TECHNICAL APPENDIX B

Hydrocarbons and Chemical Compounds Used in Aviation Fuels

BY S. D. HERON

This appendix is intended primarily for those whose curiosity may be aroused by the foregoing text. The author is far from being a chemist and realizes that this appendix is likely to arouse derision on the part of teachers of elementary high school chemistry. He has experienced the mental confusion which is suffered by the average mechanical engineer (who is usually almost without training in chemistry) when he is first exposed to the chemistry of the hydrocarbons and other compounds used in fuels. The author has found that the general line of attack used in this appendix at least partially removes fuel chemistry from the class of pure magic as regards engineers and mechanics.

The compounds discussed here involve only six chemical elements: the gases — hydrogen, oxygen and nitrogen; the solids — carbon and lead; and the liquid — bromine. The chemical symbols for these six elements are:

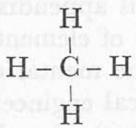
Element	*Chemical Symbol*
Hydrogen	H
Oxygen	O
Nitrogen	N
Carbon	C
Lead	Pb
Bromine	Br

The atom is the smallest possible division of an element. Many elements, however, cannot exist alone as single atoms and the smallest actual division is a molecule containing two or more atoms, thus: hydrogen $H-H = (H_2)$. A compound consists of two or more dissimilar atoms linked together and its smallest division is also a molecule, thus: water $H-O-H = (H_2O)$.

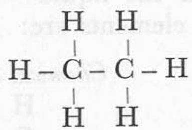
The hydrocarbons used in aviation fuels consist almost entirely of paraffins, naphthenes, and aromatics. Olefins are used only in very low concentration since they show certain performance disadvantages and are restricted in amount by specifications. Olefins, while of very minor interest for actual use in aviation fuels, are nevertheless of great importance since many of the most important aviation fuel hydrocarbons are manufactured from them.

1. Paraffins

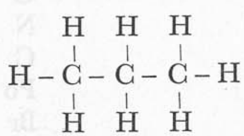
The simplest hydrocarbon is the paraffin

methane  sometimes known as marsh gas and by far the largest constituent of natural gas. It consists of one atom of carbon — which has four "bonds" with which it may be linked to other atoms — and four hydrogen atoms each having only one "bond." This system of bonds is fundamental to the carbon and hydrogen atoms in that it never varies throughout the entire field of hydrocarbon chemistry. Several carbons may be linked together chain fashion with their remaining "bonds" satisfied by hydrogen atoms, thus:

ethane



propane



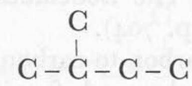
It should also be noted that no "bonds" may be left dangling — all must be linked if the compound is to exist as such. This principle obviously makes possible the construction (at least on paper) of an infinite number and variety of hydrocarbon molecules.

As these variations in number and variety are obviously determined by the possible *carbon* linkages, the molecular structure of hydrocarbons may be considered only in terms of the linkage of their carbon atoms which can be arranged in chains as in paraffins and olefins or in rings as in naphthenes and aromatics.

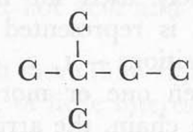
In the normal or straight chain compounds, the carbon atoms in the molecule are linked together in so-called straight chains in which no carbon atom is linked to more than two other carbon atoms, thus:[1]

C – C – C – C – C *normal pentane*

If more than three carbon atoms are contained in the molecule, the atoms can be arranged in what is called a branched chain, thus:

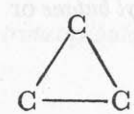


isopentane



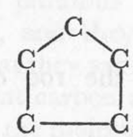
neohexane

In the ring compounds the basic structure of the ring may contain as few as three carbon atoms, thus:

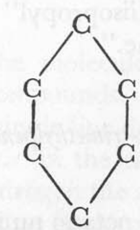


cyclopropane (a gas used for anesthesia)

Cyclopropane is the simplest possible naphthene or "ring" paraffin. The naphthenes with five and six carbon atoms in the ring are the only ones, however, of interest for aviation fuels, thus:



cyclopentane and *cyclohexane*



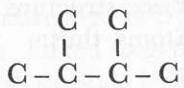
[1]For simplicity skeleton formulas will be used, in which the hydrogen positions are implied.

As the molecules of the paraffins and naphthenes are fully saturated, they cannot accept additional hydrogen.

