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Hydrocarbon Cracking Reactions on Nickel

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The cracking reactions of several low molecular weight hydrocarbons on a nickel carbide catalyst have been studied in the absence of added hydrogen. Kinetic measurements have shown that the Arrhenius parameters for product methane formation, from different reactants, were closely similar, and this is considered to be evidence that the reaction which immediately precedes the product methane desorption step is rate-controlling. During such cracking reactions, in which product carbon was deposited on the solid phase, a small concentration of metallic nickel was maintained in the catalyst. It seems probable, therefore, that crystalline nickel was the active solid in cracking and that crystalline nickel carbide was not a necessary intermediate in nickel-catalyzed cracking and hydrocracking reactions.

The results obtained in the present study are compared with data for other reactions occurring at nickel surfaces and the significance of the obedience of the Arrhenius parameters, measured for these reactions, to the compensation law is considered. It is concluded that the compensation effect results from the establishment of surface equilibria, the position of which is determined largely by hydrogen availability, on the active surface of the solid catalyst. Such surface equilibria involve species formed by dissociation of gaseous products and reactants and (possibly) also surface metal atoms.

Studies designed to elucidate the mechanism of the nickel-catalyzed cracking reactions of hydrocarbons have been reported by many different groups of workers. These investigations have shown that the reaction of a hydrocarbon with a nickel surface may result in complex dissociation equilibria, where the most abundant chemisorbed species may vary with changes in experimental conditions (*1–3*). The chemical properties of such surface radicals have not been fully characterized and agreement has not been reached on the steps which control the rate of hydrocarbon hydrocracking on nickel. Taylor and co-workers (*4–7*) concluded that the rate-limiting step in the hydrocracking reaction was rupture of a C–C bond in the chemisorbed hydrocarbon radical. Anderson and Baker (*8*), however, believe that the reaction rate was controlled by the process which resulted in product methane desorption. Galwey (*9*) has shown that the kinetic characteristics of methane formation on hydrogenation of hydrocarbon residues, chemisorbed on nickel, were similar to those observed for nickel carbide hydrogenation (*10*) and concluded that here the methane production step was rate-limiting.

The present article reports kinetic measurements for the cracking reactions of hydrocarbons on nickel carbide in the absence of added hydrogen. It was expected that this study might yield information concerning (i) the rate-limiting step in hydrocarbon cracking reactions; (ii) whether nickel carbide was a necessary intermediate in nickel-catalyzed cracking reactions; and (iii) the effect of saturation of the metallic phase with carbon on the catalytic activity of the metal. The authors are unaware of any previous study of the activity of nickel carbide as a cracking

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catalyst. Some measurements of the rate of propane hydrocracking over the same catalyst preparation were made for comparative purposes.

We use the terms "hydrocracking" and "cracking" to refer to hydrocarbon breakdown reactions in the presence and absence of added gaseous hydrogen, respectively.

EXPERIMENTAL

The apparatus was similar to that previously used to study the reduction of nickel carbide (*10*). Yields of methane, the most abundant gaseous product, were measured using gas-solid chromatography and a katharometer detector. Other volatile products were identified, and estimated, by gas-liquid chromatography and a radioactive ionization detector, using appropriate liquid phases and column lengths. The cracking of benzene and of octacosane ($C_{28}H_{58}$) were studied in the apparatus previously used to investigate the nickel carbide–water vapor reaction (*11*).

Nickel carbide, from a single preparation (a gift from the International Nickel Co.) was used for all experiments. The method of preparation, the composition, and both physical and chemical measurements made for this particular sample of nickel carbide have been detailed elsewhere (*10–12*). Reactant gases, supplied by Matheson and Co. were outgassed and fractionally distilled before use.

Experimental procedure. A fresh catalyst sample was used for each reactant gas studied. About 0.1 g of nickel carbide was weighed (±0.2 mg), dispersed on glass wool in the reaction vessel, and evacuated to $\sim 10^{-6}$ torr at 300° for 3 hr. A measured volume of gaseous reactant (a standard quantity, 0.85 ± 0.02 ml STP at 50 ± 2 mm, unless otherwise stated) was admitted to the reaction vessel and remained in contact with the catalyst at known temperature for a measured time. The contents of the reaction vessel were then almost completely removed by expansion into the Toepler bulb for subsequent chromatographic analysis and a new volume of reactant was admitted. Product yields were measured at appropriate time intervals for each of a number of reaction temperatures. For most of the reactants, measurements were repeated on a second catalyst sample to confirm reproducibility. Studies were largely confined to reaction conditions under which the yield of the most abundant product (methane) represented a small fraction of the reactant dose admitted.

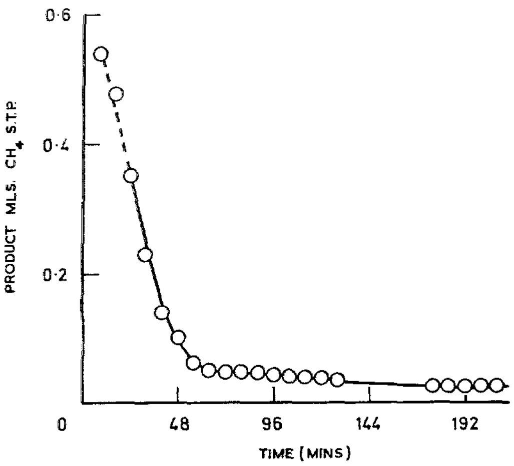

FIG. 1. Approach of reaction to constant rate of methane production. Readings were made at 8-min intervals during reaction of successive volumes of ethane at 50 mm on 0.15 g of a fresh sample of nickel carbide. (Calibrations were uncertain in dotted region.)

