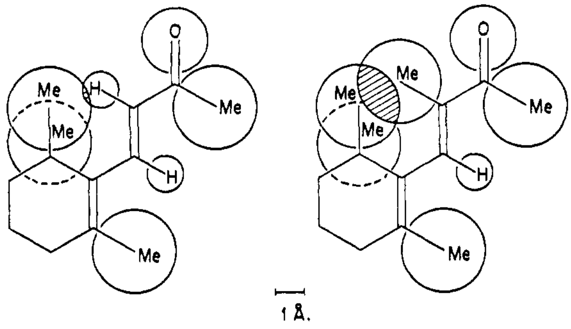

β-Ionone *β-i-Methylionone*

Fig. 1.

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RECEIVED SEPTEMBER 8, 1949

SOME CHARACTERISTICS OF A CRYSTALLINE COMPOUND DERIVED FROM VITAMIN B$_{12}$

Sir:

Vitamin B$_{12}$,[1] 23.7 mg., was stirred with 80 mg. of platinum catalyst in an atmosphere of hydrogen for twenty hours at atmospheric pressure as described by Kaczka and co-workers.[2,3] During the period, 1.12 ml. of hydrogen was taken up, corresponding to about 3 mols. The color changes described elsewhere[2] were noted. About 18 mg. of red crystals (I) was obtained from acetone–water solutions of the resultant product. Further purification, accompanied by the removal of brown material, was accomplished by silicic acid chromatography, using the same procedure employed for vitamin B$_{12b}$,[4] followed by recrystallization. The absorption spectrum maxima following this procedure and after drying at 110° for twenty hours at 1 mm. over phosphorus pentoxide, were as follows: 273 mμ, $E^{1\%}_{1\,\text{cm.}}$ 132; 351 mμ, 159; 525 mμ, 54. These maxima and extinction coefficients are characteristic of vitamin B$_{12b}$. Upon adding sodium hydroxide to a concentration of 0.01 *N*, the absorption spectra of I and of vitamin B$_{12b}$ were found to undergo identical bathochromic shifts of the two main absorption bands to 357 mμ and 536 mμ, respectively. No such shifts were observed with vitamin B$_{12}$. The infrared absorption spectrum[5] of I was similar to that of vitamin B$_{12b}$ and both showed the absence of a band at 2140 cm.$^{-1}$. The presence of a band at this point was observed with vitamin B$_{12}$.[6] The biological activity of I was compared with those of vitamins B$_{12}$ and B$_{12b}$ using *L. leichmannii*[7] and chicks.[8] All three preparations had the same activity within the limits of error of the assay methods. In contrast, vitamin B$_{12a}$, also produced by hydrogenation of vitamin B$_{12}$,[2] was reported to have only 20% of the activity of vitamin B$_{12}$ for *L. leichmannii*[2,9] and 30 ± 15% of the activity vitamin B$_{12}$ for chicks.[2] A band in the absorption spectrum of vitamin B$_{12a}$ was reported at 315 mμ ($E^{1\%}_{1\,\text{cm.}}$ 80).[2] This band was absent from the absorption spectra of both I and vitamin B$_{12b}$.[6] The present experimental results indicate that, under our conditions, vitamin B$_{12b}$ was produced by hydrogenation of vitamin B$_{12}$.

[1] Purchased from Merck and Co., Rahway, New Jersey.

[2] E. Kaczka, D. E. Wolf and K. Folkers, THIS JOURNAL, **71**, 1514 (1949).

[3] The hydrogenation was carried out by Mr. W. Fulmor.

[4] J. V. Pierce, A. C. Page, Jr., E. L. R. Stokstad and T. H. Jukes, THIS JOURNAL, **71**, 2952 (1949).

[5] Kindly measured by Dr. R. C. Gore, Stamford Research Laboratories, American Cyanamid Company.

[6] J. V. Pierce, A. C. Page, Jr., E. L. R. Stokstad and T. H. Jukes, THIS JOURNAL, **72**, in press (1950).

[7] C. E. Hoffmann, E. L. R. Stokstad, B. L. Hutchings, A. C. Dornbush and T. H. Jukes, *J. Biol. Chem.*, **181**, 635 (1949).

