indicate that the reactions undergone by aliphatic aldehydes C₂-C₄ with hydrogen in the presence of a Ni-SiO₂ catalyst to yield volatile products can be represented by





Over the whole range of experimental conditions (130-200°C and 0.01-2 atm hydrogen pressure) reaction (I) has been found to be the predominant reaction, with reaction (II) accounting for <4 % of the total stoichiometry, and reaction (III) insignificant below 180°C.² Both reactions (II) and (III) increase in significance with increasing temperature; at 300°C at 2 atm hydrogen pressure methane and water are the only products. However, it is reaction (I), the principal reaction in the experimental temperature range, which is the subject of detailed study in this paper. Almost exclusive cleavage of the carbon-carbon bond at the alpha position has been observed, cleavage of bonds further along the carbon chain amounting to 2-3 %, as a proportion of the volatile products in the case of both straight- and branched-chain aldehydes at temperatures up to 180°C.

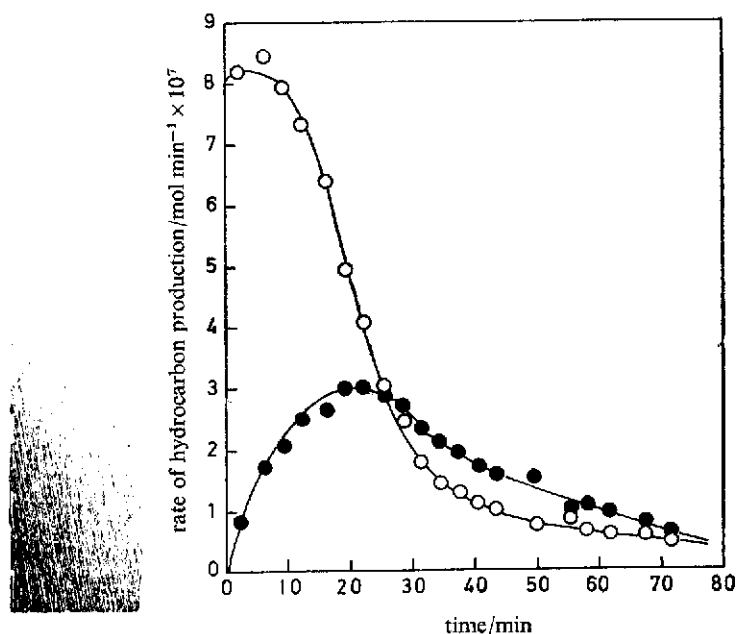
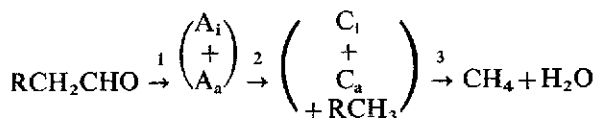


FIG. 2.—Rates of production of ethane and methane against time for the hydrogenolysis of propanal at 177°C: (○) ethane production; (●) methane production.

When an aliphatic aldehyde is introduced into a previously activated Ni-SiO₂ catalyst column, under the above reaction conditions, the two hydrocarbons from reaction (I) are generated as a result of two separate rate processes. Under the conditions studied, the methane production was invariably slower than the production of the higher hydrocarbon. Fig. 2 illustrates the process in the case of propanal, where the rates of methane and ethane production are plotted against time for an experiment in which 4.8 mg of propanal was syringe-injected into a previously activated 3 m Ni-SiO₂ column at 177°C. The principal features of the plots are that both rates pass through a maximum and decay away with time, that the methane production is zero at zero time, and the rate of production of ethane has a non-zero starting value. The areas under the profiles give a measure of the total stoichiometry of the reaction; under the conditions of fig. 2, approximately 2.3×10^{-5} mol of

ethane, 1.3×10^{-5} mol of methane and $< 10^{-7}$ mol of propane were generated from an injection of 8.3×10^{-5} mol of aldehyde. The balance of carbonaceous material which remains on the catalyst, and which reacts only slowly at the reaction temperature was substantially recovered as methane when the column was heated to 350°C under hydrogen and the catalyst restored to its original condition.