RESULTS

Methane Formation

The most detailed kinetic studies were concerned with the methane formation reaction. The rate of production of this substance, from the cracking reaction and using a fresh sample of catalyst, progressively decreased from a relatively rapid initial value to a constant rate which was approached in an approximately asymptotic manner (Fig. 1). This constant rate was apparently not further decreased thereafter by carbon deposited by reactions such as $2\ C_2H_6 \rightarrow 3\ CH_4 + C$. After a change in the catalyst temperature, the reaction rate underwent a comparatively rapid change during the first 30 min and thereafter the rate of change decreased but remained appreciable for 2–3 hr. Following changes in reaction conditions (temperature and reactant pressure) the establishment of the constant rate of reaction required a considerable equilibration interval. Care was taken to ensure that such equilibration had occurred before recording measurements reported in the present article. Changes in reactant contact time, however, were followed by rapid establishment (two-three readings) of the new constant rate of reaction.

Typical plots of methane yield against contact time for the cracking reactions of ethane and of butane are shown on Figs. 2 and 3, respectively. A linear increase in product yield with reaction time was observed and extrapolation of the line to zero methane yield showed short induction periods to reaction ($t' = 1$ to 5 min). In general, t' values tended to increase with the number of carbon atoms in the reactant molecule and with decrease in reaction temperature.

Arrhenius parameters found from the kinetic measurements (linear rates of reactions studied 250–330°) for the hydrocarbon cracking reactions which were included in the present investigation are reported in Table 1. Kinetic data for the cracking reaction of octacosane were not obtained, since only trace amounts of methane were formed by the relatively severe cracking conditions of 30 min contact with the catalyst at 330°.

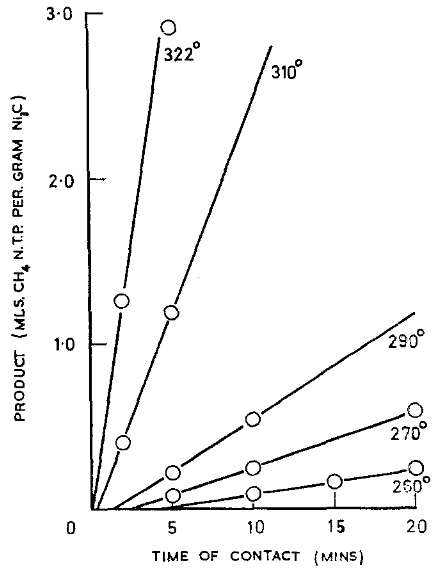

FIG. 2. Typical kinetic measurements for the production of methane on cracking ethane over nickel carbide.

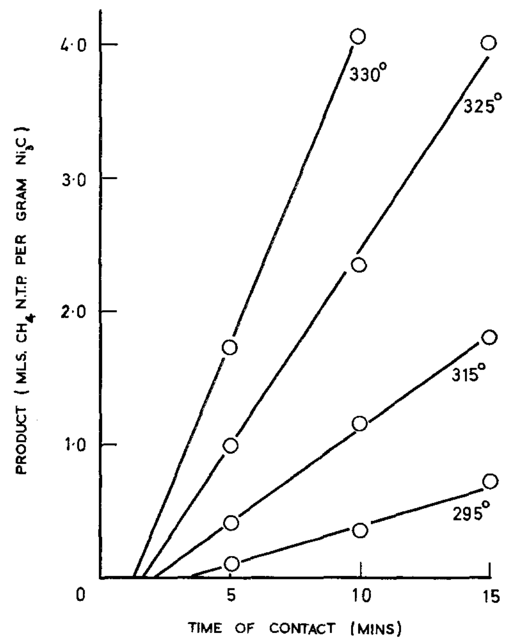

FIG. 3. Typical kinetic measurements for the production of methane on cracking butane over nickel carbide.

Reaction rate–pressure dependency measurements were made for cracking ethane and propane. Comparison of rates before and immediately following a change in

TABLE 1
SUMMARY OF KINETIC DATA FOR METHANE FORMATION FROM HYDROCARBONS[a]

Compound	E	$\log_{10}A$	$k_{315°} \times 10^{12}$
Ethane	38	25.7	0.40
Ethylene	37	24.9	0.183
Acetylene	40	25.9	0.126
Propane	36	24.8	0.319
Propylene	38	25.5	0.230
Cyclopropane	38	25.5	0.230
Butane	44	27.8	0.282
1-Butene	44	27.8	0.282
Benzene	57	31.3	0.016

[a] $k_t°$ and $\log_{10}A$ are expressed as molecules cm^{-2} sec^{-1} and the error in $\log_{10}A$ is ±0.7. E is in kcal per mole and the error is ±10%.

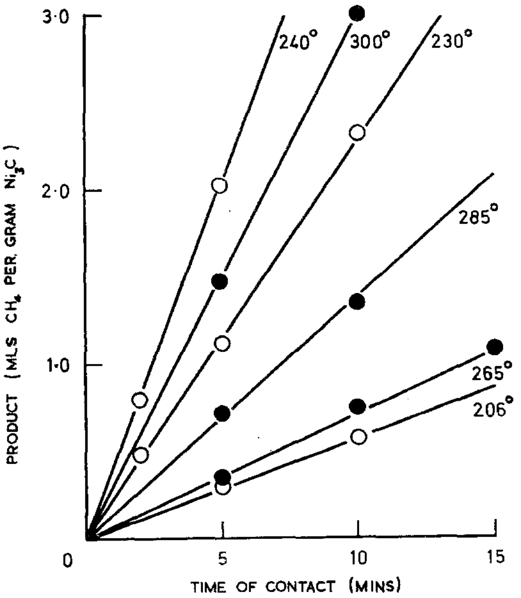

FIG. 4. Typical kinetic measurements for the production of methane on hydrocracking propane over nickel carbide: Mixture I, ●; Mixture II, ○; Table 2.

reactant pressure indicated direct proportionality but, after equilibration, the rate dependency reduced to ∝ (hydrocarbon pressure)$^{0.3}$.

