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The Kinetics and Mechanism of the Reaction between Steam and Hydrocarbons over Nickel Catalysts in the Temperature Range 350–500°C, Part 1

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The reactions of *n*-heptane and *n*-hexane with steam over a nickel–alumina catalyst powder were investigated at 200 psig over a temperature range of 360–450°C. For most of this range, the reaction rate was proportional to (hydrocarbon pressure)$^{0.3}\cdot(H_2O)^0$ and the activation energy for the reaction was 21 ± 1 kcal. The results were interpreted by a Langmuir kinetics mechanism, and it was shown that the relative reaction rates of hexane and heptane in mixtures depended primarily on the relative adsorption coefficients of the reactants.

INTRODUCTION

Industrial processes based on the catalyzed reaction between steam and hydrocarbons to give a methane-rich gas suitable for the manufacture of town gas are now well established (*1, 2*). In these processes, plants are generally operated in the range 400–535°C and 15–25 atm pressure. As the overall reaction is then slightly exothermic, the reactants are heated to the required temperature and allowed to react over a catalyst without further addition of heat, the heat generated being sufficient to sustain the reaction. This is in marked contrast to the other industrial process using the same reactants to manufacture a hydrogen-rich gas. Here the reaction is strongly endothermic and the reaction is carried out in externally heated tubes of narrow diameter at much higher temperature (700–900°C). This change of product composition with temperature arises because it has been found that catalysts which promote the reaction of higher hydrocarbons with steam will generally equilibrate the products by the water-gas and carbon monoxide methanation reactions, e.g.,

$$a\cdot C_xH_y + b\cdot H_2O \rightarrow \begin{cases} CO + H_2O \rightleftharpoons H_2 + CO_2 & (1) \\ CO + 3H_2 \rightleftharpoons CH_4 + H_2O. & (2) \end{cases}$$

As the equilibrium constants for these reactions are known, the composition of the final products can then be predicted if the pressure, temperature and C:H:O ratio of the reactants are known (*1–3*).

The present experiments were made to investigate the low temperature reaction using paraffinic hydrocarbons as reactants. In part 1, the kinetics of the *n*-heptane/steam reaction are described together with some experiments using *n*-hexane, both under isothermal conditions.

In Part 2, the role of the above equilibration reactions in controlling the final product composition has been investigated when the conversion of the reactants is incomplete.

Few previous investigations have been concerned with the low temperature reaction. Slovokhotova and Balandin (*4–6*) investigated the reaction of steam with a

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number of hydrocarbons but as the significance of the equilibration reactions was not then appreciated, a satisfactory interpretation of the results was not achieved. Rogers (*7*) investigated how the products of the reaction of butane with steam approached equilibrium as decomposition progressed. Recently Bhatta and Dickson (*8*) examined the kinetics of the same reaction in an investigation which partly paralleled the present work on heptane, though using a different catalyst.

EXPERIMENTAL METHODS

The experiments were carried out in a flow-reactor using the all metal apparatus shown in Fig. 1. Because only a small proportion of the feed hydrocarbon was usually reacted in F, a secondary reactor B, packed with a large quantity of pelleted catalyst was used to gasify the remaining hydrocarbon. By this means, sufficient gas was always present at the control valve K for it to maintain a steady pressure within the reactor.

Figure 2 shows in more detail the reactor which was made from stainless steel components. The usual weight of catalyst used was 0.100 g but for some experiments this was increased. The temperature along the catalyst could be scanned using the movable thermocouple.

The samples were analyzed chromatographically in three ways: (1) Using a squalane column at 50°C and a flame ionization detector, the samples were examined to identify trace products arising from the decomposition. (2) Using a Poropak Q column at room temperature, the gaseous products (H_2, CH_4, CO_2, CO, C_2H_6) were analyzed after the removal by condensation of water and higher hydrocarbons. (3) The overall conversion of the feedstock was determined using a chromatograph modified by interposing a heated copper oxide tube and a magnesium perchlorate drier between the column outlet and the katharometer detector (*9*). Trial experiments showed that if the copper oxide was maintained at 750°C and the carrier gas flow rate was set at 30 ml/min, all the separated components