[8] E. L. R. Stokstad, T. H. Jukes, J. V. Pierce, A. C. Page, Jr., and A. L. Franklin, *ibid.*, **180**, 647 (1947).

[9] D. Hendlin and H. B. Woodruff, paper presented at 116th meeting, American Chemical Society, Atlantic City, N. J.; September, 1949.

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RECEIVED DECEMBER 21, 1949

A NEW IRON CARBIDE IN HYDROCARBON SYNTHESIS CATALYSTS

Sir:

During the course of hydrocarbon synthesis investigations in this laboratory, X-ray diffraction patterns of certain catalyst samples have indicated the presence of a new iron carbide phase. Iron catalysts in the hydrocarbon synthesis process using CO and H$_2$ have been characterized by the presence of iron carbide either as Fe$_2$C (Hägg) or Fe$_2$C (hexagonal).[1] There has been great interest in these carbides because of the role they may play in the catalytic process.[2]

The catalyst used in these investigations was obtained from reduced, promoted mill scale which analyzes approximately 97.0% total iron, with minor amounts of Mn, Cu, Ni, Al, S and P, and 0.7% K$_2$CO$_3$ as promoter. The new iron carbide appeared along with Fe$_3$O$_4$ and Fe$_2$C (Hägg) during the course of a fluidized synthesis run at 27 atm. pressure and 360°, and eventually it constituted approximately 90% of the total catalyst charge.

The X-ray diffraction pattern of this carbide phase is shown in Fig. 1(b). In this pattern some faint lines are attributed to Fe$_3$O$_4$ and Fe$_2$C (Hägg).[3] For comparison, the diffraction pattern for Fe$_2$C (Hägg) is shown in Fig. 1(a), and that for α-Fe is shown in Fig. 1c. These diffraction patterns were obtained with a 0.6-mm. extruded sample in a 71.6-mm. powder camera using radia-

[1] Hofer, Cohn and Peebles, THIS JOURNAL, **71**, 189 (1949).

[2] Storch, "Advances in Catalysis and Related Subjects," Vol. I, Academic Press, Inc., New York, N. Y., 1948, pp. 115–156.

[3] Jack, *Proc. Roy. Soc.* (*London*), **195A**, 56 (1948).

