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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 II

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The products of the nickel catalyzed reaction between steam and heptane have been analyzed at different stages of decomposition of the reactants. The products approach, but do not exactly conform to, the composition which would be obtained from a system in which the water gas and carbon monoxide hydrogenation reactions are at equilibrium. The results suggest that the primary products of decomposition are hydrogen and carbon monoxide. In spite of this, the assumption that equilibrium is attained along the catalyst bed in an adiabatic reactor leads to a satisfactory correlation between bed temperature and degree of decomposition. When catalyst activity is lost for the reforming process, a comparable loss of activity also occurs for the equilibrating reactions.

INTRODUCTION

When hydrocarbons are completely decomposed with steam over a nickel catalyst to give a gas which is a mixture of methane, carbon monoxide, carbon dioxide, and hydrogen, it has been found (*1–4*) that the product gas composition satisfies the water-gas [Eq. (1)] and carbon monoxide-methanation [Eq. (2)] equilibria at the reactor outlet temperature and pressure.

$$CO + H_2O \rightleftharpoons H_2 + CO_2, \quad (1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O. \quad (2)$$

To explain the phenomena observed in industrial plants, it has been suggested that these equilibria also apply when the feed is only partly decomposed (*1*). The following experiments were therefore carried out to test this hypothesis under near isothermal conditions and to see if this would give any information on the mechanism of the steam–hydrocarbon reaction. In addition, experiments were made in an "adiabatic" reactor to simulate the industrial practice of low-temperature steam-reforming, wherein heat input to an insulated reactor is solely that carried in by the preheated reactants and heat output is assumed to be that carried out by the hot outlet gases. Finally, the activity of the catalyst for the above reactions was compared with that for the overall hydrocarbon steam reaction. The experiments were all made using a hydrocarbon feed of *n*-heptane and the same catalyst as in Part I (*8*), namely, coprecipitated 75% nickel–alumina.

Two previous papers have described similar experiments for butane and steam,

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with conflicting conclusions. Bhatta and Dixon (*5*) found that equilibrium was achieved at all points along a catalyst bed of 15% nickel–alumina; Rogers and Crooks (*6*, *7*) using a 75% nickel–alumina catalyst found that it was not. In the following, the catalyst was similar to that used by Rogers, but heptane replaced butane.

Experimental Methods

The apparatus has been fully described in Part I (*8*). The conversion of heptane was measured on a specially adapted chromatograph as previously described, but in most of the experiments the greatest interest was in the dry gas composition after condensation and removal of unreacted heptane and excess steam. This was determined chromatographically using a Poropak Q column at room temperature. Besides methane, carbon monoxide, carbon dioxide, and hydrogen, which were always present, ethane was occasionally detected, but the amounts were always small in relation to the methane and carbon dioxide. Carbon monoxide was also always at a low concentration—usually <1% (v/v) of the total dry gas. The outlet steam partial pressure was calculated from a knowledge of the proportions of heptane and steam in the feed, the fraction of heptane decomposed, and the gas composition.

It was not possible to suppress completely the development of a temperature variation along the catalyst when using the "isothermal" reactor at a fairly high conversion of the feed (>30%). The use of a helium gas diluent and high steam: distillate ratios was of considerable help but the temperature scans along the catalyst made with the movable thermocouple still indicated variations of approximately 5 to 10° depending on the amount of conversion. Where gas compositions are related to temperature, therefore, the outlet temperature is given. In the "adiabatic" experiments, the reactor was wrapped in several layers of insulating ceramic fiber before being placed in the furnace and helium was not added to the reaction mixture.