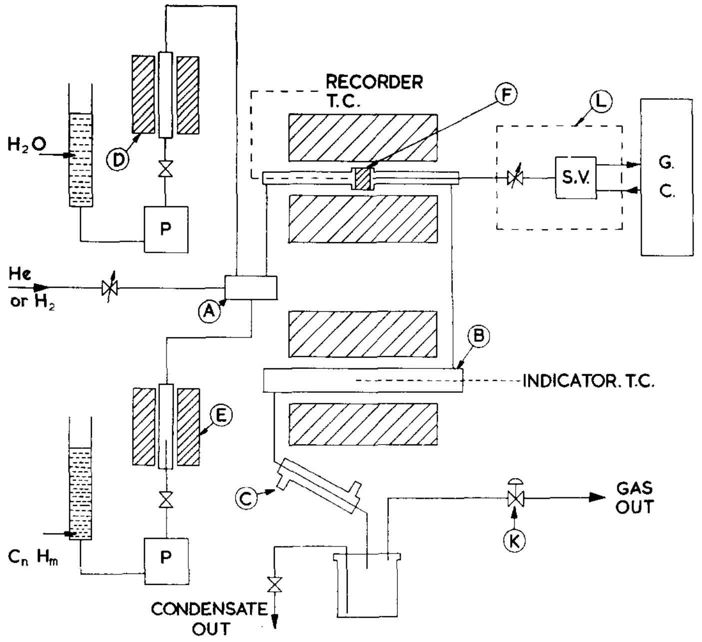

FIG. 1. Apparatus for catalyst activity measurement in a pressurized flow system. A, heated mixing vessel; B, secondary reactor; C, condenser; D, E, evaporating furnaces; F, catalytic reactor with thermocouple T.C.; L, heated box containing sample valve S.V. for gas chromatograph G.C.; K, pressure control valve; and P, metering pumps.

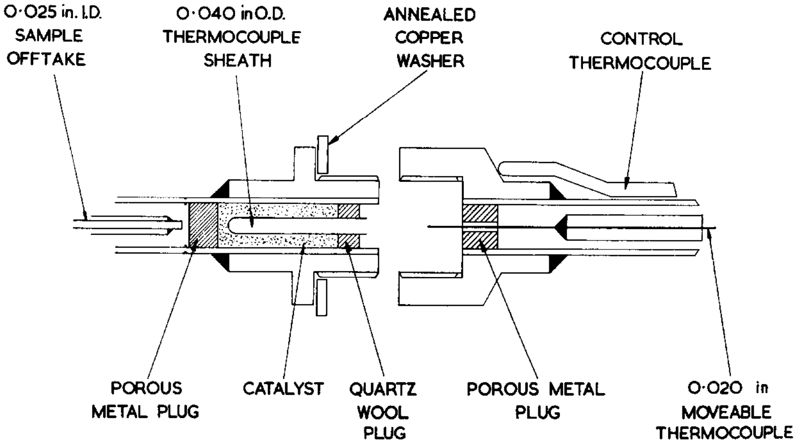

FIG. 2. Details of containment of catalyst in stainless steel reactor.

were oxidized to carbon dioxide and water. Thus, following the absorption of the water produced by this oxidation and present in the sample originally, each compound was eluted as a quantity of carbon dioxide, the amount of which was proportional to its concentration in the sample and its carbon number. The merit of this procedure was the elimination of the need to calibrate the chromatograph for all the expected product gases and the avoidance of separating the C_1 gases and hydrogen individually. The column used was 15% squalane on HMDS-treated Celite, maintained at 75°C, which gave adequate separation of hydrocarbons, though C_1–C_3 hydrocarbons were not completely resolved. In practice it was found that the traces of ethane and propane in the products were a negligible proportion of the C_1 products and therefore the first peak represented the combined amounts of carbon monoxide, carbon dioxide, and methane in the sample. Hydrogen which was also eluted at this stage was of course completely oxidized and absorbed as water. Each peak was integrated and the conversion was thus measured in terms of the integrator counts I.

$$\% \text{ conversion} = \frac{I \text{ (products)}}{I \text{ (products)} + I \text{ (feed remaining)}} \times 100.$$

For the heptane or hexane, the products other than C_1 gases were usually negligible so that for heptane for example

$$\% \text{ conversion} = \frac{I_1}{I_1 + I_7} \times 100.$$

The procedure for the experiments was as follows:

The reactor was packed with catalyst, assembled, and pressure tested. After the reactor was brought to temperature in a stream of helium, the catalyst was then reduced overnight at the operating pressure (usually 200 psig) in a flow of 2 ft^3/hr of hydrogen at 400–450°C.

Helium and steam were passed into the apparatus approximately 30 min before discontinuing the hydrogen flow and simultaneously starting the hydrocarbon feed. The usual reactant flows used as "standard" conditions were 21 ml of hydrocarbon, 26 ml of water and 28.3 liters helium per hour. This corresponded to a molar rate of hydrocarbon:steam of approximately 1:10. This ratio was necessary for satisfactory continuous operation of the industrial process.

Helium was present in the reaction mixture for two reasons: (i) it enabled the partial pressure of either reactant to be changed while keeping the other constant; and (ii) it reduced the sharp temperature gradients observed along the catalyst, when decomposition was appreciable. The only satisfactory method of eliminating these gradients was to select experimental conditions so that conversions were about 10% or less and to keep the catalyst volume as small as possible. Dilution of the catalyst with aluminum powder to increase the thermal conductivity of the catalyst mass was also used when it was required to operate at high feed conversion but this was only partially successful for reasons which are evident from the work of Mischke and Smith (*10*).

