under pyrolytic conditions[4a] but not in refluxing aqueous solution[4c] while 1-methylgramine methiodide reacts rapidly with aqueous sodium cyanide at the reflux temperature to yield a mixture of the isomeric nitriles IX and X.[5,6a]

Acknowledgment.—The authors are indebted to the Electrochemicals Department of the du Pont Company for gratuitous supplies of furan and 2-methylfuran.

Summary

1. An improved method is described for the synthesis of Mannich bases derived from 2-methylfuran.

2. Furfuryltrimethylammonium iodide and the corresponding 5-methyl compound have been found to undergo amine exchange with piperidine, but the hydrochlorides of furfuryldimethylamine and the corresponding 5-methyl compound do not react with piperidine in refluxing *n*-hexanol differing in this respect from analogous indole compounds.

3. Furfuryltrimethylammonium iodide and the corresponding 5-methyl compound react with sodium cyanide to yield nitriles only at temperatures above 180° thus distinguishing themselves again from the indole Mannich bases. Furfuryltrimethylammonium iodide unlike furfuryl chloride with sodium cyanide yields mainly furfuryl cyanide and only traces of 2-methyl-5-cyanofuran.

4. The synthesis of N-furfurylaniline has been improved and N-methyl-N-furfurylaniline has been synthesized.

NOTRE DAME, INDIANA RECEIVED AUGUST 18, 1949

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

Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers from Cobalt Catalyst[1]

BY R. A. FRIEDEL[2] AND R. B. ANDERSON[2]

The composition of synthetic liquid fuels, such as are obtained in the Fischer–Tropsch process, are of interest both in studying reaction mechanism and in determining applicability as fuels. Little quantitative work on these products has been reported; general product-distribution studies have been reviewed by Storch.[3] The first comprehensive information on the isomeric composition of Fischer–Tropsch hydrocarbons was published by von Weber.[4] By determining boiling points and molecular weights of fractions, von Weber estimated that the mole fractions of branched hydrocarbons were 0.15, 0.27 and 0.40 for the C_6, C_8 and C_{10} ranges, respectively. Later, Koch and Hilberath[5] determined isobutane content and showed qualitatively the presence of the various monomethyl paraffin isomers in the C_5–C_7 range. Traces of more highly-branched paraffins were reported, but none involving a quaternary carbon atom were claimed to exist. The present paper deals principally with the product distribution from C_1 to C_{20} and with the quantitative analysis of paraffin isomers in the C_5–C_8 range.

Product Distribution, C_1 to C_{20}

The distribution of hydrocarbon products from tests of precipitated cobalt catalysts in small reactors with 2 hydrogen to 1 carbon monoxide gas at atmospheric pressure, space velocity of 100 and about 190°, was obtained by fractional distillation of the liquids and mass spectrometer analysis of the gases. The liquid products were fractionated in a 6-foot, 25 mm. diameter, Podbielniak column, at atmospheric pressure up to C_{13} and at 40-mm. pressure from C_{13} to C_{20}. Plate values for the atmospheric distillation varied between about 50–80 theoretical plates. Fractionations were carried out on both the original sample and on a hydrogenated portion. The molecular weight distributions obtained from the boiling point curves were identical for the two distillations. Estimated accuracies for the distribution vary from 5% at C_6 to 25% at C_{20}. Qualitative tests by ferrox paper, 2,4-dinitrophenylhydrazone, and spectrometric methods showed the presence of oxygenated compounds in various fractions. For the over-all distribution to C_{20} no further separation or analysis was undertaken.

The distribution according to carbon number fraction is given in Fig. 1a. The yield of methane was large followed by a minimum at C_2, a broad maximum from C_5 to C_{11}, and a gradual decrease to C_{20}. Ten per cent. of the products was above C_{20}, the average molecular weight of this residue being 309. This distribution is similar to that reported by Craxford[6] for C_1 to C_{13}, but differs considerably from those reported by Underwood[7] for C_1 to C_{32} and by Herington[8] for C_5 to C_{11} in which the weight fraction decreased continually with increasing carbon number above C_5.[9]

Herington[8] considered the formation of hydro-

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(1) Not subject to copyright.

(2) Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pennsylvania.

