THE ALKYLATION OF ISOBUTANE WITH BUTENE-2

By

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THE ALKYLATION OF ISOBUTANE WITH BUTENE-2

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PREFACE

This study was undertaken with the objective of investigating

the rate of alkylation of isobutane with butene-2, in the liquid phase,

using sulfuric acid as a catalyst. Since there is very little published

information concerning the rate of this alkylation reaction, it was felt

that such information would be useful to refiners with alkylation units.

The guidance and encouragement extended by Dr. J. M.

Marchello is acknowledged, and appreciation is expressed for the as-

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The help and encouragement extended by my wife, Judy, have

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INTRODUCTION

The oil refining industry of today is faced with an ever increasing demand for larger and larger quantities of high octane, low sensitivity fuels for use in modern internal combustion engines. As compression ratios continue to climb, refiners will have to produce even higher octane-number fuels to allow knock-free operation of these engines. The use of "alkylate", the reaction product of isobutane and butene, as a blending component in gasoline offers an excellent method of upgrading our present motor fuels.

Alkylate has a number of characteristics that make it an ideal blending component in motor gasolines.(1, 2, 3). It has a high susceptibility to tetraethyllead by itself, and it retains this high susceptibility in blended gasoline. It has a low sensitivity, that is, there is little difference between the research and motor octane numbers of alkylate. Also, its performance in supercharged engines is superior to catalytic polymerization gasoline. Alkylate is a completely saturated product with respect to carbon-carbon bonds, giving it low gum forming tendencies.

The fact that both isobutane and olefins are converted in the process is of major importance. The olefins are produced as a by-product of catalytic cracking operations, and are not particularly desirable in gasolines because of their gum forming tendencies. Isobutane is a high octane material, but its volatility precludes its use as a blending component in large quantities.

At the present time, two processes for the production of "alkylate" may be considered as commercial. These are the sulfuric acid catalyzed and the hydrofluoric acid catalyzed processes. A third process, chiefly of academic interest although some work has been done on the process, is the uncatalyzed gas phase reaction. The gas phase reaction is at least partially amenable to treatment by the theory of absolute reaction rates.

The first commercial alkylation units were constructed in the late 1930's to produce aviation gasoline.(4,5). When the United States entered World War II in 1940, the demands for aviation gasoline increased tremendously, and a number of alkylation units were constructed over a short period of time. Basic research into the process was severely limited, since the great need for gasoline justified the use of any equipment that would produce it. Efficiency, economy of operation, and required capital investment became secondary considerations.

The commercialization of the alkylation processes was the result of the pooled efforts of the research staffs of the Anglo-Iranian Oil

Company, Ltd., Humble Oil and Refining Company, Shell Development Company, Standard Oil Development Company, and The Texas Company. These companies were all separately engaged in research directed toward commercialization of an alkylation process. However, in order to aid the war effort and to prevent duplication of research effort, they pooled their knowledge of the process.

When the war ended there was very little demand for large quantities of aviation gasoline and a number of units were shut down. Because of the increased octane requirements of modern automotive engines, these units are again operating, and new units are being built.

Research on alkylation was largely limited to the qualitative effects of the various operating variables on the quantity and quality of the reaction products, as measured by the ASTM distillation curve and motor octane number. (7, 8, 9, 10).

Some attention was given to the quantitative effects of the operating variables on the quantity and quality of the alkylate. Little work was done on the reaction mechanisms and, apparently, no successful attempt was made to determine reaction rate constants.

Many different parameters affect the commercial alkylation process; however, reaction temperature, mass transfer, and chemical kinetics appear to be the dominant factors. The main purposes of this study were: to predict the rate of the gas phase thermal alkylation reaction from the absolute reaction rate theory; and, to investigate experimentally the rate of the liquid phase sulfuric acid catalyzed alkylation of isobutane with butene.

The declining profit margins in the refining industry make it imperative that refining and conversion units operate as efficiently as possible. It is hoped that this study may be of some value to those concerned with alkylation units.

CHAPTER II

REVIEW OF THE LITERATURE

Reaction Mechanisms

A number of reaction mechanisms have been proposed, but none have been fully accepted. This is quite logical considering the apparent complexity of the reaction and the difficulties encountered in separating and identifying the products of the reaction.

Using butene-2 as an example, the over-all reaction may be written as

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3 \quad + \quad CH_3 - CH = CH - CH_3 \longrightarrow PRODUCTS$$

(isobutane)   (butene-2)

Birch and Dunstan (11) suggested that the initial step in the sulfuric acid catalyzed reaction was the formation of a complex compound between the sulfuric acid and the isoparaffin. This complex compound then reacted with olefins to form the products. Robey (8), however, was unable to substantiate this experimentally.

Caesar and Francis (13) proposed a mechanism which accounted for many of the observed isomers resulting from the sulfuric acid catalyzed alkylation of isoparaffins. They postulated that the

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alkylation occurs as a result of an initial carbon-to-carbon bond cleavage of the isoparaffin prior to addition to the olefin. However, the mechanism fails to explain many of the reactions that are known to take place.

The reactions that are known to occur during the sulfuric and hydrofluoric acid catalyzed addition of olefins to isoparaffins are: alkylation, polymerization, depolymerization, cyclization, dehydrogenation, hydrogenation, and isomerization. Since these reactions are all taking place simultaneously, the actual reaction path leading to any given product is apt to be quite complicated.

The carbonium-ion theory, as postulated by Whitmore (14), and applied by Ciapetta (15) to the acid catalyzed alkylation reaction, is able to explain these reactions and predict the reaction products. The carbonium-ion intermediate offers an explanation for the marked similarity of the products of the reactions of isobutane with butene-1, isobutylene and the copolymerization of isobutene with the normal butenes. The theory is also able to explain the apparent slight reversibility of the alkylation reaction.

The amphiprotic nature of sulfuric acid and hydrofluoric acid, and the large value of their autoprotolysis constants indicate that these acids are an excellent catalyst for proton transfer reactions.(15). Proton transfer reactions include reactions such as hydrogenation-dehydrogenation, hydrogen exchange, isomerization, polymerization, and depolymerization.

In acid-base catalysis, amphiprotic solvents are those solvents which have the ability to add a proton to form lyonium ions or lose a proton to form lyate ions (16). Aprotic solvents are those with negligible acidity or basicity. In concentrated sulfuric acid, for example, the lyonium ion is H_3SO_4 and the lyate ion is HSO_4. For solutions of constant ionic strength in any solvent, the product of the lyonium and lyate ions is a constant, the autoprotolysis constant of the solvent.

The alkylation of isobutane with the butenes may occur as follows (15):

Initial Step.

(isobutane)   (carbonium ion)   (proton) (electrons)

Reaction of the carbonium ion with Butene-2.

shift of a methyl group

(2, 2, 3 - trimethylpentane)

shift of a hydrogen atom

(2, 3, 4 - trimethylpentane)

(2, 3, 3 - trimethylpentane)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}} + CH_2 {*} CH - CH_2 - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - C^*H - CH_2 - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_2 - CH_2 - CH_3$$

(2, 2 - dimethylhexane)

shift of a methyl group

shift of a hydrogen atom

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C^*} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3$$

(2, 4 - dimethylhexane)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - C^*H - CH_2 - CH_2 - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C^*} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3$$

(2, 2 - dimethylhexane)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_2 - CH^* - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C^*} - CH_2 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$$

(2, 5 - dimethylhexane)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}} + CH_2 {*} \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - C^* - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$$

$$\xrightarrow[2e]{+H^+}$$

(2, 2, 4 - dimethylpentane)

shift of a methyl group

shift of a hydrogen atom

$$CH_3 - C^* - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$$

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - C^*H - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C^*} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \xrightarrow[2e]{+H^+} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$$

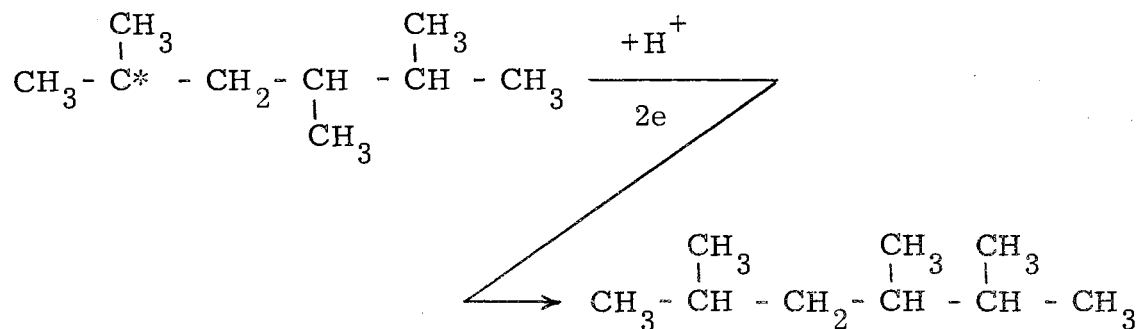(2, 3, 4 - trimethylpentane)

The product obtained in the alkylation of isobutane with butenes contains a number of components both lighter and heavier than the expected octanes. The presence of isopentane and 2, 2, 5-trimethylpentane, for example, can be explained by the partial depolymerization of the carbonium ion which gives 2, 3, 4-trimethylpentane on hydrogenation, into a mixture of propylene and pentanes.(15).

