sufficient to examine only the gaseous products through C_5 as a preliminary measure and then only if these compounds showed a significant activity to proceed with a complete radioanalysis of the higher carbon numbers.

Product ratios and percentage conversions are in agreement with the earlier integral experiments and are not quoted here. The data are collected in Table IV. Again note that the coke activity was measured at the end of the cracking run.

TABLE IV

RADIOACTIVITY OF PRODUCTS FORMED ON CRACKING CETANE AT 372° OVER A SILICA–ALUMINA CATALYST CONTAINING RADIOACTIVE COKE

Substance	C.p.m./ mg. carbon	Total, cc.	Total counts	$\frac{\text{SA product}}{\text{SA coke}}$
CH_4				
C_2H_4	18	1.3	24	1.8×10^{-3}
C_2H_6				
C_3H_8	9	14.8	222	0.9×10^{-3}
C_3H_6	10	11.2	179	1.0×10^{-3}
i-C_4H_{10}	14	26.8	778	1.4×10^{-3}
i-C_4H_8 1-C_4H_8	9	6.4	128	0.8×10^{-3}
n-C_4H_{10}				
cis + *trans*-C_4H_8	7	8.6	120	0.7×10^{-3}
Pentanes and pentenes	2	9.6	58	0.2×10^{-3}
Coke	10,200	54 (mg.)	550,000	1

The results of this experiment clearly indicate that coke exchange plays a negligible role in determining the activity spectrum of our previous results. Still the fact that about 0.5% of the total activity of the coke plus that of the gaseous product activity is found in these products is surprising and perhaps significant. Incidentally, it might be remarked that from the fact that the propane radioactivity is no higher than that of the other hydrocarbons one has fair assurance that the radioactivity transferred to the gas phase is not due to a hydrogen transfer to residual chemisorbed propylene that might have been left from the coking step itself.

One final way of summarizing coking formation that actually took place during the regular tracer experiments in the integral runs given in paper I is to summarize the ratio of the percentage of the total radioactivity in the coke divided by the percentage of the feed gas converted to coke. These ratios were found to be 1.5, 0.3, 0.3, 3.8 and 3.4 for the runs using radioactive propylene, radioactive propane, radioactive normal butane, radioactive heptene-1 and radioactive normal heptane, respectively. It is easy to understand why the ratio for propylene and heptene-1 are both much greater than the ratios for propane and normal butane because in general olefins are more prone to form coke than are the saturated hydrocarbons. However, it is difficult to understand why the ratio is so high for normal heptane. The answer to this latter observation will have to wait further experimental work.

Acknowledgments.—Thanks are due to the Atomic Energy Commission for supporting this work under contract No. AT 301–2008, and to the Leeds & Northrup Co. for the donation of two recorders used throughout the work.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

The Kinetics of Propane Cracking on Nickel[1]

BY DOUGLAS W. MCKEE

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The catalytic cracking of propane on unsupported nickel has been studied over the temperature range 100–200°. Methane, small amounts of ethane and a carbonaceous surface residue of variable composition were the products of the reaction, which proceeded with an activation energy of 15 ± 1 kcal./mole. A zero-order dependence of the rate of reaction on the partial pressure of propane was generally found, although poisoning of the catalyst by strongly adsorbed residues became increasingly important at higher temperatures. Possible mechanisms of the cracking reaction are discussed.

Introduction

Comparatively little information is available concerning the chemisorption and dissociation of saturated hydrocarbons on metal surfaces. Thus, in spite of the fact that the subject of hydrocarbon cracking on silica–alumina and oxide materials has a very considerable literature and the reactions and intermediates involved are fairly well understood, few detailed studies have been made with metallic catalysts and the mechanism of carbon–carbon cleavage on metal surfaces is not well defined. Most of the studies which have been made, such as those of Morikawa, Trenner and Taylor,[2a] are concerned mainly with hydrocracking, in which both hydrocarbon and hydrogen are present in the gas phase. The situation here is probably different from that which occurs when the hydrocarbon is present alone. A recent study from this Laboratory[2b] has shown that the C–H bonds in ethylene can be broken at as low as −78° on a nickel catalyst, whereas C–C bond cleavage did not become appreciable until 80°. In the case of ethylene the deposition of involatile carbonaceous residues on the surface during the course of the reaction seemed to play an important role in the activity of the metal. As a continuation of this work, it was decided to compare the behavior of

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(1) This work was made possible by the support of the Advanced Research Projects Agency (Order No. 247-61) through the United States Army Engineer Research and Development Laboratories under Contract Number DA-44-009-ENG-4853.

