

Summary

1. *cis*- and *trans*-2-aminocyclohexyl benzoate hydrochlorides on treatment with one equivalent of alkali yielded the corresponding oily 2-aminocyclohexylbenzoates which were identified by their conversion to crystalline tosyl derivatives.

2. The presence of alkali greatly facilitated the rearrangement of the diastereomeric 2-amino-

cyclohexyl benzoates to the corresponding benzamidocyclohexanols. Prior to the appearance of rearrangement product, transitory solution of the aminoester occurred; the phenomenon is attributed to the formation of an alkali-soluble ortho-acid derivative.

3. A mechanism for the O→N acyl migration has been presented.

SZEGED, HUNGARY

RECEIVED MARCH 9, 1950

[CONTRIBUTION FROM THE INSTITUTE FOR GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF SZEGED]

The Examination of a System Carbon and Hydrogen in the Temperature Range 1100-2600°

BY ZOLTÁN SZABÓ

Introduction

Since the beginning of our century the equilibrium between carbon and hydrogen has been the subject of numerous investigations. Pring and Hutton¹ heated a carbon bar electrically in a hydrogen atmosphere. Their experimental values scattered markedly. Other authors (Mayer, Bone, etc.),² also could not obtain more accurate data. Later Pring and his co-workers³ again investigated this methane equilibrium, especially the role of the catalyst in respect to the site of the equilibrium. Wartenberg, Wedensky, etc.,⁴ worked out the theoretical side of this problem.

The work of these authors was characterized by a comparatively primitive experimental technique and by defective, even incorrect, thermodynamic considerations. During the glowing, the carbon bar easily becomes inactive and reacts afterward very slowly. The temporarily constant values have been considered as equilibrium values. But when these values changed in the presence of certain catalysts, some authors^{3a,b} advocated the point of view that the equilibria could be changed by a catalyst, which would be equivalent to the realization of the perpetuum mobile of second kind. The wall effect has been also neglected, although this circumstance has a great influence on the concentration.

Our aim has been to investigate the system of carbon and hydrogen by modern experimental technique.

Carbon has been glowed electrically in pure hydrogen atmosphere, the carbon only being at a high but well-defined temperature. The reaction

(1) Pring and Hutton, *J. Chem. Soc. (London)*, **89**, 1591 (1906).

(2) Mayer and Altmayer, *Ber.*, **40**, 2134 (1907); Bone and Coward, *J. Chem. Soc. (London)*, **93**, 1197, 1975 (1908); *ibid.*, **97**, 1219 (1910); Coward and Wilson, *J. Chem. Soc. Industry*, **40**, 445 (1912).

(3) (a) Pring, *J. Chem. Soc. (London)*, **97**, 498 (1910); (b) Pring and Fairlie, *ibid.*, **99**, 1796 (1911); **101**, 91 (1912).

(4) (a) Berl and Bemman, *Z. physik. Chem.*, **A162**, 71 (1932); (b) Morris Travers, *Trans. Faraday Soc.*, **34**, 580 (1938); (c) Wartenberg, *Z. physik. Chem.*, **61**, 366 (1907); (d) Wedensky-Frost, *Chem. Zentr.*, **104**, II, 1928 (1933).

products have been immediately frozen out after leaving the zone of high temperature (see the discussion of the reaction space below). Moreover, we endeavored to employ accurate analytical methods.

Experimental and Analysis

The carbon was arc lamp carbon 7 mm. in diameter with a free length of 70 mm. which was heated between water-cooled electrodes in a 5-liter glass bulb, or in a cylindrical steel vessel of the same volume by current from a low-voltage transformer. The pressure of hydrogen, except for the low pressure experiments, was atmospheric. The temperature of the glowing carbon was measured by means of an optical pyrometer, with an accuracy of ± 3 -5°. The samples for the analysis were taken into a gas analytical buret during the glowing. The experiments were made at a constant volume.

At very high temperatures special care must be taken with the fastening of the carbon bar, in order to preserve the contact and to allow free dilation and contraction. Therefore both ends of the carbon bar were set into precisely bored copper bars as seen in Fig. 1. One of these was fixed in a water-cooled, copper block; the other could slide in the bore hole of another copper block, also cooled by water. By this arrangement the carbon bar has sufficient mobility. The electrical contact and the cooling were also quite satisfactory.