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C^*} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \longrightarrow$$

$$CH_3 - CH = CH_2$$
(propene)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_3$$
(2-methylbutene-2)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH = CH_2$$
(3-methylbutene-1)

$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 - CH_3$$
(2-methylbutene-1)

$+ H^+$
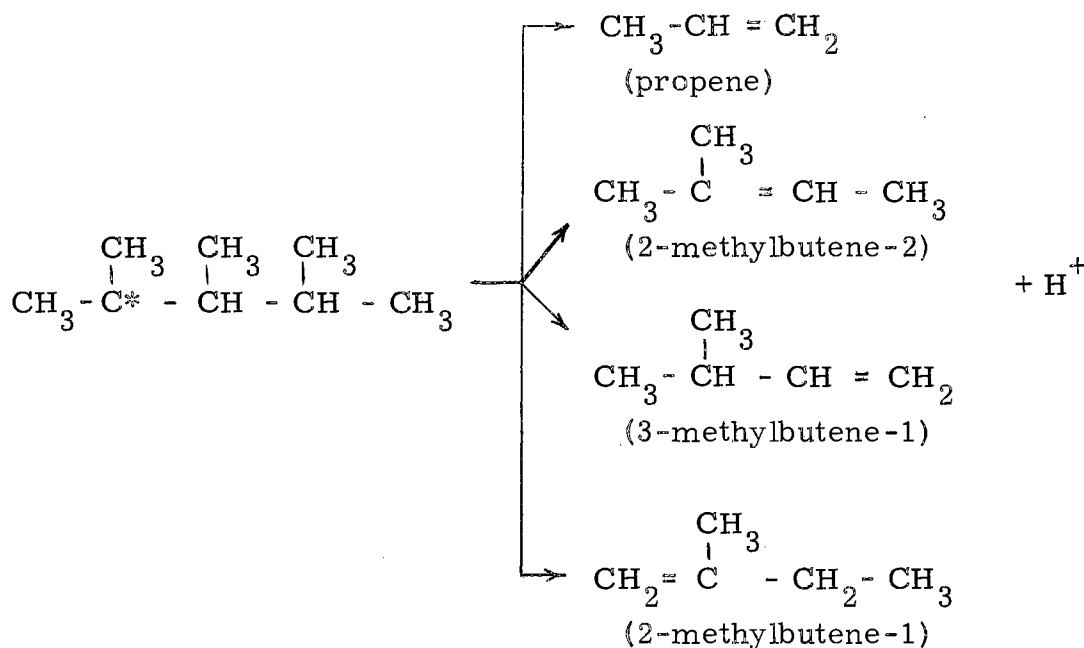
These olefins may then react with the carbonium ion formed from isobutane to give heptanes and nonanes. For example, 3-methylbutene-1 could react to give 2, 2, 5-trimethylheptane and 2, 3, 5-trimethylhexane. (15).

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}} + CH_2 = CH - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \longrightarrow CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - C^*H - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \qquad +H^+$$

$$2e$$

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3 \longleftarrow$$

$$\underset{\overset{|}{CH_3}}{CH_3} - \overset{\overset{CH_3}{|}}{C^*} - CH_2 - \underset{\overset{|}{CH_3}}{CH} - \overset{\overset{CH_3}{|}}{CH} - CH_3 \quad \xrightarrow[\quad 2e \quad]{+H^+}$$

$$\longrightarrow \quad CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_2 - \overset{\overset{CH_3}{|}}{CH} - \overset{\overset{CH_3}{|}}{CH} - CH_3$$
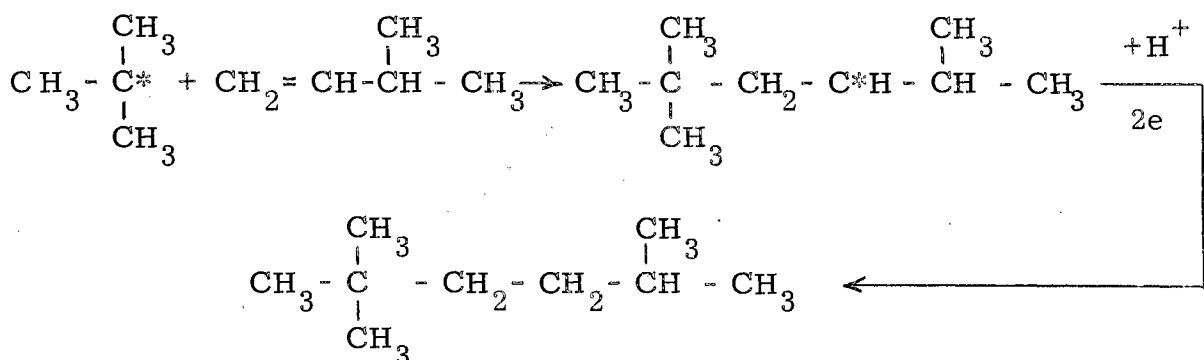
The extent of the depolymerization reaction would depend on the struc-ture of the carbonium ion and its rate of hydrogenation to the corre-sponding saturated hydrocarbon.

The thermal alkylation of paraffins is generally postulated to be the result of a free radical chain mechanism.(17, 18).

Initially

$$CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_3 \longrightarrow C^*H_3 + CH_3 - \underset{\overset{|}{CH_3}}{C^*H} \quad .$$
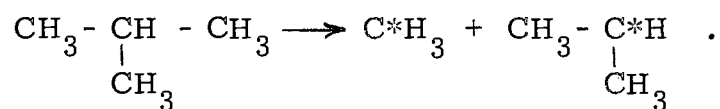
The methane radical then reacts with more isobutane:

$$CH_4 + CH_3 - \overset{\overset{CH_3}{|}}{\underset{\overset{|}{CH_3}}{C^*}} \qquad (2\text{-}1)$$

$$C^*H_3 + CH_3 - \underset{\overset{|}{CH_3}}{CH} - CH_3$$

$$CH_4 + CH_3 - \underset{\overset{|}{CH_3}}{CH} - C^*H_2 \qquad (2\text{-}2)$$

Reaction of (2-1) with butene-1 :

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C*}} \;+\; CH_2 = CH-CH_2-CH_3 \longrightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-\overset{\overset{\textstyle C*H_2}{|}}{CH}-CH_2-CH_3 \quad (2\text{-}3)$$

$$\longrightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-C*H-CH_2-CH_3 \quad (2\text{-}4)$$
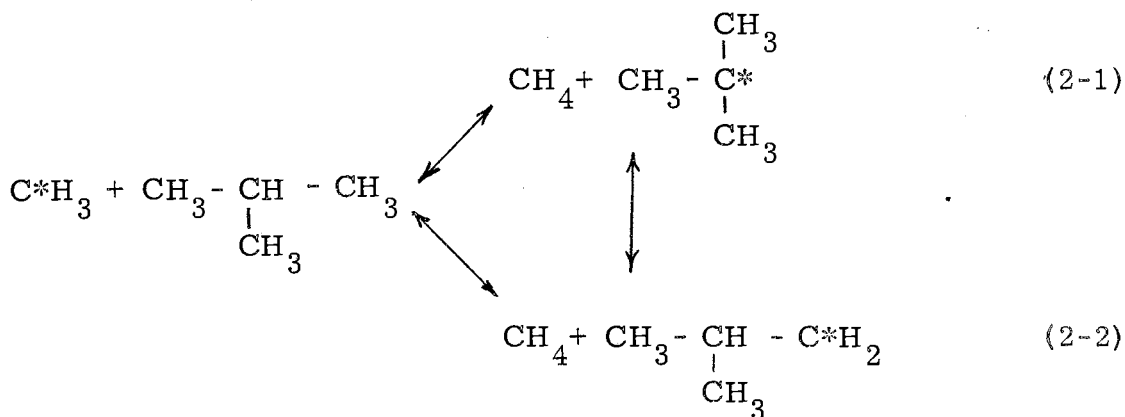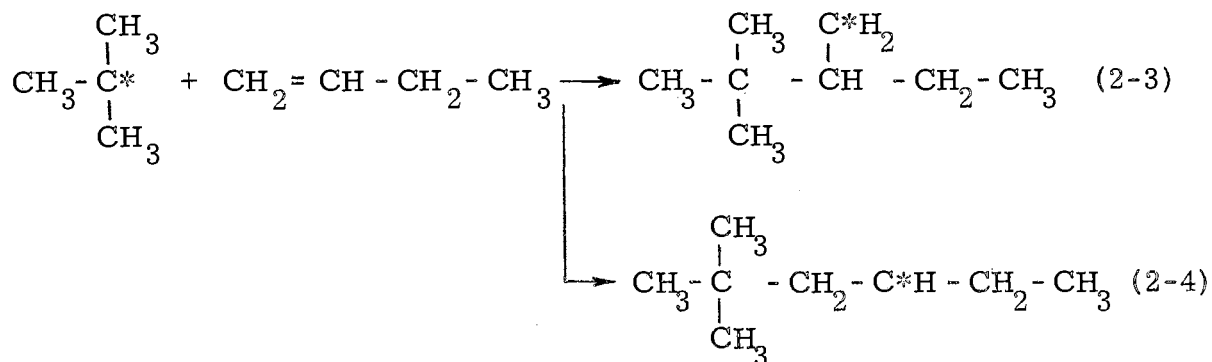
Reaction of (2-3) with more isobutane to form a product and another

radical:

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-\overset{\overset{\textstyle C*H_2}{|}}{CH}-CH_2-CH_3 + CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{CH}} \longrightarrow$$

$$\longrightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-\overset{\overset{\textstyle CH_3}{|}}{CH}-CH_2-CH_3 + CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C*}}$$

(2, 2, 3-trimethylpentane)
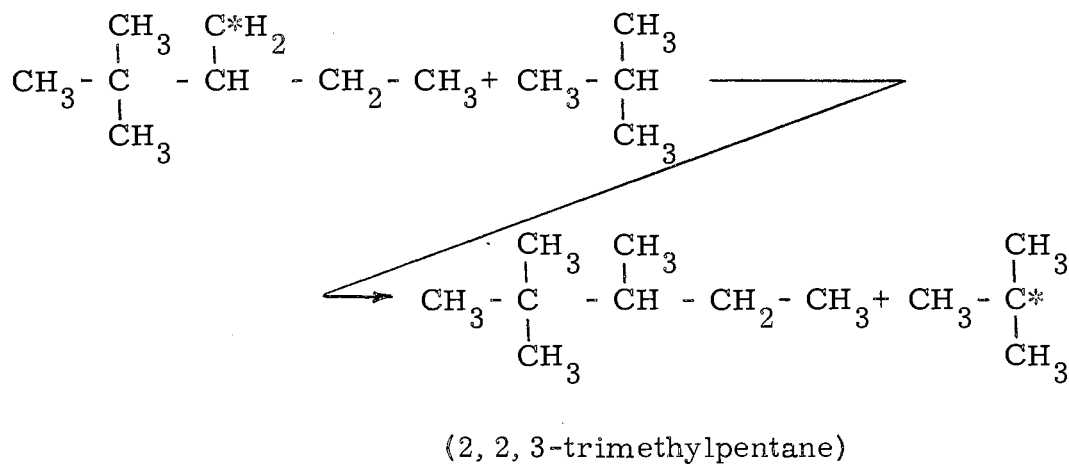
Reaction of (2-4) with more isobutane:

$$CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-C*H-CH_2-CH_3 + CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{CH}}$$

$$\longrightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3 + CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C*}}$$

(2, 2-dimethylhexane)

Reaction of (2-2) with butene-1 :

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - C*H_2 + CH_2 = CH - CH_2 - CH_3 \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - C*H - CH_2 - CH_3 \quad (2\text{-}5)$$

$$\longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\overset{C*H_2}{|}}{CH} - CH_2 - CH_3 \quad (2\text{-}6)$$
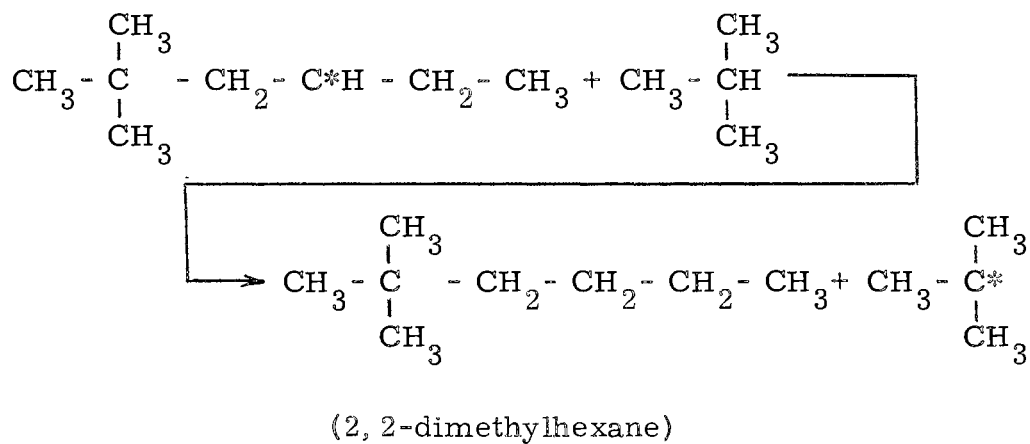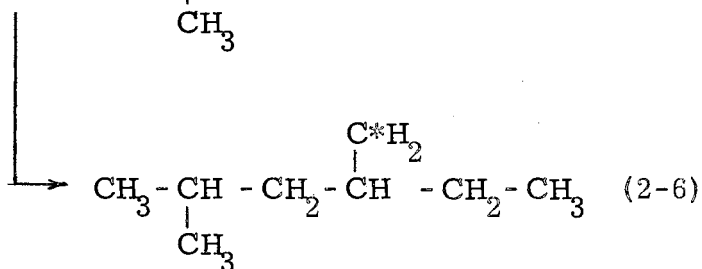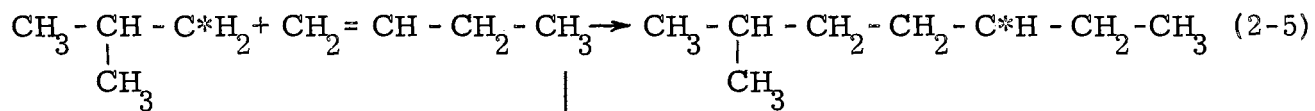
Reaction of (2-5) with more isobutane:

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - C*H - CH_2 - CH_3 + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} \longrightarrow$$

$$\longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C*}}$$

(2-methylheptane)
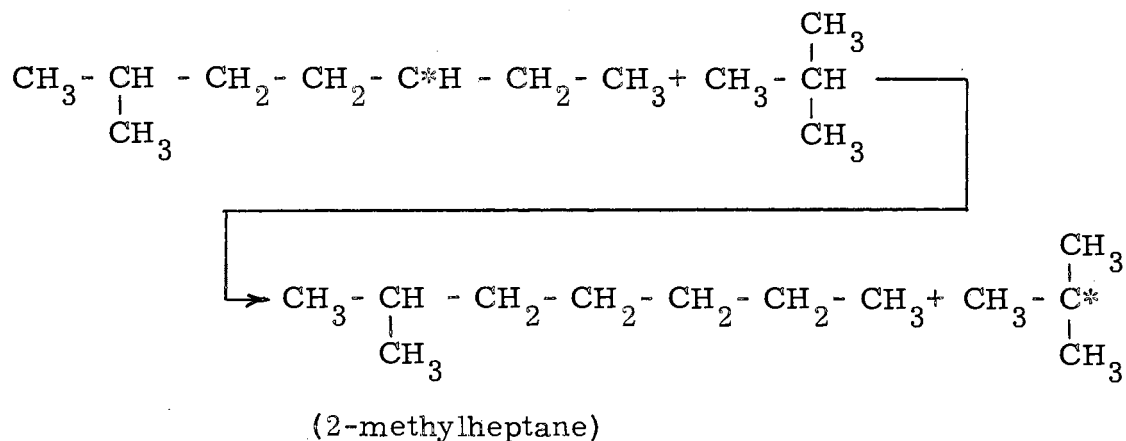
Reaction of (2-6) with more isobutane:

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\overset{C*H_2}{|}}{CH} - CH_2 - CH_3 + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} \longrightarrow$$

$$\longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\overset{CH_3}{|}}{CH_2} - CH_2 - CH_3 + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C*}}$$

(2, 4-dimethylhexane)

Reaction of (2-1) with butene-2 :