(2) (a) K. Morikawa, N. R. Trenner and H. S. Taylor, *J. Am. Chem. Soc.*, **59**, 1103 (1937); (b) D. W. McKee, *Nature*, **192**, 654 (1961); *J. Am. Chem. Soc.*, **84**, 1109 (1962).

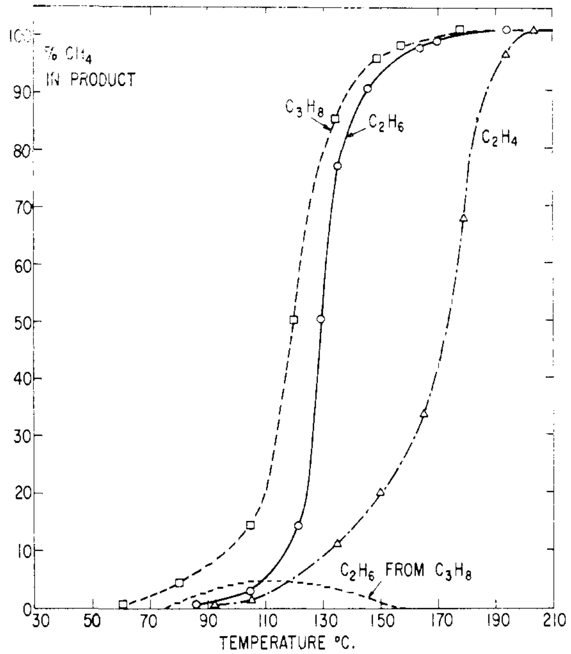

Fig. 1.—Extent of cracking of C_3H_8, C_3H_8 and C_2H_4 after 4 hr. contact with 14.8 g. nickel; initial pressure ≅ 6 mm.

ethylene with that of propane under the same conditions, in the hope that some insight could be gained into the nature of the cracking reactions on the surface of a "d-band" metal.

Experimental

Apparatus.—A static volumetric technique was used similar to that employed in the previous investigation.[2b] Pellets of pure carbonyl nickel were sealed into the adsorption apparatus and protected from mercury vapor by means of gold foil traps. A measured volume of propane was allowed to stand over the catalyst for varying periods of time and changes in pressure were followed by means of a wide-bore mercury manometer. Samples of the gas phase in contact with the metal were condensed in demountable traps cooled in liquid nitrogen. The contents of the traps were then analyzed by means of an F. & M. Temperature Programmed Gas Chromatograph, using a 2.4-m. silica gel column and helium as carrier gas. By this means the products of reaction were studied as a function of time, temperature and pressure. In most of the experiments, the initial pressure of propane in the storage part of the apparatus was adjusted to about 7.1 mm. After expansion into the catalyst chamber, the initial pressure over the metal was about 5.6 mm. in a total gas volume of 117.7 ml. The temperature of the catalyst was generally kept constant to within ± 0.5° and the pressure measurements were accurate to ± 0.01 mm. At the conclusion of each run, the metal was evacuated at 400° for a period of one hour and then reduced in a stream of pure hydrogen at 400° for at least four hours. The hydrogen for this purpose was purified by diffusion through a palladium thimble and was maintained at a pressure of about 5 cm. over the metal. Finally the metal was evacuated for at least 12 hours at 400° to a residual pressure less than 2×10^{-6} mm. Less stringent activation techniques led to unreproducible results.