It appears from these observations, and particularly from the zero methane production rate at zero time, that the reaction generates products as a result of consecutive reactions, which could be represented by the following scheme :



where A and C represent adsorbed species. The stoichiometric results (*e.g.*, those above) indicate that, at the experimental temperature, only a proportion of these species, labelled A_a and C_a , is active, and the balance is inactive (labelled A_i and C_i), only reacting when the temperature is raised. We now turn attention to the investigation of the kinetics of the reaction occurring in the experimental temperature range indicated by the horizontal processes, 1, 2 and 3 in the above scheme.

From the observation that the rate of ethane production in fig. 2 has an initial non-zero value it is concluded that the adsorption process 1 is rapid compared with further steps. In the development of the kinetic equations for product formation process 1 can, therefore, be eliminated. The possible factors which, at a constant temperature, could control the rate of generation of the two hydrocarbon products from the catalyst surface are : surface concentrations of A and C, surface concentration of hydrogen, and hydrogen gas pressure. Under conditions of constant hydrogen pressure, the last of these will be absorbed into an experimental rate constant and further, if the hydrogen pressure is such as to render the available catalyst sites effectively fully covered with adsorbed hydrogen (*i.e.*, the situation prevailing at the top of the hydrogen adsorption isotherm), the surface hydrogen concentration will be given by the total number of available sites less those occupied by other surface species.

By setting up differential equations corresponding to the various dependences of the rate of generation of the hydrocarbons on these factors, solving these equations numerically and comparing with the experimental data, it was possible to identify those rate equations which generated functions most closely followed by the experimental data. The simplest of these rate equations are as follows :

$$\frac{dA_a}{dt} = -k_2 A_a (M - A_a - C/n), \quad (1)$$

and

$$\frac{dC_a}{dt} = Bk_2 A_a (M - A_a - C/n) - k_3 C_a \quad (2)$$

where A_a represents the surface concentration of that species, C represents the total concentration of the C_a and C_i species, and M is a parameter which is a measure of the total number of available sites on the catalyst surface which are involved in the reaction. n is a parameter which takes into account the different numbers of active sites occupied by C relative to A. k_2 and k_3 are rate constants and B is a parameter which represents the proportion of species A_a which reacts to give the reactive species

C_a . Thus $(M - A_a - C/n)$ represents the concentration of hydrogen on the catalyst surface, and the equations can be solved by writing C in terms of A_a and C_a from the total stoichiometry, and inserting a boundary condition that the initial concentration of A occupies a fraction f of the total surface sites. It is important to observe that these rate equations which gave optimum agreement with the experimental data, indicate that species A_a reacts at a rate controlled by surface hydrogen, and species C_a reacts with a rate independent of surface hydrogen.

TABLE 1.—COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES FOR THE RATES OF PRODUCTION OF HYDROCARBONS IN THE HYDROGENOLYSIS OF PROPANAL ON Ni-SiO₂ AT 177°C

time /min	rate of production of hydrocarbon/mol min ⁻¹ × 10 ⁷			
	ethane		methane	
2.3	8.31	(8.69)	0.83	(0.64)
6.4	8.45	(8.56)	1.71	(1.69)
9.4	7.94	(8.10)	2.07	(2.26)
12.4	7.33	(7.37)	2.50	(2.66)
16.4	6.40	(6.12)	2.64	(2.94)
19.4	4.94	(5.11)	3.00	(2.98)
22.4	4.06	(4.14)	3.00	(2.90)
25.5	2.98	(3.26)	2.86	(2.75)
28.5	2.44	(2.51)	2.71	(2.53)
31.4	1.78	(1.91)	2.34	(2.29)
34.4	1.48	(1.42)	2.11	(2.03)
37.4	1.30	(1.05)	1.97	(1.78)
40.4	1.15	(0.77)	1.71	(1.54)
43.4	1.03	(0.56)	1.57	(1.32)

Theoretical values shown bracketed.