Results

Outlet Gas Compositions Under Isothermal Conditions

The outlet gas composition was determined at different values of the overall conversion of the heptane. For a fixed ratio of hydrocarbon:steam:helium at constant reactor conditions, the different values of conversion were obtained, either by changing the total feed rate, or by allowing the catalyst activity to decay over a long period of time. The results obtained by

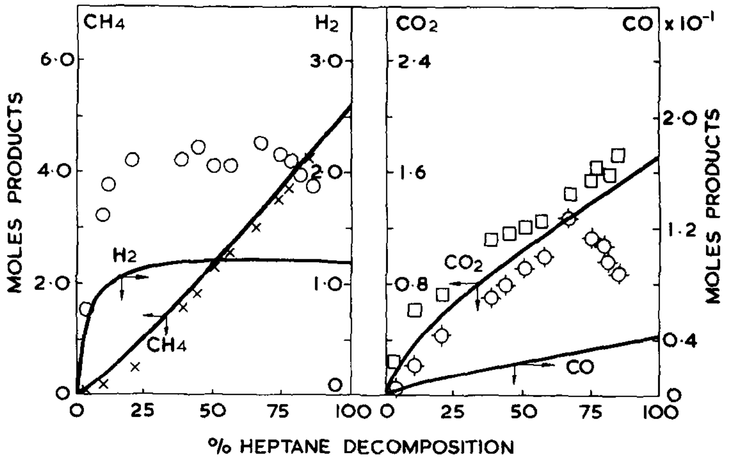


FIG. 1. Experimental and theoretical product gas composition in moles of product per mole of heptane fed: conditions: 450°C; 14.7 atm. Lines indicate amounts if products are at equilibrium; experimental point: ⊙, H_2; ×, CH_4; □, CO_2; -◇-, CO.

both these methods could not be distinguished from one another which indicated that the product composition was probably a function of the conversion of the feedstock only.

Figure 1 shows the results of an experiment at 450°C and 14.7 atm pressure with a helium:steam:heptane ratio of 8.3:10:1 *M*. Similar experiments were made at 400°C, and with a 25:25:1 helium:steam:heptane mixture at 425 and 450°C. In Fig. 1, they are compared with the gas compositions which would have been obtained had the product gas and residual steam been at equilibrium according to Eqs. (1) and (2). The method of computing the composition is given by Dodge (*9*), the values for the equilibrium constants being obtained from Ref. (*10*). In the calculation it was assumed that only the products and steam are involved and that the undecomposed hydrocarbon acts, together with the helium, as a diluent gas. The yields are expressed in moles of gas produced per mole of heptane fed which enables the buildup of the individual products to be followed.

TABLE 1

VALUES OF THE EQUILIBRIUM FUNCTIONS AT DIFFERENT HYDROCARBON CONVERSIONS AT 450°[a]

	Conversion (%)	K_1	K_2
	85.4	0.213	0.00535
	80.1	0.232	0.00919
	78.2	0.227	0.0151
	74.9	0.226	0.0208
	56.7	0.255	0.0260
	51.3	0.230	0.0316
	44.7	0.209	0.0367
	33.1	0.187	0.0701
	21.0	0.187	0.0777
	(°C)		
Theoretical values at	400	0.086	0.000066
	450	0.135	0.0009
	500	0.204	0.0093

[a] $K_1 = (CO)(H_2O)/(CO_2)(H_2)$

$K_2 = (CO)(H_2)^3/(CH_4)(H_2O)$.

An alternative method of presenting the results is to calculate the equilibrium functions corresponding to the outlet gas compositions, again assuming that the residual heptane and helium can be regarded as diluents. The results of such calculations are shown in Table 1. The reproducibility of measurements, particularly of K_2 was not good because small errors in the analysis were magnified by the power expressions in the formula for K_2.

The values given are typical of many similar experiments; both constants were consistently higher than would have been expected at equilibrium at the reaction temperature. K_2 usually showed a gradual decrease in value as the conversion decreased but K_1 only decreased appreciably as complete reaction was approached. The discrepancies were obviously too large to be attributed to small errors in temperature determination.

Conversion Measurement in an Adiabatic Reactor as a Function of Outlet Temperature

A lagged reactor was used in these experiments in which the steam:heptane ratio in the feed was 9.5:1 *M*, the total pressure 14.5 atm, and the inlet temperature 450°C. As the amount of conversion changed, it was determined by analysis of the outlet gases, and the outlet temperature was measured with the movable internal thermocouple. The results are shown in Fig. 2, superimposed on a curve calculated using the equilibrium assumptions previously mentioned, with the additional feature that the reactions were assumed to take place in a thermally isolated reactor. The method of calculation is given in the Appendix.