Hydrocracking of propane. Typical plots of product yield–time for the hydrocracking reaction of propane on nickel carbide are shown on Fig. 4. There was no appreciable reaction induction period ($t' = 0$) and reaction rates rapidly reached a new constant value after each change of catalyst temperature. Arrhenius parameters for the linear reaction rates, found for all the mixtures studied, and for the propane cracking reaction, are listed in Table 2. A composite Arrhenius plot, using the data from Tables 1 and 2, and a line (A), for propane hydrocracking on nickel, calculated from data reported by Anderson and Baker (*8*) is given in Fig. 5.

PRODUCTS OTHER THAN METHANE

Hydrogen. The cracking reactions of ethane, ethylene, and acetylene gave approximately equal yields of hydrogen and the amount increased with reaction temperature and decreased somewhat at longer reaction times. After 4 min at 300°, 8.0 ml of ethane yielded 0.9 ml of hydrogen and this decreased to 0.6 ml after 10 min ["ml" used here, and below, refers to the volume (STP) of reactant (or product) reacting with 1.00 g nickel carbide].

TABLE 2

SUMMARY OF KINETIC DATA FOR METHANE FORMATION FROM PROPANE AND PROPANE-HYDROGEN MIXTURES[a]

Mixture	$p_{C_3H_8}$ (mm)	p_{H_2} (mm)	E	$\log_{10}A$	$k_{250°} \times 10^1$
Propane	50	0	36	24.8	0.006
I	43.4	6.6	24	20.6	0.038
II	43.8	36.2	26	23.0	0.676
III	50.3	109.7	39	27.4	0.178

[a] Legend: As for Table 1.

C_2 compounds. The cracking reaction of ethane gave small traces of ethylene, but the yields did not vary significantly with reaction time or temperature. The amount of ethane formed during the ethylene cracking reaction increased linearly with time and, from rate constants found at 240–300°, the activation energy for formation of this compound was 30 ± 3 kcal mole^{-1}; at lower temperatures (190–230°) the value was significantly smaller (~4 kcal mole^{-1}).

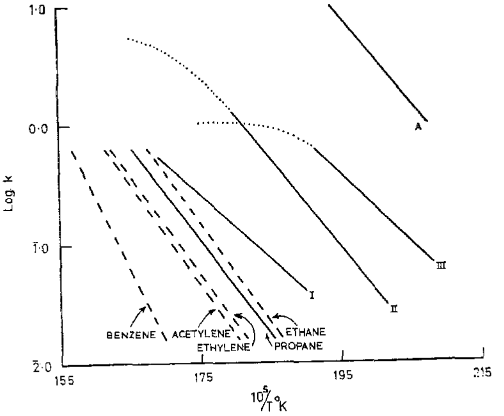

FIG. 5. Composite Arrhenius plot for cracking and hydrocracking reactions of hydrocarbons over nickel or nickel carbide catalysts. Named organic compounds refer to cracking reactions, Roman numerals refer to mixtures detailed in Table 2 and line A was derived from propane hydrocracking over nickel films from data reported by Anderson and Baker (*8*).

Ethylene cracking also formed a small amount of acetylene.

The ethane yield from the propane cracking reaction was ~5% that of product methane and the activation energy for the formation of this compound was 30 ± 3 kcal mole^{-1} (250–300°); trace amounts of ethylene and acetylene were also detected. Ethane was the only significant C_2 product formed in propane hydrocracking; the yield was comparable with that from the cracking reaction. Propylene cracking gave both ethane and ethylene, yields being comparable with those from propane cracking. The kinetic behavior of the formation of these products was, however, complex; typical product yield–time plots are shown in Fig. 6. Thus, reactions of the type $C_3 \rightarrow C_2 + C$ did not contribute significantly to product yields.

Benzene and toluene. The accuracy with which kinetic data for the production of these compounds could be obtained, using the radioactive ionization detector, was less than that achieved for methane formation.

The cracking reactions of propylene, ethylene, and acetylene formed benzene, the yields from cracking 9.0 ml of reactant 10 min at 300° were 0.0025, 0.0005, and 0.0005 ml, respectively. Benzene yields were directly proportional to reaction time <300° and the activation energy for the formation of this product, from all three reactants, was 40 ± 5 kcal mole^{-1} (250–300°). The toluene yield was always close to 0.5 that of benzene and no systematic change in this ratio with variation in reaction time or temperature could be detected. Both products were formed by reaction at 100° but yields below 250° were below the limits required for kinetic investigation.

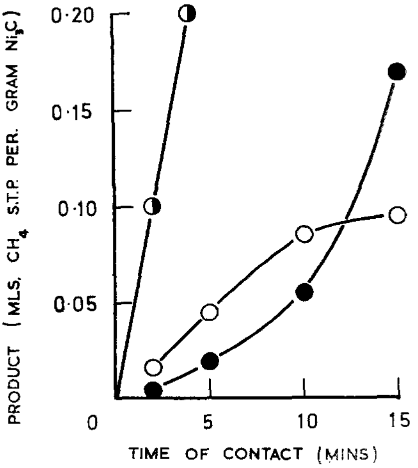

Fig. 6. Variation in product yields with time for the cracking reaction of propylene at 300°: ◑ methane; ●, ethane; and ○, ethylene.

