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# The Reactions of Nickel Carbide with a Number of Hydrogen-Containing or Oxygen-Containing Gaseous Compounds

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The kinetics of reaction of nickel carbide with a number of gases which contain hydrogen and/or oxygen have been studied in the temperature range 200–500°C. The results can be classified as showing evidence of three main types of reaction: (1) No reaction below the temperature at which nickel carbide decomposes. Both carbon dioxide and ammonia showed this type of behavior; the latter reacted above 400°C with the products of the thermal decomposition of the carbide to form methane. (2) Reaction occurred in the temperature range 200–350°C to give a mixture of a small number of gaseous products (for example $CH_4$, $CO_2$, and CO) by a reaction in which the rate was proportional to pressure of the reactant gas and the weight of unreacted carbide. Reaction of water vapor and sulfur dioxide showed this behavior. The cracking of ethane was also included in this class though reaction rate did not decrease with time; it was believed that the carbide phase was regenerated during the reaction. (3) Reaction gave a complex mixture of products and kinetics showed evidence of two periods of reaction, an initial deceleratory process followed by a long slow main reaction period, which is believed to occur at a solid–solid interface. Reactions of hydrogen chloride and of hydrogen sulfide with nickel carbide were examples of this type of behavior.

Mechanisms are proposed to account for the reactions of each of the gases studied with nickel carbide.

## INTRODUCTION

A recent study (*1*) of the cracking of small amounts of different hydrocarbons chemisorbed on a cracking catalyst of high area nickel, supported on silica, showed that methane was the almost exclusive product of reaction in excess hydrogen. The kinetics of methane formation were identical for a number of different adsorbed saturated organic molecules. Further work (*2*) showed that the presence of oxygen in the adsorbed molecule did not influence the kinetics of methane formation but the presence of chlorine or of iodine considerably reduced reaction rate. The cracking reactions of adsorbed saturated hydrocarbons were explained by a mechanism in which nickel carbide was postulated as a possible reaction intermediate. Results of a study (*3*) of the kinetics of reduction of nickel carbide with hydrogen were similar in many respects to the cracking of adsorbed hydrocarbon radicals, mentioned above, supporting the suggestion that nickel carbide may be an intermediate in cracking reactions on a nickel catalyst. Apart from a paper by Bahr and Bahr (*4*), however, few data are available on the reactions of nickel carbide with gases, other than hydrogen, and it was apparent from the results mentioned above that adsorbed chlorine influences the rate of reaction of hydrogen with carbon adsorbed on the nickel surface while oxygen does not. The present work was undertaken, therefore, to obtain kinetic data which might give information about the mechanisms of reactions of nickel carbide with a number of inorganic gases containing oxygen or hydrogen, and those compounds which may act as a poison in catalytic reactions (e.g., $H_2S$) were selected as being of particular interest.

## EXPERIMENTAL

The reaction vessel described previously (*3*) was used to study the reaction of nickel carbide with all gases except water vapor and the reaction vessel used in this study is described below. Products were analyzed in a standard Pye Argon Chromatograph and a detailed account of the use of this instrument for the determination of permanent gases has been given (*5*). Preliminary studies, made with each reactant gas, were used to determine the most suitable chromatograph column conditions for the separation and determination of the products; calibrations of the response of the instrument were made whenever analytical conditions had been changed and were repeated at intervals throughout the work. In kinetic studies of the reaction of nickel carbide with ammonia, with ethane, and with sulfur dioxide, the elution of large peaks due to unchanged reactant, which would mask the response of the product gases, was accelerated. Just prior to elution of the reactant peak the analytical column was removed from the instrument and a hot zone, given by a Bunsen flame, was slowly moved down the column while the argon flow was maintained.

The sources of $H_2$, $N_2$, $CH_4$, $CO_2$, CO, $NH_3$, and $SO_2$ and purification before use in calibrations or as reactants were as given previously (*5*). Cylinder ethane was condensed in liquid nitrogen, outgassed, the first-boiling fraction evacuated, and thereafter stored at −195°C. Hydrogen chloride was prepared by dehydration of hydrochloric acid A.R., with sulfuric acid A.R., dried by passage through sulfuric acid A.R., condensed, outgassed and stored at −195°C. Hydrogen sulfide was prepared by the action of water on aluminum sulfide, and passed through sodium sulfide solution and dried by passage over first calcium chloride, then phosphorus pentoxide, and finally through a trap at −80°C. It was outgassed and stored at −195°C.

The nickel carbide used throughout was from the same batch as used previously (*3*) and was originally supplied as a gift by the International Nickel Company (Mond) Ltd. After each experiment the solid products of the previous reaction were removed before the introduction of the subsequent sample of reactant. After each series of experiments involving a particular gaseous reactant, the taps of the vacuum apparatus were cleaned, regreased, and the system was thoroughly outgassed before a new series of experiments involving a different reactant was started.