Materials.—Phillips "Research Grade" 99.98% pure propane was used throughout this work; the gas was condensed and fractionally distilled from a liquid nitrogen trap before being admitted into the apparatus.

High purity 325 mesh "Inco D" carbonyl nickel was used, the sample being pressed loosely into 6-mm. pellets. The weight of metal was 14.8 g. and the total surface area of the sample was 1.41 m.^{2} as determined by the B.E.T. method, using krypton adsorption at −195°.

Results

Cracking of Ethylene, Ethane and Propane Compared.—In order to compare the cracking behavior of propane, ethane and ethylene under the same conditions, the same initial pressure of each gas was allowed to stand over the reduced metal for the same time at each of a series of temperatures between 50 and 300°. The amounts of methane produced under one set of conditions are compared for the three gases in Fig. 1. Methane was the sole gaseous product from both ethane and ethylene, but the cracking of propane also produced a small amount of ethane in the range 80 to 150°. Propane cracked more readily than the other two gases, the production of methane first becoming noticeable from the former at 65°. It was not possible to compute activation energies for cracking from the data of Fig. 1 as the extent to which the systems have approached equilibrium vary considerably from point to point.

Propane Cracking.—Measurements of the rate of methane formation from propane were made at temperatures ranging from 100 to 200°. The reaction could be followed by measuring the change in pressure over the sample, however an unambiguous interpretation of the rate of pressure rise could not be obtained at short contact times as it was found that rapid irreversible chemisorption of propane took place immediately the gas came into contact with the metal, resulting in an initial rapid decrease in pressure. This chemisorption was appreciable at temperatures too low for cracking to be observed. At 80 , the volume of propane chemisorbed was found to be 0.19 ml. STP and 0.20 ml. STP at 106°, at which temperature the production of methane was just measureable after 1 hr. contact time.

The area occupied by a molecule of propane in an adsorbed monolayer can be calculated approximately by assuming that the packing is the same as in the liquefied adsorbate. Then the molecular area $A_m = 4 \times 0.866 \left(\frac{M}{4\sqrt{2}\,Nd_L}\right)^{2/3}$ where M is the molecular weight and d_L, the liquid density of the adsorbate and N is Avogadro's number. A value of 27.4 Å.^{2} is found by this method in the case of propane. This procedure, which ignores orientation effects in the monolayer, has been found to give consistent results in the case of the physical adsorption of propane on silica gel.[4] In the present case, using a value of 27.4 Å.^{2} for the monolayer area of the propane molecule and the measured area of the metal sample, the observed adsorption value of 0.19 ml. STP was found to correspond very closely to the completion of a monolayer on the metal surface. It thus appears that a monolayer of chemisorbed propane was formed before the cracking reaction began.

The yield of methane as a function of time is shown at three different temperatures in Fig. 2, the methane content of the gas being found by direct analysis. Each data point in these and subsequent diagrams represents a separate determina-

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(3) S. Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, N. J., 1945, p. 287.

(4) D. W. McKee, *J. Phys. Chem.*, **63**, 1256 (1959).