Benzene and toluene yields from the cracking reactions of ethane, propane, and butane were 0.03, 0.1, and 0.1, respectively, those from the reaction of propylene (10 min at 300°). In contrast to the behavior of the unsaturated compounds, yields from the alkanes were largely independent of contact time, 250–300°. Aromatic hydrocarbon yields from propane hydrocracking (Mixture II) were significantly less than those from the cracking reaction. Small amounts of benzene and toluene were formed on cracking octacosane 30 min at 300°.

Other products. The radioactive ionization detector showed the formation of several products, other than those mentioned above, from cracking reactions at 250–300°. *Acetylene* formed at least 20 further hydrocarbon products, including butane, cyclohexane, and isomers of pentane and hexane. Yields of most products were directly proportional to contact time. At least four higher hydrocarbons (> ~C_9) were present in a sublimate from the heated zone. Quantitative measurements showed that 9.0 ml of acetylene at 300° yielded 0.008 ml min^{-1} of unsaturated C_4 isomers. The cracking reaction of *ethylene* also gave further hydrocarbons, but the yields showed relatively minor variation with changes in reaction time or temperature. Ethylene (9.0 ml) reacted 10 min at 300°, yielded 0.08 ml of unsaturated C_4 isomers; propane, C_5 and C_6 isomers and higher hydrocarbons (> ~C_9) were also detected. No further products were identified from the *ethane* cracking reaction. There was evidence that very small traces of further products were probably formed during *propane* cracking. Yields of butene isomers from *propylene* cracking were similar to those from the acetylene reaction and other hydrocarbon products were also detected.

Octacosane reacted at 300° to yield isomers of C_2-C_8 hydrocarbons; yields of hydrocarbons containing an even number of carbon atoms were greater than those of the C_3, C_5, and C_7 isomers. Except for toluene, C_7 and C_8 products were not detected from the cracking of any other reactant.

Blank reactions in which ethylene and acetylene were heated under reaction conditions, in the absence of nickel carbide, gave yields of C_4 hydrocarbons and benzene which were always small ($<2\%$) compared with those from the catalytic reaction.

X-RAY DIFFRACTION STUDIES ON THE CATALYST

The original reactant consisted principally of nickel carbide (*10*) and it contained no significant amount of nickel metal. Similar X-ray examination of the catalyst after use in the cracking reactions of acetylene (the most carbon-rich reactant) and of propane showed that, in addition to the carbide phase, small amounts of nickel were also present. Thus, despite carbon deposition during cracking, crystalline nickel was formed from the carbide phase, in a mixture which did not originally contain it. After nickel carbide had been used in those hydrocracking reactions which employed a high proportion of hydrogen, metallic nickel was the only crystalline phase which could be detected in the used catalyst. Complete reduction of the carbide phase had occurred.

COMPENSATION DATA FROM THE LITERATURE

On making comparisons between the present results and published kinetic parameters for several other reactions involving methane formation at nickel surfaces, we observed correlations which have not been reported previously. The points on Fig. 7 summarize all the available data for such rate process, in which the Arrhenius pre-exponential factor, A, could be converted to the units mol. cm^{-2} sec^{-1}. These reactions include (i) nickel carbide hydrogenation (×) (*10*); (ii) hydrogen desorption during chemisorption of methane and of ethane on nickel (*13*) and propane cracking (*14*) (○); (iii) methane exchange and "higher temperature range" exchange of ethane (●) (*1*, *15*); and (iv) hydrocarbon hydrocracking (△) (*8*, *16*). The data reported by Morikawa *et al.* (*5*, *6*) (▽) also fall on this line if it is assumed that the area of their catalyst was comparable with those used by Yates *et al.* (*16*), i.e., 10 m^2 g^{-1}. Thus, despite the apparent diversity of the chemical processes involved in these reactions, there is a marked compensation effect.

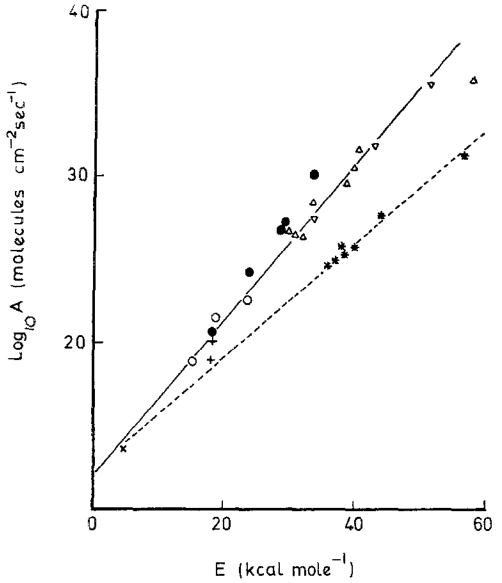

FIG. 7. Compensation plot for Arrhenius parameters measured for various methane formation reactions involving catalysis by nickel or nickel carbide. For legend see text.