A major difficulty which was encountered during this work was change of catalyst activity. It fell sharply during the initial hour or so of operation; thereafter the decline was gradual under constant conditions but was susceptible to changes in conditions. Several percent of the measured activity could be lost during a day's operation. Therefore the practice was adopted of interpolating all measurements of activity between two readings at fixed "standard" conditions, and to express the measurements in relative terms.

Nearly all kinetic measurements were made under conditions of differential operation and the results were interpreted using the simple equation for flow system in a fixed bed reactor.

$$W/F = x/r \qquad (3)$$

where W = mass of catalyst; F = feed rate of hydrocarbon; x = conversion measured as fraction of reactant converted; and r = rate of reaction per unit weight of catalyst per unit time. Calculation showed that the volume change on reaction remained small at low conversion when steam was initially in excess, and therefore the average compositions within the reactor could be estimated for the purpose of evaluating orders of reaction. The product composition depended on the reaction conditions as will be shown in part II; at 425° a typical analysis of the dry, helium-free product gas was (%): H_2, 68.4; CO, 0.4; CH_4, 6.2; CO_2 25.

Reactants

Most of the experiments were made using *n*-heptane which was commercially available (Esso Petroleum Ltd.) at better than 99.5% purity. This was desulfurized by refluxing over freshly prepared Raney nickel for 8 hr followed by distillation. The *n*-hexane (British Drug Houses) was used without further treatment. The sulfur content of both feedstocks was <1.0 ppm. The water used was freshly distilled.

The catalyst used was a coprecipitated nickel–alumina catalyst containing in its reduced form 75% nickel, 25% alumina. X-Ray investigations have shown that the alumina was predominantly present in a poorly crystalline γ-form. The catalyst was prepared by coprecipitation from mixed nickel and aluminum nitrates with potassium carbonate following the procedures outlined in British Patent 969,637 (*11*). The total area of the freshly reduced catalyst, determined by BET nitrogen adsorption, was 144 m^2/g. The nickel area separately determined by hydrogen adsorption at room temperature was 46 m^2/g of catalyst.

Apart from the experiments in which the effect of altering the particle size was investigated, the catalyst particles were 211–195 μ (52–72 BSS) in diameter in the calcined but unreduced form. A slight shrinkage took place on reduction.

RESULTS

Effect of Temperature on the Reaction

Figure 3 shows the results obtained when reacting heptane and steam over a catalyst sample of gradually decreasing activity. For sets of experiments at different temperatures, the total feed rates were adjusted so that the conversions were all approximately in the same range for each set. On plotting the reaction rate against $1/T$, the activation energy remained unchanged showing that it was unlikely that loss of catalyst activity was resulting in a change in the rate-controlling reaction. The activation energy found, ~21 kcal/mole, excluded the possibility of mass transfer to the catalyst surface being a rate controlling factor as this would have given activation energies of a few kcalories. Similar results were obtained for hexane. The possibility that diffusion coupled with reaction within the catalyst pellets was

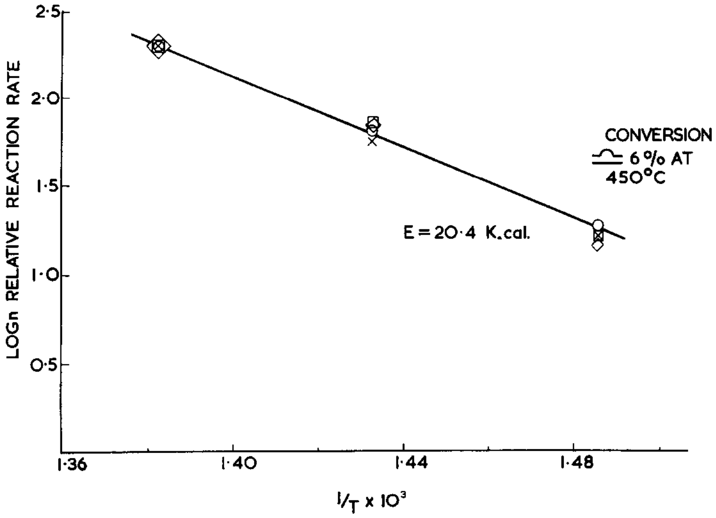

FIG. 3. Activation energy plots of a single catalyst at different levels of activity: □, standard feed rate 21 ml of heptane, 26 ml of water, 28.3 liter of helium, per hour; ◇, 0.75 × standard rate; ○, 1.25 × standard rate; and X, 1.5 × standard rate.

rate controlling was checked by repeating experiments with particles of different size ranges. The following activation energies were observed for the sizes indicated: (853–1002 μ), 21.2 kcal; (211–295 μ), 20.3 kcal; (124–178 μ), 22.3 kcal. Had diffusion processes become important, a fall in activation energy would have been observed to a limiting value of about half the true one (*12*, p. 66) when the particle size was increased. Such an activation energy (10 kcal) was observed when a catalyst of ⅛ in. equant cylindrical pellets was used. Under the usual experimental conditions it is therefore unlikely that diffusion processes were affecting the rates measured.