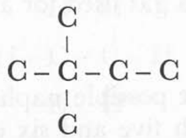
Characteristics of the Paraffins

Paraffins are the "back bone" of aviation gasoline, those of principal interest including the five-carbon molecule as the smallest and the eight-carbon molecule as the largest. Within this range many important structural differences are encountered. The most highly "branched" molecules have the highest antiknock properties and are preferred. Aviation gasolines, therefore, contain large percentages of "isopentanes," "isohexanes," and "isooctanes." The isooctanes are the main constituents of "alkylate" (see p. 704).

As the arrangement of the carbon-to-carbon bonds is so important, a convention is widely used for its specification. When the hydrocarbon chain is represented on paper, the carbon atoms are assigned positions — 1, 2, 3, etc., reading from left to right. Thus when one or more branches are linked to the carbon atom of a chain, the arrangement is denoted thus:

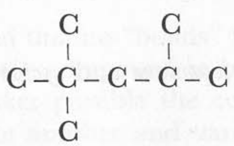


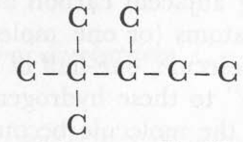
2, 3, dimethyl butane or

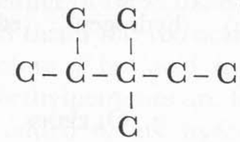


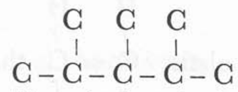
2, 2 dimethyl butane

Both are isohexanes, and each is sufficiently important to possess also a "trade" name. The 2, 3 isohexane is known as "diisopropyl" while the 2, 2 compound is called "neohexane."

2, 2, 4-trimethylpentane  is the 100 octane of the octane number scale.

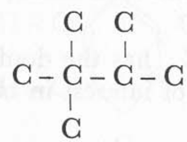
2, 2, 3-trimethylpentane  is the best of the octanes and is a very sensitive paraffin like triptane.

2, 3, 3-trimethylpentane  is also very sensitive.

2, 3, 4-trimethylpentane  is a sensitive paraffin contained in hot acid and phosphoric acid octanes and in alkylate.

Paraffins with more than eight carbon atoms in the molecule are, in general, of little interest in aviation fuels and will not be discussed.

Triptane is the seven-carbon atom paraffin

2, 2, 3 trimethylbutane 

While of excellent performance characteristics, it cannot be made in the enormous quantities necessary for practical use.

2. Forms of Linkage

The paraffins contain all the hydrogen the molecule can accept, and they are known as saturated compounds. The fact that they are saturated is shown by only a single line linking adjacent carbon atoms, thus: C — C or *ethane*. In the case of olefins the molecule does not contain all the hydrogen the molecule can accept. This is shown by a double line (known as a double bond) linking adjacent carbon atoms, thus: C = C or *ethylene*. When two atoms (or one molecule) of hydrogen are added to an olefin molecule, one-half of the double bond must be used to "hook on" to these hydrogens. The double bond then disappears and the molecule becomes "saturated," thus:

$$\underset{\text{(ethylene)}}{C=C} + \underset{\text{(hydrogen)}}{H_2} \rightarrow \underset{\text{(ethane)}}{C-C}$$

3. Olefins

Ethylene, the simplest olefin $\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$ that can exist, is a gas and only of interest for manufacture of aviation fuels. It is used as an anesthetic.

The position of the double bond is also quite important. The convention employed to describe its location consists in adding a numeral at the end of its name, thus:

Butene-1 C = C – C – C has the double bond at the "end" of the chain. It is a gas of interest in manufacture of alkylate and hot acid octane.

Butene-2 C – C = C – C is an important gas used in the manufacture of alkylate and other octanes.

Isobutylene $\begin{array}{c} C = C - C \\ \;\;\;\;| \\ \;\;\;\;C \end{array}$ is the gas used in manufacture of cold acid octane and is important is making hot acid octanes and alkylate.

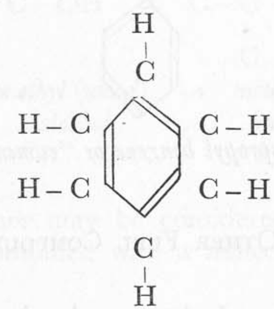
2, 4, 4-trimethylpentene-1 or *diisobutylene* $\begin{array}{ccccccccc} & & & & & & C & & \\ & & & & & & | & & \\ C & = & C & - & C & - & C & - & C \\ & & | & & & & | & & \\ & & C & & & & C & & \end{array}$ and

2, 4, 4-trimethylpentene-2 or *diisobutylene* $\begin{array}{ccccccccc} & & & & & & C & & \\ & & & & & & | & & \\ C & - & C & = & C & - & C & - & C \\ & & | & & & & | & & \\ & & C & & & & C & & \end{array}$

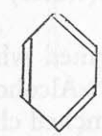
are formed when two molecules of isobutylene are combined (or polymerized) into one molecule. When two atoms of hydrogen are added to either of these molecules 2, 2, 4-trimethylpentane is formed, and this is the 100 octane of the octane number scale. In manufacture of hot acid and phosphoric acid octanes a variety of trimethylpentenes are first formed, and these then have hydrogen added or are hydrogenated to form the octanes.