For analysis, samples of 90-100 ml. of gas were collected. Because of the large volume of the vessel, the pressure did not change considerably during the sampling. Below 1700° the formation of only methane and carbon monoxide was observed, the latter from impurities containing oxygen; but its amount never exceeded a few hundredths of 1%. We have found that the final methane concentration is not influenced by varying carbon monoxide amounts, as was also found by Pring.^{3a} For the determination or for the removal of carbon monoxide a neutral solution of cuprous chloride was employed according to Bayer.⁵ The methane was measured through explosion.

Above 1700° acetylene and ethylene also form. The temperature limit of the formation of these gases was determined to be 1750° in special experiments. Still higher temperatures showed the CN-group too. In this case the sample was treated with alkali. The acetylene was determined with mercuric cyanide solution. It is indispensable that the sample for analysis be taken during the glowing; otherwise, the selective

(5) Bayer, "Gasanalyse," Stuttgart, 1941.

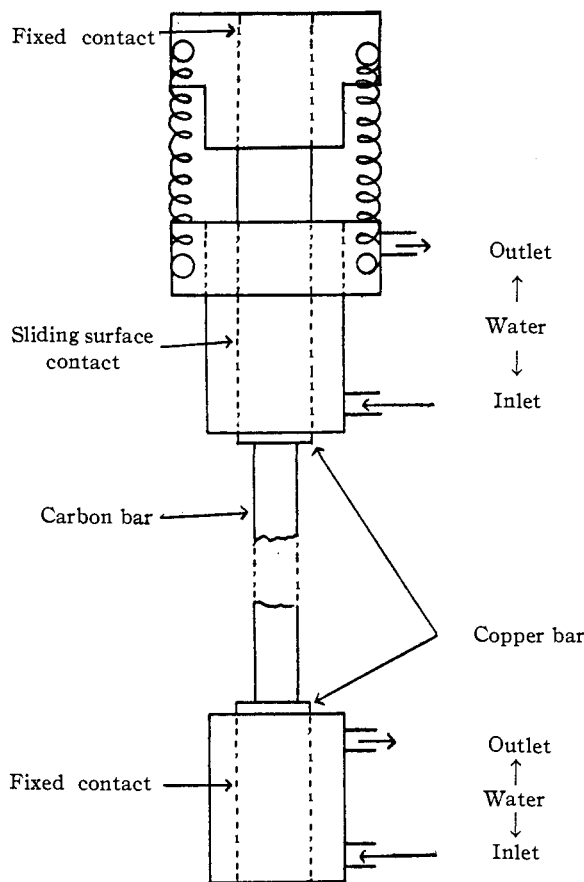


Fig. 1.—Diagram of fastening of the carbon bar. The spring helps at contraction.

adsorption of carbon strongly alters the methane concentration.

Correction of the Temperature Observation and Discussion of the Problem of the Reaction Space.—The temperature of the carbon bar was not the same everywhere, because the leading-in and -off blocks lowered the temperature on both ends. The distribution of the temperature along the carbon bar was independent of the temperature. It was established graphically, as shown in Fig. 2.

The optical pyrometer was calibrated against hot filaments of known temperatures and no black body corrections were used. The glass absorption was determined experimentally and taken into account. This correction was almost negligibly small. The temperature measured on the middle of the carbon bar had to be reduced by 15° to obtain the average temperature.

The investigations of Schwab and Pietsch⁶ have shown that the decomposition of methane on a glowing catalyst-thread goes on quite heterogeneously. Only those molecules will decompose which collide with it. In consequence of this fact only the layer closest to the glowing surface

(6) G. M. Schwab and E. Pietsch, *Z. physik. Chem.*, **121**, 189 (1926).

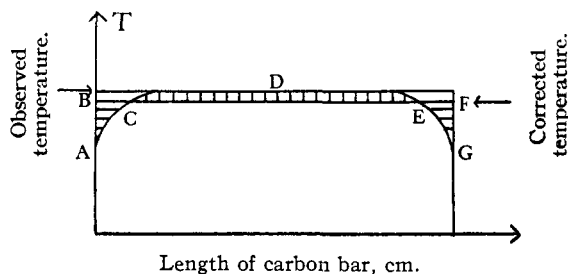


Fig. 2.—Diagram for the correction of the temperature readings: area ABC + EFG = area CDE.

can be considered as a reaction space. The thickness of this layer does not exceed molecular dimensions. This point of view is also valid for the reaction of hydrogen with carbon to form CH_4 or CH_2 fragments; this reaction does not take place in the gaseous phase, but only on the glowing surface of carbon. This statement is in agreement with the enormously great sublimation heat of carbon, so that its tension at our highest temperature does not exceed 10^{-30} mm. Carbon atoms or molecules do not occur in the gaseous phase.