TABLE 2.—VALUES OF PARAMETERS WHICH GAVE OPTIMUM CORRESPONDENCE BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS IN THE HYDROGENOLYSIS OF ALDEHYDES

reactant	temp/°C	$M/\text{mol} \times 10^5$	$k_2/\text{mol}^{-1} \text{min}^{-1}$	k_3/min^{-1}	n	B	f
propanal	155	4.2	860	0.022	3	0.27	0.71
propanal	161	3.45	2200	0.030	3	0.29	0.65
propanal	174	3.4	3100	0.057	3	0.43	0.74
propanal	177	3.1	3900	0.066	3	0.58	0.64
n-butanal	151	11.0	170	0.019	4	0.28	0.48
n-butanal	162	6.6	420	0.026	4	0.61	0.48
n-butanal	172	6.9	920	0.048	4	0.55	0.48
2-methyl propanal	152.5	11.0	200	0.019	4	0.41	0.50
2-methyl propanal	160	8.8	480	0.026	4	0.39	0.68
2-methyl propanal	173	8.7	1000	0.050	4	0.47	0.65

The results of curve fitting the experimental data to the functions of eqn (1) and (2) are shown in table 1, for the reaction of propanal at 177°C. A close correspondence is observed between the experimental values and the predicted values for the rates of production of the two hydrocarbon products. The values of the various parameters found for optimum correspondence, for different temperatures and different reactant aldehydes, are shown in table 2.

As would be expected, the value of M , which represents the number of sites involved in the reaction, increases with increasing size of reactant molecule, and this trend is also reflected in the fraction f of these sites which are initially occupied

by reactant, which decreases with increasing reactant molecular size. The value of M also decreases with rising temperature, and this may be due to the increase in velocity of the adsorption process. As expected the rate constants increase with temperature; k_3 at a fixed temperature has a value which is approximately invariant with reactant molecule, while k_2 decreases by a factor of ≈ 4 on going from propanal to the butanals. This suggests that the step 3 (characterised by k_3) is essentially the same in all cases while step 2 changes in character with reactant molecule.

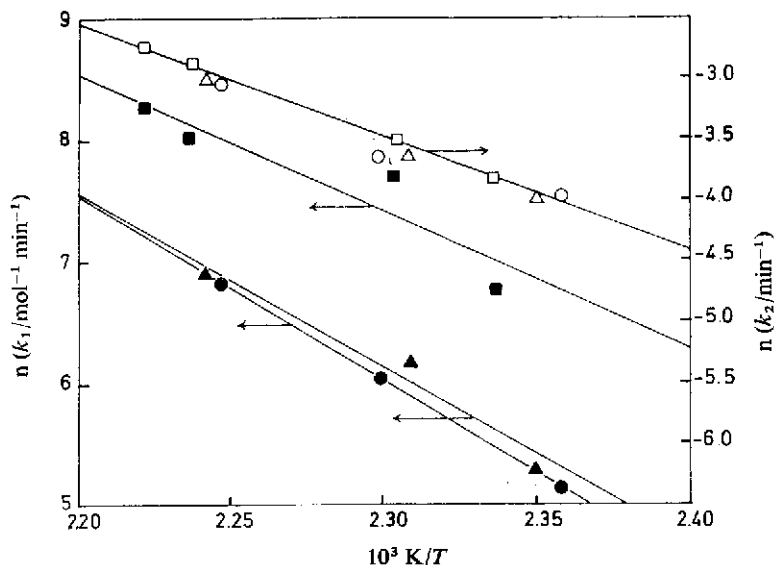


FIG. 3.—Arrhenius plots for the production of hydrocarbons in the hydrogenolysis of aldehydes: ●, propane production from n-butanal; ▲, propane production from 2-methyl propanal; ■, ethane production from propanal; ○, methane production from n-butanal; △, methane production from 2-methyl propanal; □, methane production from propanal.

The parameter n has no great influence on the curve fitting in the range 3-6, and so values were chosen in this range to correspond to the expected carbon numbers of the species A relative to C. The factor B increases with rise in temperature; this is expected since it reflects a crude species activity distribution, and a greater proportion will react at higher temperatures.

TABLE 3.—ARRHENIUS DATA FOR THE HYDROGENOLYSIS OF ALDEHYDES ON Ni-SiO₂ AT 2 atm HYDROGEN PRESSURE

reactant	RCH ₃ production rate		methane production rate	
	log ₁₀ (A/ min ⁻¹ mol ⁻¹)	E /kJ mol ⁻¹	log ₁₀ (A/ min ⁻¹)	E /kJ mol ⁻¹
propanal	14.6 ± 0.5	94 ± 10	8.1 ± 1.0	80 ± 5
n-butanal	17.8 ± 0.5	130 ± 5	6.7 ± 0.5	70 ± 5
2-methyl propanal	17.1 ± 0.5	120 ± 5	7.5 ± 0.5	75 ± 5

The Arrhenius plots for the production of methane and the higher hydrocarbon RCH₃ from propanal, butanal and 2-methyl propanal, are shown in fig. 3 and the Arrhenius parameters are listed in table 3. This table shows that both the pre-exponential factor, and the activation energy of the reaction step which leads to the

higher hydrocarbon, increase with increasing reactant molecular weight, but the parameters associated with the formation of methane are unaffected within experimental error. This is expected if the species which is hydrogenated to give methane is the same in each case.