A sketch of the reaction vessel used in the study of the $Ni_3C$–$H_2O$ reaction is shown in Fig. 1. This apparatus was evacuated before each experiment by several strokes of the Toepler pump which drew water vapor through the reaction vessel while the furnace around it was being rap-

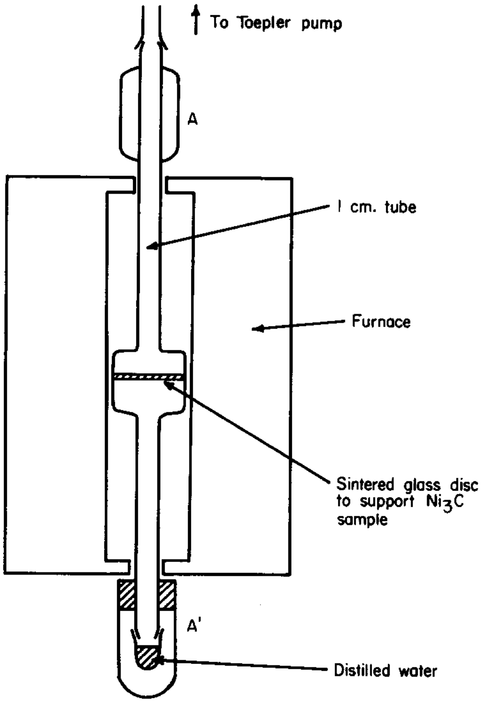

FIG. 1. Sketch of reaction vessel used in study of nickel carbide–water vapor reaction.

idly raised to reaction temperature. A thermometer was clamped in such a position that the bulb was held close to the sintered glass disc which supported the reactant. The pressure of water vapor over the catalyst was controlled by the temperature of the small reservoir A′ which contained distilled water and this was maintained at a constant known temperature by water circulated through A and A′ from a large thermostated bath. Condensation on the inner surface of A and in the Toepler pump showed that diffusion of water through the reaction vessel readily occurred. It has been assumed in the interpretation of the results that reaction occurred in a pressure of reactant equal to the vapor pressure of water at the temperature of the thermostated bath; this approximation takes no account of the small interval which must occur between withdrawal of a sample and re-establishment of equilibrium conditions.

In the study of the reactions of nickel carbide with HCl and with $H_2S$ a wider range of higher boiling point products was found than had been observed for the other reactants. Analyses of products were made almost exclusively on a 120-cm chromatograph column of dinonylphthalate, supported on Celite, and information about the nature of the complex mixture of products was obtained from comparisons of their retention distances with those of pure known compounds determined under identical analytical conditions. Good linear log(retention time)—boiling point plots were obtained with this column for the alkanes, monochloroalkanes, and the limited range of thioethers available. During the work with HCl and with $H_2S$ a short column of solid NaOH was included between dosing volume and chromatographic column to remove corrosive gases, as described previously (*5*). This somewhat increased the peak width of the products with short elution times and due account has been taken in the measurement of retention times.

## Results and Discussion

Results of observations of the reactions of nickel carbide with each of the gases studied are presented and discussed in the following sections.

### *Ammonia*

The reaction of ammonia with nickel carbide only became appreciable at temperatures above 400°C to give a mixture of hydrogen and nitrogen in volume ratio close to 3:1; traces of methane were also found. These results are in good agreement with those of Bahr and Bahr (*4*). Arrhenius plots of the zero order rate constants for the methane formation reaction, for three different samples of carbide, gave an energy of activation of $38 \pm 2$ kcal/mole between 400° and 500°C. The rate of methane formation from unit weight of carbide, at a given temperature, varied considerably between different samples of the solid. On allowing ammonia to stand in contact with the carbide overnight the gaseous products were found to contain a high proportion of methane.

Since nickel carbide decomposes (*6*) into its elements at about 400°C and since it is known (*7*) that nickel films catalytically decompose ammonia at about this temperature, it must be concluded that hydrogen and nitrogen were formed by catalytic decomposition of ammonia on nickel metal rather than from reaction with the carbide. Methane may be formed subsequently by two possible mechanisms. One is by reaction of adsorbed hydrogen, from ammonia decomposition, with graphite, formed by carbide decomposition, at the nickel–graphite interface. Alternatively, it is possible that a small amount of carbon may have remained in the bulk nickel phase, in equilibrium with graphite at the surface, and this may have been hydrogenated at the metal–gas interface. These possibilities cannot be distinguished on the evidence given here. Both are consistent with the observed variation in rate of reaction from specimen to specimen, since the surface area of the metal and the dispersion of product graphite on it may both be expected to be sensitive to the thermal history of the sample. The constant energy of activation indicates that the same chemical process was occurring on the different specimens of the solid reactant.

### *Carbon Dioxide*

No appreciable reaction of carbon dioxide with nickel carbide was detected below about 300°C, but above this temperature carbon monoxide was found in the product gases in an amount which did not depend on the time of contact of the reactants or the weight of nickel carbide in the reaction vessel. This is therefore identified as an equilibrium rather than a kinetic process. The proportion of carbon monoxide in the equilibrium increased between 350° and 500°C and the free energy of reaction, determined from change in equilibrium constant over this temperature interval, was 9.8 kcal/mole, which agrees reasonably well with that calculated (10.6 kcal/mole) from thermochemical data for the equilibrium

$$CO_2 + Ni \rightleftharpoons CO + NiO \qquad (1)$$

Bogatskii (*8*) reports $\Delta F^\circ_{298} = 9{,}352$ cal/mole for equilibrium (1) in the temperature range 500–1,100°C. The value obtained in the present work did not agree with the calculated value, 28.1 kcal/mole, for the equilibrium

$$\tfrac{1}{2}CO_2 + \tfrac{1}{2}C \rightleftharpoons CO$$

It is known (*6*) that nickel carbide decomposes above 350°C and this result, taken with the above calculations, leads to the conclusion that carbon dioxide does not react appreciably with nickel carbide but may, at higher temperatures, oxidize nickel metal formed by thermal decomposition of the carbide.