Results for methylamine hydrocracking (+), where nickel carbide formation occurred, were also close to the line on Fig. 7 (*18*). Data from the present study (*) fall below the line in Fig. 7; this will be discussed below. Values of Arrhenius parameters for exchange reactions on nickel, listed by Bond (*17*), fall, with appreciable scatter, about a line +3 (approximately) in log A above the full line in Fig. 7 and parallel with it. Data for aromatic hydrocarbon desorption from nickel oxide (*19*) fall about a line, again approximately

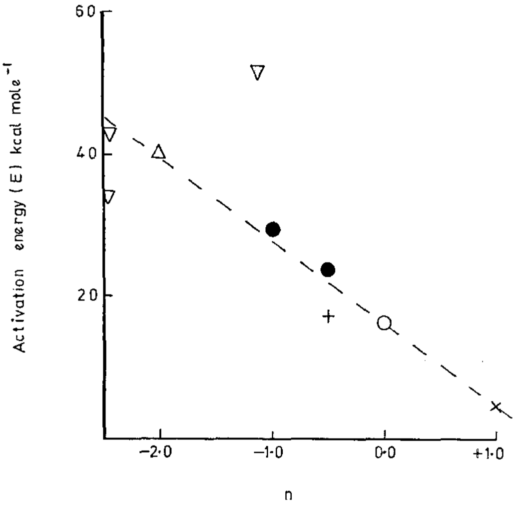

FIG. 8. Trend of variation of activation energy with exponent of hydrogen pressure dependency (n) for some of the reactions included in Fig. 7.

parallel to but well below (—5 in log A) that in Fig. 7. The data used in Fig. 7 show (with one exception) the trend illustrated in Fig. 8 between activation energy and the exponent of the dependence of reaction rate on hydrogen pressure (n).

Fewer studies of appropriate series of reactions on metals other than nickel could be found in the literature. The available measurements have been collected and results are summarized in Table 3, from which it may seen that at least four metals showed similar behavior to that described for nickel. The Arrhenius parameters for reactions of different types (i.e., cracking or exchange) on a particular metal gave different lines on the compensation diagram.

DISCUSSION

The data reported above show that, during cracking reactions on nickel carbide, surface processes of considerable complexity occur. Since simultaneous rate processes proceed on the solid, it is necessary to subdivide the discussion, but it is emphasized that several different chemical changes may be occurring concurrently. Such reactions may be grouped as follows: (i) cracking, which yielded the most abundant product, methane; (ii) hydrogenation and dehydrogenation; (iii) polymerization; (iv) reactions involving at least two chemical processes, e.g., polymerization followed by cracking, or vice versa, which are possible routes for the formation of C_5 hydrocarbons and toluene; (v) deposition of carbon on the catalyst; and (vi) formation of crystalline nickel. Each reactant did not yield every possible product and the relative importance of these processes varied significantly between different reactants, e.g., (i) alkenes gave greater yields of polymeric products than alkanes and (ii) small amounts of metallic nickel were formed during cracking, whereas hydrocracking resulted in complete reduction of the carbide phase.

The Active Solid Catalyst

The kinetic data showed that, after the initial decrease in reaction rate, carbon deposition did not progressively reduce the rate of the cracking reaction. Elemental analyses of catalyst samples, after use in the cracking reactions of propane (15 hr at

TABLE 3

PARAMETERS DEFINING COMPENSATION LINE FOR CATALYTIC REACTIONS ON DIFFERENT METAL SURFACES

Metal	Reaction of hydrocarbon	Intercept A when $E = 0$ (molecules cm^{-2} sec^{-1})	Slope of compensation line $\left(\frac{\text{molecules cm}^{-2}\text{ sec}^{-1}}{\text{kcal mole}^{-1}}\right)$
Ni	Cracking	12.0	0.45
Pd		12.8	0.40
Pt		12.4	0.37
Ni	Hydrogen exchange	15.6	~0.45
Pd		16.0	0.42
Pt		14.3	0.39
Pt	Oxidation	16.7	0.41
W	Cracking	12.0	0.57
W	Exchange	~14	~0.8

330°) and acetylene (10 hr at 325°) showed that these contained 0.7% and 31.8%, respectively, more carbon than that in the original catalyst preparation. Despite this carbon deposition, nickel crystallites, sufficiently large to be detected by X-ray diffraction, were formed during the cracking reaction.

The kinetics of oxidation of carbon in a sample of catalyst, which had been used in the propane cracking reaction, were compared with data for the original preparation (*12*). Results showed that some of the carbon in the former sample underwent comparatively rapid oxidation initially, but the greater part of the carbon dioxide appeared only as result of a relatively very slow reaction. This shows that there is a considerable change in the reactivity of the carbon as a result of the catalytic reaction, attributable to extensive redistribution (aggregation?) of carbon within the solid phase.

From the above observations, it is concluded that both nickel and carbon atoms undergo extensive lattice reorganization during cracking reactions. Such movements may be expected to occur readily since cracking reactions were studied in the temperature range immediately below that in which nickel carbide decomposition becomes significant (*20*). Furthermore, Ehrlich (*21*) has shown that chemisorption on active solids may be accompanied by movements of surface atoms. We believe, therefore, that, during the catalytic reaction, migrations of atoms at, and from, the surfaces of solids results in the establishment of equilibria between the chemisorbed cracking intermediate and (at least) three solid phases (nickel carbide, nickel metal, and elementary carbon). These equilibria result in the preservation of a constant effective catalyst area, presumably on nickel crystallites and/or at phase boundaries. The maintenance of a proportion of metallic nickel in the active solid may result from one, or more, of the following effects: (i) thermal decomposition of nickel carbide, (ii) reduction of nickel carbide, and (iii) removal of deposited carbon from the active surface by migration to growth regions of carbonaceous material.

