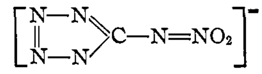
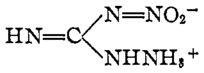
acid (I) together with its mono- and di-basic salts have the same peak at 277 mμ, it is reasonable to assume that both the singly charged anion (III) and the doubly charged anion (VII)


VII

absorb at the same frequency, possibly with a difference in extinction coefficients. For this to be so, it is necessary to conclude that the initial proton removed is from the nitramine group in the singly charged anion (III). For the hydrogen to be removed initially from the ring, yielding the singly charged anion (II) would result in a large hypsochromic shift and a corresponding decrease in extinction coefficient. Accordingly, another peak should have been resolvable. This was not found to be the case.

It will be noted (Table I) that di-(diethylammonium)-5-nitroaminotetrazole (V) deviates by a large amount from Beer's law in contrast to the other compounds which follow Beer's law to approximately 10%. This may indicate incomplete dissociation.

The absorption frequency at the major peak of nitroaminoguanidine (VI) in comparison with nitramide,[3] NH_2NO_2, is found shifted by a very large amount toward the visible region. Nitramide has an absorption maximum at 225 mμ and a molecular extinction coefficient of 5900, whereas VI has its major peak at 267 mμ with a molecular extinction coefficient of 14,200. These data may be readily explained by considering that in neutral aqueous solution, a "*zwitterion*" species VIII is present, the large increase in conjugation



$$\mathrm{HN{=}C}\left\langle\begin{matrix}\mathrm{N{=}NO_2^-}\\ \mathrm{NHNH_3^+}\end{matrix}\right.$$

VIII

accounting for the large shift in frequency and an increase in extinction of better than 2.5. These arguments are strengthened by the identical ultraviolet spectra data for nitroguanidine in acid, neutral and basic media (Table I). In 5-nitroaminotetrazole (I) the shift of 10 mμ to the visible is then due to the addition of another double bond to extend the already conjugated system. Work along these lines is being continued in order to further substantiate the "zwitterion" structure for nitroaminoguanidine and related nitroammonocarbonic acids.

Experimental

Measurements.—All measurements were made with a Beckman ultraviolet quartz spectrophotometer Model D-U, using 0.999 and 0.997 cm. quartz cells. All compounds were run in concentrations from 1×10^{-4} *M* to 1×10^{-5} *M*.

Materials.—The preparation and purity of 5-nitroaminotetrazole and its salts have been described in a separate communication.[2] Nitroaminoguanidine has also been previously described.[2] Aniline hydrochloride was prepared by precipitation of an ether solution of redistilled aniline and dry hydrogen chloride and recrystallization. (*Anal.* Calcd. for C_6H_8NCl: Cl, 27.36; N, 10.81. Found: Cl, 27.39; N, 10.80.)

Acknowledgment.—The support of the U. S. Naval Ordnance Test Station, Inyokern, China Lake, California, under Research Contract N-123S-61517 is gratefully acknowledged.

CHICAGO, ILL. RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Hydrocarbon Synthesis Catalyst Studies. Use of Deuterochloric Acid

BY H. I. WECK, S. MEYERSON AND H. S. SEELIG

Iron catalysts that have been used in hydrocarbon synthesis studies liberate hydrogen and hydrocarbons when dissolved in hydrochloric acid. By the use of deuterochloric acid instead of hydrochloric acid, it has been proved that these hydrocarbons are derived from iron carbide and the acid and are not adsorbed synthesis products that were liberated when the catalyst dissolved. From an examination of the methanes formed it has been concluded that stable iron alkyls do not exist on the catalyst. No exchange was observed between the hydrogen in a sample of *n*-pentane absorbed on metallic iron and the deuterium in the acid used to dissolve the iron.

Introduction

Promoted iron catalysts[1] have been employed frequently for the synthesis of hydrocarbons from carbon monoxide and hydrogen. As the starting material, iron oxides are generally used and these are reduced, usually with hydrogen, before an active catalyst is obtained. In some instances the reduced metal is further treated with carbon monoxide to yield the carbide,[2] but this is not necessary. During the synthesis, changes take place in the composition of the catalyst; the metallic phase tends to disappear and oxides and carbides of iron are formed.[3] In addition carbon and wax are deposited on the catalyst.