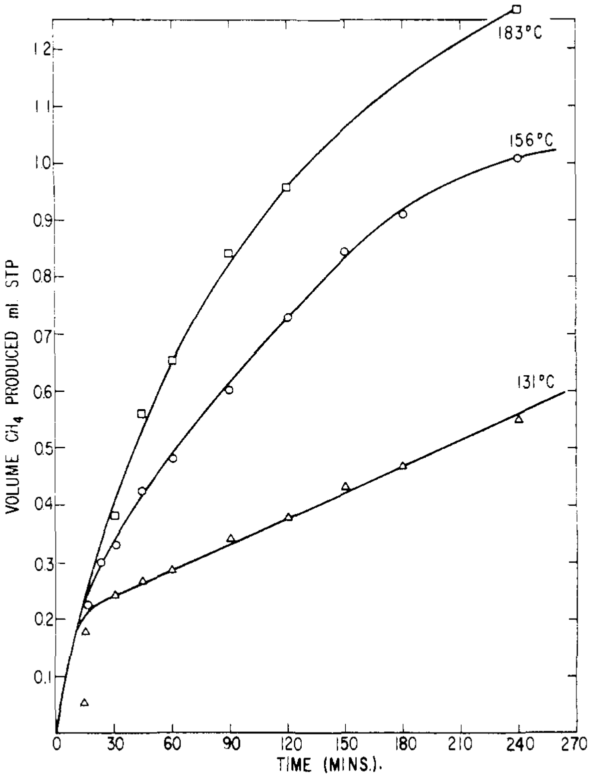


Fig. 2.—Rate of CH_4 production at 131, 156 and 183°; initial C_3H_8 pressure = 5.6 mm.

tion, the metal being reduced and evacuated as described above after the completion of each measurement. The volume of methane produced was closely linear with time at 131°, although this linearity did not extend to the origin. These results indicate that a zero order reaction was taking place, the rate being independent of propane partial pressure. At short times the rate was dependent on propane pressure until the monolayer was complete. A small amount of ethane was also formed at this temperature, although its concentration did not exceed 1–2%. At 156°, the time dependence of methane yield was more complex, the central portion of the plot being linear but with deviations at both extremities. At 183°, the rate of disappearance of propane was given approximately by the expression

$$- \mathrm{d}P_{C_3H_8}/\mathrm{d}t = kP_{C_3H_8}^{1.32}$$

though, as discussed below, self-poisoning of the surface was rapid in this case. No ethane was observed in the products at 183° or above.

In addition to the gaseous product of the cracking reaction, a nonvolatile residue was left on the surface, as in the case of ethylene dissociation.[2b] An average composition of this surface residue could be calculated in the form $(CH_n)_x$, by performing a mass balance on the total reactants and products. Hence

$$n = \frac{8(n'_{C_3H_8} - n_{C_3H_8}) - 6n_{C_2H_6} - 4n_{CH_4}}{3(n'_{C_3H_8} - n_{C_3H_8}) - 2n_{C_2H_6} - n_{CH_4}}$$

where $n'_{C_3H_8}$ is the number of moles of propane introduced initially and the other molar quantities refer to the amounts of the various gases present

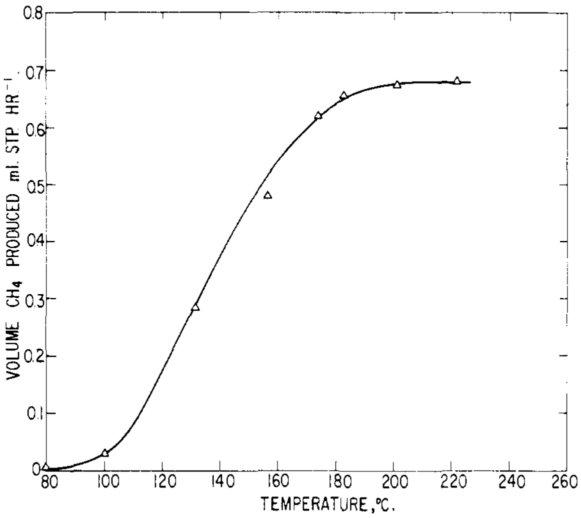


Fig. 3.—CH_4 yield as a function of temperature, 1 hr. contact time.

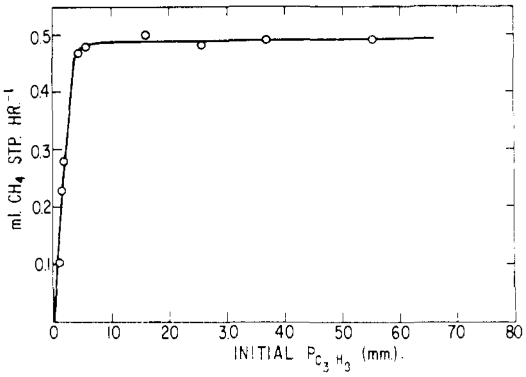


Fig. 4.—CH_4 yield *vs.* initial C_3H_8 pressure at 156°, 1 hr. contact time.

at the end of the run. The value of n varied somewhat with temperature and extent of reaction, but an average value of 1.5–1.7 was found in most cases.