The Effect of Change in Heptane Partial Pressure on the Reaction Rate

These experiments were carried out using a constant feed of water and changing the feed rates of heptane and helium so that the total molar flow remained constant. Thus the steam partial pressure remained constant and the change in rate of reaction could be correlated with the change in partial pressure of the heptane. The results were fitted to the empirical equation: Reaction rate $= k'P^n$ ($P =$ mean partial pressure of heptane in psia) and the plot of log P vs. log (rate) at different temperatures is shown in Fig. 4.

At all temperatures, deviations from linearity were observed at the lower pressures. Over a limited range, however, the order of reaction was fairly constant: at 380°C it was zero but at the other temperatures which are shown it was approximately 0.3. These results may be interpreted in terms of a Langmuir kinetic mechanism where the apparent order of reaction will increase from 0 to 1 as surface coverage decreases.

One experiment was made with ⅛ in. pellets to see the effect of diffusion on the order of reaction. At 415°C, the apparent order had increased to 0.8.

The Effect of Change of Steam Partial Pressure on the Reaction Rate

Several attempts were made to detect a change of reaction rate when the steam pressure was altered, particularly in view of the first-order term found for butane decomposition (*8*). The alterations that were possible were limited because it was always necessary to maintain an excess of steam present to minimize the loss of catalyst activity. Several series of experiments were made at 425 and 450°C, changing

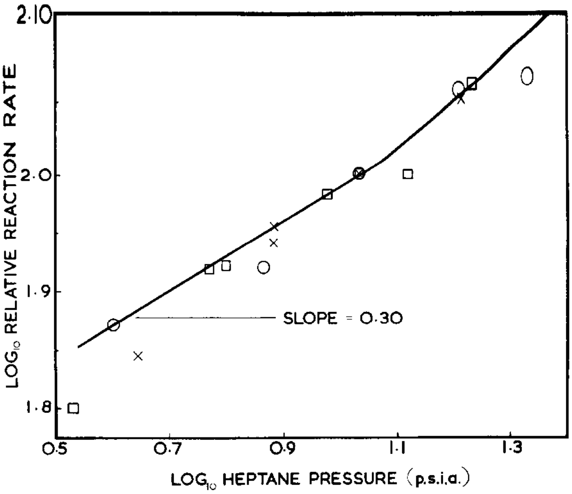

FIG. 4. Effect of heptane partial pressure on reaction rate at low conversions of heptane. Plot of: rate = $k'P^n$; slope = n = 0.3; X, 400°; ○, 425°; □, 450°.

the steam partial pressure between 4 and 9 atm with a constant hydrocarbon pressure of 0.42 atm. Most of the series indicated zero order for steam but a few gave slightly negative orders, between —0.15 and 0.0.

The Effect of Change of the Pressure of Both Reactants on the Reaction Rate

For confirmation of the orders of reaction found, further experiments were made in which the total pressure of the reactants was varied either (a) by altering the helium flow at constant reactor pressure, or (b) by altering the reactor pressure while maintaining constant flows of the reactants and helium.

(a) When the helium flow was changed from 1.2 to 3.6 moles/hr while the heptane and water flows were kept constant at 0.145 and 1.450 moles/hr, respectively, a change in conversion of heptane from 15.7 to 12.5% was observed at 450°C. Assuming the reaction rate equation

$$r = k'[P_7]^{0.3} \cdot [P \cdot \mathrm{H_2O}]^n,$$

and taking an average value for the hydrocarbon partial pressure (P_7) in each case, calculation gave $n = +0.07$.

(b) The effect of total pressure on the reaction rate was measured at high conversion to see if the reaction orders found under differential conditions were still applicable. This, however, meant that an integrated form of the rate equation had to be used for calculating the expected changes. Assuming

$$\text{Rate} = k'[P_7]^{0.3} \cdot [P \cdot \mathrm{H_2O}]^0,$$

$$\frac{W}{F} = \int_0^x \frac{dx}{k' \cdot [P_7^0(1-x)]^{0.3}}$$

$$= \frac{1}{0.7k'\,[P_7^0]^{0.3}}[1-(1-x)^{0.7}],$$

where P_7^0 is the inlet pressure of heptane. As W/F remains constant, and P_7^0 is proportional to the total pressure P_t

$$\left[\frac{(P_t)_1}{(P_t)_2}\right]^{0.3} = \frac{1-(1-x_1)^{0.7}}{1-(1-x_2)^{0.7}}.$$

Using this equation the following changes in conversion were calculated for pairs of experiments for which the total pressures were $(P_t)_1$ and $(P_t)_2$ (Table 1).