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}} \quad + \quad CH_3-CH=CH-CH_3 \longrightarrow \quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-C^*H-CH_3 \quad (2-7)$$

shift of a
methyl group

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C^*H-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 \quad (2-8)$$
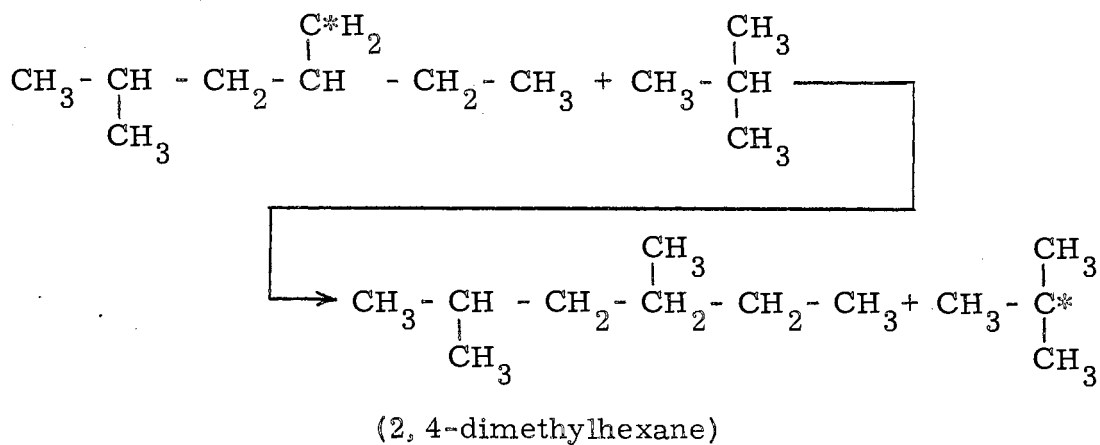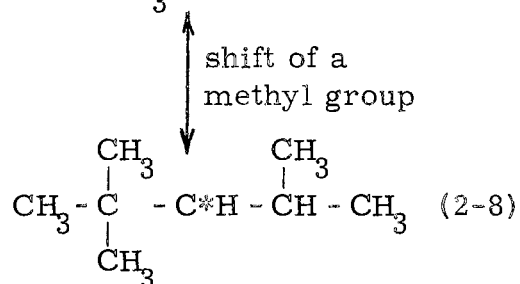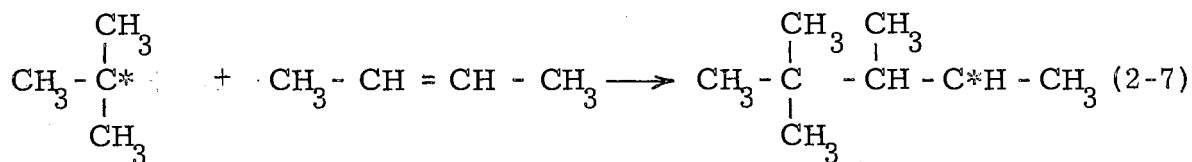
Reaction of (2-7) with more isobutane:

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}-C^*H-CH_3 + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}$$

$$\longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_3 + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}}$$
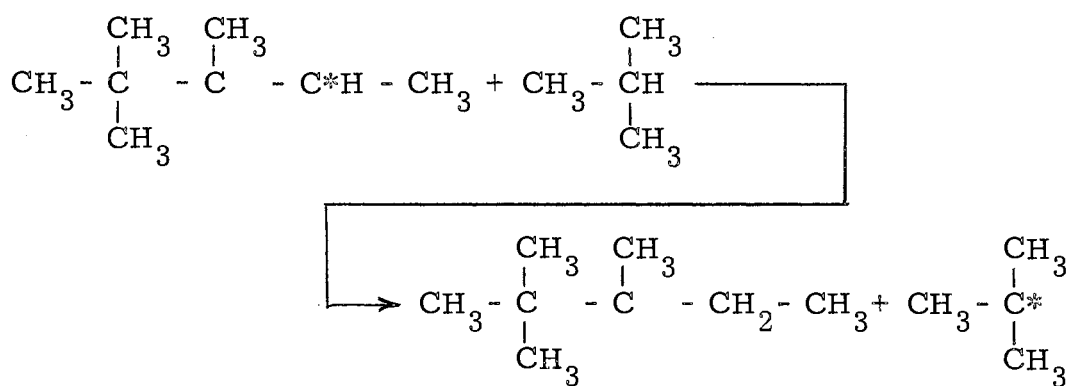
(2, 2, 3-trimethylpentane)

Reaction of (2-8) with more isobutane:
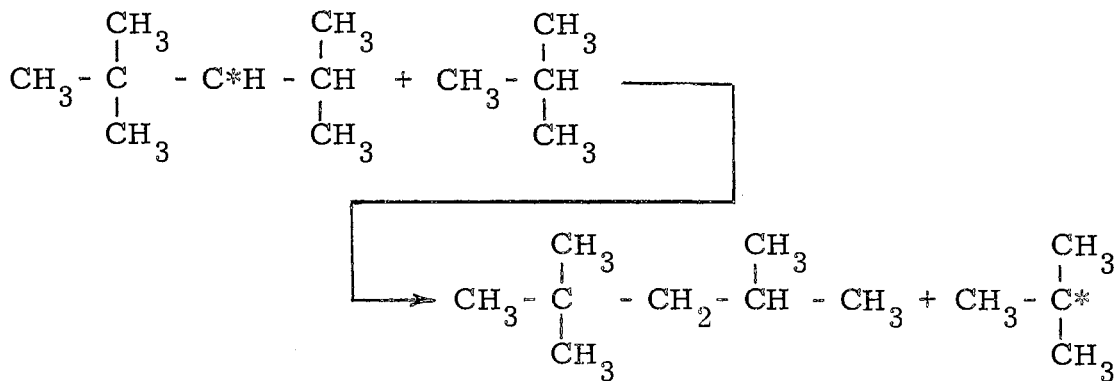
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C^*H-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}$$

$$\longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^*}}$$

(2, 2, 4-trimethylpentane)

Reaction of (2-2) with butene-2 :

$$CH_3-CH-C*H_2 + CH_3-CH=CH-CH_3 \longrightarrow CH_3-CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-C*H-CH_3 \quad (2\text{-}9)$$
$$\underset{\underset{CH_3}{|}}{}$$

↕ shift of a methyl group

$$CH_3-CH-CH_2-C*H-\underset{\underset{CH_3}{|}}{CH}-CH_3 \quad (2\text{-}10)$$
$$\underset{\underset{CH_3}{|}}{}$$
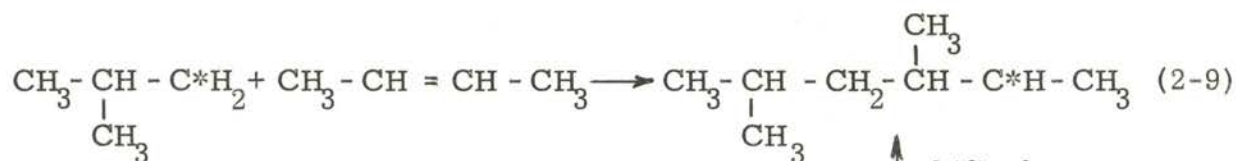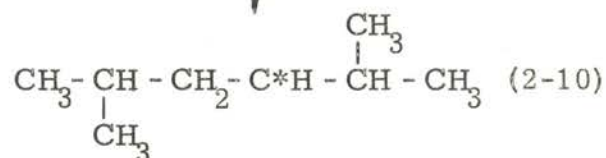
Reaction of (2-9) with more isobutane:

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\overset{CH_3}{|}}{CH}-C*H-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH} \longrightarrow$$

$$\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\overset{CH_3}{|}}{CH}-CH_2-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}*$$

(2, 4-dimethylhexane)
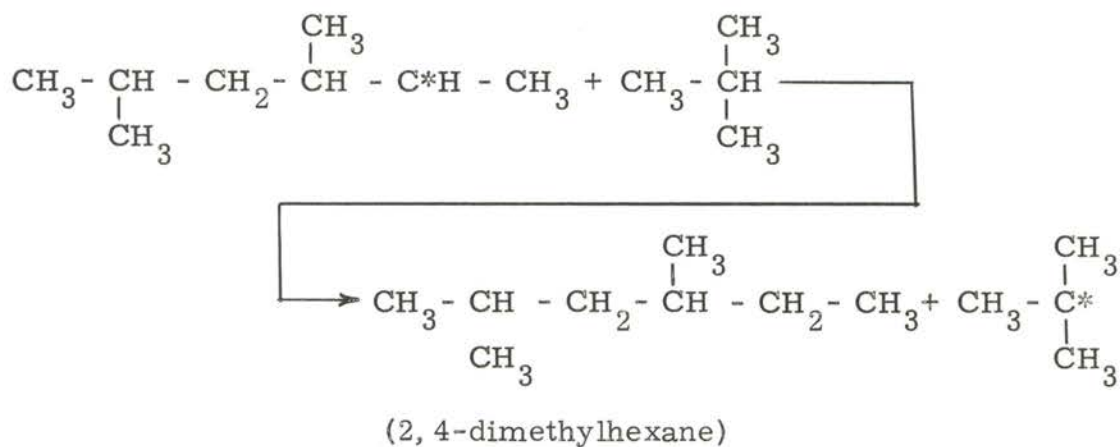
Reaction of (2-10) with more isobutane:

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-C*H-\underset{\overset{CH_3}{|}}{CH}-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH} \longrightarrow$$

$$\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\overset{CH_3}{|}}{CH}-CH_3 + CH_3-\underset{\underset{CH}{|}}{\overset{CH_3}{\overset{|}{C}}}*$$

(2, 5-dimethylhexane)
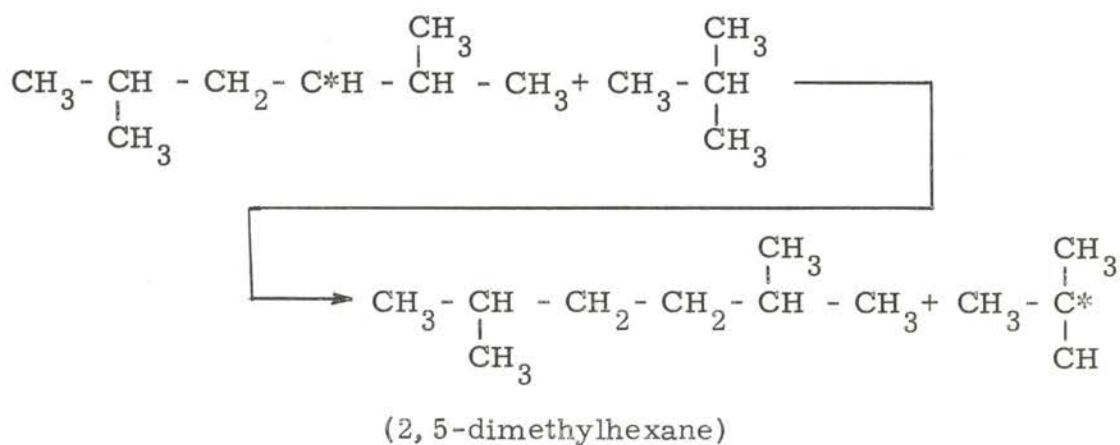
The complexity of the reaction path leading to any given product is obvious, since the above reactions are only a portion of the total number that can take place.