To follow the complex changes of the catalyst during the synthesis reaction, a chemical method of analysis was devised. The hydrocarbons liberated when the catalyst is dissolved in hydrochloric acid were assumed to have come from iron carbide (Fe_2C) and the quantity of this material was calculated accordingly. The purpose of the experiments to be described was to determine by the use of deuteriochloric acid whether these liberated hydrocarbons were adsorbed on the catalyst, were present as iron alkyls, or came from iron carbide.

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(1) F. Fischer and H. Tropsch, *Brennstoff Chem.*, **4**, 276 (1923).

(2) H. Pichler, Report to Kaiser Wilhelm Institute for Kohlenforschung in Mülheim-Ruhr, Sept. 10, 1940; T. O. M. Reel 101; British Admiralty Report PG-21574-NID; M. Leva, Translation of German Documents on the Development of Iron Catalysts for Fischer-Tropsch Synthesis, Part I, Office of Synthetic Liquid Fuels Report, Pittsburgh, 1947.

(3) Anderson, Hofer, Cohn and Seligman, THIS JOURNAL, **73**, 944 (1951).

Experimental

The deuterium oxide (99.8% D_2O) was obtained through the United States Atomic Energy Commission. The phosphorus pentachloride was Merck and Co., Inc., reagent grade. The *n*-pentane was secured from the National Bureau of Standards. All gas samples were analyzed by the mass spectrometer.

Preparation of Deuteriochloric Acid.—Two solutions of deuterium chloride in deuterium oxide were prepared. The first was prepared by adding slowly 6.1 g. of phosphorus pentachloride to 1.5 ml. of D_2O and absorbing the generated DCl in 23.5 ml. of D_2O. The acid solution was found to contain phosphate as indicated by an ammonium molybdate test. Removal of this phosphate was effected by means of a simple distillation. The acid strength of the solution was 14.6 wt. %, as indicated by titration with 0.1 *N* NaOH to a phenolphthalein end-point. The light isotope concentration in the deuteriochloric acid was determined by decomposing the acid with zinc; the hydrogen content of the hydrogen plus deuterium was 3.18 ± 0.03 mole %.

Since the sample of D_2O contained only 0.2% H_2O, a second sample of acid was prepared using greater care to exclude moisture and air. Phosphorus pentachloride was sublimed under vacuum in a sealed glass system in order to remove any water or hydrogen chloride that might have been present. The strength of the acid prepared from this PCl_5 was found to be 12.8 wt. % and the concentration of the light isotope was 2.69 ± 0.03 mole %. The improvement in purity achieved by subliming the phosphorus pentachloride was only 0.49 mole %. The high concentrations of the light isotope in the acid samples may be due in part to the differences in the overvoltages of hydrogen and deuterium.

Treatment of Catalysts with Hydrochloric and Deuteriochloric Acid.—Three samples of catalyst were obtained during the course of hydrocarbon synthesis runs conducted at 315°, 250 p.s.i. pressure, with a synthesis gas having a H_2/CO ratio of two, and using a fluidized iron catalyst promoted with 0.5 wt. % K_2O. These were dissolved in 19 wt. % hydrochloric acid and the liberated gases were analyzed to provide the results shown in Table I. Samples of the same catalysts were also treated with deuteriochloric acid. The percentages of the light isotope in the total hydrogen (hydrogen plus deuterium) present in the gases liberated by DCl are given in Table II. Because the mass-spectrometer patterns of the higher-molecular-weight deuteriocarbons are not well established, the individuals of only the methane series could be identified,[4] and of these, only CD_4 and CD_3H were present in sufficient quantities to be determined. The deuterium content of the higher molecular weight hydrocarbons was estimated from the mass spectra without identifying the individual components.

TABLE I

COMPOSITION OF GASES EVOLVED FROM USED CATALYSTS BY TREATMENT WITH HCl

Catalyst sample	A	B	C
Catalyst age, hours	120	120	92
Component		Mole %	
H_2	88.8	88.5	88.8
CH_4	5.4	4.8	4.9
C_2H_4	1.2	1.2	1.1
C_2H_6	0.7	0.8	0.9
C_3H_6	1.1	1.3	0.8
C_3H_8	0.5	0.7	0.8
C_4H_8	.8	1.2	1.0
i-C_4H_{10}	.1	...	...
n-C_4H_{10}	.4	0.3	0.3
C_5H_{10}	.5	...	.5
i-C_5H_{12}	.2	.2	.3
n-C_5H_{12}	Trace	.5	.1
C_6H_{12}	0.3	.3	.3
C_6H_{14}	...	.2	.2
Total	100.0	100.0	100.0