4. Aromatics

The basis of all aromatic compounds is the six-carbon benzene ring in which every other carbon-to-carbon linkage is a "double" bond, thus:

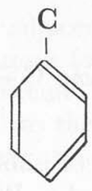


The benzene ring is conventionally represented by the simple form

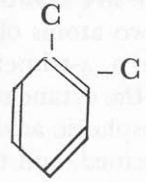


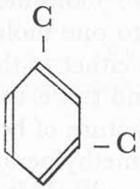
the carbon and hydrogen positions being implied.

Side chains of all varieties can be combined with the benzene ring to produce a whole host of compounds, some of which are also important aviation gasoline components. These are:

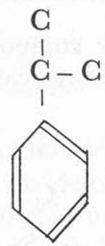


toluene





ortho-xylene *meta-xylene* *para-xylene*



isopropyl benzene or "cumene"

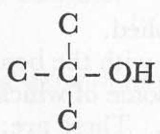
5. Other Fuel Compounds

(a) Alcohols

An alcohol is formed when a molecule of water is combined with a molecule of an olefin, thus:

C = C (ethylene) + H_2O (water) → C — C — OH *ethyl (grain) alcohol*

Similarly an olefin is formed when a molecule of water is removed from an alcohol. Alcohols may be of a variety of types having straight or branched chains, thus:



tertiary butyl alcohol

(b) Ethers

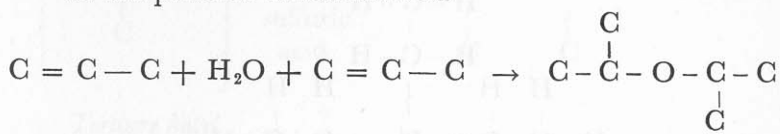
An ether is formed when a molecule of water is combined with two molecules of olefin, thus:

C = C + H_2O + C = C → C – C – O – C – C

ethylene + water + ethylene → diethyl (anesthetic) ether

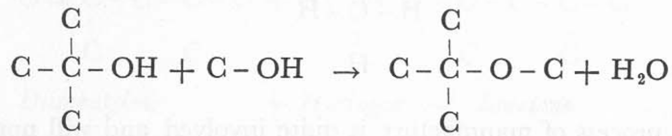
and thus:

In the presence of sulfuric acid



propylene + water + propylene → diisopropyl ether

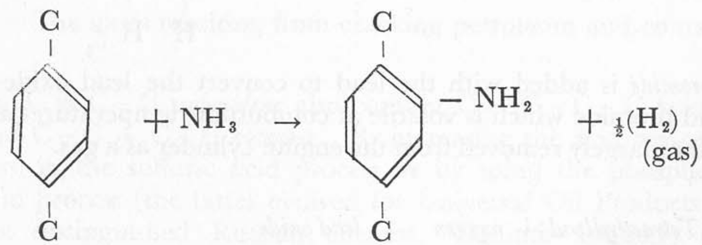
Ethers are often (in fact generally) made by removing one molecule of water from two molecules of alcohol, thus:



tertiary butyl alcohol   methyl (wood) alcohol → methyl tertiary butyl ether + water

(c) Aromatic Amines

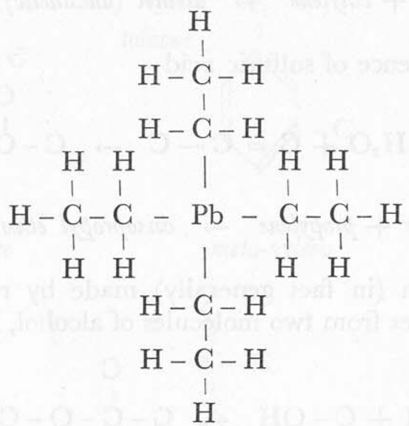
Aromatic amines may be considered as a molecule of ammonia (NH_3) combined with a molecule of an aromatic, thus:



Para-xylene + ammonia forms para-dimethyl amino benzene + hydrogen (xylidine)

(*d*) *Lead Antiknock Compound*

Tetraethyllead (lead) is a complex compound in which four ethyl (C_2H_5) groups have been added to an atom of lead, thus:



The process of manufacture is quite involved and will not be discussed here.