Figure 3 shows the yield of methane after one hour contact as a function of temperature. The total volume of methane evolved approached a limiting value at high temperatures, due probably to the poisoning of the surface with carbonaceous deposits. These residues could not be removed by pumping at the reaction temperature but, as in the case with the residues from ethylene dissociation,[2b] prolonged reduction with hydrogen at a temperature of about 400° was necessary to restore the metal to its previous activity.

The effect of initial propane pressure on the rate of methane formation at 156° is illustrated in Fig. 4. For initial propane pressures above 5 mm., the volume of methane produced in 1 hr. was constant over a ten-fold range in pressure. This result confirms that the kinetics of cracking at this temperature and below were zero order with respect to the propane partial pressure. The initial propane pressure required to cover the surface with a monolayer were calculated to be 1.5 mm. (assuming 27.4 Å.[2] for the cross-sectional area of C_3H_8), a result which agrees well with the beginning

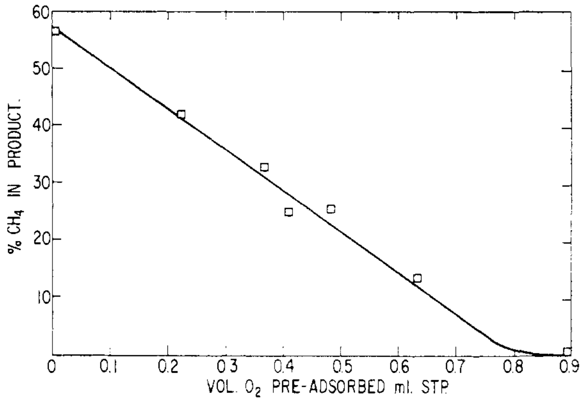


Fig. 5.—CH_4 yield as a function of pre-adsorbed O_2; 156°, 1 hr. contact time.

of methane evolution from Fig. 4. For small initial pressures of propane, the rate of reaction was approximately first order, but the data in this region are rather limited.

Owing to the rapid adsorption of propane which occurred at the beginning of each measurement, it was not possible to calculate the activation energy for the cracking reaction from the initial rate of pressure increase. However, comparison of the rate of methane formation in the nearly linear portions of the curves for the three temperatures of Fig. 2, gave an apparent activation energy of 15 ± 1 kcal./mole. The specific zero-order rate constants (k) for unit area of metal surface were 0.41×10^{11} molecules $sec.^{-1}$ $cm.^{-2}$ at 131° and 1.27×10^{11} molecules $sec.^{-1}$ $cm.^{-2}$ at 156°, and the pre-exponential, or frequency factor A was approximately 6×10^{18} molecules $sec.^{-1}$ $cm.^{-2}$.

Effect of Pre-adsorbed Oxygen and Water.—In order to determine whether a metallic surface is necessary for C–C bond cleavage, the effect of pre-adsorbed oxygen on the rate of methane formation was studied. The yields at 156° after 1 hr. are shown in Fig. 5 and indicate that the presence of pre-adsorbed oxygen inhibited the cracking reaction, the volume of CH_4 produced being inversely proportional to the volume of chemisorbed oxygen present. The calculated value for monolayer coverage of the metal surface is 0.38 ml. O_2 STP, assuming 14.1 $Å.^2$ for the cross-sectional area of the oxygen molecule. This value is about half that required to reduce the methane yield to zero; however, there is abundant evidence that multilayers of oxide are formed rapidly on freshly reduced nickel surfaces,[5] and can diffuse readily into the interior[6] of the metal. These results indicate that cracking did not occur on the oxide covered surface. The oxidized surface was inactive catalytically up to about 200°, when it began to function as an oxidation catalyst, converting propane completely to carbon dioxide and water.[7]

Several attempts also were made to investigate the effect of water vapor on the cracking reaction. Water adsorbed rapidly on the reduced metal at room temperature and above, the volume adsorbed being 0.046 ml. STP/g. at 156° and 0.031 ml. STP/g. at 183°. However the adsorption appeared to be reversible and after evacuation of the metal at the adsorption temperature, the rate of the subsequent cracking reaction with propane was unchanged.