TABLE II

LIGHT ISOTOPE CONCENTRATIONS IN GASES EVOLVED FROM USED CATALYSTS BY TREATMENT WITH DCl (MOLE % H IN H + D)

Catalyst sample	A	B	C
Total gas sample	2.33 ± 0.03[a]	1.61 ± 0.02	1.86 ± 0.02
Non-condensables	2.42 ± 0.03	1.67 ± 0.02	1.93 ± 0.02
Methanes only	2.0 ± 0.1	1.6 ± 0.1	1.7 ± 0.1
Condensables[b]	5.5 ± 3	5.6 ± 1.7	8.3 ± 2

[a] The probable errors listed are due entirely to uncertainties in the reading of peak heights on mass spectrometer records. [b] C_2 and heavier material held up at liquid nitrogen temperatures.

TABLE III

OBSERVED AND CALCULATED COMPOSITION OF METHANES

Catalyst	A		B		C	
sample	Obsd.	Calcd.[a]	Obsd.	Calcd.	Obsd.	Calcd.
CD_4	91.9	90.99	93.6	93.72	93.1	92.76
CD_3H	8.1	8.68	6.4	6.13	6.9	7.03
CD_2H_2	..	0.31	..	0.15	..	0.20
CDH_3	..	.0049	..	.0016	..	.0025
CH_4	..	.0000	..	.0000	..	.0000

[a] Statistical distribution calculated from light isotope fraction in the total sample.

The concentrations of the individual deuteriomethanes are presented in Table III, and are compared with the theoretical methane distributions calculated from the light isotope concentration in the total gas sample.

Exchange Reaction between Hydrogen and Deuterium.—About 0.1 ml. of pure *n*-pentane was added to 1.0 g. of a reduced iron catalyst. The catalyst containing the absorbed *n*-pentane was decomposed by deuteriochloric acid. Analysis showed that no deuterium was introduced into the pentane by this treatment and therefore no exchange between the deuterium in the acid and the hydrogen in the pentane had taken place.

Discussion

The percentages of light isotope (H/H + D) in the gas liberated from DCl solutions by zinc are higher than the percentages found in the gases evolved from the catalyst samples. This was unexpected since the catalyst would appear to be a likely source of hydrogen dilution. However, the zinc experiments were done on a smaller scale with an excess of metal, and any error due to the presence of minute traces of water would be larger. Therefore, since the total gases from the catalysts contained 90% hydrogen and deuterium, the percentages of light isotope in these samples appeared to more nearly represent the actual hydrogen concentration in the deuteriochloric acid than did the results obtained by decomposing the acid with zinc. Accordingly, the lower percentages were used to calculate the methane distributions in Table III.

The concentrations of the light isotope in the non-condensable and methane fractions are the same as in the total catalyst gas samples (Table II). These hydrocarbons appear to have been produced directly from iron carbide and deuteriochloric acid. The concentration of hydrogen in the condensable fraction is greater than in the total catalyst gas. Some adsorbed hydrocarbons do appear to be present, but the quantity is small, and the error introduced into the carbide calculation is less than 5%.

The observed percentage of CD_3H in the methane fraction does not differ appreciably from the percentage calculated from statistical considerations. Although there is some uncertainty in the contribu-

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(4) J. Turkevich, L. Friedman, E. Solomon and F. M. Wrightson, THIS JOURNAL, **70**, 2638 (1948).

tion of CD_2H_2 to the mass spectrometer pattern, it is safe to assume that the concentration did not exceed the calculated amount in Table III. These results do not eliminate the possibility that iron alkyls exist on the catalyst surface during synthesis but no evidence was found for their presence in the used catalyst samples.

WHITING, IND. RECEIVED NOVEMBER 3, 1950

[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

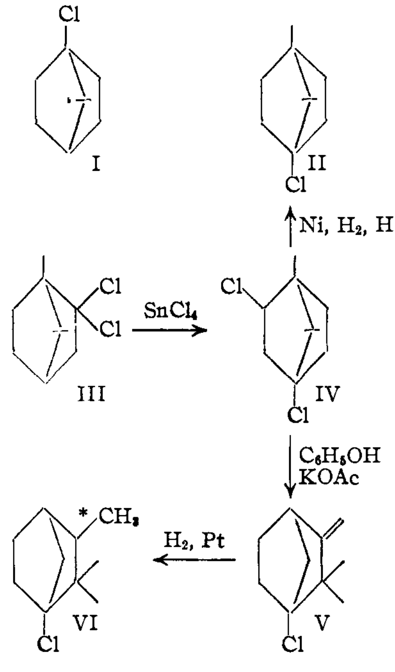
4-Chlorocamphane[1]