The Effect of Loss of Catalytic Activity on the Different Reactions

Since the gas composition at a given heptane conversion was independent of the overall catalyst activity, it seemed likely that the activities of the catalyst for the

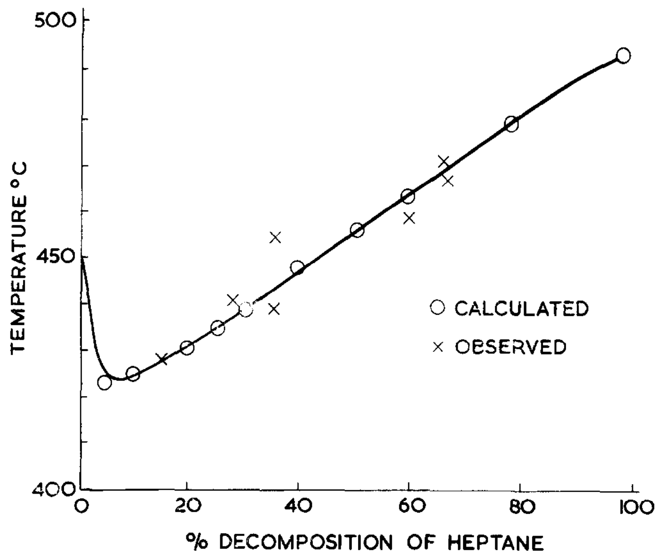


FIG. 2. Experimental and theoretical catalyst temperature in an adiabatic reactor at 14.7 atm: —, temperature if products are at equilibrium; ×, observed measurements.

different reactions occurring thereon were interrelated. Thus the overall heptane conversion of a catalyst was compared with its activity for the water-gas and carbon monoxide-methanation reactions. The water-gas activity was measured as the fractional amount of carbon monoxide reacted when a mixture of carbon monoxide, steam, and helium (molar hourly flows 0.40, 1.4, 1.2) was passed over the catalyst at 272°C and 14.7 atm pressure. Methane formation by secondary reaction was negligible. The activation energy for the reaction was 14.7 kcal.

The carbon monoxide-hydrogen reaction activity could not be measured in a similar way because of the high exothermicity of the reaction. When a reactor was gradually heated in a flowing CO/H_2 stream (molar hourly flows 0.097, 0.266), a sharp increase in the internal temperature was noted when reaction commenced, and this temperature differential—about 60°—was maintained on cooling the reactor until the catalyst temperature had fallen to a point (T) at which the reaction was only just self-sustaining. On further cooling, a sharp drop in temperature occurred. This "threshold" temperature (T) proved to be a reproducible measure of the catalyst activity. It increased as the methanating activity decreased.

In the complete experiment, the overall heptane conversion was measured during the course of an experiment lasting several days, at times immediately prior to the interruption of the steam/hydrocarbon flow for measurement of the activity of the subsidiary reactions by the above methods. In Fig. 3, the methanating and water-gas activities are compared with the relative overall activity (i.e., conversion of heptane/original conversion). It is evident that the activities for all the processes decline together.

DISCUSSION

The consequences of the tendency for the product gases and unreacted steam to equilibrate are twofold. Firstly there is a change in the dry gas composition as the amount of reaction increases; at the temperature and pressure of the present experiments, the composition changes from predominantly hydrogen and carbon oxides initially, to predominantly methane when the feed has been nearly all consumed. Secondly, in an adiabatic reactor, these