The results from both experiments (a) and (b) give a good confirmation that the orders determined differentially could not be greatly in error and (b) also indicates

TABLE 1

OBSERVED AND CALCULATED EFFECT OF TOTAL PRESSURE ON CONVERSION

$(P_t)_1$ (psia)	$(P_t)_2$ (psia)	Conversion at $(P_t)_1$ (%)	Conversion at $(P_t)_2$ (%) Observed	Conversion at $(P_t)_2$ (%) Calculated
204	303	71.7	75.9	78.7
303	204	70.5	67.5	63.0
205	94	70.4	64.5	61.3

that there was little if any interference with the reaction by the products, though this could account for the small differences found. This was further examined by deliberate introduction of products with the feedstock.

The Influence of the Products on the Reaction Rate

Hydrogen. It was not possible to do any quantitative experiments with hydrogen present in the feed because the reaction became strongly exothermic, making temperature control difficult. Qualitatively it could be shown that conversion increased, presumably as a result of an exothermic hydrogenation reaction, confirming plant observations that the catalyst was active for hydrogenation.

Methane. Three experiments were carried out in which natural gas was added to the feed in place of part of the helium supply. The added gas contained 81% methane, 12.6% ethane, 3.0% propane and 3.3% butane with traces of inerts. The molar feed rates of the reactants were in the proportions

$$\text{heptane:gas} = 0.10:1.95,$$

and the reaction temperature, 400°C.

When the activity of the catalyst was such that without added gas 94% of the heptane was being converted, no change was observed on admitting methane. However, when the initial conversions were lower at 37 and 26%, methane reduced the conversion to 22 and 10–15%, respectively (at low conversions it became difficult to obtain repeatable values for the C_1 gas formed from heptane in the presence of large quantities of added methane). Analysis of the outlet gas showed that the methane itself reacted with steam to increase the CO_2 content of the gas and also that 50% of the ethane remained unchanged.

The overall conclusion was that there was a slight retardation of the reaction by comparatively large amounts of methane when the conversion was low, but when conversion was high (and therefore when there was already an appreciable amount of methane in the system), the effect was negligible.

Carbon monoxide. Jurgens (*13*) has reported that the presence of carbon monoxide strongly interfered with the hydrogenation of hydrocarbons. It was therefore considered likely that inhibition might also occur in the present experiments so the concentration of carbon monoxide added to the reactants was initially kept small. Thus a mixture was made of 0.24% (v/v) CO in the helium gas used in the experiments. Using relative molar flows of 2.4 moles of He–CO mixture to 0.100 moles of heptane, no noticeable effect was observed when the initial decomposition of heptane was 47% with pure helium gas. The experiments were then repeated using a helium supply which contained 5.3% added carbon monoxide. Again no effect was noticed in a system in which heptane decomposition was initially 16%.

Experiments with Mixed Feedstock

Though experiments under nondifferential conditions (20–100% decomposition) were attempted with individual hydrocarbons, the results obtained were not satisfactory and it was considered that a better guide to the later stages of the decomposition could be obtained if measurements could be made that were independent of the absolute reactivity of the catalyst, but still depended on the form of the kinetic law followed by the reaction. As *n*-hexane was unlikely to differ in this latter respect from *n*-heptane, use could be made of measurements of the relative rates of reaction in an equimolar mixture of the two hydrocarbons. Thus if P_6 and P_7 are the partial pressures of hexane and heptane