### *Ethane*

Between 230° and 330°C ethane reacted with nickel carbide to give a mixture of methane and hydrogen in approximately 10:1 volume ratio. Initially, and after any change in reaction temperature, the reaction rate showed a slow change with time before reaching a value which remained constant thereafter. After this initial period, successive doses of ethane at 60 ± 3 mm pressure admitted to the reaction vessel formed methane and hydrogen by a reaction which showed zero order kinetics providing samples were withdrawn before an appreciable fraction of the dose of ethane admitted had reacted. Zero order rate constants were measured after the constant rate of reaction had been attained, at several temperatures within the range 230–330°C, on each of four different samples of nickel carbide. All the rate constants so obtained, when each had been divided by the weight of reactant carbide, fell on a single straight line on an Arrhenius plot, from which an energy of activation of 21 ± 1:5 kcal/mole was found.

After a sample of carbide had been heated above 420°C in ethane, the subsequent rate of the methane formation reaction at temperatures below 330°C returned to the value observed before heat treatment, after the time necessary for reestablishment of the constant reaction rate.

From the observed zero order kinetics of the methane formation reaction at constant temperature and constant weight of reactant carbide it is concluded that reaction of successive doses of equal pressure of ethane occurred on a surface of constant composition and area. It is suggested that reaction occurred by dissociation of ethane, adsorbed on the surface of the carbide, and the adsorbed hydrogen atoms so formed may then react with adsorbed carbon atoms to form methane and, at the same time, a small proportion is desorbed unchanged. This reaction is summarized

$$2C_2H_6 \rightarrow 3CH_4 + C$$

The energy of activation is identified with the breakdown of ethane on the surface; it is somewhat lower than the value reported by Kemball and Taylor (*9*) for the decomposition of ethane on a supported nickel catalyst (40 kcal/mole) but is close to the values reported by Wright, Ashmore, and Kemball (*10*) (18.3 and 20.7 kcal/mole) for the dissociative adsorption of ethane on nickel films at 60–100°C. An alternative mechanism for this reaction in which ethylene is formed and the hydrogen released reacts with the carbide to form methane is untenable since it is inconsistent with zero order kinetics, ethylene was not detected in the reaction products, and McKee has shown *(11)* that ethylene chemisorbed on nickel is cracked to methane at 200°C.

The carbon released in the cracking reaction may be incorporated into the bulk of the metal but excess was presumably precipitated as graphite since more carbon was deposited than could react with the nickel metal available. This is consistent with the observation that nickel carbide formed by reaction between a hydrocarbon and the metal contains graphite. Initially, after any temperature change and after heating above 400°C the time lapse before zero order kinetics were observed shows that an appreciable interval was necessary to re-establish equilibria between surface radicals and the carbon content of the bulk phase.

### *Water Vapor*

The reaction vessel used to study the nickel carbide–water vapor reaction has been described above.

Nickel carbide reacted with water vapor between 240° and 410°C to give a mixture of hydrogen, methane, and carbon dioxide. The total volume of gaseous products, formed on completion of reaction of unit weight of carbide, decreased with increasing reaction temperature from 240° to 330°C and more rapidly above 340°C. The total quantity of carbon which appeared as carbon dioxide and methane was always less than about half the carbidic carbon in the reactant *(3)*. Below about 325°C in 30 mm pressure of water vapor, the reaction products fitted the equation given by Bahr and Bahr *(4)*:

$$C + 2H_2O \rightarrow 2H_2 + CO_2 \qquad (2)$$

with, in the present work, some 15% of the hydrogen present as methane. The yield of methane increased with decreasing water vapor pressure, some 30% of the hydrogen being present as methane after reaction in 5 mm of water vapor pressure. Between 240° and 325°C the ratio of volumes of product $(H_2 + 2CH_4)$: $CO_2$ was close to 2:1 from Eq. (2). Accurate quantitative agreement could not be expected since small amounts of oxygen remain in the reaction vessel after the outgassing procedure. The proportion of carbon dioxide in the products decreased above 340°C; reaction in 5 mm of water at 400°C yielded small quantities of hydrogen and methane (2:1 volume ratio) and a negligible quantity of $CO_2$.

Kinetic experiments showed an initial short acceleratory period, almost certainly due to the interval necessary to establish thermal equilibrium in the reaction vessel, followed by a reaction which yielded all three products at an almost constant rate during the main reaction period. Reaction was completed after a brief, strongly deceleratory period. A typical set of results for the main reaction period of an experiment at 265°C is shown on Fig. 2. The rates of all reactions were measured from the mean slope of the volume of products–time plot for the main reaction period and these were found to be directly proportional to the vapor pressure of water at the temperature of the thermostated jacket (A, Fig. 1). This was good evidence that reaction was not opposed by reduced rate of diffusion of reactant in the presence of the product gases. Rate constants for the main reaction period found in this way, between 250° and 350°C, each divided by the weight of solid reactant, gave an Arrhenius energy of activation $15 \pm 1$ kcal/mole for the formation of all three products. The rate of reaction above 350°C was less than that predicted from extrapolation of the Arrhenius plot.