Discussion

As a result of experiments on the hydrocracking of ethane and propane on nickel and iron catalysts, Cimino, Boudart and Taylor[8] postulated that dissociation of the hydrocarbon takes place on the metal surface into adsorbed radicals and chemisorbed hydrogen

$$C_2H_6 \rightleftarrows (C_2H_x)_a + (6 - x)/2H_2$$

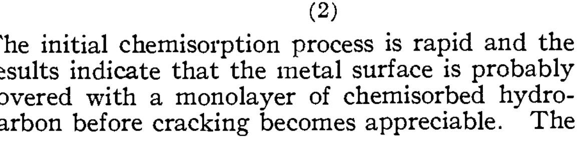
This reversible dissociation was believed to be followed by the breaking of C–C bonds on the surface by interaction of the adsorbed residues with surface hydrogen

$$(C_2H_x)_a + H_2 \rightleftarrows CH_y + CH_z$$

This was believed to be the slow step in the reaction, the removal of the mono-carbon fragments as CH_4 being rapid. By assuming that the fraction of the metal surface covered with hydrogen was proportional to the hydrogen gas pressure, a kinetic expression was deduced which fitted the observed dependence of the rates on the pressures of hydrogen and ethane. A similar mechanism was proposed for the hydrocracking of propane, the initial step being the dissociation

$$C_3H_8 \rightleftarrows C_3H_x + (8 - x)/2H_2$$

These mechanisms are plausible for the cracking of hydrocarbons when hydrogen gas is present in quantity in the gas phase, but it is likely that the rate determining step is different in this case than when hydrogen is absent. Recent work on the cracking of ethane on evaporated films of rhodium[9] in the absence of hydrogen, has failed to detect the production of hydrogen by dissociation, the sole gaseous product of the reaction being methane. In the present work also, no hydrogen was detected in any of the experiments. It seems likely that, in the absence of hydrogen, propane is initially rapidly chemisorbed on the metal surface, followed by dissociation of the chemisorbed species into mono- and di-carbon fragments. Some C–H bond splitting also may occur



$$\begin{tikzcd} & & C_2H_x + CH_y \\ C_3H_8(g) \arrow[r] & C_3H_8(ads.) \arrow[ur, "(1)"] \arrow[dr, "(2)"'] & \\ & & C_3H_n + (8 - n)H \arrow[uu] \end{tikzcd}$$

The initial chemisorption process is rapid and the results indicate that the metal surface is probably covered with a monolayer of chemisorbed hydrocarbon before cracking becomes appreciable. The

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(5) J. J. Chessick, Y. F. Yu and A. C. Zettlemoyer, "Proceedings of Second World Congress on Surface Activity," Vol. II, Academic Press, New York, N. Y., 1957, p. 269.

(6) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.* (*London*), **A177**, 62 (1940).

(7) D. W. McKee, to be published.

(8) A. Cimino, M. Boudart and H. S. Taylor, *J. Phys. Chem.*, **58**, 796 (1954).

(9) R. W. Roberts, *Nature*, **191**, 170 (1961).

rate determining step is probably the dissociation of the C–C bond by reaction 1. Reaction 2 involving C–H bond scission is likely to be more rapid than (1).

Owing to the high speed of migration of hydrogen atoms along the metal surface, the subsequent surface reaction between mono-carbon fragments and chemisorbed hydrogen will be a rapid process

$$^{*}CH_y + (4 - y)H^{*} \longrightarrow CH_4(g)$$

The fact that the concentration of ethane in the gas phase is always small, indicates that the addition of chemisorbed hydrogen to the di-carbon fragments

$$^{*}C_2H_x + (6 - x)H^{*} \longrightarrow C_2H_6(g)$$

may not occur to any appreciable extent; however, the disappearance of ethane at the higher temperatures suggests that catalytic cracking of the ethane initially formed also may take place.