(3) H. H. Storch, *Chem. Eng. Progress*, **44**, 469 (1948).

(4) U. von Weber, *Angew. Chem.*, **52**, 607 (1939).

(5) H. Koch and F. Hilberath, *Brennstoff-Chem.*, **22**, 135, 145 (1941); **23**, 67 (1942).

(6) S. R. Craxford, *Fuel*, **26**, 119 (1947).

(7) A. J. V. Underwood, *Ind. Eng. Chem.*, **32**, 449 (1940).

(8) E. F. G. Herington, *Chem. and Ind.*, **65**, 347 (1946).

(9) C. W. Montgomery and E. B. Weinberger, *J. Chem. Phys.*, **16**, 424 (1948), calculated the distribution curve of paraffin hydrocarbons in terms of temperature, methane to ethane ratio and carbon to hydrogen ratio assuming thermodynamic equilibrium, and were able to satisfactorily approximate the distribution data of Underwood.

carbons by one carbon atom additions to a hydrocarbon chain growing at the catalyst surface, assuming that hydrocracking reactions are not important. He defined a quantity β_n, the probability that a hydrocarbon chain of length n on the catalyst will appear as product of length n divided by the probability of growing at the surface to appear in the products as a hydrocarbon of greater chain length, by equation (1).

$$\beta_n = \phi_n \Big/ \sum_{n+1}^{\infty} \phi_i \qquad (1)$$

where ϕ_i is the number of moles of hydrocarbons of length i in the product.

Further consideration of Herington's approach leads to

$$\beta_n = \frac{1 - \alpha_n}{\alpha_n} \text{ or } \alpha_n = \frac{1}{1 + \beta_n} \qquad (2)$$

where α_n is the probability of growth of a chain of length n. It can be shown that for any range of constant value of β_n

$$\phi_{n+1} = \phi_n \frac{1}{1 + \beta} = \phi_n\,\alpha \qquad (3)$$

and

$$\phi_n = \phi_x\,\alpha^{n-x} \qquad (4)$$

Also

$$W_n \cong 14\,n\,\phi_x\,\alpha^{n-x} \qquad (5)$$

where W_n is the weight of hydrocarbons of length n. The weight distribution curve of equation (5) exhibits a maximum at $n = -1/\log_e \alpha$, but the mole distribution curve (equation (4)) decreases monotonically. A plot of log ϕ_n against n (equation (4)) should be linear.

Figure 1b presents a plot of β_n for the data of Fig. 1a. For the range C_5 to C_{15} the value of β_n is approximately 0.2 ($\alpha_n = 0.83$). This differs considerably from the distribution of Herington where β_n was about 0.3 ($\alpha_n = 0.77$), and reflects the differences in the distribution curves. For $\beta = 0.2$ a maximum in the weight distribution is predicted at $n = 5$, while for $\beta = 0.3$ the maximum is predicted at $n = 4$. A plot of log ϕ_n against n of the data of Fig. 1a was linear as should be expected from the relative constancy of β_n.

Olefin percentages in the C_2, C_3, C_4 and C_5 fractions were, respectively, 0 (none detectable), 39, 47 and 43%. The percentages of olefins in the higher fractions decreased steadily with molecular weight, similar to the data of Herington.

Analysis of C_5–C_8 Paraffin Isomers

Liquid product from one of the catalyst-testing units, employing a cobalt–thoria–kieselguhr (100:18:100) precipitated catalyst (conditions above), was distilled in a 10-plate column and topped at 160°. A 55-cc. aliquot portion of the distillate was percolated through a silica-gel adsorption column in order to separate quantitatively paraffins, olefins and oxygenated plus other components (Table I). The total paraffin mixture was fractionally distilled into five molecular-weight cuts, C_5–C_8, for analysis of isomers by a Consolidated mass spectrometer.[10] Liquid samples were introduced into the instrument by means of a 0.001-cc. self-filling micropipet.[11] Accuracy was tested in the usual way by analysis of synthetic blends. Results for two of the blends which simulated Fischer–Tropsch products are given in Table II. Ethyl and dimethyl derivatives were not found in preliminary work on the unknown samples and so were not included in the blends. But, to test the accuracy of analyses for these isomers a C_7 blend was analyzed for 3-ethylpentane, 2,3- and 2,4-dimethylpentane, with the negligible results shown in parentheses in Table II.[12] A C_8 blend was analyzed for 3-ethylhexane, 2,3-, 2,4- and 2,5-dimethylhexane. Because of the complexity of the system and the smallness of all concentrations except that of n-octane, the results were not negligible; however three of the four isomers were calculated to be 1% or less.