The effect of water on the reaction rate was investigated by performing the experiments using a carrier gas saturated with water vapour at 0°C. The reaction followed a similar pattern as under dry conditions with similar rates, but the specific activity of the catalyst was reduced, and the reactant occupied a longer section of the reactor column. This resulted in approximately the same molar flux of products from the column as under dry conditions, but the width of the stop-flow peaks indicated that reaction was occurring in a section of catalyst approximately twice as long.

INFLUENCE OF HYDROGEN PRESSURE ON REACTION

The differential equations which were found to correspond to the experimental rate plots in the foregoing section indicate that the reaction of the surface species A_s (to yield the higher hydrocarbon) depended upon the concentration of surface hydrogen, while the reaction of species C_s (to yield methane) was independent of the hydrogen surface concentration. The influence of the hydrogen gas pressure was, therefore, of importance.

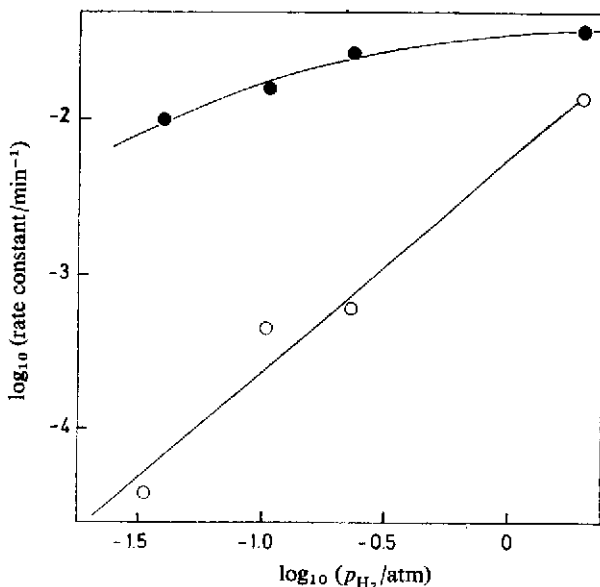


FIG. 4.—Effect of hydrogen pressure on the rate of formation of (○) methane and (●) ethane in the hydrogenolysis of propanal.

A series of experiments were carried out in which propanal was reacted in a catalyst column using a nitrogen + hydrogen mixture as a carrier gas. The composition of the mixture was adjusted to give hydrogen partial pressures ranging from 0.01 to 2 atm. The rates of production of methane and ethane (expressed as pseudo-first-order rate constants) are plotted against the hydrogen partial pressure using logarithmic axes in fig. 4.

by reactant, which decreases with increasing reactant molecular size. The value of M also decreases with rising temperature, and this may be due to the increase in velocity of the adsorption process. As expected the rate constants increase with temperature; k_3 at a fixed temperature has a value which is approximately invariant with reactant molecule, while k_2 decreases by a factor of ≈ 4 on going from propanal to the butanals. This suggests that the step 3 (characterised by k_3) is essentially the same in all cases while step 2 changes in character with reactant molecule.