We have also another direct experimental evidence for the delimitation of the reaction space. In the decomposition of hydrocarbons in a homogeneous process, soot separates. Our glass bulb, however, remains quite clean even during long reactions. Even the cooled metal surface remains entirely free of soot, provided it has been brought close to the glowing carbon surface. Thus apparently decomposition of methane in the gaseous phase does not take place.

If now only a monomolecular layer is considered as reaction space, then the temperature of this reaction space will be the same as the temperature of the surface of the carbon measured by means of optical pyrometry.

If the gas were at the same temperature as the carbon, the whole vessel would, of course, be just as hot as the carbon and then we should be dealing with a static method and the measurements would give the true equilibrium. However, our reaction system is not static, but dynamic. Thus our system may be compared with flowing methods in which the hot reaction vessel is our reaction space surrounding the hot carbon rod, around which the gas circulates automatically so long as the temperature gradient exists between the hot carbon rod and the cold gas in the vessel. The extreme smallness of the reaction space permits the reacting gases only to remain a very short time in this space, thus the delay is commensurate with, or even less than, the time needed for the total reaction of the gases in the reaction space. This involves a stationary character of the system⁷ discussed particularly further

(7) This phenomenon is very similar to that already found by Haber and König in 1907 (F. Haber and A. König, *Z. Elektrochem.*, **13**, 725 (1907)). They produced an electric arc in a cooled quartz capillary tube, thus obtaining far higher NO concentrations than

on. This stationary state can be approached and reproduced from both sides; from the hydrogen as well as from the methane side. The gas flowing around the hot carbon bar changes its composition until this stationary state sets in.

Naturally, there exists a very great temperature gradient between the surface of the glowing carbon and the remaining volume of the reaction vessel. It is well known that gas mixtures can be separated in such a temperature gradient, if the other conditions are also favorable for this.

In numerous previous investigations we have pointed out that the geometric conditions of our reaction equipment do not permit the formation of a concentration gradient. In order to test this factor in the present work we have chosen a vessel of such geometrical dimensions as to produce in a mixture of hydrogen and carbon dioxide a great separation of the two gases due to thermal diffusion (see Fig. 3a). Then we let successively the dimensions of this separating model approach our reaction vessel (Fig. 3b-e) and observed the diminution of the thermal diffusion effect as a function of the dimensions by analysis of samples taken from the top and the bottom of the vessel and at half height in the neighborhood of the hot filament, as well as from a more distant point. Early in this series, before the conditions of our reaction vessel had been approached, we reached a point where there was no evidence of any separation by thermal diffusion, *i. e.*, the analysis of the four samples agreed closely.

Our wide cylindrical vessel, which was also suitably short, having a ratio of width to length of 1:2.5, and the relatively short glowing carbon bar (Fig. 3f), are conducive to a relatively small separation by thermal diffusion. The stormy convection, the thermosiphonic effect and the diffusion keep the gas mixture so much in motion that no separation detectable by analysis can take place.

Besides the geometrical conditions, however, the thermal separation depends on the material composition. In our experiments the mixture of hydrogen and methane from the point of view of the separation was still more unfavorable than in the case of hydrogen and carbon dioxide.

Although in this manner thermal diffusion was not to be found in macroscopic dimensions, the possibility of one in microscopic dimensions is not at all excluded. Some differences between the measured and calculated methane concentrations point to a concentration gradient between the reaction space of molecular thickness and the surrounding gas. The consequences arising from this possibility will be discussed later.

Experimental

Experiments at Normal Pressure.—We endeavored to reach the methane equilibrium from those which would have corresponded to thermodynamic equilibrium. (Also at this reaction the direct role of the ions is negligible, agreeing with other experiments, *e. g.*, P. Günther and H. Theobald, *Z. physik. Chem.*, **B40**, 1 (1938); M. Bodenstein, *Roczniki Chem.*, **18**, 374 (1938) (*C. A.*, **33**, 6534 (1939)).