The research octane number of the major components in aviation and motor fuels is presented in Table I to indicate the value of the various reaction products.

The actual product distribution varies with the operating conditions employed. The main process variables for the sulfuric acid and hydrofluoric acid processes are, in order of decreasing importance (2, 8, 10):

(1) Reaction temperature

(2) Isobutane to olefin ratio

(3) Acid strength

(4) Degree of mixture dispersion

(5) Isobutane to n-butane ratio

(6) Acid to hydrocarbon ratio

Table II presents the product distribution data obtained by McAlister and co-workers (20) for the sulfuric acid alkylation of iso-butane with butene-2.

A more complete product breakdown of a "typical" alkylate is presented in Table III. The olefin feed to the alkylation unit which produced the alkylate contained 3.5 mole % propylene, 90.0 mole % butenes, and 6.5 mole % pentenes.(21).

TABLE I

OCTANE NUMBERS OF THE MAJOR COMPONENTS IN
AVIATION AND MOTOR FUELS (19)

	Clear	3ml TEL
Isopentane	92.3	+1.0
n-Pentane	61.6	84.6
n-Hexane	24.8	65.3
2,2-Dimethylbutane	91.8	+0.6
2,3-Dimethylbutane	+0.3	--
n-Heptane	0.0	43.5
2,2-Dimethylpentane	92.8	+0.4
2,3-Dimethylpentane	83.1	96.6
2,3-Dimethylpentane	91.1	+0.3
2-Methylhexane	42.4	73.2
3-Methylhexane	52	74.7
n-Octane	(-15)	24.8
2,2-Dimethylhexane	72.5	93.3
2,5-Dimethylhexane	55.5	81.6
2,4-Dimethylhexane	65.2	87.3
2,3-Dimethylhexane	71.3	91.7
3,3-Dimethylhexane	75.5	94.6
2,2,4-Trimethylpentane	100.0	+3.00
2,2,3-Trimethylpentane	+1.2	--
2,3,4-Trimethylpentane	+0.22	--
2,3,3-Trimethylpentane	+0.61	--
2,2,5-Trimethylhexane	--	--
2,3,5-Trimethylhexane	--	--
2,2-Dimethylheptane	50.3	77.2

Numbers following a plus sign, indicate that the octane number
is equivalent to that of 2,2,4-trimethylpentane plus the indicated num-
ber of mls. of tetraethyllead.

TABLE II

OBSERVED PRODUCT DISTRIBUTION FOR THE LIQUID PHASE SULFURIC ACID CATALYZED ALKYLATION OF ISOBUTANE WITH BUTENE-2 (20)

Observed Product	WT %
Isopentane	4-6
2, 2, 4 trimethylpentane	34-38
2, 3, 4 trimethylpentane 2, 3, 3 trimethylpentane	51-55

TABLE III

A TYPICAL COMPONENT BREAKDOWN OF A TOTAL ALKYLATE (21)

Component		L. V. %
2, 3	Dimethylbutane	4. 2
2, 2	Dimethylpentane	
2, 4	Dimethylpentane	
3, 3	Dimethylpentane	3. 3
2, 3	Dimethylpentane	2. 2
2, 2, 4	Trimethylpentane	30. 4
2, 3, 3	Trimethylpentane	37. 7
2, 3, 4	Trimethylpentane	
	Dimethyl hexanes	4. 9
	Isononanes	5. 2
	Isodecanes	11. 1
	Total	100. 0

Rate Data

The author has been unable to find any extensive amount of rate data in the literature. The small amount of information available indicates that a fairly large amount of such information is probably available in the research files of private companies.

Some recommended reaction times for maximum product quality and quantity as a function of temperature and olefin identity for the hydrofluoric acid catalyzed alkylation of isobutane are presented in Table IV.(17).

TABLE IV

RECOMMENDED REACTION TIMES FOR THE HYDROFLUORIC
ACID CATALYZED ALKYLATION OF
ISOBUTANE WITH OLEFINS (17)

Temperature ^{o}C	Reaction Time, Minutes		
	Butene-2	Butane-Butene Mixtures	2-Butene-Isobutane Mixtures
50	0.02-0.08	0.004-0.1	0.0005-0.01
40	0.07-0.36	0.02-0.4	0.002-0.05
30	0.35-1.78	0.06-1.6	0.008-0.20
20	2-10	0.25-6.3	0.04-1.1
10		1.6-39.4	0.19-4.7

Table V presents the available data on the gas phase thermal alkylation of isobutane with ethylene.(18). Runs A and B were conducted at constant pressure with extensive turbulent flow mixing of the reacting gases. Run C was made at constant volume with no mechanical mixing of the reacting gases.

TABLE V

AVAILABLE DATA ON THE THERMAL ALKYLATION OF
ISOBUTANE WITH ETHYLENE (18)

	Run Number		
	A	B	C
Temperature, (^{O}F)	940	968	941
Pressure (psig)	4500	2500	4700
Average reaction time, (minutes)	3.2	4.3	5.1
Charge composition			
C_2H_4 (weight percent)	7.8	9.8	16.5
(volume percent)	15.0	18.4	29.1
i-C_4H_{10} (weight percent)	92.2	90.2	83.5
(volume percent)	85.0	81.6	70.9
C_2H_4 in effluent stream (weight percent)	1.6	1.0	0.1
Products, (weight percent)			
Pentenes	3.5	5.7	4.4
Pentanes	6.2	17.2	23.8
Hexenes	2.9	4.5	2.7
Hexanes	46.0	39.9	17.5
Heptenes	2.7	2.5	1.1
Heptanes	9.3	7.9	5.6
Octenes	2.9	3.9	3.4
Octanes	11.0	8.0	17.2
Heavier gasoline	13.7	7.9	20.5
Tar	1.8	2.5	3.8
Octane number of gasoline fraction	85	--	--

CHAPTER III

SOME OF THE THEORY OF CHEMICAL KINETICS

Derivation of Rate Equations for Simple

Bimolecular Gas Reactions

The rate of a reaction is expressed as the change in the number of units of mass of some component participating in the reaction per unit of time θ per unit of volume V. Mathematically, then

$$r = -\frac{1}{V}\frac{dn}{d\theta} \quad . \tag{3-1}$$

If it is possible to segregate the effects of the amounts of the various components from the other variables, the rate equation may be written as (22, 23)

$$r = -\frac{1}{V}\frac{dn}{d\theta} = k\, F(n_a n_b \ldots) \quad . \tag{3-2}$$

The term k is referred to as the specific reaction rate, rate coefficient, or rate constant. The nature of the function F is established by the law of mass action (23).

Consider the reaction

$$aA + bB \longrightarrow lL + mM \quad . \tag{3-3}$$
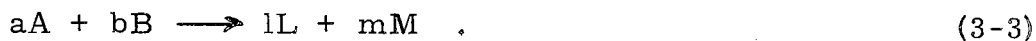
Let n_{ao} and n_{bo} be the initial amounts of the reactants and let n_a and n_b be the amounts present at any time θ. Then the rate of disappearance of A is expressed by

$$r_a = -\frac{1}{v}\frac{dn_a}{d\theta} = k\left(\frac{n_a}{v}\right)^a\left(\frac{n_b}{v}\right)^b \qquad (3\text{-}4)$$

assuming the stoichiometric equation represents the mechanism of the reaction.

