Catalysis and Carbonium Ions in Petroleum Formation

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IN THREE RECENT PAPERS (*4, 5, 6*) some evidence was presented that active surface minerals, in the strata in contact with petroleums, or the heavy bitumen that preceded typical petroleum, played an essential role in the formation of petroleums. It was suggested that such minerals have acted as catalysts and that the many hydrocarbons now found in petroleum were formed by chemical reactions through a carbonium ion mechanism. Two recent papers (*9, 15*) have brought forward experimental evidence that in industrial catalytic cracking with certain types of catalysts the reactions that take place involve a carbonium ion mechanism. There is much evidence that the two sets of phenomena are related. All of the evidence cannot be reviewed here but the more important considerations are:

(1) Petroleums appear to have been formed from original organic source material laid down in marine sediments, changing slowly through heavy bitumens progressively with age and depth (*2, 5*) to petroleums containing light and heavy oils, except in certain unusual circumstances (see par. 5).

(2) Both the geological (*10*) and chemical (*3*) facts are conclusive as proving a low temperature history, in most cases not exceeding about 140° F.

(3) Calculations from the known rates of cracking at 750° F, or higher, indicate that at the temperatures in oil reservoir rocks substantially no change in hydrocarbon oils could have been effected by *heat alone* during elapsed geologic time (*13*) even to the Ordovician, and most of our American petroleums are not older than Cretaceous.

(4) Sedimentary rocks, shales, and sands, having marked catalytic activity, as measured by the polymerization of unsaturated hydrocarbons, are much more common and widely distributed than was formerly supposed. This activity is not limited to special clays of the type of fuller's earth (*4*).

(5) Heavy petroleums are known that contain little or no light oils and are old enough (Cretaceous or older) to have been converted to an average petroleum containing 25 to 30 percent gasoline. Such heavy oils occur usually in limestone reservoir rocks which have no catalytic activity, as for example the heavy Panuco oil of Mexico found in a Cretaceous limestone, a heavy crude devoid of gasoline found in the Arbuckle limestone (Ordovician) in northern Oklahoma and Kansas, and heavy black oils produced from limestone in Wyoming. In other cases, relatively light crudes may have been formed before migrating into a limestone reservoir. It has recently been found (*5*) that the tar sand in Athabasca, which is Cretaceous, is a clean quartz sand free from clay or fines and is noncatalytic, as tested for polymerizing activity (see following discussion of catalyst activity). Since this sand is not consolidated or lithified the tar probably impregnated the sand early in its history.

(6) The percentages of individual hydrocarbons in petroleums bear no consistent relation, even in the case of a single petroleum, to any calculated equilibrium mixture or ratios, for any particular temperature. If temperature alone were the controlling factor then all oils of substantially the same age and temperature history should be substantially the same and individual hydrocarbons, as for example the isomeric hexanes, should be found in the same relative proportions. This is not even approximately true.

(7) Crude petroleums of widely different composition are known that occur in strata separated vertically by only a hundred feet or so, with no unconformity between them, and whose age and temperature histories are thus substantially the same. Such differences, heretofore very puzzling, are readily accounted for by wide differences in catalytic activity of the rocks with which they are in contact.

(8) The percentages of cyclopentanes and cyclohexanes in all gasolines that have been investigated cannot possibly be accounted for by thermal degradation of any marine source material containing such C_5 and C_6 rings (*6*). Substances containing cyclopentane rings are exceedingly rare in nature. High yields of a trimethyl cyclopentane have been formed from isobutene under polymerizing conditions.

(9) A study of the catalytic action of fuller's earth and several synthetic alumina-silica catalysts on propylene, at 350° C, below common cracking temperatures, showed that isoparaffins and olefins of C_5, C_6, C_7, C_8, and C_9 and higher molecular weight hydrocarbons were formed (*8*). This showed that paraffin syntheses, hydrogenation, and carbon chain splitting occurred. The results obtained in this investigation, as well as the products obtained by commercial catalytic cracking, varied with the nature of the catalyst.