X-ray examination of the residue from a reaction at 300°C, cooled *in vacuo*, showed nickel metal to be the main solid product, but there was evidence for a small amount of nickel oxide. Kinetic experiments in which atmospheric oxygen was admitted to the reaction vessel at reaction temperature showed that methane and hydrogen were not detected in the products while gaseous oxygen was present.

From the close similarity of the kinetics of formation of all three products it is concluded that the rate-determining step in the reaction is the dissociative adsorption

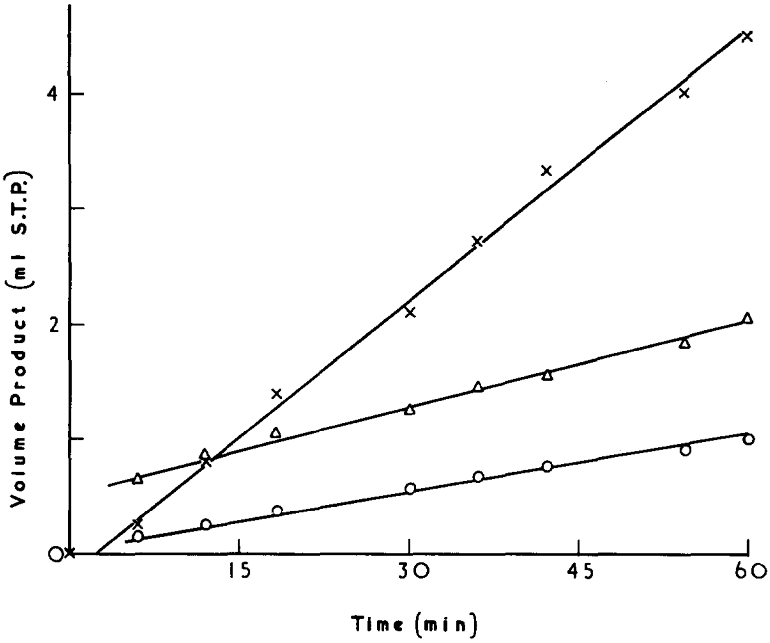

FIG 2. Plot of volume of product hydrogen (+), methane (○), and carbon dioxide (△) against time for reaction of water vapor with nickel carbide at 265°C for initial period of reaction only.

of water. Adsorbed hydrogen atoms are readily displaced from the surface when reaction occurs in high pressures of water vapor (30 mm) but with decreasing pressure of reactant there was an increase in probability of reaction with surface carbon to form methane, presumably by the same reaction as discussed previously (*3*) for the hydrogenation of nickel carbide. This is supported by the equal energies of activation for the hydrogen and the methane formation reactions.

The results reported above show that carbidic carbon is not quantitatively converted to gaseous products below the temperature at which thermal decomposition of nickel carbide becomes appreciable (~340°C). It is concluded, therefore, that the radicals present on the surface may provide an alternative mechanism of graphite deposition, possibly through the decomposition of a reaction intermediate on the surface. During the main reaction period it is concluded that, below about 350°C, reaction occurred at the original surfaces of the sample and shows approximately zero order kinetics until most of the carbon in the carbide phase has reacted. The brief, pronounced deceleratory period was observed during reaction of the last traces of the carbon.

Above 350°C both rate of reaction and volumes of products decrease. It seems probable that appreciable oxidation of the nickel occurs since some oxidation was detected in the X-ray examination of the residue from reaction at 300°C, and, furthermore, carbon dioxide can react with nickel metal above 350°C, as seen above, and this accounts for the decrease in yield of this product at higher temperatures. The reduction in yield of hydrogen and methane can be accounted for by the competing reaction, the thermal decomposition of the carbide phase, known to occur at these temperatures (*6*).

Inhibition of the hydrogen formation reaction by the presence of atmospheric oxygen is presumably due to the oxidation of adsorbed hydrogen. Gaseous oxygen can, however, react with surface carbon as shown by the relatively large volumes of carbon dioxide formed when it was present. This also accounts for the large initial volume shown in the first reading of the results in Fig. 2, gaseous oxygen being present as a result of incomplete outgassing.

### *Sulfur Dioxide*

Nickel carbide reacted with sulfur dioxide in the temperature range 250–400°C to give carbon dioxide as the main reaction product in total yield slightly less than that calculated for complete oxidation of the carbidic carbon. Carbon dioxide formation was a deceleratory rate process throughout the reaction, though in the initial region it could be approximated to a linear reaction rate. Initial zero order rate constants, corrected to rate for unit weight of carbide, gave an energy of activation of 10 ± 1.5 kcal/mole over the temperature interval 240–350°C. After heating nickel carbide above 450°C subsequent reaction with sulfur dioxide below 350°C gave small traces of $CO_2$ as the only gaseous product.

At about 350°C the reaction may be summarized by the equation

$$Ni_3C + SO_2 \rightarrow NiO + CO_2 + (Ni + CO + Ni_3S_2)$$

the products in the bracket being in small amounts and the sulfide suggested from observations by Rumyantsev and Chizhikov (*12*) who state that above 450°C the following reaction occurs

$$7Ni + 2SO_2 \rightarrow Ni_3S_2 + 4NiO$$

There was no conclusive evidence to show the final sulfur-containing product but it may be assumed to form one of the sulfides of nickel or elemental sulfur, the latter being sublimed from the reaction vessel.

