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LETTERS TO THE EDITORS

# The Formation and Influence of Methyl Carbonium Ions in the Catalytic Cracking of Propane, Isobutane, and *n*-Butane

Some time ago, Franklin and Nicholson carried out experiments leading to the surprising conclusion that the catalytic decomposition of propane, isobutane, and 2-methylbutane was first order with respect to the partial pressure of the hydrocarbon whereas that of *n*-butane, *n*-pentane, and *n*-hexane was three halves order (*1*). Recently in an effort to check these results and if possible explain them, we carried out a series of rate measurements on several of these hydrocarbons in an apparatus in which the reactants were continually recirculated rapidly over the catalyst. The first experiments indicated that the catalyst rapidly lost activity during a given run. Also it was noted that the olefin products at first increased and then decreased. With a view to ascertaining the part played by the olefin products a run was made in which the olefins were completely removed from the circulating gas by $Hg(ClO_4)_2$ supported on firebrick. The alteration in the reaction rate and the nature of the products formed in the absence of olefins was so striking as to warrant reporting some of our observations in the present letter. It appears that we have found conditions under which methyl carbonium ion is the principal carbonium ion on the catalyst surface. Furthermore, propane, isobutane and normal butane all appear to decompose many times more rapidly in the absence of the olefins than in their presence.

A static reactor assembly with gas circulation similar to that described in detail by Kallo (*2*) was used for our experiments. A gas sampling valve built into the gas circulation path (the volume of the valve, 0.18 cc was negligible compared to the total volume of the system, about 190 cc) made possible gas chromatographic analysis of the system at regular intervals, 5 or 10 min. A vacuum system, calibrated gas buret, manometer and U-tube [which as desired could be filled with $Hg(ClO_4)_2$ on firebrick-22 (*3*)] completed the setup. The gas circulating pump actuated by a square wave generator provided a circulation rate of about 1000 cc min. For all the runs 34.8 g of a Davison cracking catalyst (13% $Al_2O_3$) was used.

Figures 1, 2, and 3 present a set of rate curves for the catalytic decomposition of propane, isobutane, and normal butane, respectively, and for the production of products. The curves marked with "Hg" as a subscript refer to experiments in which the olefins were being continually removed. In a few cases the mercury perchlorate filling became exhausted before completing the individual run. Such a point is shown in Fig. 2 and in Fig. 3 by an arrow on the time scale.

The experiments are characterized by three surprising and unexpected results, as follows:

(1) After a few minutes in the runs in which the olefins were being continually removed, the decomposition of the reactant hydrocarbons accelerated rapidly and for a given partial pressure of reactant became as much as 25 times as fast as in runs in which the olefins were permitted to accumulate.

(2) When the olefins were being re-

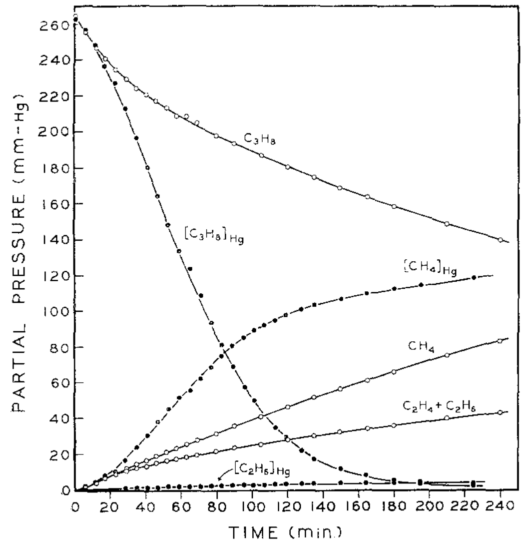

FIG. 1. The catalytic decomposition of propane over a silica-alumina catalyst at 500°C. The curves labelled with "Hg" as subscript represent the runs in which the olefins were being continually removed by a trap of mercury perchlorate in the circulating system. Propylene, iso-$C_4H_{10}$, and $n$-$C_4H_{10}$ were reduced from values of 4.6, 2.9, and 3.1 mm in the standard run to zero in the runs containing the mercury perchlorate trap.

moved, methane was the principal saturated hydrocarbon product; in addition, minor amounts of ethane and, for the decomposition of the two butanes, very small quantities of propane were detected.