Consider the special case of Equation (3-3) where a, b, and l are unity and m is zero, i.e. a second order reaction.

$$A + B \longrightarrow L \qquad . \qquad (3\text{-}5)$$

The rate equation with respect to component A then becomes

$$r = -\frac{1}{V}\frac{dn_a}{d\theta} = k\left(\frac{n_a}{V}\right)\left(\frac{n_b}{V}\right) \quad . \qquad (3\text{-}6)$$

Since

$$n_b = n_{bo} - n_{ao} + n_a \quad , \qquad (3\text{-}7)$$

$$r = -\frac{1}{V}\frac{dn_a}{d\theta} = k\left(\frac{n_a}{V}\right)\left(\frac{n_{bo} - n_{ao} + n_a}{V}\right) \quad . \qquad (3\text{-}8)$$

Separating the variables

$$\int_{n_{ao}}^{n_a}\frac{V\,dn_a}{n_a(n_{bo} - n_{ao} + n_a)} = -k\int_0^\theta d\theta \quad . \qquad (3\text{-}9)$$

Integrating at constant volume, we have

$$\frac{V}{n_{bo} - n_{ao}}\ln\left[\frac{n_a(n_{bo})}{n_{ao}(n_{bo} - n_{ao} + n_a)}\right] = -k\theta \quad . \qquad (3\text{-}10)$$

Equation (3-10) is used for the calculation of k, the specific reaction rate, for simple homogenous, isothermal reactions at constant volume.

If the reaction takes place at constant pressure, as is the probable case with a flow reactor, the volume term becomes a function of the system composition, temperature, and pressure, and can no longer be taken out from under the integral sign.

If we assume that the ideal gas law holds, then

$$V = \frac{n_t \, RT}{P} \quad .$$

(3-11)

From Equation (3-5)

$$n_t = n_a + n_b + n_c$$

(3-12)

$$n_c = n_{ao} - n_a \quad .$$

(3-13)

Substituting Equations (3-7) and (3-13) in Equation (3-12) and canceling like terms gives

$$n_t = n_a + n_{bo} \quad .$$

(3-14)

Therefore

$$V = \frac{(n_a + n_{bo}) \, RT}{P} \quad .$$

(3-15)

Substituting Equation (3-15) into Equation (3-9) gives

$$\int_{n_{ao}}^{n_a} \frac{RT \, (n_a + n_{bo}) \, dn_a}{P n_a (n_{ao} - n_{bo} + n_a)} = - k \int_{o}^{\theta} d\theta \quad .$$

(3-16)

Integrating, we obtain

$$\frac{RT}{P} \left\{ \ln \left(\frac{n_{bo} - n_{ao} + n_a}{n_{bo}} \right) + \frac{n_{bo}}{n_{bo} - n_{ao}} \ln \left[\frac{n_{bo} \, n_a}{(n_{bo} - n_{ao} + n_a) n_a} \right] \right\} = - k\theta \quad .$$

(3-17)

Equation (3-17) is used to calculate values of k for simple, homogenous, isothermal reactions taking place at constant pressure. Note that the equations just derived are strictly valid only for simple reactions, a simple reaction being defined as a reaction uncomplicated by consecutive, side or reverse reactions or by physical resistances.

Fugacities could have been used instead of pressures. However, this refinement seemed unwarranted considering the extent and accuracy of the data available.

Arrhenius Equation

The effect of temperature on the specific reaction can be accurately represented by Equation (3-18), an empirical equation obtained by Arrhenius in 1889 to explain the rate of inversion of sucrose by acids.(22).

$$k = Ae^{-\frac{E}{RT}} \qquad (3-18)$$

The terms A and E are referred to as the frequency factor and activation energy, respectively.

Absolute Reaction Rate Theory

Transition state theory, also called absolute reaction rate theory, postulates an "activated" or "transition" state through which a system would be expected to pass in going from reactants to products. The "transition state" may be thought of as an elevated energy state in which sufficient energy is present to drive the

reacting molecules over the barrier separating the reactants and products.

The theory predicts the following equation for the specific reaction rate.(24, 25).

$$k = \frac{k^*T}{h} \cdot \frac{Q^o_{\ddagger}}{(Q^o_a)^a (Q^o_b)^b} e^{-\frac{E_o}{RT}} \tag{3-19}$$

where

$$k \quad = \quad \text{specific reaction rate}$$

$$k^* \quad = \quad \text{Boltzman's constant}$$

$$h_o \quad = \quad \text{Planck's constant}$$

$$Q^o_a \quad = \quad \text{total partition function/cc for component A}$$

$$Q^o_b \quad = \quad \text{total partition function/cc for component B}$$

$$Q^o_{\ddagger} \quad = \quad \text{total partition function/cc for the activated complex}$$

$$E_o \quad = \quad \text{activation energy at the absolute zero of temperature.}$$

By using order of magnitude figures for the partition functions in the temperature range of interest, the terms

$$\frac{k^*T}{h} \cdot \frac{Q^o_{\ddagger}}{(Q^o_a)^a (Q^o_b)^b}$$

can presumably be evaluated to within two or three powers of ten. (22, 24). This leaves E_o, the activation energy at absolute zero of temperature, the only unknown in Equation (3-19).

Bimolecular reaction activation energies have been correlated with bond energy data by Hirschfelder (26). For exothermic four atom reactions of the type AB + CD = AC + BD, Hirschfelder found that the activation energy was 28 percent of the sum of the energies of the bonds being broken.

The Hirschfelder rule estimates the activation energy E rather than E_o. However, if the estimated activation energy is fairly large, and the temperature is not excessively high, E is approximately equal to E_o, since

$$E_o = E_a - mRT \qquad (3\text{-}20)$$

where m lies between $-3/2$ and $1/2$ (24).

Since all the quantities in Equation (3-19) are known, or can be estimated, it is theoretically possible to calculate specific reaction rates to within a few powers of ten.

CHAPTER IV

EQUIPMENT AND PROCEDURES

Equipment

A glass lined autoclave of two gallon capacity, manufactured by the Pfaudler Company, was used for the reaction vessel. The autoclave was jacketed around the sides and bottom so that a cooling medium could be circulated around the reaction chamber. A glass coated anchor type agitator, driven by an electric motor through a V-belt drive, was used to mix the reacting fluids. The agitator speed was variable by using various diameter sheaves on the motor shaft. The unit was fitted with a pressure gauge isolated from the reactor by a tantalum diaphragm, and a glassed thermometer well.

As received, the autoclave had no provision for introducing materials into the reaction chamber under pressure, no provision for removing a sample of the reacting mixture, and no provision for draining the reaction chamber. However, two flanges on the head of the unit were available for modification. One of the flanges was blind and the other was fitted with a rupture disk assembly.

The blind flange was modified by drilling a hole through the flange and cutting threads at both ends for stainless steel 1/4 inch

male tube to pipe fittings. A 1/4 inch stainless steel tube was shaped to run down the inside wall of the reaction chamber, past the agitator, to the bottom of the vessel. Another piece of 1/4 inch stainless steel tubing connected the inner tube to the sampling system and, alternately, to the drain.

A new flange was made to replace the flange fitted with the rupture disk. A hole was drilled through the center of the flange and threads were cut for a stainless steel 1/4 inch male tube to pipe fitting. A short piece of 1/4 inch stainless steel tubing and a 1/4 inch stainless steel female Hoke needle valve completed the system for the introduction of hydrocarbons into the reaction vessel under pressure. A Teflon gasket was made to provide the seal between the flange and reaction chamber.

The reactor cooling system consisted of a 55-gallon drum to hold ice and ice water, and a small centrifugal pump used to circulate ice water from the bottom of the drum, through the autoclave jacket and back to the top of the drum where it splashed over ice.

A schematic flow diagram of the system is presented in Fig. 1, and photographs of the apparatus are presented as Plates 1 and 2. The cooling system is visible in Plate 2. The hydrocarbon charging system is shown in both photographs. The sampling and reactor drainage system is also shown in Plate 2.

A schematic diagram of the sample trapping assembly is presented as Fig. 2. Two stainless steel male valves and one stainless
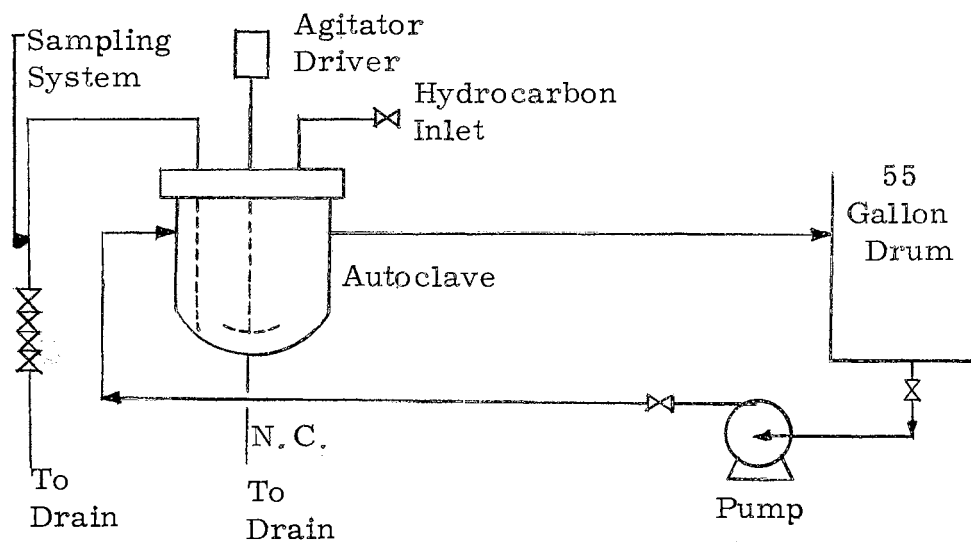
Fig. 1. Schematic Flow Diagram of the Experimental Equipment
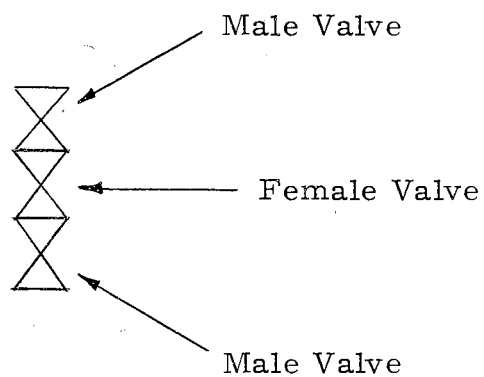
Fig. 2. Schematic Diagram of a Sampling Assembly