X-ray examination of the residue from a partially completed kinetic experiment at 420°C (cooled *in vacuo*) showed nickel oxide to be the main solid product with small amounts of nickel metal and a third unidentified product, present in trace amounts only, which was presumably the sulfide of nickel.

Over the whole temperature range studied the total volume of product gases contained about 10% carbon monoxide; the volume in any one sample was, however, largely independent of the interval between readings. Traces of other compounds detected will be mentioned below.

From the results given above, the carbon dioxide formation reaction was seen to depend on the amount of carbidic carbon present since this reaction was deceleratory throughout and little reaction was observed on a sample which had previously been heated above its decomposition temperature. It is suggested that carbon is oxidized at the surface of the carbide by oxygen atoms formed from the dissociative adsorption of sulfur dioxide and that adsorbed carbon monoxide and oxysulfide radicals are probable intermediates. Adsorbed sulfur may reduce the strength of adsorption of carbon monoxide so that this compound can be detected in the products, in contrast to the reaction with water vapor where this compound was not found. It seems probable that gaseous carbon monoxide in the products may be readsorbed and oxidized when present in appreciable concentration since the volume detected was largely independent of contact time between the reactants. The observed quantitative conversion of carbidic carbon to carbon dioxide and carbon monoxide also contrasts with the reaction with water vapor and it is concluded that the graphite formation reaction, through decomposition of an adsorbed intermediate, postulated above, does not occur.

In addition to the oxides of carbon, traces of carbonyl sulfide, identified by its chromatograph retention distance, were detected in the latter stages of reaction in amounts representing some 0.001% of the carbon oxidized. Another compound was detected as a chromatograph response trace between the $CO_2$ and COS peaks and the amounts found fitted none of the kinetic laws tested. The low yield of this substance makes investigation difficult and attempts to obtain an infrared spectrum were unsuccessful. It is tentatively suggested that this may be SO or CS but further work is necessary to make a positive identification.

### *Hydrogen Chloride*

In contrast to the small number of products detected in the reactions reported above, at least 14 different products were detected from the reaction of nickel carbide with dry hydrogen chloride. This mixture was separated on the dinonylphthalate chromatograph column maintained at constant analytical conditions throughout the work and detector response peaks were observed at characteristic retention distances. In subsequent discussion it has been assumed that the area of the detector response trace for each substance was directly proportional to the volume of that substance given by the reaction (*5*) and where the term "total volume" has been used it is based on this assumption.

The reaction was studied at 250–350°C and chromatograph response peaks, each identified by a reference letter, were observed at the following characteristic retention distances (in arbitrary units): 12(A), 18(B), 21(C), 25(D), 31(E), 45(F), 53(G), 61(H), 77(J), 160(K), 470(L), 820(M), and 1850(N). A consisted of at least two different substances.

From a plot of total volume of A against time it was seen that the reaction could be divided into (i) an initial reaction which was deceleratory throughout (Fig. 3a) and (ii) the main reaction period in which a brief acceleratory period (Fig. 3a) was followed by a long slow deceleratory period (Fig. 3b). A short time elapsed between readings shown on Fig. 3a and those on Fig. 3b and since accurate allowance for the effect of this on the time variable cannot be made, the time intervals on Fig. 3b are shown measured from a second zero.

**Initial reaction.** Products A to G (A in largest yield) were formed between 280° and 350°C by a rate process which was deceleratory throughout. A detailed analysis of the kinetics of the reaction forming A could not be made since the main reaction obscured the latter stages, but from initial reaction rates an energy of activation of $18 \pm 2$ kcal/mole was estimated. The volume of A evolved on completion of the initial reaction was directly proportional to the weight of reactant nickel carbide.

**Main reaction.** A series of experiments, similar to that illustrated in Fig. 3, was made under a variety of experimental conditions in which the slope of the approximately linear middle period of the reaction was used as a measure of reaction rate. Reaction rate was independent of variation in length of small intervals between readings but at larger intervals this decreased as reactant gas was consumed. It was not practicable to make an analysis of the kinetics of formation of all the products since the response peaks overlapped but qualitative observations suggested that the formation of all the products obeyed the same laws.

Results showed that the rate of reaction was directly proportional to the pressure of hydrogen chloride, and some of the evidence for this, studied in greater detail in other experiments, can be seen on Fig. 3b where a few results for reaction in 30 mm HCl have been included on the plot for reaction in 60 mm HCl. The rate of formation of A increased with temperature from a comparatively small value at 150°C to a broad maximum value at 225–350°C and thereafter decreased to a small value at ~400°C. Kinetic experiments, interrupted by heating the carbide above the decomposition temperature, returned to approximately the same rate as previously on cooling to 300°C.

**Other experiments.** Two experiments were made under identical conditions to those used above where hydrogen chloride at 60 mm reacted with intimate mixtures of (a) graphite and $NiCl_2 \cdot 6H_2O$ (34:66 by weight) at 300°C and (b) graphite and NiO (56:44 by weight) at 290°C. Both reactants gave products having retention distances the same values as substances A to E. Reaction of mixture (a) was deceleratory throughout the 3 hr during which it was studied. A slow reaction of mixture (b) occurred for 24 hr, and in the latter stages of reaction response peaks were observed at 94 and 220 (same units as above).