$$\frac{-dP_6}{dt} = k'_6[P_6]^n \text{ and } \frac{-dP_7}{dt} = k'_7[P_7]^n,$$

$$\frac{-dP_6}{k'_6[P_6]^n} = \frac{-dP_7}{k'_7[P_7]^n}.$$

For $n = 1$, first order

$$\log \frac{P_6}{P_6^0} = \frac{k'_6}{k'_7} \log \frac{P_7}{P_7^0} \quad (4)$$

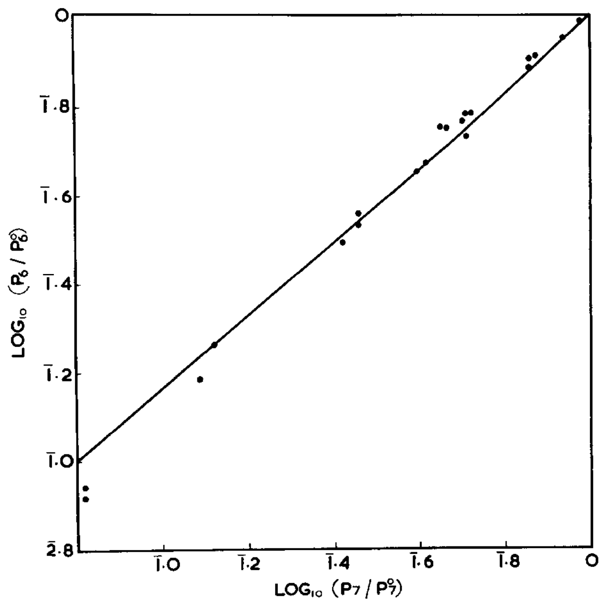

FIG. 5. Plot of Eq. (4): slope $k_6A_6/k_7A_7 = 0.83$.

Figure 5 shows that this expression (4) holds for most of the reaction for experiments carried out at 425°C, which is difficult to reconcile with the fractional order found by the differential experiments. However, if Langmuir kinetics are considered to apply to the mixed hydrocarbons and the k_6 term includes terms arising from adsorption of the steam

$$\frac{-dP_6}{dt} = \frac{k_6A_6P_6}{1 + A_6P_6 + A_7P_7},$$

and it may be seen that this and its analogous equation for heptane would give the same expression as (4) with $k'_6/k'_7 = k_6A_6/k_7A_7$. In any case, in a Langmuir system, a change to first order kinetics would be expected at low reactant concentration. The slope of the graph gives a value of k_6A_6/k_7A_7 of 0.83.

Experiments to Determine the Relative Reaction Rates of Hexane and Heptane

It has recently been shown how adsorption and reaction rate constants may be calculated from kinetic data obtained during the decomposition of mixtures of competing reactants (*14*) if Langmuir kinetics may be assumed. Thus for n-hexane (and analogously n-heptane), the following may be derived if the surface coverage is fairly complete, i.e., $A_6P_6 \gg 1$.

Reaction rate of hexane alone

$$= \frac{k_6A_6P_6}{1 + A_6P_6} \simeq k_6,$$

Reaction rate of hexane in a mixture

$$= \frac{k_6A_6P_6^*}{1 + A_6P_6^* + A_7P_7^*}$$

$$\simeq \frac{k_6}{1 + (A_7P_7^*/A_6P_6^*)},$$

where A_6,A_7 = the adsorption constants; k_6,k_7 = reaction rate constants; P_6 = partial pressure of pure hexane; and P_6^*,P_7^* = partial pressures of reactants in mixture.

$$\text{Thus, relative reaction rate } \frac{r \cdot C_6 \text{ pure}}{r \cdot C_6 \text{ mixt}} = 1 + \frac{A_7}{A_6}\frac{P_7^*}{P_6^*}, \quad (5)$$

and A_7/A_6 can be determined by doing experiments with mixtures giving different values of P_7^*/P_6^*.

Further, the relative reaction rates within a particular mixture will be given by

$$\frac{r \cdot C_7 \text{ mixt}}{r \cdot C_6 \text{ mixt}} = \frac{k_7A_7P_7^*}{k_6A_6P_6^*}. \quad (6)$$

This will permit the determination of k_7A_7/k_6A_6 from which k_7/k_6 may then be calculated. This may finally be checked by determining the relative reaction rates of pure hexane and pure heptane which should be k_7/k_6.

The experiments were made at 406°C with mixtures of *n*-hexane and *n*-heptane, the mole ratio of the two components being adjusted so that approximately $P_6^*:P_7^* = 1:1$ or $2:1$.

A lower helium flow (0.6 moles) than usual and a slightly increased hydrocarbon flow ensured a higher hydrocarbon partial pressure and consequently a closer approach to zero order kinetics. The relative molar rates of decomposition of the components of the mixtures were determined and plotted against the relative partial pressures. These were determined as the average pressure of each hydrocarbon in the mixture after making allowance for the different amount of each decomposed. Each experiment with a mixture was bracketed by experiments with pure hexane. As may be seen from Eq. (5), the slopes of the graphs shown in Fig. 6 give $(A_7/A_6) = 1.70$ and $(k_7A_7)/(k_6A_6) = 1.58$, whence $k_7/k_6 = 0.93$. In separate experiments with pure components, the same masses of hexane and heptane were converted under the same conditions in the range 12–30% conversion. In molar terms $k_7/k_6 = 6/7 = 0.86$, in reasonable agreement with the above.