The observed activation energy of 15 ± 1 kcal./mole agrees with the value found by Roberts for the cracking of ethane on evaporated rhodium films[9] and is also close to the value of 20–25 kcal./mole obtained by Cimino, Boudart and Taylor[8] for ethane cracking on iron catalysts. It is probable that the rate determining step with both propane and ethane involves C–C bond fission. The observed zero order kinetics at 131 and 156° are consistent with the idea that the rate determining step is a surface reaction, the concentration of chemisorbed propane being independent of gas phase propane pressure except at very low concentrations. Although at 183°, the rate is apparently a function of propane partial pressure, this effect is probably due to surface poisoning.

According to Morikawa, Trenner and Taylor,[2a] appreciable quantities of ethane as well as methane are found in the product of hydrocracking of propane on Ni-kieselguhr at 157°. It is likely that some of this ethane arose by hydrogenation of the residues on the metal surface. The kinetics of the hydrocracking reaction were found to be strongly inhibited by hydrogen, which apparently competes with the hydrocarbon for adsorption sites on the metal surface. The activation energy for the hydrocracking of propane was found to be 34 kcal./mole.

The formation of strongly adsorbed residues which act as catalyst poisons is apparently of general occurrence in hydrocarbon reactions on metal surfaces. Thus they have been found to play an important role in the dissociation of ethylene[2b] and in the hydrocracking[10] and exchange[11,12] of isomeric pentanes and hexanes on nickel and other metals. The building-up of these residues may give rise to spurious kinetics and activation energies. Although the breaking of C–C bonds in simple hydrocarbon molecules probably involves activation energies of the order of 20 kcal./mole or less,[9] values as high as 54 or 69 kcal./mole have been reported.[10] It seems likely that these values arise, at least in part, from variations in the yield of surface residues at different temperatures.

The build-up of strongly adsorbed and multiply bonded surface residues is also probably responsible for the limiting methane yield shown in Fig. 3. A similar effect has been noted by Galwey and Kemball[11] in the case of exchange of ethane with D_2 over nickel. The activity of the catalyst increased between 0 and 75° but with falling activation energy, between 90 and 150° the catalyst was almost inactive but recovered again between 160 and 200°. In this case hydrogen or D_2 was present and could effectively remove the residues at elevated temperatures, as found in the present work. In the absence of hydrogen, however, the accumulation of residues can retard the dissociation reactions and eventually completely poison the catalyst. In a typical experiment at 156°, 1 ml. STP of C_3H_8 was converted to CH_4 and a surface residue in about 6 hours. Assuming that an active site on the surface occupied 27 Å.[2] (the cross-sectional area of propane in the adsorbed monolayer), this corresponds to a conversion of about 5 molecules of propane per site. This low "turnover number" would render the metal unattractive from a practical standpoint and, in fact, the metal is almost behaving as a reagent in this reaction. A similar buildup of surface deposits has been noted by Franklin and Nicholson[13] for cracking on silica–alumina catalysts. Although prolonged reduction in hydrogen at elevated temperatures is necessary to remove these residues in the gas phase, it has recently been demonstrated[14] that efficient removal of the complexes from propane dissociation on platinum can be carried out electrochemically in a fuel cell operating at 65°.

Acknowledgments.—The author wishes to thank E. J. Cairns and W. T. Grubb for many helpful discussions during the course of this investigation.

(10) J. R. Anderson and B. G. Baker, *Nature*, **187**, 937 (1960).

(11) A. K. Galwey and C. Kemball, *Trans. Faraday Soc.*, **55**, 1959 (1959).

(12) F. G. Gault and C. Kemball, *ibid.*, **57**, 1781 (1961).

(13) J. L. Franklin and D. E. Nicholson, *J. Phys. Chem.*, **60**, 59 (1956).

(14) W. T. Grubb, to be published.