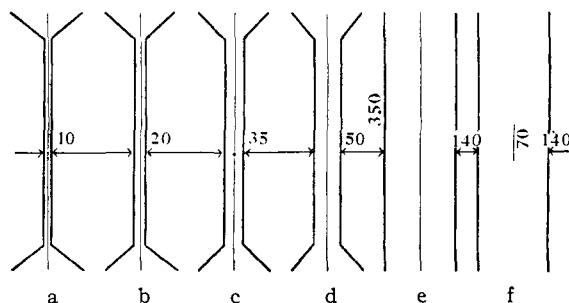


Fig. 3.—Test-tubes for investigation of the thermal diffusion equilibrium in mixture of hydrogen and carbon dioxide. The hot filament extends along the whole tube a—e: tube a, great separation; b, middle separation; c, small separation; d, no separation; e, no separation; f, our experimental vessel; dimensions in mm.

the hydrogen, as well as from the methane, side.

Methane is one of the most stable gases. The decomposition only starts above 650–700°. The rate of the decomposition depends strongly on the surface activity. To reach quickly the final concentration we employed hydrogen containing some methane, instead of pure methane. The carbon bar was glowed alternately in hydrogen or in a hydrogen–methane mixture. As a result, the carbon surface became active and the equilibria were reached quickly. The lower the temperature of the decomposition, the greater was the activity of the freshly deposited carbon layer. The experiments were continued until the concentration of methane became constant at a fixed temperature.

Experiments at Lower Pressure.—If one denotes the fractions of the total pressure p present as hydrogen and methane, respectively, by h and Ch_4 , one obtains at equilibrium $k = h^2p^2/Ch_4p$, and from this $Ch_4 = kh^2p$. The fraction of methane is proportional to the total pressure. These experiments show such a relationship. The same is also valid for ethylene $2C + 2H_2 = C_2H_4$, but not for acetylene, since this latter reaction $2C + H_2 = C_2H_2$ proceeds without variation in the number of moles.

The results of all measurements are given in Table I and on a graph (Fig. 4). The accuracy of these values is, however, different. In the case of methane the error is estimated at several units in the second decimals.

Discussion of the Experimental Results

The methane concentrations plotted against increasing temperature in Fig. 4 show initially a decrease in methane concentration reaching a minimum at 1450° followed by an increase in methane concentration until 2000°. Above this the methane concentration decreases. Since thermodynamically methane should decrease in stability with temperature over the entire range, a simple equilibrium involving CH_4 cannot

(8) C. D. Hurd, "The Pyrolysis of Carbon Compounds," N. Y., 1929.

TABLE I
 MEASUREMENTS OF THE HYDROGEN-METHANE EQUILIBRIUM

Temp., °C.	CH ₄ , ^a %	Time, hr.	Volume %			Time, hr.	Volume %		
			CH ₄	C ₂ H ₂	C ₂ H ₄		CH ₄	C ₂ H ₂	C ₂ H ₄
Hydrogen pressure, 760 mm.									
1145	0	2	1.18	4	1.28
1145	0	3	1.30	5	1.24
1145	2.20	1	1.45	3	1.20
1145	2.20	2	1.18	4	1.22
1450	0	1	0.20	2	0.26
1450	5.50	1	1.24	3	0.27
1450	5.50	2	0.28
1600	0	1	.59	2	0.57
1600	0	1.5	.60
1600	1.50	1	.62	2	0.59
1600	1.50	1.5	.54
2000	0	0.1	.70	0.42	0.70	0.33	1.25	0.42	0.47
2000	4.00	0.1	1.31	0.35	0.30	0.4	1.25	0.45	0.45
2200	0	2	1.06	1.18	1.06	5	1.12	1.18	0.83
2200	4.20	4	1.04	1.12	0.85
2400	0	1	0.81	1.15	0.93	4	1.07	1.34	1.07
2400	4.00	2	1.19	1.86	1.07	4	1.05	1.43	1.00

^a Initial volume per cent. of CH₄.