TABLE I

FRACTIONATION OF C_5–C_9 FISCHER–TROPSCH COBALT-CATALYST LIQUID PRODUCT BY SILICA-GEL ADSORPTION AND DISTILLATION

Component	Volume per cent.
Paraffins	71.7
Olefins	19.2
Residual (oxygenated material, etc.)	9.1
	100.0
Per cent. of total liquid product	37.8

TABLE II

MASS-SPECTROMETER ANALYSES OF SYNTHETIC BLENDS

Component	Blend composition	Anal. #1	Anal. #2
		Volume per cent.	
C_7 Synthetic blend			
n-Heptane	76.7	76.1	76.2
2-Methylhexane	11.1	11.2	11.3
3-Methylhexane	12.2	12.7	12.5
3-Ethylpentane	0.0		(−0.6)
2,3-Dimethylpentane	.0		(.1)
2,4-Dimethylpentane	.0		(.1)
C_8 Synthetic blend			
n-Heptane	5.2	4.5	4.9
n-Nonane	3.2	3.9	3.5
n-Octane	74.8	75.3	73.2
2-Methylheptane	7.0	7.0	6.9
3-Methylheptane	6.9	6.4	7.2
4-Methylheptane	2.9	2.9	4.3

Analyses of paraffin isomers in the C_5–C_8 molecular-weight cuts are given in Table III. Isomeric percentages are given for each C-group on the basis of 100%. Of particular interest is the slight but progressive decrease of the straight-chain isomers, the major components, with molecular

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[10] R. A. Brown, R. C. Taylor, F. W. Melpolder and W. S. Young, *Anal. Chem.*, **20**, 5 (1948); R. C. Taylor, R. A. Brown, W. S. Young and C. E. Headington, *ibid.*, **20**, 396 (1948).

[11] R. A. Friedel, A. G. Sharkey, Jr., and C. R. Humbert, *ibid.*, in press.

[12] This method is described by Kent and Beach, *ibid.*, **19**, 290 (1947).

weight. von Weber's[4] results predicted this effect but to a greater degree than found in the present work. Results from attempted analyses for various ethyl and dimethyl derivatives are given in Table III in parentheses. In all cases percentages were very close to zero, being either slightly positive or negative. These data were considered valid evidence for the absence of appreciable concentrations, but did not allow precluding the presence of traces. In these calculations only one isomer containing a quaternary carbon atom, 2,2-dimethylbutane, was investigated, and this was found to be absent (−0.4%). No indication of this or any other compound of this type has been found.

TABLE III

MASS-SPECTROMETER ANALYSES OF C_5–C_8 PARAFFIN ISOMERS FROM FISCHER–TROPSCH COBALT-CATALYST LIQUID PRODUCT

Component	Composition, volume, %
C_5s	
n-Pentane	94.9
Isopentane	5.1
C_6s	
n-Hexane	89.6
2-Methylpentane	5.8
3-Methylpentane	4.6
2,2-Dimethylbutane	(−0.4)
2,3-Dimethylbutane	(.04)
C_7s	
n-Heptane	87.7
2-Methylhexane	4.6
3-Methylhexane	7.7
3-Ethylpentane	(−0.7)
2,3-Dimethylpentane	(− .02)
2,4-Dimethylpentane	(− .6)
C_8s	
n-Octane	84.5
2-Methylheptane	3.9
3-Methylheptane	7.2
4-Methylheptane	4.4
3-Ethylhexane	(0.1)
2,3-Dimethylhexane	(neg.)[a]
2,4-Dimethylhexane	(neg.)
2,5-Dimethylhexane	(neg.)

[a] No definite negative percentages can be given because the C_8 results are the summed analyses of 7 fractions.