(3) The formation of all normal and isobutane during propane cracking, and the formation of normal and isopentane during the cracking of isobutane and normal butane were completely blocked by the olefin removal. The isomerization of $n$-butane to isobutane and of isobutane to normal butane was almost eliminated by the removal of the olefins.

In explaining the results one is first inclined to suspect the transport to the catalyst of some product acompanying the picking up of olefins by the mercury perchlorate. However, no new products appeared when the olefins were being removed. That the change in rate and nature of products was not due to a release of water vapor from the perchlorate was shown by inserting and noting the absence of any effect of a tube of magnesium perchlorate in the circulating gas stream between the mercury perchlorate and the catalyst. Furthermore, analysis of the

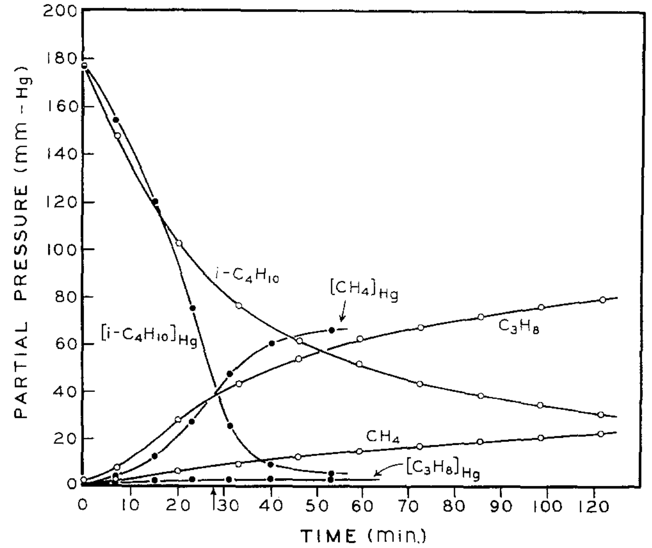

FIG. 2. The catalytic decomposition of isobutane at 450°C over a silica-alumina catalyst. The curves labelled with "Hg" as a subscript represent runs in which the olefins were being continually removed by a trap of mercury perchlorate in the circulating system. The partial pressures of the $C_2$ fraction, $n$-butane, and iso-pentane were reduced from values of 21.3, 18.6, and 7.7 to 6.4, 1.4, and 0, respectively, by inserting the mercury perchlorate trap.

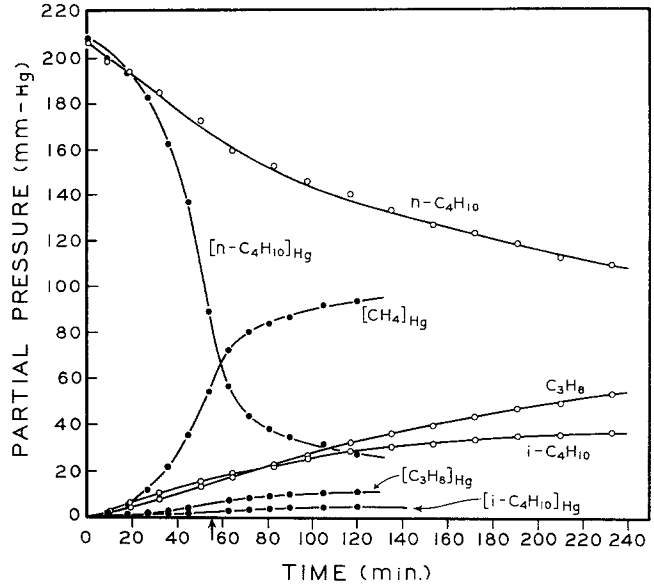

Fig. 3. Catalytic decomposition of *n*-butane at 400°C. Runs in which a mercury perchlorate trap was added to the circulating system to remove olefins are marked by a "Hg" subscript. In the normal run the methane reached a final value of 14.2 mm of Hg; the $C_2$ fraction, iso-pentane, and normal pentane reached values of 9.8, 3.5 and 1.2 mm, respectively. With the mercury perchlorate present the methane was as shown in the figure; the $C_2$ fraction increased to 18.7 mm and the iso-$C_5H_{12}$ and $n$-$C_5H_{12}$ were not detectable.

$Hg(ClO_4)_2$ trap, after completion of the run, showed the complete absence of chloride ion. Finally, the rapid drop in the rate of decomposition of the reactants at the point at which the mercury perchlorate became exhausted showed the effects produced are apparently due entirely to the removal of olefins. This is what would be expected if the olefins are removed, as claimed, by π-bonding to the mercury perchlorate (*4*).