LOWER PRESSURES OF HYDROGEN

Temp., °C.	Initial		Time, hr.	Volume %				Time, hr.	Volume %			
	H ₂ , mm.	CH ₄ , ^a %		Obs.	CH ₄	Cor. ^b	C ₂ H ₂		C ₂ H ₄	Obs.	CH ₄	Cor.
1145	510	0	2.5	0.80	1.19	3.5	0.83	1.23
1145	530	3.50	4.5	.86	1.23	5.5	.84	1.21
1450	460	0	1	.19	0.31	2	.17	0.28
1450	460	1.50	2	.16	0.26	2.5	.17	0.28
1600	560	2.70	1.5	.54	2.5	.40	0.55
1600	500	0	2	.39	0.59
2000	460	0	0.5	.72	1.19	0.36	0.36	1	.74	1.22	0.33	0.41
2000	460	4.50	1	.71	1.18	0.39	.39
2200	435	0	0.04	.62	1.08	1.06	.44
2200	455	4.70	.03	.69	1.15	1.07	.46	0.06	.65	1.09	1.10	0.45
2400	510	0	.03	.72	1.07	1.44	.64	0.06	.64	0.96	1.37	0.56
2400	490	3.80	.03	.66	1.02	1.40	.66

^a Initial volume per cent. of CH₄. ^b Corrected to 760 mm. hydrogen pressure (vol. % = 760/p).

explain the results. If one considered the data below 1450°, the equilibrium constants, assuming

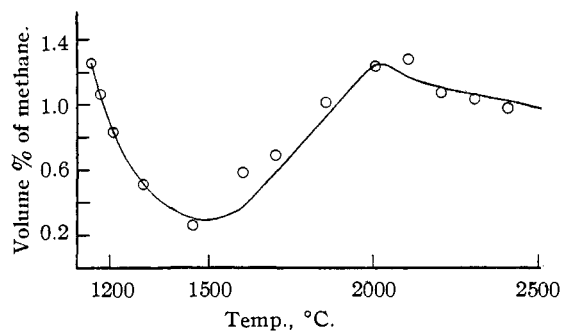


Fig. 4.—The methane concentration as a function of the temperature: O, measured values; — calculated values. The measured values represent the average values, each of which is approached from the hydrogen as well as from the methane side. The approaches quite agree within the experimental error (see also the Table I).

that the methane concentrations correspond to equilibrium at the temperature of the rod, are somewhat higher than those given in the literature. Table II gives these constants compared with the data of Schenck⁹ and Schultze.¹⁰

TABLE II
METHANE EQUILIBRIUM CONSTANTS MEASURED, CALCULATED AND EXTRAPOLATED

t, °C.	T, °K.	CH ₄ found vol. %	—log K _p (P _{H₂} = 1 atm.)—		
			Author	Schultze	Schenck
1145	1418	1.25	-1.90	-2.03	-2.13
1180	1453	1.06	-1.97	-2.11	-2.20
1210	1483	0.83	-2.08	-2.16	-2.26
1300	1573	0.51	-2.29	-2.33	-2.43
1450	1723	0.26	-2.59	-2.56	...

The calculated results given by Schultze depend upon specific heats extrapolated from below 1000°. More exact specific heats might probably yield higher equilibrium concentrations and might

(9) F. Schenck, *Z. anorg. allgem. Chem.*, **164**, 145 (1937).

(10) Landolt-Börnstein, "Physikalisch-chemische Tabellen."

give better agreement between the equilibrium results and the concentrations obtained in this work. However, the calculations of Prosen, Pitzer and Rossini¹¹ which are based on the heat of formation of methane obtained from heats of combustion and the entropy of methane give equilibrium concentrations about one-third lower than those observed in this work. Accordingly, unless the heat capacity values are greatly in error, it hardly seems likely that the experimental results reported in the present paper for temperatures up to 1450° can be considered as representing the true equilibrium values.

The cause of the threefold difference between the experimental results found in the present work and the calculated values of Rossini and his collaborators is not known with certainty at the present time. However, as pointed out above, the possibility exists of a thermal diffusion effect causing a difference in composition between the gas in the cold part of the reaction vessel and the gas in the hot vessel immediately adjacent to the carbon rod. Certainly the deviations between the results observed in the present work and those calculated by Rossini are in the right direction to be taken into account by such a microscopic thermal diffusion effect. However, it should be emphasized that at the most this effect can only help explain the difference between the measured concentrations of the methane and the true equilibrium values. It cannot cause the increase in the absolute value of methane concentrations that takes place above 1450°.