Plate I. The Reaction Vessel
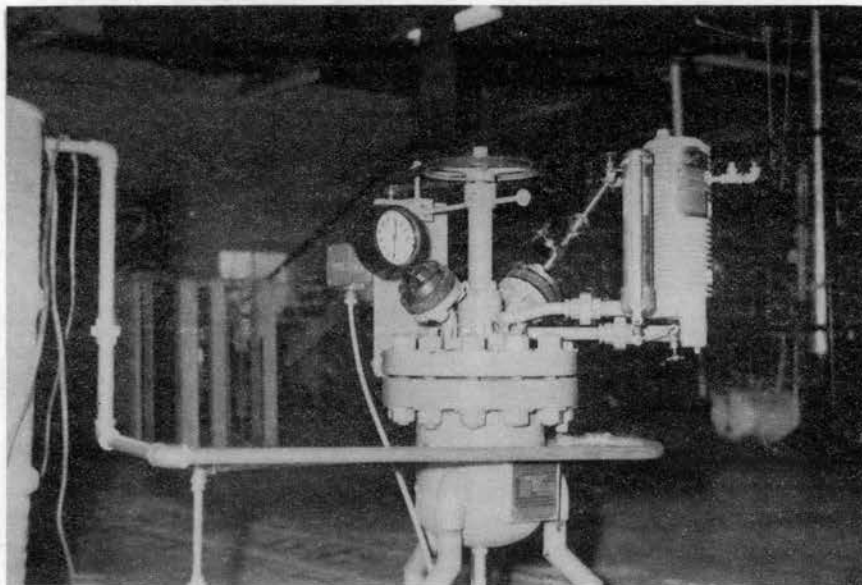
Plate II. The Autoclave and the Cooling System
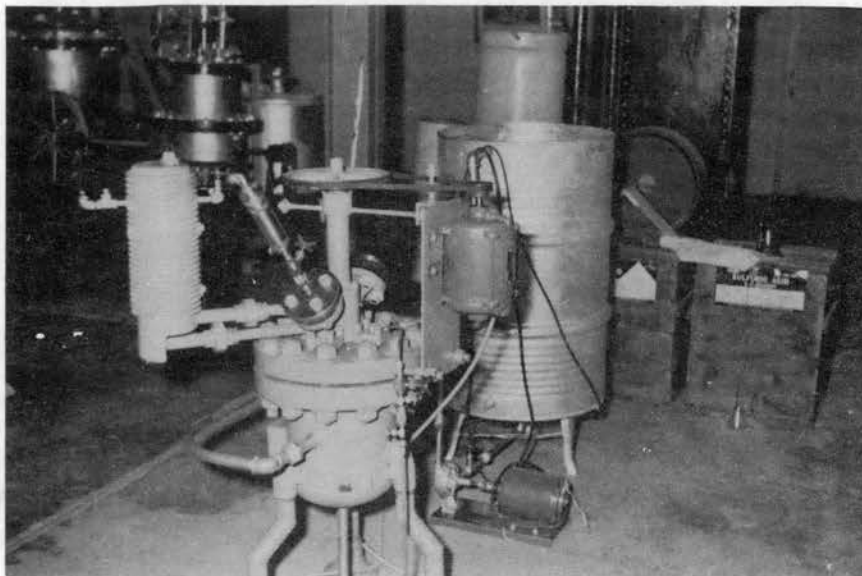
steel female valve comprised the assembly. The male to female to
male hook-up of the valves provided a two-compartment trap (with the
center valve closed), and a relatively small volume of sample.

Standard stainless steel LPG corrosion test bombs were used to
transfer the isobutane and butene from the gas cylinders to the reaction
chamber. One of the bombs is shown clearly in Plate 2.

Technical grade isobutane and butene obtained from the Phillips
Petroleum Company were used in this study. Chromatographic analy-
sis of the hydrocarbons indicated the purity level to be approximately
98%.

Reactor Charging Procedure

The procedure for charging the reactor consisted of three dis-
tinct steps: (1) acid loading, (2) isobutane loading, (3) butene-2
loading. These steps are discussed below.

To charge the reactor with catalyst, concentrated sulfuric acid
was siphoned into a flask and poured into the reaction chamber through
an opening made by removing a flange. The necessary intermediate
weighings were made to allow the amount of acid in the reactor to be
determined by weight. This procedure was repeated until the desired
quantity of acid (approximately one gallon) had been transferred into
the reaction chamber. The bombs were cooled by immersion in ice
water, connected, in turn, to the inverted isobutane bottle and allowed
to fill. Following one bomb, the full bomb was disconnected from the

bottle, dried, and placed under a heat lamp. When the bomb temperature had risen to a few degrees above atmospheric temperature, it was weighed, connected to the charging system, and the isobutane allowed to drain into the reaction chamber. The bomb was then disconnected, re-weighed, and the isobutane charge determined by the change in weight. This procedure was repeated until the desired quantity of isobutane (one-half to one gallon) had been loaded into the reaction chamber.

Ice water was circulated through the autoclave jacked during the period of charging the acid and isobutane. After the temperature in the reaction chamber had stabilized, the butene-2 was charged in the same manner as the isobutane.

Sampling Procedure

Since a relatively large volume of isobutane, compared to butene, was used, the layer of isobutane above the acid should have effectively prevented much contact between the sulfuric acid and butene. Time zero for the reaction should roughly have been the time when agitation of the mixture was initiated.

When agitation of the mixture was initiated, the time was noted. The valves in the sampling assembly were opened and the lines and valves purged. The bottom valve in the sampling assembly (shown schematically in Fig. 2) was closed and the time noted. The time of closing the bottom valve was considered to be the effective time of

sampling taking. The top valve in the sampling assembly was then closed, the main valve was closed, and the assembly was removed from the sampling line. The sampling assembly was shaken to help settle the acid, the center valve closed, the bottom valve opened and the acid blown to the drain. The bottom valve was closed and the middle valve was opened to allow the sample trapped in the upper half of the assembly to expand into the full volume between the two outer valves. The other samples were taken in the same manner.

Each sample was then expanded into an evacuated mass spectrometer sample bottle, which served as a reservoir so that repeat analysis could be run on each sample.

Sample Analysis

The samples were analyzed with the chromatograph at the School of Chemical Engineering. A column four feet long packed with dinonyl phthalate was used to separate the isobutane and butene-2. A column operating temperature of 123° F and a helium carrier gas flow rate of 49 cc per minute were used.

The chromatograph was calibrated using isobutane and butene-2 from the same source as that used for reaction. The calibration curves are presented in Appendix B.

Since very precise sample sizes are necessary for an accurate chromatographic analysis, a concentration ratio method, independent of sample size, was derived to obtain the butene concentration. The

derivation is presented below.

Consider a chromatogram with component A and B peak areas of A_a and A_b , respectively. Using calibration curves, the sample sizes corresponding to these areas are S_a and S_b , respectively.

Calculate the ratio

$$\frac{S_a}{S_b} = R \quad , \text{ where } R = \frac{\text{cc's of component A}}{\text{cc of component B}} \quad ;$$

but

$$\frac{\text{cc's of component A}}{\text{cc of component B}} = \frac{\text{moles of component A}}{\text{mole of component B}} \quad ,$$

therefore

$$\frac{n_a}{n_b} = R \quad ,$$

and since

$$n_b = n_{bo} - n_{ao} + n_a \quad \text{where } n_b = \text{moles of component B present at any time}$$

$$n_{bo} = \text{moles of B present initially}$$

$$n_{ao} = \text{moles of A present initially}$$

$$n_a = \text{moles of A present at any time}$$

then

$$R = \frac{n_a}{n_{bo} - n_{ao} + n_a} \quad .$$

Solving for n_a

$$n_a = \frac{R(n_{bo} - n_{ao})}{1 - R} \quad .$$

This procedure was to be used to determine the amount of reactants present in the various samples.