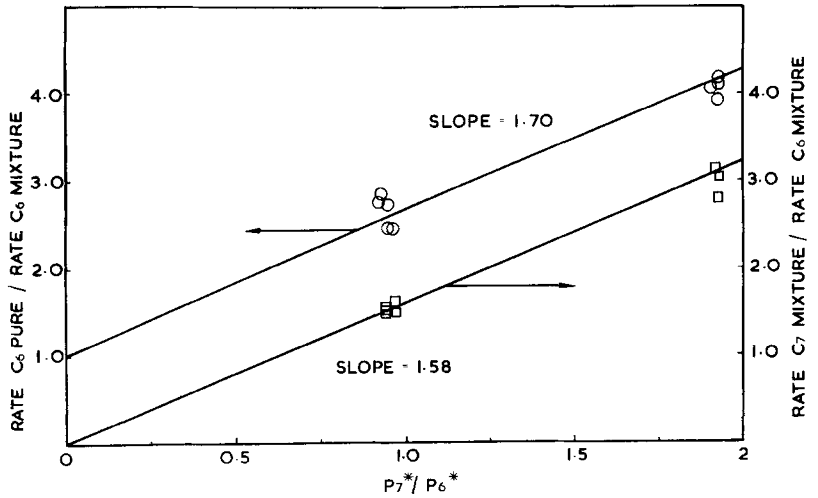

Fig. 6. ⊙, Plot of Eq. (5): reaction rate of pure hexane relative to its reaction rate in a mixture of hexane and heptane vs. partial pressure ratio of reactants; ⊡, plot of Eq. (6): reaction rate of heptane in a mixture relative to reaction rate of hexane in the same mixture vs. partial pressure ratio of reactants.

The differences in the rate of reaction of hexane and heptane in mixtures therefore stemmed mainly from differences in the values of their adsorption coefficients and not from the rate constants controlling their decomposition. This difference in the value of the adsorption coefficients was confirmed by gas chromatography using a short column of catalyst in a chromatograph in place of the normal separating column. Chromatographic theory (*15*) relates retention volume V_r to the partition coefficient B between the adsorbed and gas phase by the relation $V_r = V_d + B \cdot V_e$ where V_d is the dead volume of the column and V_e the volume of the adsorbent. On the catalyst column, though some decomposition was evident when mixtures of pentane, hexane and heptane were passed through it at temperatures between 250 and 350°C, the order of elution was qualitatively that which would be expected from the adsorption coefficients, i.e., C_5 before C_6 before C_7.

The Relative Decomposition Rates of Other Hydrocarbons

These were briefly investigated by using equimolar mixtures of hexane or heptane with other hydrocarbons so that the relative rates measured include differences in the rate constant and an adsorption term.

The results indicated that the order of reactivity for the *n*-hydrocarbons was $C_8 > C_7 > C_6 > C_5$.

Branched hydrocarbons were more stable than the corresponding normal ones, but the products from their partial decomposition contained a much greater proportion of partially decomposed molecules, particularly of smaller branched hydrocarbons than the feed. Methyl cyclohexane was slightly less reactive than heptane but toluene was more reactive. Again, partially decomposed hydrocarbons were present in the products—toluene for example was found amongst the products from methyl cyclohexane. The total amounts of these hydrocarbon fragments remained a fairly small proportion of the products—less than 5% in most cases.

DISCUSSION

Any suggested reaction scheme must offer an explanation of the following features of the reaction: (i) the reaction orders observed; (ii) the lack of lower paraffin products during the decomposition of *n*-hydrocarbons but their presence when branched chain paraffins are decomposed; (iii) the relative reaction rates of different hydrocarbons in mixtures or when reacted separately; and (iv) the effects of diffusion as demonstrated when catalysts pellets were used in place of powders.

The following reaction scheme is postulated to explain the results:

$$P(c) \underset{a_2}{\overset{a_1}{\rightleftharpoons}} C_n \underset{b_2}{\overset{b_1}{\rightleftharpoons}} (CH_x)_n + (H_2O) \xrightarrow{k} \text{Products} \underset{c_2}{\overset{c_1}{\rightleftharpoons}} \text{Product gas.}$$

gas | surface | gas

It is proposed that the hydrocarbon is initially adsorbed according to a Langmuir mechanism and, if it is a normal paraffin, that it reacts rapidly on the surface to produce entities containing one or perhaps two carbon atoms (CH_x). These fragments then react with adsorbed steam and for *n*-hydrocarbons, this reaction is rate controlling. The steam is strongly adsorbed on sites which are different from those responsible for hydrocarbon adsorption and reaction takes place following migration of one or both of the reactants to adjacent positions. The reaction products are hydrogen and molecules containing one carbon atom; they desorb and subsequently interact to form equilibrium gas mixtures.

For branched chain hydrocarbons, the rate controlling process is the formation of (CH_x) since the disruption of the original hydrocarbon produces some (CH_x) and relatively stable adsorbed species some of which may desorb before reacting further.