The essential problem in explaining petroleum formation is to discover a plausible chemical mechanism to account for the formation of the great diversity of hydrocarbons, including normal paraffins and branched chain paraffins, cycloparaffins and alkylated cycloparaffins and aromatics. If, instead of such complex mixtures, petroleums consisted of only a few hydrocarbons, as in the natural occurrences of normal paraffins in plants where the paraffins are associated with fatty acids having one more carbon atom than the paraffins, then it would be obvious or strongly indicated that the hydrocarbons were simply derived from fatty acids by loss of CO_2. However, the characteristic complexity of petroleums is strikingly analogous to the results obtained by Gayer and the results of low temperature catalytic alkylations of isoparaffins and olefins now generally believed to take place through a carbonium ion mechanism.

The choice of mechanisms that might account for such complex hydrocarbon mixtures as petroleums appears to be limited to two: free radicals and carbonium ions.

It should be kept in mind that any hypothetical mechanism should be operable within the natural and common conditions of petroleum formation, i.e., temperatures usually not exceeding about 140° F and exceptionally as high as 225° F and as low as 100° F, and contact through millions of years with certain mineral formations.

It is true that there are many chemical reactions that take place at or slightly above room temperature, and that are believed to involve a free radical mechanism. However, as shown by the work of Morris Kharasch, such reactions are catalyzed by such substances as unstable organic peroxides, or by short wavelengths of light, both of which agents are believed to form free radicals. Both catalysts are patently excluded by the environment, in deeply buried strata, in which petroleum has been formed. The other common condition for producing free radicals is thermal decomposition at temperatures much higher than can be considered in this problem.

Reactions of hydrocarbons involving a carbonium ion mechanism are not necessarily conditioned upon high temperatures, for many of them take place at low temperatures—as, for example, in alkylation processes where refrigeration is required to maintain temperatures below about 60° F. In a paper published in 1948 (*4*) it was stated:

> It is now generally accepted that all of these alkylation results are best explained by the formation of carbonium ions. The low temperature formation of the great number of hydrocarbons found in petroleum through the action of active-surface minerals must have a similar chemical mechanism. Further evidence that the catalytic active-surface minerals play an important role in the formation of petroleum is found in the nature of the hydrocarbon constituents of typical petroleums. The fact that straight-run gasolines and kerosenes contain no unsaturated or olefinic hydrocarbons is a strong indication of this. Also the complexity of such oils or, in other words, the very large number of hydrocarbons, isomeric paraffins, naphthenes and aromatic hydrocarbons, has no other plausible explanation.

B. S. Greensfelder (*9*) and his co-workers, in their study of the mechanism of catalytic cracking, state:

> The properties of carbonium ions, which are postulated to represent the reactive form of the hydrocarbon in conventional catalytic cracking, also determine the mechanism of reaction and the type of product in many other acid-catalyzed hydrocarbon reactions such as isomerization, polymerization, paraffin alkylation and hydrogen transfer reactions of olefins, also the isomerization of paraffins and the alkylation of aromatics.

In their study, likewise in the work of C. A. Thomas, good qualitative correspondence between acidity (pH and reaction of the dry solid with ammonia) and catalytic activity is established. They state that the carbonium ion mechanism of catalytic cracking is

> . . . directly coupled with the requirement that the acidic oxide type of cracking catalyst must make available reactive positive hydrogen ions (protons) capable of producing carbonium ions . . .

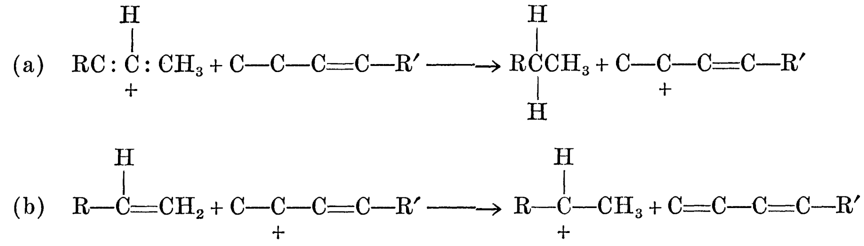
on contact with the oil. Definite experimental evidence was obtained for the strongly acidic character of silica-alumina, silica-zirconia-alumina (U.O.P. Type B) and acid-treated clay catalysts. These catalysts at ordinary temperatures are also good polymerization catalysts.