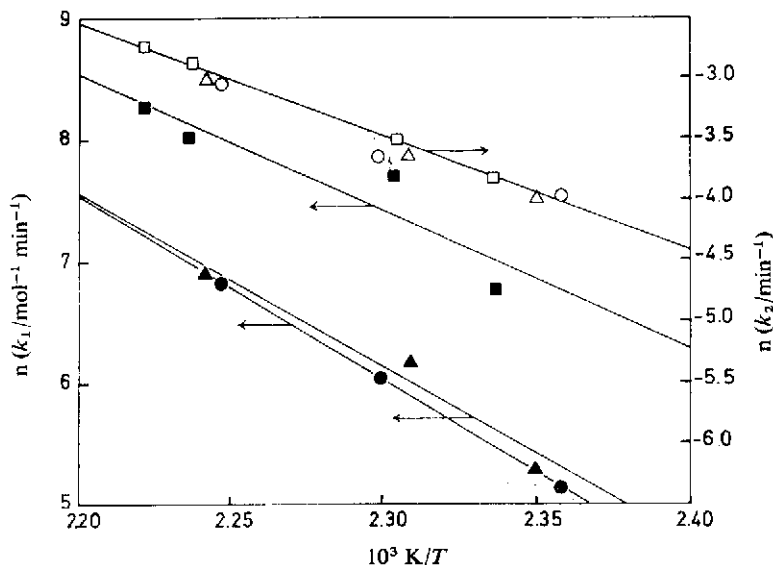


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reactant	RCH ₃ production rate		methane production rate	
	$\log_{10} (A/$ $\text{min}^{-1} \text{mol}^{-1})$	E /kJ mol ⁻¹	$\log_{10} (A/$ $\text{min}^{-1})$	E /kJ mol ⁻¹
propanal	14.6 ± 0.5	94 ± 10	8.1 ± 1.0	80 ± 5
<i>n</i> -butanal	17.8 ± 0.5	130 ± 5	6.7 ± 0.5	70 ± 5
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Fig. 4 shows that the rate of production of the higher hydrocarbon is substantially invariant with respect to the hydrogen pressure. The slight decrease in rate as the hydrogen pressure is reduced can be attributed to the lowering of the surface hydrogen concentration which would accompany the reduction in pressure. In contrast to this the methane production varies markedly with the hydrogen pressure, showing an experimental order with respect to hydrogen of $\approx +1.4$. Whereas methane production is dependent upon hydrogen pressure but independent of the surface hydrogen concentration, ethane production is independent of hydrogen pressure, but dependent upon the surface hydrogen concentration. Thus the dependence of the reactions on hydrogen is in accordance with the rate laws determined from curve fitting.

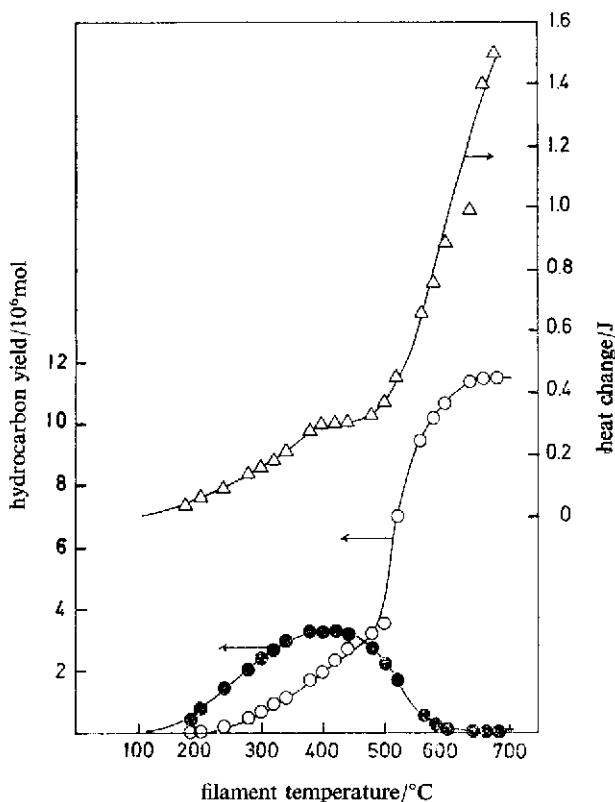


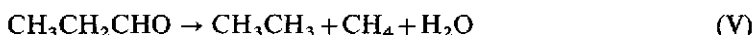
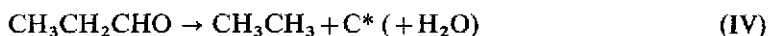
FIG. 5.—Hydrocarbon yield and heat change for the hydrogenolysis of propanal: (●) ethane yields, (○) methane yield, (△) heat change.