Analysis of products of a normal experiment over the charcoal column at 20°C showed that hydrogen, ethane, and possibly propane were present in the products but no methane was detected even after reac-

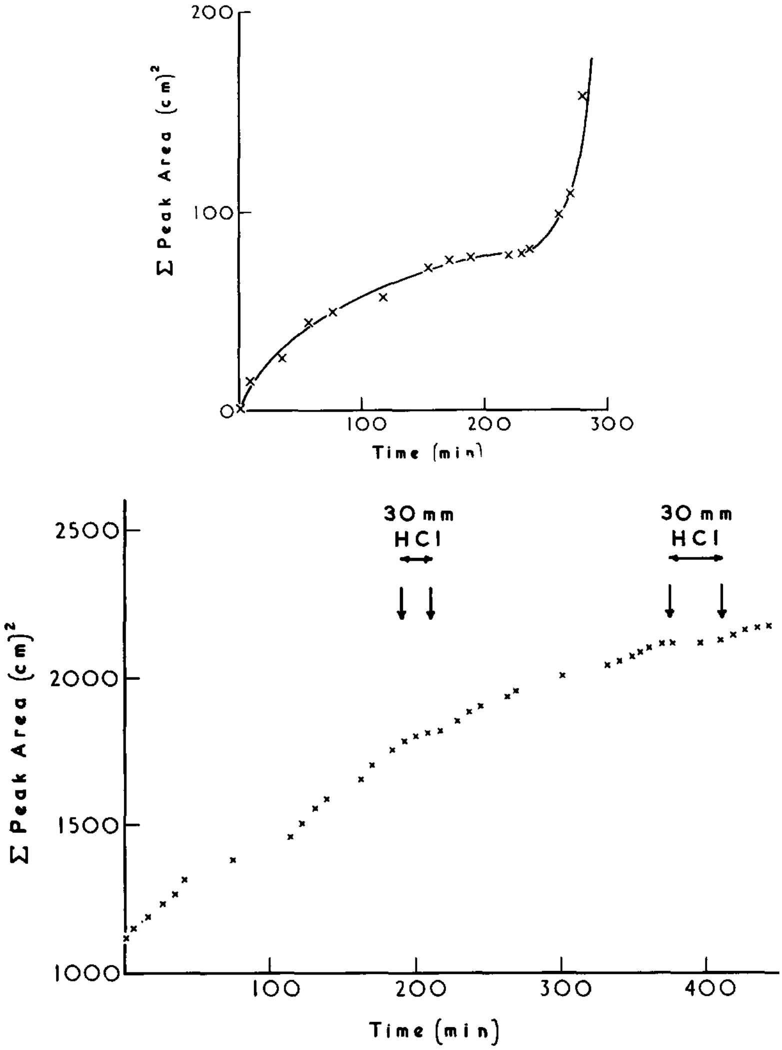

FIG. 3. Plot of sum of chromatograph response peak areas for product "A" (see text) for $Ni_3C$–HCl reaction.

a. Initial reaction and acceleratory region of main reaction.

b. Part of deceleratory region of main reaction. Two short periods of reaction with 30 mm of HCl are shown (between pairs of arrows), majority of readings for reaction of 60 ± 3 mm HCl admitted in each dose. There was a time interval between Figs. 3a and 3b and time scale 3b has been taken from a second zero. Figs. 3a and 3b show results for a single reaction.

tion of gaseous hydrogen at 300°C with the residue from a partially completed $Ni_3C$–HCl reaction.

Examination of the residue from a partially completed $Ni_3C$–HCl reaction showed: (a) part (~55%) of the residue was soluble in water and chemical analysis of the filtered solution gave the atomic ratio Ni:Cl::1:2 ± 0.2; (b) the ratio Ni:C in the dried insoluble part of the residue was 1:0.192, close to the value found (*3*) for the original carbide; and (c) an X-ray diffraction study of the solid residue showed $Ni_3C$ only.

**Discussion.** The large number of products observed from the $Ni_3C$–HCl reaction is believed to be a mixture of hydrocarbons and chlorohydrocarbons. Analyses on the charcoal column showed that ethane and possibly propane were present and these, together with any butane, would contribute to peak A. Products C, J, K, L, M, and N were close to the retention distances for normal alkanes found by direct calibration [*n*-pentane (21), *n*-hexane (73), *n*-heptane (170), and *n*-octane (420)] and extrapolation of the log (retention distance)–boiling point plot gave values for *n*-nonane as 830 and *n*-decane as 1950. Peaks E, G, and H were close to those found for *n* and isopropyl chloride and methylene chloride. These suggestions appear to be the most reasonable interpretation of the data since it seems improbable that alkenes would result from reactions in excess hydrogen chloride and if all possible branched-chain hydrocarbons were present a very much larger number of products would be observed. Accordingly it is concluded that the $C_2$–$C_{10}$ normal alkanes and the chloro derivatives of some of the lower members were the main products of reaction. Calculations using approximate values for chromatographic response sensitivities showed that the total volume of product hydrocarbons was of the same order as that expected from complete hydrogenation of the total carbon in the sample. The results are consistent with the brief notes on this reaction given by Bahr and Bahr (*4*).