There was evidence that hydrogen could accelerate the establishment of the position of the new equilibrium, following changes in reaction conditions since (i) t' was negligible in hydrocracking reactions (Fig. 4) and (ii) the value of t' in cracking reactions (the induction period in Figs. 2 and 3) was comparable with the time required to establish a small gaseous hydrogen pressure. We suggest, therefore, that chemisorbed hydrogen may facilitate migration of carbon, possibly as surface hydrocarbon radicals, on those surfaces at which the cracking reaction is proceeding. Hydrogen also influenced the position of catalyst equilibria since (i) there were differences in the kinetic behavior shown by the reactions of the different propane hydrocracking mixtures (Table 2) and (ii) the carbide phase was reduced during hydrocracking.

A model of the catalyst involving equilibria between several hydrocarbon radicals and solid phases tends to emphasize the chemical properties of the interacting solid phases and the mobile surface species; this probably includes surface-migrating nickel atoms. This representation of the active catalyst is used in the discussion below in preference to theoretical descriptions of catalytic behavior based on (i) rigid geometrical models of a static surface or (ii) variations in catalytic activity resulting from progressive changes in the properties of the electronic energy levels of the solid. Static models of the catalyst surface have not so far resulted in any accepted general theory of catalysis by metals. Dynamic models have, as yet, received less attention but progressive changes in the positions of dynamic surface equilibria would appear to provide an acceptable explanation of compensation behavior.

General Observations about Catalytic Reactions

The compensation line in Fig. 7 was defined by kinetic data for reactions involving carbon and hydrogen chemisorbed on a nickel surface and gaseous methane. This single pattern of behavior, derived from observations on several different chemical processes, strongly suggests the existence of a common feature in the reaction mechanisms. We shall assume here, as a working hypothesis, that the reactions which give points on the compensation line (Fig. 7) possess a common rate-determining step. We shall assume also, that the equilibrium concentrations of surface intermediate species may vary with different reactant mixtures. These assumptions are supported by the observations that (i) different compensation lines were given by different chemical processes occurring on a particular metal (compare data for exchange and cracking, Table 3); (ii) comparable reactions on different metals yield different lines on a general compensation plot (values for cracking and for exchange reactions on Group VIIIc metals are close but differ from those for tungsten); and (iii) compensation effects have been described (*17*, p. 194) for a particular chemical change proceeding on different metal surfaces: here identical surface reactions may occur, but there is variation in the metallic component or constituents of the surface equilibria.

Compensation lines for a particular reaction occurring on different metals will cross the comparable family of lines derived from data for different reactions occurring on a particular metal; an example of a line of the former type is given in Fig. 2, p. 194 of ref. (*17*) and a line of the latter type is shown in Fig. 7 above. The network comprised of the two families of such lines, once established, would be useful in comparing activities of different metals in particular reactions and predicting activities in untested systems. At present, however, sufficient published data to locate lines of the net are available only for a few metals and further work is necessary to investigate the properties of other elements. Such an extension could increase the potential usefulness of this theoretical scheme for the prediction of catalytic activity.

Cracking and Hydrocracking Reactions on Nickel

The points on Fig. 7 show progressive changes in the values of Arrhenius parameters with the relative availability of surface hydrogen in the sequence: (i) hydrogenation of the carbon-rich nickel carbide phase; (ii) dissociative chemisorption of methane and ethane, which is accompanied by carbon deposition; (iii) methane exchange (relatively insensitive to hydrogen pressure); and (iv) hydrocarbon hydrocracking (sensitive to pressure of gaseous hydrogen). This trend is also shown by the variation in the hydrogen pressure dependency exponent with activation energy (Fig. 8) and is consistent with the view that the position of surface equilibria varies with different reactants. Qualitatively, we regard the low frequency factor for nickel carbide hydrogenation to be due to a low concentration of chemisorbed hydrogen since the surface valence forces of the solid are satisfied by carbon. The apparent low activation energy is attributed to variation in the concentration of chemisorbed hydrogen with temperature and, therefore, the experimental value is not a true measure of the energy barrier to surface reaction. At the opposite end of the compensation scale, hydrocracking, large concentrations of surface hydrogen and hydrocarbon radicals are present (the reaction frequency factor is greater than the reactant collision frequency with the surface) and a relatively large energy is required to rupture the strong bonds between radicals and surface.

To provide a quantitative theoretical description of the compensation effect, we may define two forms of carbon, (i) C_I carbon which may be directly hydrogenated to methane and (ii) C_{II} carbon, which may not be directly hydrogenated to form methane, but which reduces the unsaturated character of the metallic surface (interstitial carbon, polymeric radicals?). Assuming that the reactions which give the compensation plot (Fig. 7) possess a common rate-determining step for methane formation, and identifying this as the reaction of hydrogen with a single carbon unit at the surface (*8–10*), the rate of this process may be expressed

$$d[\mathrm{CH_4}]/dt = k_1[\mathrm{H}]^p[\mathrm{C_I}]^v \exp(-E/RT) \quad (1)$$

where p and q are constants and the concentrations of surface species, [H] and [$\mathrm{C_I}$], are such that the surface energy of the catalyst is minimized. The concentration of species in the $\mathrm{C_I}$ layer (these are not identified but may include methyl and methylene radicals) are controlled by the availability of surface hydrogen, [H]. Equation (1) may be rewritten

$$d[\mathrm{CH_4}]/dt = k_2[\mathrm{H}]^r \exp(-E/RT) \quad (2)$$

At equilibrium the adsorption of hydrogen may be written

$$\mathrm{H_2(g)} + 2(s) \rightleftharpoons 2\mathrm{H}(s)$$

where (s) is a surface site, and, from Bond (*17*) we may write

$$[\mathrm{H}] = (s)^{1/2}[H_2]^{1/2} \exp(\Delta S/R) \exp(-\Delta H/RT) \quad (3)$$

If we now assume that (i) entropy and heat of adsorption are related in a linear manner (*22*) and (ii) the reduction in the heat of hydrogen adsorption is directly proportional to [$\mathrm{C_{II}}$] for the surface at equilibrium, we may combine Eq. (2) and (3) and rewrite as

$$d[\mathrm{CH_4}]/dt = k_3[\mathrm{H}]^n \exp\{(a\Delta \mathrm{S} - b[\mathrm{C_{II}}])/R\} \exp\{(c\Delta H + E - e[\mathrm{C_{II}}])/RT\} \quad (4)$$

where a, b, c, and e are proportionality constants.