If one now considers the data above 1450°, it is clear that methane cannot be the only species involved on the hot rod since methane becomes less stable the higher the temperature. However, CH, CH₂ and CH₃ are all formed from the elements with absorption of heat and all become more stable with increasing temperature. Thus the minimum in the methane concentration at 1450° must be attributed to the formation of an endothermic carbon hydride on the carbon rod which is converted to methane by reaction with hydrogen upon leaving the rod. Above 1450°, the concentration of methane on the surface of the hot rod must be lower than the concentration of the new carbon hydride which is less important than CH₄ below 1450°, but which becomes more important above 1450° because of its increasing stability with temperature compared to the decreasing stability of CH₄ with increasing temperature. It is not possible to say which carbon hydride is the one of importance above 1450°, but it is probably CH₃ or CH₂ rather than CH.

At higher temperatures, C₂H₂ would also be expected to become important at the rod and indeed it is observed in the cool gas. C₂H₄ is also observed due probably to the partial hydrogenation of C₂H₂ and to some extent to reaction of

CH₂ radicals with one another or of the reaction between CH₄ and one or more of the radicals CH, CH₂ or CH₃ in the cooler part of the tube. The decrease in the methane concentration above 2000° may well be due to the loss in CH, CH₂, or CH₃ radicals and to the direct loss of methane by some of these side reactions.

Data were determined at two pressures in every case which allows one to consider in more detail the mechanism at the hot rod. Unfortunately, the data for C₂H₂ and C₂H₄ are not precise enough to draw any reliable conclusions, but the methane volume fraction is proportional to the total hydrogen pressure. This is exactly what one would expect below 1450°, but the power dependence to be expected when the lower hydride becomes the main species on the hot rod is not so obvious.

If one considers possible reaction kinetics for the synthesis and decomposition of methane that would yield the observed linear relationship between the mole fraction of methane and the total hydrogen pressure, certain conclusions become evident. In the first place, if all processes leading to the formation of methane depend in an over-all way on the square of the partial pressure of hydrogen, and if, in addition, the processes leading to the disappearance of methane are proportional to the first power of the methane partial pressure, then the steady state mole fraction of methane present at a given temperature will be proportional to the pressure of hydrogen. It is difficult, however, at the present time to be sure of the exact nature of the reactions involved in the synthesis and decomposition of methane in the temperature range above 1450°. As pointed out above, it seems certain that the increase of methane to a maximum as the temperature increases must result from the increasing production of radicals such as CH, CH₂ or CH₃ as the temperature is increased. If one imagines that these radicals diffuse away from the hot zone and eventually combine in some fashion with hydrogen to form methane, it is easy to account for a second order dependence of the rate of formation of methane on the total pressure of hydrogen. Thus, for example, the rate of formation of methane in the cool part of the reaction vessel may be considered proportional to the number of CH₂ radicals diffusing from the hot zone out into the cooler part of the apparatus. In turn, the number of CH₂ molecules diffusing from the hot zone will be proportional to the number that are present near the carbon surface. This latter concentration should vary with the first power of the pressure of hydrogen. Accordingly, if one assumes that the rate of combination of CH₂ and hydrogen, in the cooler part of the vessel is proportional to the partial pressure of hydrogen, one arrives at the conclusion that the rate of formation of methane by this mechanism is proportional to the square of the partial pressure of hydrogen.

(11) E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research, Nat. Bur. of Stds.*, **34**, 403 (1943).

In summary, then, the experimental values illustrated by the curve in Fig. 4 seem to be explainable as steady state values and not as true equilibrium values. Below 1450°, the observed methane values seem to be too high in consequence of the phenomenon of thermal diffusion (considered in a microscopic rather than a macroscopic sense) and probably of some other unexplained causes. Above 1450°, it seems likely that radicals such as CH, CH₂, or CH₃ are being formed in increasing quantities as the temperature increases and that these radicals on diffusing out away from the hot zone and into the cooler regions of the reaction vessel combine in some way to form methane. Possibly the gradual decrease in the methane content above 2000° is best explained by the preferential reactions of these radicals to form C₂H₄ rather than CH₄ at the higher temperatures. The formation of acetylene in the cool gas is probably due, in part at least, to the equilibrium formation of acetylene on the hot carbon rod and to its diffusion outward into the cooler part of the reaction system.