The present results show that volatile products were formed from both carbidic and graphitic carbon in the solid reactant since (a) the carbon content of partially reacted carbide was close to the value for the original solid, (b) reaction occurred even after the carbide had been heated above its decomposition temperature, and (c) reaction in HCl occurred between graphite and solid $NiCl_2 \cdot 6H_2O$, or NiO, to give peaks at the same retention distances as the initial members of the series observed for the $Ni_3C$–HCl reaction.

The reaction kinetics observed for the $Ni_3C$–HCl reaction differ markedly from those discussed in previous sections and are similar to those sometimes found for the thermal decomposition of pure solids (*13*). Analytical data of the present work suggest that a nonvolatile solid product is formed, almost certainly $NiCl_2$, and reaction occurs at the $Ni_3C$–$NiCl_2$ interface. The initial deceleratory reaction occurred during the formation of a layer of chloride over the original surfaces of the solid. Thereafter nuclei were established which grew into the bulk of the solid giving the sigmoid-shaped curve characteristic of the thermal decomposition of some solids (see, for example, ref. *14*).

The similarity of the range of products found in the present reaction with those given by the Fischer-Tropsch reaction (*15*) suggests that a single reaction mechanism may be common to the two systems. There is some doubt as to the detailed steps involved in the Fischer-Tropsch reaction but the model involving formation of chains of carbon atoms at the reaction interface leading to desorption of normal alkanes, developed in studies of the Fischer-Tropsch reaction, satisfactorily accounts for the products observed in the present work. The evidence obtained in the present work suggests that the alkane formation reaction occurred with carbon after it had been removed from the carbide phase; this is consistent with the results from catalytic studies where it has been found that nickel carbide is inactive in the Fischer-Tropsch reaction (ref. *15*, p. 357). This mechanism is also consistent with the observation that nickel chloride may be used as a catalyst in the hydrogenation of coal (*16*). It is also believed that single carbon units on the surface are not readily hydrogenated to form methane since this gas was not detected in the products [it must be remembered, however, that the chromatograph was less sensitive to this compound than to the other products (*5*)]. It has been shown (*2*) that traces of adsorbed chlorine strongly inhibit the formation of methane at the nickel surface.

The above results are accounted for, therefore, by a model where reactions, occurring by the same process as believed to operate in the Fischer-Tropsch synthesis, occur at an interface which progresses through the reactant by growth of the nickel chloride phase. The reaction rate increases with temperature in the lower range but a decrease in rate is observed above 350°C, possibly resulting from a decrease in the volume of hydrogen adsorbed on the reactant surface at higher temperatures.

### *Hydrogen Sulfide*

The reaction of nickel carbide with hydrogen sulfide was similar in many respects to the reaction with hydrogen chloride discussed above. Two complicating factors were, however, noted: (a) incomplete removal of $H_2S$ from the product gases by the alkali occasionally masked the earlier peaks and (b) traces of $H_2S$ increased the sensitivity of the detector. Frequent changing of the NaOH (*5*) enabled kinetic studies of the type reported in the previous section to be made.

The pattern of products observed differed from that for hydrogen chloride and the chromatograph response peaks from reaction at 220–350°C were found (under identical analytical conditions to those used previously) at 10 + 15 (P), 29 (Q), 46 (R), 58 (S), 68 (T), 98 (U), 120 (V), 150 (W), 180 (X), 235 (Y), and 520 (Z). The products varied so that slightly greater proportions of the longer retention distance substances were formed at higher temperatures and in the later stages of reaction. The total volumes of products (from peak area, as above) for complete reaction of unit weight of carbide were very much less than those found for the $Ni_3C$–HCl reaction. Above 380°C hydrogen became an important product of reaction.

Plots of the total volume of product against time (as previously) were similar to those found in the $Ni_3C$–HCl reaction but the deceleratory process was very much sharper and rapid cessation of reaction was observed in a number of experiments. Results of a typical reaction (at 325°C) are summarized in Fig. 4, this reaction was interrupted and allowed to stand for a short time in $H_2S$ between the readings at the point marked by an arrow. Interruption of another reaction with evacuation for 40 min at 300°C did not change the reaction rate, and no further induction period was observed when kinetic measurements were resumed.

From measurements of the rate of the approximately linear middle region of reaction (Fig. 4), between 250° and 325°C an energy of activation of 6 ± 1 kcal/mole was found. Experiments which were interrupted with heating to temperatures at which the thermal decomposition of car-

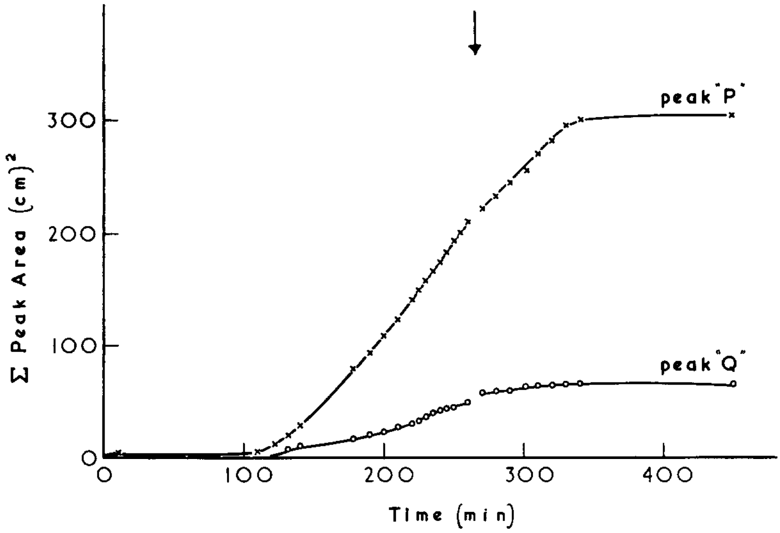

FIG 4. Plot of sum of chromatograph response peak areas for products "P" and "Q" (see text) against time for $Ni_3C$–$H_2S$ reaction.