BY W. VON E. DOERING AND E. F. SCHOENEWALDT

The bridgehead chloride, 4-chlorocamphane, has been synthesized conveniently from camphor in three steps and has been found to lose chlorine and form an inseparable mixture of C_{10} hydrocarbons on treatment with the halophilic reagents, aluminum bromide, zinc chloride and silver ion. These results are interpreted as suggestive of a difficultly formed, transitory, bridgehead carbonium ion.

The significant and original investigation by Bartlett and Knox[2] of 1-chloroapocamphane (I), in demonstrating failure to obtain reaction with silver nitrate in refluxing aqueous ethanol, has aroused our curiosity concerning the limits of unreactivity of bridgehead chlorine under more strongly halophilic conditions. In this paper a partially satisfactory description of the behavior of the homologous and easily available 4-chlorocamphane (II) is presented.

D(−)2,2-Dichlorocamphane (III, α-dichlorocamphane), prepared by the action of phosphorus pentachloride on D(+)camphor,[3,4] rearranges in the presence of stannic chloride to β-dichlorocamphane (IV),[3,4] the structure of which Houben and Pfankuch have shown to be L(+)2,4-dichlorocamphane (IV).[5] Hydrogenation of IV with Raney nickel in the presence of alcoholic alkali gives optically inactive II, the yield from camphor being 15% of the theoretical. The structure of 4-chlorocamphane is assigned to II on the grounds of consistency (1) with the method of preparation and the structure of the starting material, IV, (2) with the reduction of II to camphane by sodium and alcohol, and (3) with the *meso* nature of II. This latter hypothesis is supported by the facts that *optically active* 4-chlorocamphene (V)[4] is hydrogenated under identical conditions to the *optically active* L(−)4-chlorodihydrocamphenes (VI)[6] and that L(+)2,4-dichlorocamphane (IV) is optically and chemically stable to ethanolic alkali.



Like 1-chloroapocamphane (I),[2] 4-chlorocamphane (II) and L(−)4-chlorodihydrocamphene (VI) are stable to potassium hydroxide in refluxing 90% ethanol for two days. More strikingly II is also unaffected by ethanolic sodium ethoxide at 205° for two days.

Whereas I is reported not to form a Grignard reagent,[2] VI, which also fails to react with magnesium, does react with sodium–potassium alloy (but not with sodium sand) to give a metallic derivative, carbonation of which leads to the mixture of isocamphane-4-carboxylic acids. This result indicates that there is no inhibition to the existence of a negative charge at a bridgehead, a conclusion that seems implicit in the reported reductions of bridgehead halogen with sodium and alcohol.[4]

With silver nitrate in 90% ethanol, 4-chlorocamphane (II) shows no detectable reaction on refluxing or on heating at 160° but the reaction is complicated by the complete reduction of the silver ion at the higher temperature. At 205° suspended in *aqueous* silver nitrate, II reacts to give 59% of the theoretical amount of silver chloride, some unreacted II, and an inseparable mixture of organic

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[1] Taken from a dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939).

[3] H. Meerwein and R. Wortmann, *Ann.*, **435**, 190 (1923).

[4] J. Houben and E. Pfankuch, *ibid.*, **501**, 219 (1933).

[5] There follows a brief outline of the evidence and interpretations on which the expression for IV rests. (a) β-Dichlorocamphane and β-chlorocamphene (from D camphor) are interconvertible in a manner completely analogous with the isobornyl chloride–camphene interconversion. (b) β-Chlorocamphene reacts under the Bertram–Wahlbaum conditions to give a chlorohydrin, the structure of which is clearly L-4-chloroisoborneol on the grounds that reduction gives L-isoborneol and oxidation gives a chloroketone which in turn by an unequivocal series of reactions is converted to the known α-chlorocamphoric anhydride. (c) On the highly reasonable assumption that the reaction of hydrogen chloride with β-chlorocamphene proceeds as does the hydration, IV is L(+)2,4-dichlorocamphane.

[6] Although the ease of preparation commends the 4-chloroisocamphanes (VI) as a source of bridgehead chloride, the fact that in our hands the substance is an inseparable mixture of *endo* and *exo* isomers detracts from its usefulness.