The reaction orders observed are 0–0.3 for hydrocarbon and 0 for steam. Langmuir adsorption leads to the rate equation.

$$\text{Rate} = k\theta = \frac{ka_1P_c}{a_2 + a_1P_c + k} \quad (\theta = \text{surface coverage})$$

and if $(a_2 + k)$ is small in comparison with a_1P_c, the surface will tend to be completely covered and zero order kinetics are followed. As P_c falls (in experiments at high conversion) the order will increase, but at lower temperatures when adsorption is stronger, the kinetics approach nearer to zero order, as was found experimentally. Since the order for steam is also zero, it seems likely that adsorption leading to a nearly covered surface is again involved. However, the sites for steam adsorption must be different from those adsorbing hydrocarbon since competition for the same sites would lead to a negative order for one of the reactants. Since hydrocarbon is almost certainly adsorbed on the metal (*16*), adsorption of steam on the alumina seems likely.

Zero-order kinetics for steam would also be obtained if the rate controlling slow reaction step were b_1 since steam is not involved in this reaction. However, if this were a slow step, one might expect to observe the presence of fragments of the original feed in the gas phase. These are observed in the case of hydrogenation reactions at lower temperatures where it is generally assumed that the rate-controlling process is the scission of a carbon–carbon bond by the attack of hydrogen (*16, 17*). Since the catalyst used in the present experiments is similar to those used for hydrogenation [particularly to that used by Bazant (*17*)], one might expect the adsorption processes to be similar, but followed by a rapid breakdown of the adsorbed molecules because of the higher temperature. This type of process was suggested by Galwey (*18*) to explain hydrogenolysis processes when hydrogen was admitted into a reactor after adsorption of hydrocarbon on a nickel surface. Galwey's results also indicated that branched chain hydrocarbons were more difficult to disrupt and in accord with this are the present observations of fragments of the feedstock when these hydrocarbons are reacted.

The similarity of the reaction rates and activation energies of *n*-hexane and *n*-heptane are accounted for by the reaction scheme as one might expect the same *mass* of carbon to react in a given time provided the surface remains saturated with (CH_x). The relative reaction rates in mixtures are adequately explained by their dependence on the relative adsorptivities of the two hydrocarbons which agree qualitatively with the chromatographic results. One disagreement which does arise is between the slope of the line in Fig. 5, which shows $k_6A_6/k_7A_7 = 0.83$ at 425°, and the value for this expression calculated from the slopes of the lines in Fig. 6, 0.62 at 406°. Even allowing for the difference in temperatures, these figures cannot be reconciled because they lead to an unreasonable difference in the heats of adsorption of hexane and heptane. The most likely source of error in this case would be the catalyst temperature measurement in the experiments at high conversion.

For reaction to take place following adsorption on separate sites, there must be mobility of the adsorbed species. It has recently been suggested that OH groups on alumina are sufficiently mobile to move onto adjacent metal atoms (*19*) so reaction could take place either on the metal or on the interface between the two phases. Experiments showed that the reaction could be carried out on nickel alone, but not on alumina without nickel. It seems less likely therefore that reaction takes place following migration of the hydrocarbon residue onto the alumina surface as is suggested to occur in hydroforming reactions (*20*).

The diffusional effects found are qualitatively of the right order but it must be admitted that the activation energy of 10 kcal found with ⅛-in. diameter pellets is probably only fortuitously about half the activation energy when using a powdered catalyst, because additional complications arise when a Langmuir model is being considered (*25*). This is because decreasing the partial pressure of gas in contact with a surface by diffusion or any other way will result in the kinetics becoming first order with a different overall rate constant [rate $= k(a_1/a_2)P_c$]. The activation energy will include a positive heat of adsorption term and the approximation that the energy of activation is halved by the influence of diffusion (*12*) should really be applied to this value of E. Similarly the simpler theory on the effect of diffusion on reaction order (*25*) has to be modified and the observed order may increase more than that given by $[n+1)/2]$ (*12*, p. 66) where $n = 0.3$.

The catalyst used by Bhata and Dickson (*8*) for their experiments with butane was of 15% nickel–alumina and from the evidence of their reaction order of 1 for steam, and the activation energy of 14 ± 2 kcals (*21*), it appears to have functioned in a slightly different way. However, zero-order kinetics were still found for butane so the point had not yet been reached when the weaker adsorption of the lighter hydrocarbons would tend to give first-order kinetics as found when steam–reforming methane (*22–24*).

While reaction between steam and hydrocarbon is the predominant reaction taking place throughout, in the later stages of the reaction when an appreciable partial pressure of hydrogen has built up, some direct hydrogenation of the feed is almost certain to take place. It is not possible however to differentiate the methane formed in this way from that produced by hydrogenation of carbon oxides.

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