bide is rapid showed no further reaction when cooled to the previous reaction temperature.

Mixtures of NiO:graphite (56:44 by weight) and Ni:graphite (66:34 by weight) treated with $H_2S$ under normal reaction conditions gave very small traces of products having chromatograph retention distances similar to those found from the $Ni_3C$–$H_2S$ study. This reaction was very rapidly completed. Hydrogen was the main product from reaction of $H_2S$ with the Ni-graphite mixture. Chemical analysis of the residue from a $Ni_3C$–$H_2S$ reaction, which had almost gone to completion at 310°C, showed that it contained 6.93% carbon (12.8% carbon in the original sample). X-ray powder diffraction photographs of the residue from two different reactions at 310°C gave a pattern of lines in the positions expected from the presence of $Ni_3S_2$. It was apparent that Ni and NiS were not formed in appreciable amounts; $Ni_3C$ was present in the sample heated to 310°C only, but not in that which had been heated above 400°C during the course of the reaction. The line attributed (*3*) to graphite was present in both specimens.

The identification of the full range of products is a matter of some difficulty since pure samples of all sulfides and hydrocarbon isomers were not available. Peaks Q, Y, and Z were of similar retention distances to those measured directly for $(CH_3)_2S$, $(C_2H_5)_2S$, and $(i\text{-}C_3H_7)_2S$; the other peaks, which did not correspond to those of the normal alkane series are considered to be mixed sulfides (RSR′) and hydrocarbon isomers. The formation of appreciable amounts of monoalkyl sulfides, which were absorbed by the solid alkali, would account for the observation that a smaller total area of response peaks of all products was found here than with the $Ni_3C$–HCl reaction. Methane was sought but not found. These results are consistent with those of Bahr and Bahr (*4*).

It is believed that reaction occurs at the $Ni_3C$–$Ni_3S_2$ interface which progresses through the reactant by growth of nuclei; this process has been discussed above for the $Ni_3C$–HCl reaction. With hydrogen sulfide, however, negligible reaction occurs at the $Ni_3S_2$–graphite interface since (i) no reaction was detected after thermal decomposition of the carbide phase, (ii) very little reaction occurred on heating Ni– or NiO–graphite mixtures in $H_2S$, and (iii) analysis of the solid product of reaction suggested that the graphite in the solid had not reacted. The formation of volatile products must therefore be confined to the surface carbidic carbon, which may form chains of adsorbed carbon atoms as discussed in the previous section, but the gaseous substances formed here were different since divalent sulfur may react to form series of thioalcohols and of thioethers. The detailed reaction mechanism cannot be established from the data available but reaction may originally occur on the nickel carbide phase since it is known (*17*) that hydrogen sulfide reacts with nickel metal to give hydrogen at temperatures below those of the present study. The absence of product methane shows that the simple reaction of carbidic carbon with adsorbed hydrogen atoms is again inhibited. The rapid cessation of reaction in the deceleratory period may result from the direct decomposition of the carbide in addition to the interface reaction during the later stages of reaction.

## CONCLUSIONS

The results in the preceding sections show that the reactions undergone by the carbon in nickel carbide depend on the chemical properties of *both* the elements in the various reactant gases studied. Characteristic behavior may be divided into three classes as follows:

1. Appreciable reaction did not occur below the temperature at which the carbide decomposed. Both carbon dioxide and ammonia showed this type of behavior and the reactions observed could be shown to occur with the products of carbide decomposition.

2. Reactions occurred between the carbon of the nickel carbide and adsorbed radicals formed by dissociative adsorption of the reactant gas to give a small range of

products. The nature of the products depended on the behavior of both chemical species in the reactant since the oxygen from both water and sulfur dioxide (both included in this class) yielded carbon dioxide as a main product but the latter also gave carbon monoxide whereas the former did not. Reaction kinetics were dependent on the concentration of carbidic carbon. At the higher temperatures studied oxygen from both $H_2O$ and $SO_2$ reacted to form NiO rather than oxides of carbon. The reaction of ethane, the third member of this class, was zero order in carbidic carbon concentration since this reactant was constantly regenerated as a phase of constant composition by the reaction itself.

3. Reaction occurred at a solid–solid interface. This mechanism was suggested from results of reaction with HCl and with $H_2S$ and differs from type 2 above in that reaction of dissociated reactant with single carbon units at the surface of the carbide is inhibited by the formation of a layer of new phase. The reaction observed is that which occurred as this layer of solid product progressed through the reactant yielding a complex mixture of gaseous products by a reaction which followed kinetic laws characteristic of the thermal decomposition of solids.

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