THERMOCHEMICAL RESULTS

Samples of aldehydes were introduced into the microcalorimeter while the filament was maintained at different temperatures. The enthalpy of the reaction occurring was determined from the change in power supplied to the calorimeter as detailed previously. The stoichiometry of the reaction was determined from the integration of the peaks eluted from the chromatographic column which followed the calorimeter. By varying the calorimeter temperature it was possible to vary the proportion of injected aldehyde which underwent the various reactions (I)-(III) above, and also the partial reaction yielding the higher hydrocarbon RCH_3 and leaving a certain

amount of surface species C remaining. The results are illustrated by fig. 5 where the total enthalpy and the hydrocarbon yields are plotted against calorimeter filament temperature in an experiment where 0.15 mg aliquots of propanal were introduced by syringe. Below 150°C there is little reaction, but as the temperature is raised first the higher hydrocarbon ethane is generated, followed by an increase in the yield of methane at higher temperatures. Above a filament temperature of 400°C, the ethane itself begins to hydrogenolyse, and finally as the temperature is raised to 600°C, complete reaction occurs to yield methane and water.

The reactions undergone by the aldehyde can be expressed by the three following equations:



where C* represents the surface species which may or may not contain oxygen.

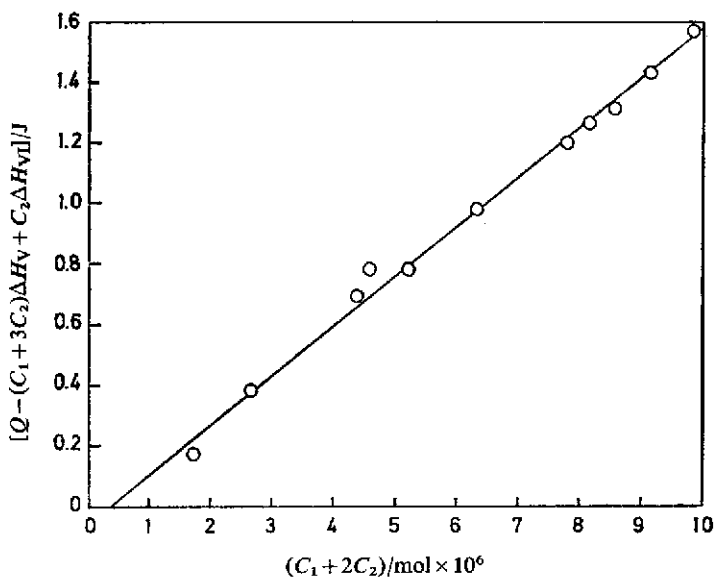


FIG. 6.—Plot of eqn (3) for propanal.

Reactions (V) and (VI) are both complete reactions with readily calculatable enthalpies while reaction (IV) is a partial reaction with a surface product. By writing down the carbon atom mass balance equations, and a thermal balance equation and solving these, it is possible to generate an expression from which the enthalpy of reaction (IV) is readily determined. For propanal this equation is:

$$Q - (C_1 + 3C_2)\Delta H_v + C_2\Delta H_{v1} = -\Delta H_{IV}(C_1 + 2C_2) + \text{constant} \quad (3)$$

where C_1 and C_2 are the molar yields of methane and ethane respectively, ΔH_{IV} , ΔH_v and ΔH_{v1} are the enthalpies of reactions (IV), (V) and (VI), respectively, and Q is the heat change measured. Fig. 6 shows a plot of eqn (3) using data in the range 180-480°C, using enthalpies of formation estimated at the mean catalyst temperature. From the slope, the heat of reaction ΔH_{IV} was calculated to be $-170 \pm 5 \text{ kJ mol}^{-1}$. Similar calculations in the case of the reaction of 2-methyl propanal gave a value of $-194 \pm 5 \text{ kJ mol}^{-1}$ for the heat of reaction (IV).

DISCUSSION

The hydrogenolysis of aliphatic aldehydes has been found to proceed with essentially exclusive terminal C—C bond cleavage under the experimental conditions outlined in this paper. This cleavage yields two fragments: an alkyl group, which is hydrogenated rapidly to the corresponding alkane in the gas phase, and a C₁ species which is hydrogenated at a measurable rate to methane in a separate rate process. From the product distribution with different reactants, it is likely that the methane originates from the carbonyl group and the higher hydrocarbon from the alkyl group since in no case in our experiments was extensive fragmentation of the alkyl group observed.