Conclusion.—I should still like to remark that the detailed investigation of such a system permits thermochemical estimations to be made which could not easily be reached otherwise. It is especially a useful way to demonstrate the existence of lower-valent species at high temperatures which cannot be obtained at ordinary temperatures. I believe that a more adequately worked out theory of the principle of this apparatus will lead to many practical advantages.

Summary

The reaction of carbon and hydrogen has been investigated between 1100–2600°. The concentration of methane, as a function of temperature shows a minimum at 1450° and a maximum at 2000°. Acetylene and ethylene are also obtained above 2000°. The results indicate that above 1450° some lower hydride, probably CH₃ or CH₂, is present at higher concentration on the surface of hot carbon rod than is CH₄.

SZEGED, HUNGARY

RECEIVED OCTOBER 22, 1948

[CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts¹

BY ROBERT B. ANDERSON, J. F. SHULTZ, BERNARD SELIGMAN, W. KEITH HALL AND H. H. STORCH

The hypothesis that metal carbides are active catalysts and/or intermediates in the Fischer-Tropsch synthesis has been popular for many years.^{2,3} Recent studies with cobalt^{4,5} and iron^{6,7} catalysts indicate that carbides of these metals are probably neither the active catalyst nor an intermediate. Nevertheless, German documents⁸ as well as unpublished results of the Bureau of Mines indicate that pretreatment of iron catalysts with carbon monoxide or mixtures of carbon monoxide and hydrogen in a manner that converts the iron or iron oxide, at least partly, to Fe₃C carbides or iron (hexagonal or Hägg carbides^{8,9}) increased their activity in the synthesis. From the German documents, it may be inferred that, other factors influencing activity being equal, the activity increases with the carbide content; however, the data are not as conclusive as may be desired.

The present paper describes the conversion

of the reduced catalyst to nitrides of iron by treatment with ammonia, a unique departure from the usual methods of pretreating iron catalysts, and considers the effect of nitriding on activity, selectivity and life of a reduced synthetic-ammonia-type catalyst. Later papers will present studies of the influence of catalyst type and composition, operation variables (temperature, flow, and type of synthesis gas), and the amounts of nitrogen and carbon in the catalyst.

The nitrides of iron have been fairly thoroughly studied. The papers of Lehrer,¹⁰ Brunauer, Jefferson, Emmett and Hendricks,¹¹ and Jack¹² describe the chemistry and structure of the iron-nitrogen system in detail. Homogeneous phases in this system are:

Phase	Nitrogen, wt. %	Atom ratio, N/Fe	Arrangement of iron atoms
α	<0.2	<0.008	Body-centered cubic
γ'	5.7–6.1	0.241–0.259	Face-centered cubic
ε	7.3–11.1	.314–.498	Close-packed hexagonal
ζ	11.1–11.3	.498–.508	Orthorhombic

The nitrides of iron are interstitial compounds similar to, and in some cases isomorphous with, the carbides of iron. Jack¹³ showed that treat-

- (1) Article not copyrighted.
- (2) Fischer and Tropsch, *Brennstoff-Chem.*, **7**, 97 (1926).
- (3) Craxford and Rideal, *J. Chem. Soc.*, 1604 (1939).
- (4) Weller, Hofer and Anderson, *THIS JOURNAL*, **70**, 799 (1948).
- (5) Anderson, Hall, Krieg and Seligman, *ibid.*, **71**, 183 (1949).
- (6) Kummer, Browning and Emmett, *J. Chem. Phys.*, **16**, 739 (1948).
- (7) Browning, DeWitt and Emmett, *ibid.*, in press; Podgurski, Kummer, DeWitt and Emmett, *THIS JOURNAL*, to be published.
- (8) For example, Pichler and Merkel, "Chemical and Thermomagnetic Studies on Iron Catalysts for Synthesis of Hydrocarbons," Bur. Mines Technical Paper **718** (1949).
- (9) Hofer, Cohn and Peebles, *THIS JOURNAL*, **71**, 189 (1949).

- (10) Lehrer, *Z. Elektrochem.*, **36**, 383, 460 (1930).
- (11) Brunauer, Jefferson, Emmett and Hendricks, *THIS JOURNAL*, **53**, 1778 (1931).
- (12) Jack, *Proc. Roy. Soc. (London)*, **A195**, 56 (1948).
- (13) Jack, *ibid.*, **A195**, 41, 56 (1948); Goodeve and Jack, *Trans. Faraday Soc.*, **82** (1948).