A study has recently been made of the acid strength of surfaces by the adsorption of various indicators (*16*). The substances investigated included silica-alumina, the silica-alumina bead catalyst used in catalytic cracking by the Socony-Vacuum Company, a synthetic silica-magnesium catalyst, alumina, and silica gel. It was concluded that pure silica gel has a very low acidity but the surface acid strength of the silica-alumina and silica-magnesia, between that of 0.1 and 1.0 *N* HCl, is an intrinsic property of these materials. The author, C. Walling, states:

> It emphasizes the possibility that many examples of heterogeneous catalysis are, fundamentally, cases of acid catalysis occurring on an acid surface . . . for which there appears to be considerable support in the literature.

He points out that activated clays are effective catalysts for acylation and alkylation of aromatic hydrocarbons (*12*), and polymerization of olefins.

According to C. A. Thomas (*15*) olefinic hydrocarbons are converted to paraffins without any external source of hydrogen. This hydrogen is supplied by converting part of the olefinic hydrocarbons into hydrocarbons having less hydrogen, and may be represented by the carbonium ion mechanism in two steps,



$$\text{(a)}\quad \mathrm{RC{:}\overset{H}{\underset{+}{C}}{:}CH_3 + C{-}C{-}C{=}C{-}R' \longrightarrow R\overset{H}{\underset{H}{C}}CH_3 + C{-}\underset{+}{C}{-}C{=}C{-}R'}$$

$$\text{(b)}\quad \mathrm{R{-}\overset{H}{C}{=}CH_2 + C{-}\underset{+}{C}{-}C{=}C{-}R' \longrightarrow R{-}\overset{H}{\underset{+}{C}}{-}CH_3 + C{=}C{-}C{=}C{-}R'}$$

Thus two olefin molecules can be converted into a paraffin and a diolefin and

> By repeating the same type of process, the diolefin may be converted to a triolefin and on to an aromatic hydrocarbon.

The formation of the aromatic hydrocarbons found in petroleum oils has always been difficult to account for by purely thermal means in view of the fact that A. W. Francis (*7*) and others (*14*) have stated on thermodynamic grounds that aromatic hydrocarbons cannot be formed from paraffins with splitting off of hydrogen under about 500° C, a temperature far outside the possibilities in petroleum formation. The formation of aromatic hydrocarbons from unsaturated hydrocarbons by hydrogen disproportionation by the action of catalysts such as fuller's earth has long been known, as for example the conversion of certain terpenes to *p*-cymene and *p*-menthane. This is an instance of the type of reaction involving a carbonium ion mechanism discussed by Thomas.

It was also suggested by Thomas that the presence of a small amount of an olefin may be necessary to start the carbonium ion chain reactions, and at high temperatures, as in commercial catalytic cracking reactions, the olefins believed to be necessary are formed by thermal decomposition, and then

> . . . the carbonium ions produced continue the reaction chainwise via the hydride ion exchange mechanism proposed by Bartlett [*1*] for the alkylation of olefins with paraffins.

However, it has been shown (*11*) that in the isomerization of butane, which is also believed to occur through a carbonium ion mechanism, 0.01 percent of butenes suffices to initiate the reaction. It is uncertain whether or not the lower boiling fractions of petroleum oils now contain olefinic hydrocarbons in any such proportions, but any conceivable organic source material for petroleum must have contained unsaturated fatty acids or their polymers. Petroleum in transition stages must have contained more than sufficient olefinic substances to initiate such carbonium ion reactions if the butane isomerization reaction is any indication of the proportions necessary.

It may be supposed that a mechanism of petroleum formation involving carbonium ion reactions would require the presence, somewhere in the strata, of carbonized residues such as are formed in commercial catalytic cracking processes, but the presence of substantial percentages of aromatic hydrocarbons, which have been otherwise difficult to account for, is one very good answer. Also highly unsaturated hydrocarbons are readily polymerized, as mentioned in the summary in the first part of this paper. Most petroleums contain heavy residues having high carbon-hydrogen ratios which have never been satisfactorily characterized. Oils free from heavy residues and having very high percentages of gasoline are generally believed to have been the result of partial purification by adsorption during migration.

It is submitted that hydrocarbon reactions involving carbonium ions and initiated by the catalytic action of acid silicate minerals, particularly clays, explain satisfactorily many of the problems of petroleum formation hitherto not understood.

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