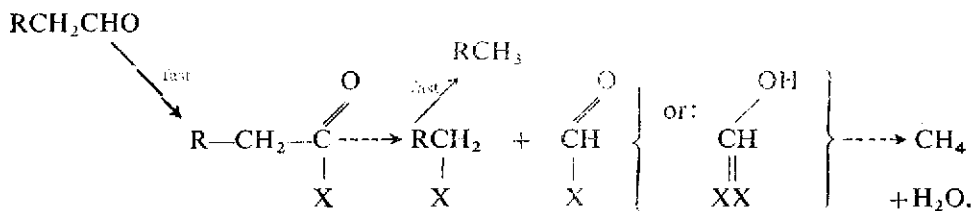
The C—C bond cleavage reaction which yields the higher hydrocarbon appears from the kinetic dependences of its formation and by the order of the reaction with respect to hydrogen pressure, to follow the Langmuir-Hinshelwood mechanism and exhibits an apparent activation energy of 90-130 kJ mol⁻¹, which is a value very much smaller than that reported for the hydrogenolysis of alkanes at 1 atm hydrogen pressure⁷ where values of between 360-550 kJ mol⁻¹ were observed.

Essentially to achieve C—C bond cleavage catalytically, the catalyst must provide an environment in which the C—C bond energy is reduced. It has recently been shown⁷ that the probable mechanism by which this occurs in alkane hydrogenolysis on Ni-SiO₂, is through the formation of multiple bonds from the carbon atoms adjacent to the C—C bond to the metal surface. As each of these are formed (endothermically in a series of surface equilibrium reactions) hydrogen is released into the gas phase which gives a large positive entropy effect and consequently a large pre-exponential factor in the experimental Arrhenius equation. At the same time the endothermicity of the equilibrium steps accumulates in the apparent activation energy, which is correspondingly very large. The reaction appears to exhibit a non-catalytic activation energy but does in fact proceed at very low temperatures as a result of the large value of the pre-exponential factor. Here the catalytic environment produces reduction of the C—C bond energy and, therefore, a low real activation energy, but this process involves a series of endothermic reactions the enthalpies of which make the activation energy appear larger.

In aldehyde hydrogenolysis, the requirement that the C—C bond energy be reduced remains, if the reaction proceed catalytically. However, the Arrhenius parameters observed in this case are quite "normal", and so the reduction in effective C—C bond energy must be caused by some other mechanism, for which the presence of the carbonyl group must ultimately be responsible. The thermochemical measurements indicate that the C—C bond cleavage reaction in the case of aldehydes is considerably exothermic, with a heat of reaction of some -(130-150) kJ mol⁻¹, after allowing for the heat of adsorption of the reactant molecule. If this heat of reaction were due to the large heat of adsorption of species C compared to that of A, some of this energy could be utilized in the C—C bond cleavage in a concerted reaction, in which the C—C bond is broken as a new bond is formed between C and the surface. The cleavage reaction could then proceed with only perhaps one or two C—metal bonds to the surface in species A, thus giving the normal Arrhenius parameters observed.

From the kinetic rate equations, and the dependence of the reaction on hydrogen pressure, the methanation of species C remaining after the C—C bond cleavage has taken place, appears to proceed *via* a Rideal-Eley mechanism, with the surface species C reacting with hydrogen in the gas phase. Infrared studies³ have indicated the presence of acyl groups and what appears to be adsorbed CO on a Ni surface after exposure to acetaldehyde. The acyl groups may well correspond to the species

A, while the adsorbed CO would correspond to the species C. If this is correct, the kinetics of the methanation of C should be close to those of the CO methanation reaction. The order of the reaction of C with respect to the hydrogen pressure is very close to that found for the CO methanation (+1.4 in both cases),⁸ and the activation energies are also similar (75 and 80-120 kJ mol⁻¹, respectively). Van Herwijnan *et al.*⁹ report that a Langmuir type model can be used to describe the methanation of CO and suggest that an enolic species on the metal surface reacting with hydrogen is the rate limiting step, although they were not able to distinguish between Langmuir-Hinshelwood and Rideal-Eley behaviour since the variation in hydrogen pressure was small in their experiments. It seems that the intermediates may well be the same in the two cases: either adsorbed CO or the enol form. The reaction could then be represented by:



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