Precise fractionation originally was not thought necessary, so there was appreciable overlapping between carbon number fractions; but accuracy was not decreased appreciably, if at all. For example, after the C_7 and C_8 cuts were analyzed, they were combined and redistilled on a precision column; this time the C_8 components were fractionated into seven cuts for re-analysis. The largest change for any of the C_8 isomers from the original one-fraction analysis was 1.1%. Further, no additional isomers were discovered.

Infrared spectrometry was applied to these samples and synthetic blends. Qualitatively this method was helpful but on fractions covering these comparatively large boiling ranges sufficient quantitative accuracy was not obtained. The infrared spectra of normal and monomethyl isomers are much too similar; on the other hand, the mass spectra of such compounds are quite characteristic.

Analysis of Olefins

Approximate analyses of olefin types in the C_6–C_8 range were carried out on the olefin portion from the silica-gel separation (Table I). The infrared spectrometric method used was essentially that described in recent publications.[13,14] Results showed the predominance of internal double-bond olefins over the alpha form; this predominance increased with molecular weight. Further, the *trans*-configuration was found in greater concentration than the *cis*-form of internal olefins (Table IV). Without all the necessary calibration compounds chain branching is detectable in olefins only if the substituents are on the carbon atoms of the double bond; such isomers were not detected.

TABLE IV

GENERAL OLEFIN TYPES, C_6–C_8

Fraction	Alpha olefins	Internal double-bond olefins	
		trans-	*cis-*
	Volume per cent.		
C_6	36 ± 2	39 ± 3	25 ± 3
C_7	28 ± 2	42 ± 5	30 ± 5
C_8	18 ± 2	52 ± 5	30 ± 5

Iron-Catalyst Products

Similar analyses have been carried out on gaseous and liquid products from iron catalysts and will be reported at the completion of a more extensive program. Preliminary results indicate that less paraffins are formed and that again only monomethyl-branched isomers are found, but in higher percentages than in cobalt products. The distribution of gaseous products from iron catalysts, shown in Table V, indicates a minimum of C_2 products[15] which was less pronounced than that observed for products from cobalt catalysts. Sizable amounts of ethylene were formed, and the olefins in the C_3, C_4 and C_5 hydrocarbons exceeded 70%. The olefin content in the C_6–C_9 portion is also high, being approximately 2.5 times greater than in liquids from cobalt catalysts. Olefins from the iron product are predominantly alpha rather than internal double-bond olefins. Some evidence has shown that chain branching in the olefins is nearly the same as that of the paraffins. The amount of material strongly adsorbed on silica gel (oxygenated compounds, aromatics, etc.) is roughly three times as great in iron-catalyst products.

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(13) R. W. B. Johnston, W. G. Appleby and M. O. Baker, *Anal. Chem.*, **20**, 805 (1948).

(14) J. A. Anderson, Jr., and W. D. Seyfried, *ibid.*, **20**, 998 (1948).

(15) Graves, *Ind. Eng. Chem.*, **23**, 3181 (1931), noted a minimum at C_2 in the catalytic synthesis of higher alcohols.

TABLE V

GASEOUS PRODUCTS FROM IRON CATALYSTS[a]

Catalysts			Fused Fe_3O_4–MgO–K_2O Fe:MgO:K_2O = 100:6.8:0.83	Pptd. Fe_2O_3–CuO–K_2CO_3 Fe:Cu:K_2CO_3 = 100:10:0.5
Hydrocarbon products	C_1	g./cu. m.	13.8	6.2
	C_2	g./cu. m.	8.6	5.6
		olefin, %	22.1	41.0
	C_3	g./cu. m.	14.3	8.7
		olefin, %	76.8	82.4
	C_4	g./cu. m.	8.0	2.7
		olefin, %	79.4	77.4
	C_5	olefin, %	77.7	72.0

[a] Tests were made with 1 hydrogen to 1 carbon monoxide gas at 7.8 atmospheres and space velocity of 100. The average temperatures of testing of the fused catalyst and precipitated catalyst were 260 and 235°. The fused catalyst was reduced in hydrogen at 450° prior to use, and the precipitated catalyst was inducted in 1 hydrogen to 1 carbon monoxide gas at 235° and atmospheric pressure.