The definition of [$\mathrm{C_{II}}$] above shows this parameter to be controlled by surface equilibria and it is seen from Eq. (4) that variation in the concentration of $\mathrm{C_{II}}$ results in the compensation effect. Thus, the above model provides a theoretical explanation of the data in Fig. 7. An equation similar to (4) above has previously been proposed (*1*) and the present work is intended to extend the description of the rate processes occurring on the catalyst surface and to apply the theory to an increased range of reactants.

In support of the above model we may also mention a theoretical derivation of the Elovich equation in which (*23*) it was assumed that the kinetics of chemisorption depended on the extent of surface coverage; such a representation is comparable to the formation of a $\mathrm{C_{II}}$ layer.

It should also be mentioned that an important alternative rate-determining step has been suggested for the hydrocracking reaction (*4–6*, *16*). The model described above, in which methane desorption is rate-limiting, provides a theoretical scheme which is applicable to a wider range of reactants and for this, and other reasons stated below, we conclude that this mechanism gives a more satisfactory basis for theoretical discussion.

Hydrocarbon Cracking Reactions on Nickel Carbide

From the results given in the previous section and the above discussion, we may make the following points: (i) The kinetics of methane formation on carbide reduction (*10*) were quite different from those of the cracking reaction on the same solid. (ii) Yields of products other than methane varied significantly, between different reactants, but such reactions did not appreciably influence the kinetics of the cracking process. (iii) The rate of methane formation at 315° was proportional to the H:C ratio for the reactant molecule (Fig. 9), indicating a direct dependence of rate of methane formation on the availability of hydrogen from the dissociated reactant. (iv) Kinetic measurements for reactions involving nickel carbide gave a compensation line (dotted in Fig. 7) which was not coincidental with that for nickel. The nickel carbide line was located through data for (a) hydrogenation (*10*), (b) methylamine hydrocracking (*18*), (c) the early stages, before significant solid product formation had occurred, of gaseous product evolution from the reactions of water vapor and of sulfur dioxide with nickel carbide (*11*), and (d) the present study. (v) Activation energy values for cracking reactions on nickel carbide were close to those for hydrocracking on nickel, but the

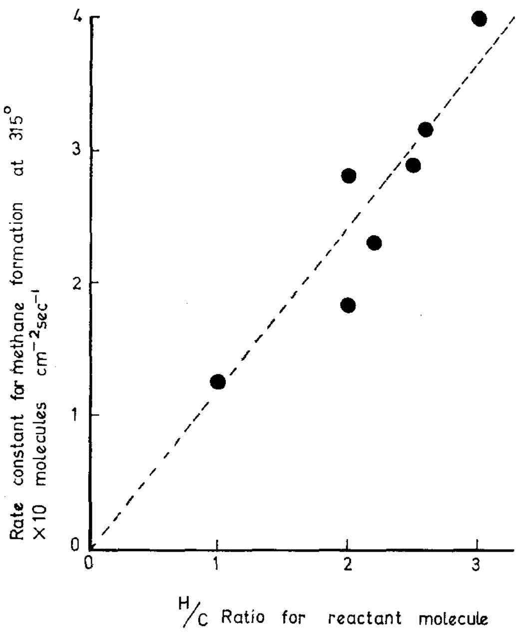

FIG. 9. Variation of rate constant for methane formation at 315° with H/C ratio in the reactant hydrocarbon, for those compounds studied in the present work.

frequency factors were significantly lower (Fig. 7). (vi) Arrhenius parameters for the cracking reactions of different hydrocarbons on nickel carbide were closely similar (Table 1). It has previously been suggested that the rate-controlling step in hydrocarbon hydrocracking was either (a) the rupture of a C–C bond in a chemisorbed hydrocarbon (*4–7*), or (b) the methane desorption process (*8*). The data in Table 1 show that methane production is very largely independent of structure and degree of saturation of the reactant hydrocarbon and this leads us to conclude that this reaction is not controlled by the properties of the original molecules (with the exception of benzene). Therefore, we identify the rate-determining step in methane formation as that reaction, between hydrogen and a single carbon unit of the C_I layer, which directly precedes methane desorption (*8*). While the hydrocarbon species involved has not been identified, we suggest the following possibilities: $CH_3 + H \rightarrow CH_4(g)$ or $CH_2 + H_2 \rightarrow CH_4(g)$. And, (vii) the activation energy reported previously (*11*) for the cracking reaction of ethane on nickel carbide (21 kcal $mole^{-1}$) was determined from reaction rates measured after short periods of equilibration (~30 min) following changes in catalyst conditions. It seems probable that in this short interval (Fig. 1) carbon in the C_{II} layer had not reached equilibrium and that surface conditions were more closely comparable with those which obtained during dissociative adsorption on nickel (*11, 13*); these differed from conditions which were reached after the long periods of equilibration used in the present study.