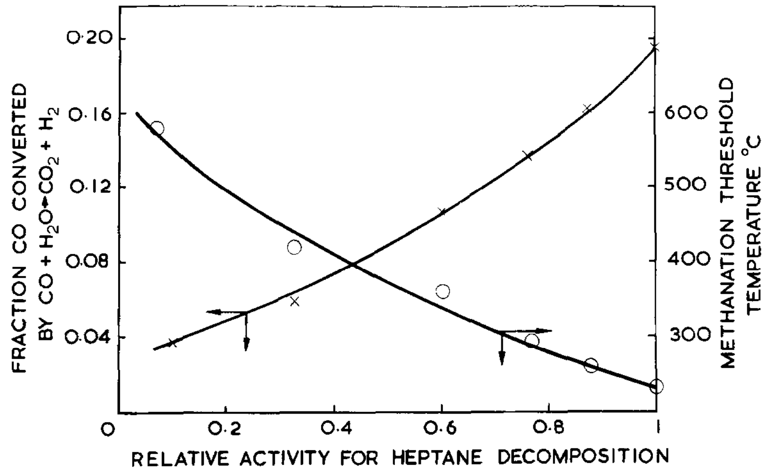


FIG. 3. Activities of methanation and shift reactions relative to overall catalyst activity for decomposition at 425°C (see text for explanation): ○, threshold temperature for methanation; ×, CO conversion by shift reaction.

changes are accompanied by changes in the temperature of the catalyst bed.

Qualitatively these effects are not difficult to comprehend. When the amount of decomposition is low, the small amounts of carbon-containing products are formed in the presence of a relatively high partial pressure of steam. Thus the equilibria [Eqs. (1) and (2)] will favor the production of carbon dioxide and hydrogen no matter what the initial products might be.

The overall reaction is then endothermic and if carried out adiabatically, a reduction in bed temperature will be observed. For example at 450°C, when only 5% of the heptane has decomposed, the reaction is approximately

$$C_7H_{16} + 8H_2O \rightarrow 4CO_2 + 3CH_4 + 10H_2 + 85 \text{ kcals.}$$

As decomposition progresses, the steam partial pressure is decreased not only by its consumption by reaction, but also by dilution with the product gas since there is an overall increase in volume. Thus the proportion of methane produced increases progressively at the expense of hydrogen. This trend is enhanced by pressure because of the diminution of volume accompanying the forward reaction [Eq. (2)]. The overall reaction also becomes progressively more exothermic giving rise to temperature distributions similar to those shown in Fig. 2.

It is thought that these equilibrating reactions may be relatively rapid in comparison to the initial decomposition, since little evidence has been obtained for inhibition of the reaction by products (*8*). Unless methane production was fairly rapid some inhibition could be expected, as decomposition of the heptane to carbon oxides and hydrogen would be limited thermodynamically to about 20%.

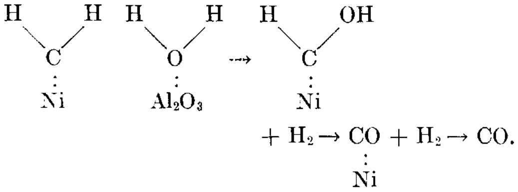
The deviations observed from the equilibrium compositions enable suggestions to be made as to which are the primary reaction products. The results of all the experiments undertaken show the same trends as exhibited in Fig. 1, viz., a deficiency of methane and an excess of carbon oxides and hydrogen in the earlier stages of the reaction. As reaction proceeds, the excess of hydrogen and carbon oxides decreases, with the implication that methane is being formed from them and that they are the primary reaction products.

Unless most of the methane is formed in this way, it is difficult to imagine how amounts of hydrogen and carbon oxides in excess of their equilibrium amounts could be attained, or conversely, how the methane could be reduced to less than its equilibrium amount. This is not to say that at some stage in the reaction when sufficient hydrogen has accumulated in the products, there will not be some methane produced directly from the feedstock by hydrogenation, but its direct formation by the steam–hydrocarbon reaction seems unlikely by any simple mechanism.

It is more difficult to decide which of the carbon oxides is first formed as both are present in excess of the equilibrium amounts. It is not sufficient to say that because the carbon dioxide accumulates in greater quantities than the carbon monoxide, it is the initial product; it is necessary to compare its excess with the carbon monoxide excess. Table 1 shows that the expression $(CO)(H_2O)/(CO_2)(H_2)$ is always greater than at equilibrium. Now if CO_2 were an initial product, together with an excess of hydrogen, it seems unlikely that sufficient CO could be formed to make $(CO)(H_2O) > (CO_2)(H_2)$, but if CO and H_2 were initially present, the rate of CO_2 production could be just slow enough for the above inequality to occur. This reaction would however be faster than the methanation reaction. It is unlikely that the methane is formed directly from carbon dioxide as it is shown in (*11*) that the reaction will not proceed if the pressure of carbon monoxide exceeds 10^{-4} atm.