Thermodynamic Considerations

The products from the Fischer–Tropsch synthesis from both cobalt and iron catalysts are not present in amounts corresponding to thermodynamic equilibrium between products and their formation must result from the selectivity of the catalytic process. First, oxygenated compounds and olefins are thermodynamically unstable with respect to paraffins. Second, olefin isomers show a greater amount of alpha olefins than predicted from equilibria between olefin isomers, the isomers with internal double bonds usually being more stable than the alpha isomers. Third, branched paraffin and olefin isomers have a greater stability than corresponding normal isomers. Fourth, of paraffin molecules, the formation of methane is the most likely thermodynamically.

Acknowledgment.—We wish to acknowledge the help of Julian Feldman, Irving Wender and Dr. Milton Orchin for their extensive work in preparing the samples.

Summary

The distribution of Fischer–Tropsch synthesis products has been given from C_1 to C_{20} for precipitated cobalt catalysts, using 2 hydrogen to 1 carbon monoxide gas at atmospheric pressure and 190°. Quantitative analysis of C_5–C_8 paraffin isomers by mass spectrometery showed only the presence of monomethyl isomers. The predominant components, the straight-chain isomers, decreased with increasing molecular weight. Approximate analyses of olefins showed that internal double-bond olefins were the major constituents. Preliminary results on iron-catalyst products also are reported.

BRUCETON, PENNSYLVANIA RECEIVED JANUARY 12, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION RUBBER CO., LTD.]

Derivatives of *p*-Chlorobenzenesulfonic Acid

BY MARSHALL KULKA

In the manufacture of DDT from chlorobenzene and chloral using sulfuric acid as condensing agent, *p*-chlorobenzenesulfonic acid is a by-product. Up to the present time, this by-product has found limited use in industry and has created a disposal problem. The purpose of this investigation was to prepare derivatives of *p*-chlorobenzenesulfonic acid to be tested as possible insecticides and fungicides. Several new sulfones, sulfonic esters and N-substituted sulfonamides were perpared and their properties noted.

The sodium salt of *p*-chlorobenzenesulfonic acid was converted to *p*-chlorobenzenesulfonyl chloride (I) and fluoride (II) by means of the corresponding halosulfonic acid in the presence of a chlorinated solvent and the optimum conditions for the conversion were developed. The use of chlorinated solvent made unnecessary the large excess of the halosulfonic acid usually employed in the preparation of various arylsulfonyl halides from sodium arylsulfonates.[1]

The sulfones (IV) were prepared by reducing (I) or (II) with excess aqueous sodium sulfite to *p*-chlorobenzenesulfinic acid (III) and condensing the sodium salt of (III) with suitable halogen derivatives. When the halogen compound employed was dichloroacetic acid, condensation and decarboxylation occurred simultaneously and the product was *p*-chlorophenyl chloromethyl sulfone.[2]

$$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{X} \xrightarrow{\text{Na}_2\text{SO}_3} p\text{-ClC}_6\text{H}_4\text{SO}_2\text{H} \xrightarrow[\text{RCl}]{\text{NaOH}} p\text{-ClC}_6\text{H}_4\text{SO}_2\text{R}$$

(I, X = Cl) (III) (IV)
(II, X = F) (R = alkyl or aralkyl)

The esterification of primary alcohols with the sulfonyl halides (I) and (II) proceeded normally in the presence of sodium hydroxide or pyridine. However, when glycerol α-monochlorohydrin ($HOCH_2CHOHCH_2Cl$) was esterified with *p*-

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[1] Green, Marsden and Scholfield, *J. Chem. Soc.*, **85**, 1432 (1904); Heumann and Köchlin, *Ber.*, **15**, 1118 (1882); Zincke and Kempf, *ibid.*, **44**, 418 (1911); Goldyrev and Postovsky, *J. Applied Chem., U. S. S. R.*, **11**, 316 (1938); *C. A.*, **32**, 5800 (1938).

[2] Smadel and Curtis, "Manufacture of Insecticides, Insect Repellents and Rodenticides," I. G. Farbenind., A. G. Leverkusen and Elberfeld, Combined Intelligence Objectives Sub-Committee Report No. XXIII-20 (PB Report No. 240, U. S. Department of Commerce).