The activation energy values found for the hydrocarbon cracking reactions were closely similar to those for the hydrocracking reactions but the pre-exponential factors for the former process were smaller by a factor of $\sim 10^4$. The real reduction in this term may be somewhat greater if allowance is made for the effect of hydrogen pressure. From these observations we conclude that nickel carbide is not an active cracking catalyst and the reactions studied proceeded on the surface of metallic nickel crystallites maintained in constant concentration by the solid phase equilibria. The pre-exponential factor for cracking reactions on the nickel carbide catalyst preparation used here was low because (i) much of the nickel remains in the carbide phase, (ii) solid surfaces may be partially coated with deposited carbonaceous material, and (iii) the area of the catalyst may be reduced from the original value through sintering.

The high activation energy for the benzene cracking reaction indicates relative stability of the aromatic nucleus, which may be chemisorbed through π-bonding to the surface (*9*) and which may not undergo dissociation to the methane precursor radicals as readily as the aliphatic chemisorbed species. The relatively great stability of chemisorbed aromatic radicals has been discussed (*9*), (*24*). Also, there were indications that aromatic nuclei may participate in surface equilibria since (i) data for the benzene cracking reaction fell on the nickel carbide line in Fig. 7 and

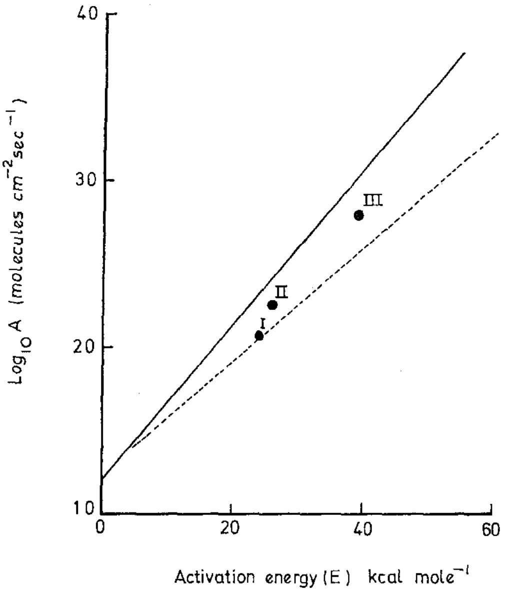

FIG. 10. Arrhenius parameters for the propane hydrocracking reaction on the compensation plot. Full and dotted lines are compensation effects found for nickel and nickel carbide, respectively (see Fig. 7 and text below). Numbers refer to mixtures mentioned in Table 2.

(ii) product benzene and toluene were formed with the same activation energy as that for methane production.

Propane Hydrocracking on Nickel Carbide

Arrhenius parameters, measured for the three mixtures studied, are shown on the compensation plot, Fig. 10. Points for Mixtures I and II, which contained insufficient hydrogen to result in complete conversion of the propane present to methane, gave Arrhenius parameters in the median region of the compensation plot. It is concluded that reaction proceeded on the nickel surfaces of the catalyst which consisted of a nickel/nickel carbide mixture and the surfaces of the former solid contained a significant proportion of C_{II} carbon. The properties of this active surface apparently were approximately comparable with those which obtained during the dissociative adsorption of hydrocarbons on nickel. Both Arrhenius parameters for the mixture containing the higher proportion of hydrogen (II) were slightly greater than those found for Mixture I. Arrhenius parameters for reaction of Mixture III, where complete reduction of the carbide phase occurred, approached the values for hydrocracking reactions on nickel. The somewhat smaller value of the pre-exponential term may result from (i) irreversible poisoning of a part of the surface during carbide preparation or (ii) sintering (the surface area of the solid was measured before use as a catalyst).

Products Other Than Methane

Reactions yielding these products were controlled by the properties of the reactant and the establishment of the mechanisms of the several concurrent rate processes was not possible. Some generalizations may, however, be made. (i) These reactions were dependent on the nature of the reactant but apparently did not influence the methane formation process. It is not known on which phase these reactions proceeded but it seems probable that the species involved do not directly enter the equilibria which control methane formation. (ii) In general, greater yields of "further products" were obtained from unsaturated reactants, whereas smaller yields of a more restricted range of substances, the amounts of which apparently underwent little variation with changes of contact time, were formed on cracking saturated reactants. Those products which were apparently not formed by a rate process may be directly desorbed from the solid when the product gases were withdrawn for analysis. (iii) Reactions at low temperatures (~100°) yielded polymeric products, whereas at higher temperature there was evidence of (a) polymerization, (b) isomerization, and (c) polymer cracking reactions. Cracking of octacosane also yielded a range of hydrocarbon products, but, since the formation of methane from this reactant was very slow, it seems probable that surface polymer may be an intermediate in "further product" formation; however, it is not the species from which methane is directly derived. (iv) The chemisorbed aromatic ring showed considerable stability since product benzene was detected from all reactants studied and, as suggested above, this species may be an intermediate in the surface equilibria during cracking.

CONCLUSIONS

1. Crystalline nickel carbide was not a necessary intermediate in nickel-catalyzed cracking and hydrocracking reactions. The reaction immediately preceding product methane desorption is the rate-determining reaction.

2. The compensation effect results from changing equilibria in the active catalyst regions, and such equilibria involve both dissociated gaseous radicals and surface atoms. A general compensation plot for different reactions on different metals may be of use in correlating and predicting catalytic behavior and so indicate the most efficient solid for use in a particular chemical change.

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