When lead alone is added to a fuel, the combustion process produces lead oxide which tends to accumulate in the cylinder of the engine.

Accordingly, a bromine compound: $Br-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Br$ *ethylene dibromide* is added with the lead to convert the lead oxide to lead bromide which is volatile at combustion temperatures and is thus largely removed from the engine cylinder as a gas.

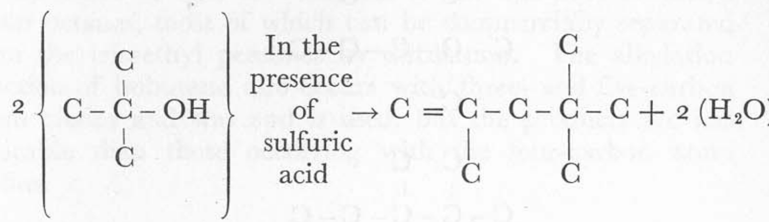
Tetraethyllead + *oxygen* → *lead oxide*

Ethylene dibromide + *oxygen* → *hydrobromic acid*

Lead oxide + *hydrobromic acid* → *lead bromide*

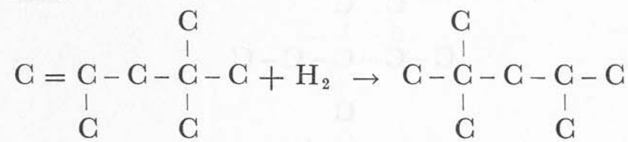
6. Manufacture of Isooctanes

(*a*) *Original processes used by Edgar*



Tertiary butyl alcohol → *Diisobutylene* + *Water*

then

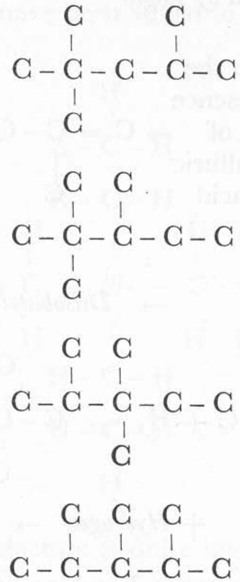


Diisobutylene + *Hydrogen* → *Isooctane*

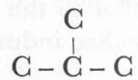
A similar process, using isobutylene in the presence of sulfuric acid, produces diisobutylene which can then be hydrogenated to the isooctane. Such a process was the first to be installed industrially and was known as the cold acid process.

(*b*) *Hot Acid and Phosphoric Acid Processes*

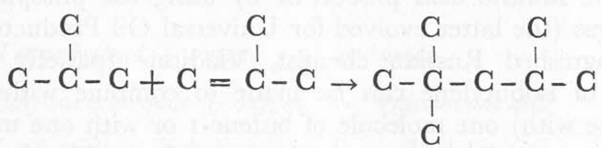
The gases resulting from cracking petroleum and containing $C=\overset{C}{C}-C$ *isobutylene* also contain $C=C-C-C$ *butene-1* and $C-C=C-C$ *butene-2*. By increasing the acid temperature in the sulfuric acid process or by using the phosphoric acid process (the latter evolved for Universal Oil Products by the distinguished Russian chemist, Vladimir Ipatieff) one molecule of isobutylene can be made to combine with (or polymerize with) one molecule of butene-1 or with one molecule of butene-2 giving a product known as hot acid polymer, phosphoric acid polymer, or more simply as codimer. The codimer, when hydrogenated, becomes hydrocodimer and consists mainly of the four possible trimethyl pentanes as follows:



(c) Alkylation process

The gases used in (b) above also contain  *isobutane.* Isobutane also occurs in considerable quantities in natural gas.

Isobutane in the presence of sulfuric or anhydrous hydrofluoric acids will add a molecule of isobutylene, butene-1, or butene-2. Thus, one molecule of a four-carbon atom paraffin (isobutane) combines with one molecule of a four-carbon atom olefin to form an eight-carbon atom paraffin, thus:



Isobutane + *Isobutylene* → *Isooctane*

The reaction shown above occurs as do similar reactions with butene-1 and butene-2. The alkylate which results from the reactions contains all four of the trimethyl pentanes shown in (b) above as well as a number of less desirable branched chain octanes, most of which can be commercially separated from the trimethyl pentanes by distillation. The alkylation reaction of isobutane also occurs with three- and five-carbon atom olefins and was and is used, but the products are less desirable than those occurring with the four-carbon atom olefins.