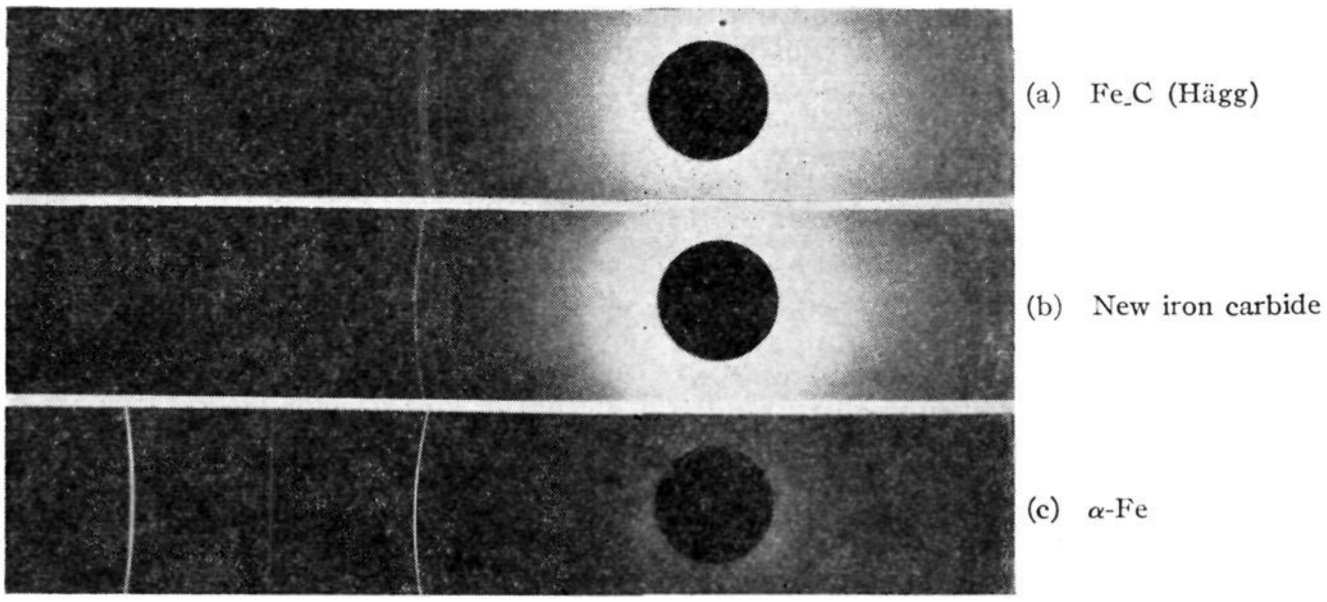

Fig. 1.—X-Ray diffraction patterns obtained from hydrocarbon synthesis catalyst.

tion from an iron target X-ray tube monochromatized with a pentaerythritol crystal.

The d/n values and relative line intensities obtained for this compound are given in Table I. The d/n values were obtained with a 214.86-mm. powder camera using an iron target X-ray tube with manganese oxide filters. An internal standard of NaCl was used. The relative line intensities were obtained from Fig. 1(b).

TABLE I

X-RAY DIFFRACTION DATA FOR THE NEW IRON CARBIDE

d/n, kX. units	Relative intensity	d/n, kX. units	Relative intensity
1.112	10	1.346	15
1.128	10	1.716	15
1.144	25	1.801	30
1.149	25	2.012	100
1.167	30	2.115	45
1.201	35	2.250	35

The new carbide is ferromagnetic and, within the limits of our experimental error, its Curie temperature is the same as that of Fe_2C (Hägg) which is 250 ± 3°.

After heating the sample of the new carbide for ten minutes at 600°, an X-ray diffraction pattern showed that the new carbide had been converted partially to cementite, Fe_3C; after thirty minutes an X-ray diffraction pattern showed that all the carbide had been converted into Fe_3C.

The chemical analysis is complicated by the presence of condensed hydrocarbon products and free carbon. After magnetic separation in a solution of xylene to reduce the amounts of these materials, chemical analysis gave 77.4% iron and 17.4% carbon. This gives an iron to carbon atom ratio of 0.96 so that the new phase could be equivalent to "FeC."

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RECEIVED NOVEMBER 16, 1949

EFFECT OF *p*H IN THE MUTAROTATION AND HYDROLYSIS OF GLYCOSYLAMINES

Sir:

A study of the behavior of the glycosylamines in the presence of acids and bases has revealed a striking dependence of the reactions of these compounds on the *p*H of the solution. Attention was first called to this important property when it was discovered that if a glycosylamine is mixed quickly with one or more equivalents of strong acid, hydrolysis requires a period of many hours, but if the acid is added dropwise to an aqueous solution of the amine, hydrolysis is complete in a few minutes. It has been found that glycosylamines in general undergo a mutarotation reaction involving establishment of an equilibrium of the various modifications. The mutarotation is followed by a hydrolysis reaction that is remarkable in that it takes place rapidly only in a limited *p*H range. Both reactions may be studied by means of the accompanying changes in optical rotation. An investigation is now in progress on the properties of a number of glycosylamines; results are reported here for L-arabinosylamine and the properties of this compound may be considered typical of the group.

Samples of L-arabinosylamine were dissolved in buffer solutions at various *p*H values, and the ensuing reactions were followed by observing the change in optical rotation. Two reactions occurred, the relative rates of which depended upon the *p*H of the solution. The first of these, which in the case of L-arabinosylamine was accompanied by a decrease in optical rotation, is ascribed to a mutarotation reaction; the second, accompanied by an increase in optical rotation, is ascribed to hydrolysis of the amine to the corresponding sugar. In solutions less alkaline than about *p*H 8, the mutarotation was too fast to be measured, and in more alkaline solutions, the hydrolysis was negligibly slow.

By application of the customary equation for a pseudo-unimolecular reaction, satisfactory rate