The increase in the rate of propane decomposition by removing the olefins can probably be explained by assuming the following reaction scheme:

$$C_3H_8 + H^+ = C_3H_7^+ + H_2 \qquad (1)$$

followed by

$$C_3H_7 \rightleftarrows C_3H_6 + H^+ \qquad (2)$$

or

$$C_3H_7 \rightleftarrows CH_3^+ + C_2H_4 \qquad (3)$$

and

$$CH_3^+ + C_3H_8 = CH_4 + C_3H_7^+ \qquad (4)$$

The removal of olefins tends to unblock* the acid sites by removing $C_3H_7^+$ by shifting both reactions (2) and (3) to the right. Apparently reaction (4) is very fast.

The accelerated decomposition of the normal butane when olefins are being removed can be explained again by an unblocking process illustrated by the scheme

$$\begin{array}{ccl} & C_4H_8 + H^+ & \\ & \overset{(5)}{\rightleftarrows} & \\ n\text{-}C_4H_9^+ & \overset{(6)}{\rightleftarrows} & CH_3^+ + C_3H_6 \overset{(7)}{\rightleftarrows} \text{iso-}C_4H_9^+ \\ & \overset{(8)}{\rightleftarrows} & \\ & C_2H_5^+ + C_2H_4 & \end{array} \qquad (5)\text{–}(8)$$

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* Obviously, the reaction of $C_3H_8$ with a propyl carbonium ion would form a new propane molecule and hence would not contribute to the disappearance of the reactant, propane. This would also be true of *n*-butane reacting with *n*-butyl carbonium ion and isobutane reacting with isobutyl carbonium ions. Accordingly acid sites can be blocked by propyl, *n*-butyl, and isobutyl carbonium ions in the decomposition of propane, *n*-butane, and isobutane, respectively.

The methyl and ethyl carbonium ions are apparently rapidly removed by normal butane by reactions analogous to reaction (4) to form methane and ethane, respectively. Presumably $n$-$C_4H_9^+$ does not isomerize directly to iso-$C_4H_9^+$ but goes instead by way of a combination of reactions (6) and (7), in agreement with a suggestion recently made by Greensfelder and Samaniego (*5*). Removal of propylene will tend to block the reaction (7) and hence the isomerization of the $n$-butane.

The decomposition of isobutane apparently also is influenced by removing the olefins. The formation of surface methyl carbonium ions is effected presumably by shifting reaction (7) from right to left in the above scheme.

Further details of interpretation will be reserved for the more complete paper now being prepared covering our kinetic studies on the cracking of propane, isobutane, normal butane, and also normal hexane. The relation of the present observations to the kinetics of the decomposition of these hydrocarbons without removal of olefins will also be discussed in the fuller report of the work.

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# Proton Acids as Electron Acceptors on Aluminosilicates

Perylene and other polynuclear aromatics are converted to cation radicals upon adsorption on silica-alumina, zeolites, and certain other acid catalysts. Several investigators have attributed this fact to the presence of strong Lewis acid centers on these catalysts (*1–4*).

Aalbersberg *et al.* (*5*) have reported that molecular oxygen, in the presence of strong Bronsted acids, converts these aromatics to cation radicals. Radical-ion formation was found to strongly depend on the acid strength of the medium. The results were interpreted on the basis that oxygen was the electron acceptor. Stringent removal of oxygen, such as by hydrogen treatment at elevated temperatures, markedly reduces or eliminates the formation of cation radicals by silica-alumina (*3, 6–8*). Accordingly, it has been suggested that the electron acceptor on silica-alumina is adsorbed oxygen rather than Lewis sites (*6, 8*).

Hirschler and Hudson (*8*) found that the $H_R$ acid strength of solid acids influenced the extent of perylene radical-ion formation in a manner similar to that observed by Aalbersberg (*5*) for liquid Bronsted acids, and showed that for both solid and liquid acids the ability to generate radical ions substantially ceased below an $H_R$ acid strength corresponding to about 57–60% $H_2SO_4$. It was therefore proposed that on silica-alumina, adsorbed oxygen accepted an electron from perylene under the catalytic influence of Bronsted acids.

We would now like to suggest an alterna-