Re-examination of the results of Rogers and Crooks (*6*) showed that if the results given in their Table 1 were plotted in the form of our Fig. 1, exactly the same trends were observed during their decomposition of butane at 400°C, but at 500°C, the departures from the equilibrium gas compositions were small. This could arise because at 500°C, the methane content of the gases at equilibrium is substantially lower and therefore less hydrogen and carbon oxides have to react to achieve this equilibrium quantity, which can, therefore, be attained more readily.

The actual reaction which gives rise to the first products must still be a subject for speculation. It was suggested in Part I that on the basis of the kinetics, a satisfactory model is the reaction of adsorbed single carbon species with water. The following scheme is similar to that of Balashova *et al.* (*12*) and would give the products we propose:



No positive evidence was ever obtained for the existence of any aldehydic constituents in the products from partly decomposed heptane. These might have been expected from such a scheme if the reacting carbon species contain several carbon atoms.

The temperature profile in the adiabatic reactor is similar to that found in industrial and larger pilot plant reactors, and it reflects the change in product composition along the catalyst bed arising from the tendency of the products to attain equilibrium. Although the isothermal experiments showed that this was not completely established, the thermal consequences of this in an adiabatic reactor were small as is shown by the agreement between the calculated and observed temperature profiles. Besides, as Rogers and Crooks showed, the magnitude of the deviations decreases at the higher temperatures of the adiabatic reactor outlet. Loss of catalytic activity results in the displacement of the temperature profile towards the outlet of the catalyst bed. The results given in Fig. 3 show that when this occurs, activity for both decomposition and equilibrating reactions is lost with the implication that similar sites are required for both sorts of reactions.

Slovokhotova *et al.* (*13*) suggested that different decomposition reactions with different activation energies were necessary to account for the changing product composition from steam–hydrocarbon reactions. It can now be seen that this can arise from the effects of temperature and pressure on the equilibrating reactions. The results corroborate those of Rogers and Crooks rather than Bhatta and Dixon in that there is a tendency for the products of partial decomposition to be poorer in methane than equilibrium would allow. This could be a further manifestation of the differences in the properties of the catalysts used; other differences between the 75 and 15% nickel-on-alumina catalysts have been previously mentioned (*8*).

APPENDIX. CALCULATION OF THE RELATION BETWEEN GAS TEMPERATURE AND FRACTIONAL DECOMPOSITION IN AN ADIABATIC BED IN WHICH THE PRODUCTS AND STEAM ARE EQUILIBRATED BY THE METHANATION AND SHIFT REACTIONS

The calculations were made using prepared sets of tables for each reaction mixture, with the pressure and C/H_2 and C/O_2 ratios being defined for each set. Each set consisted of a series of tables at increments of 5% decomposition of the feed hydrocarbon from 5 to 100%. Each table listed the gas composition which would be obtained at temperatures from 300–600°C, the composition being calculated at every 5°C by a method similar to that described in (*9*). In addition, a quantity referred to as the total heat was listed for each gas consumption. This was defined as the sum of the total enthalpy, and gross heat of combustion of all the products and steam, the standard state being taken as the usually existing state at 25°C and 1 atm. Values of these properties for pure hydrocarbons and the products of combustion are listed in Ref. (*14*). The total heat in the adiabatic system will remain constant and will be equal to the total heat of the ingoing reactants at the inlet temperature. Thus the total heat of the products (including the unreacted steam) will be the difference between the total heat of the reactants and the total heat of the unreacted hydrocarbon. This difference is calculated over the expected temperature range and compared with the total heat values listed in the tables for the appropriate percentage decomposition, interpolating where necessary, to find the temperature at which both values are equal. The temperature thus calculated is that attained by the mixture of products, unreacted steam, and unreacted hydrocarbon when the composition satisfies both the water-gas shift and methanation reactions.

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