CHAPTER V

RESULTS

Experimental Results

The results of the experimental work on the liquid phase sulfuric acid catalyzed reaction of butene-2 with isobutane are presented in Table VI. Only three runs were made since it became obvious after the third run that much lower temperatures than were obtainable with the cooling system being used would be required to slow down the reaction. The materials of construction used in the cooling system precluded the use of brine solutions to obtain lower temperatures.

The zero values reported by the chromatograph for the butene-2 concentration in the samples were unexpected. These values were checked by injecting a small quantity of butene-2 into one of the samples and reanalyzing. The presence of butene-2 was clearly shown on the resulting chromatogram, indicating that the quantity of butene-2 present in the original sample was minute enough to be undetectable.

TABLE VI

EXPERIMENTAL RESULTS - LIQUID PHASE SULFURIC
ACID CATALYZED ALKYLATION OF ISOBUTANE
WITH BUTENE-2

Run number	1	2	3
Initial concentration, (pounds)			
Butene-2	0.55	0.90	1.12
Isobutane	3.57	3.22	3.14
Sulfuric acid, (pounds)	16.32	16.13	14.75
Mixer speed, (rpm)	2240	1750	1750
Temperature, ($^{\circ}$F)	54.4	50.1	41.1
Sample number	$\frac{1}{60.0}$	$\frac{1}{13}$	$\frac{1}{5}$
Elapsed time, (seconds)			
Butene-2 concentration, (lb. moles)	0.0	0.0	0.0
Sample number	$\frac{2}{150}$	$\frac{2}{30}$	$\frac{2}{14}$
Elapsed time, (seconds)			
Butene-2 concentration, (lb. moles)	0.0	0.0	0.0
Sample number	$\frac{3}{240}$	$\frac{3}{38}$	$\frac{3}{25}$
Elapsed time, (seconds)			
Butene-2 concentration, (lb. moles)	0.0	0.0	0.0
Sample number	$\frac{4}{320}$	$\frac{4}{49}$	$\underline{4}$
Elapsed time, (seconds)			
Butene-2 concentration (lb. moles)	0.0	0.0	

Reaction Rates Calculated from Data in the Literature

The data of Frey, presented previously as Table V, on the gas

phase alkylation of isobutane with ethylene were used to calculate the

specific reaction rates presented in Table VII.

TABLE VII

SPECIFIC REACTION RATES FOR THE GAS PHASE
ALKYLATION OF ISOBUTANE WITH ETHYLENE

Run Number	A	B	C
Temperature, ^{o}F	940	968	941
Pressure, psia	4500	2500	4700
Reaction Time, Seconds	192	258	306
Initial Compositions, Mole %			
Ethylene	15.0	18.4	29.1
Isobutane	85.0	81.6	70.9
Calculated Specific Reaction Rate, $ft.^{3}(lb. Mole)^{-1} (sec)^{-1}$	0.058	0.0585	0.1145

These specific reaction rates were calculated using Equation (3-17)

for Runs A and B and Equation (3-10) for Run C.

Since the flow regime for Runs A and B was similar, the specific

reaction rates calculated for these runs were used to estimate the

Arrhenius activation energy and the frequency factor at 4500 psia. For

the calculation it was assumed that the activation energy was independent

of pressure and that the frequency factor was proportional to the square

of the pressure. The calculation gave values of 168,000 Btu/lb. mole

and 9.8×10^{24} ft.^{3} (lb. mole)$^{-1}$ (sec)$^{-1}$ for the activation energy and frequency factor, respectively.

Reaction Rates Estimated from Theory

Table VIII presents the gas phase reaction rates estimated by transition state theory using the equations presented in Chapter III. E was estimated to be 45 Kcal/g. mole (27) and $\dfrac{k'}{h} \dfrac{Q^o_{\ddagger}}{Q^o_a Q^o_b}$ was estimated to be 10^{-11}. Calculations were made for both ethylene and butene in order that the same techniques used to make the theory give comparable values of the specific reaction rate for the ethylene-isobutane reaction would be used for the butene-isobutane reaction. The results of these calculations for six temperatures are presented in Table VIII.

TABLE VIII

CALCULATED THEORETICAL VALUES OF THE
SPECIFIC REACTION RATE FOR ETHYLENE
AND BUTENE ALKYLATION OF ISOBUTANE

Temperature ^{o}F	Specific Reaction Rates, ft.^{3}(lb.mole)$^{-1}$(sec)$^{-1}$	
	Ethylene + Isobutane	Butene + Isobutane
600	2.5×10^{-19}	2.5×10^{-20}
800	2.8×10^{-12}	2.8×10^{-13}
1000	2.0×10^{-7}	2.0×10^{-8}
1200	2.6×10^{-4}	2.6×10^{-5}
1400	3.6×10^{-2}	3.6×10^{-3}
1600	1.5	1.5×10^{-1}

CHAPTER VI

DISCUSSION OF RESULTS

The experimental results indicate that the sulfuric acid catalyzed alkylation of isobutane with butene is rather fast. The data presented in Table VI are substantiated to some extent by the data of Abrams and Kuhn, presented previously in Table IV, although the data are not compatible in the sense that different catalysts were used.

Stewart and Calkins (28) noted that for the sulfuric acid catalyzed reaction, an induction period of several minutes was required before reaction began. They concluded that during this period the concentration of intermediate complexes was increased to some steady state value.

If this is actually the case, then the extremely short reaction times noted in Table VI are indicative of the time required for reaction of the carbonium ion with butene-2, since isobutane was in contact with sulfuric acid during the total period of loading the reaction chamber with hydrocarbons. The loading time for the hydrocarbons was approximately two to three hours.

To be considered also is that in a small reactor of this type, one would expect fairly efficient mixing of the phases with rapid dispersion

of the hydrocarbon phase in the acid. In the large industrial reactors using relatively high residence times it is quite possible that mass transfer is the controlling factor rather than the reaction rate.

For the gas phase thermal alkylation of isobutane the comparison between the activation energy calculated from Frey's data and the activation energy calculated by the use of the Hirschfelder rule is not particularly good, although they differ by only a factor of 2. It must be remembered, however, that small changes in specific rates can have a large effect on the calculated activation energy.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

It has been demonstrated that the experimental equipment used in this study is unsatisfactory for studying the sulfuric acid catalyzed alkylation of isobutane with butene-2. Any further work on this reaction should utilize equipment and techniques designed to eliminate, or at least minimize, the difficulties encountered with the present equipment.

Any future equipment constructed to study this sulfuric acid catalyzed reaction should be physically capable of meeting the performance criteria discussed below. These criteria are considered to be rather critical in determining the success or failure of subsequent experiments and the validity of the data obtained.

Serious consideration should be given to the use of a flow system, rather than a batch type of system, in any future studies. A flow system has certain inherent advantages over a batch system, the main advantage being that of steady-state operation. A continuous flow system, operating under steady-state conditions, would allow self checking through multiple samples and notation of the operating variables. The effect of agitating time on the degree of mixture dispersion (i. e., the

fact that the dispersed phase drop size decreases with time in agitated batch systems), and consequent change in the surface available for mass transfer, would be eliminated. The system should be designed to cover a wide range of isobutane to olefin and hydrocarbon to acid ratios, and provision should be made for recycling the reactants back through the reactor.

Since reaction temperature plays such an important role in the velocity of chemical reactions, it is imperative that the reaction temperature be controllable. The use of a small refrigeration unit, equipped to control the pressure or temperature of the refrigerant in the evaporator, should be entirely adequate for this service. The capacity of the unit should be such that it could handle the heat liberated by the reaction, the sensible heat load necessary to cool the reactants to the lowest reaction temperature to be studied, and any heat leak into the system. The refrigerant used should allow the temperature to be varied over a fairly wide range, possibly from as low as 15° F to as high as 70° F.

Of prime importance, to the end of obtaining valid reaction times, is the necessity of being able to achieve a rapid separation of the sulfuric acid and hydrocarbon phases to stop the reaction. Possibly the most promising method of obtaining a rapid phase separation would be through the use of a hydroclone, a separator similar to the conventional cyclone separator but operating on two liquid phases rather than gas and liquid or solid phases.

The reaction vessel should probably be a small volume stirred tank type of reactor. The unit should be fitted with internal cooling coils to provide better temperature control than is obtainable with jacketed apparatus. Some provision should also be made to obtain at least a qualitative measure of the degree of mixture dispersion prevailing. Perhaps the determination of the power input per unit volume, the impeller velocity, or some other criterion would adequately characterize this variable.

It is suggested that analysis of the samples be by high speed temperature programmed chromatography. The use of a temperature programmed analyzer would permit the analysis of the samples through ten carbon hydrocarbons and provide information about the distribution of the reaction products. Such data would be a valuable addition to the literature by itself, and the opportunity exists for correlating the effect of the various operating variables on the product distribution.

One object of any future experimental program should be the determination of the range over which this free-interface heterogenous reaction changes from a dynamic regime (diffusion controlled) to a chemical regime. The transition region should be rather narrow and fairly easy to locate if a mixer with a variable speed motor is employed. A method of presenting the mixing effect data and graphically showing the effect of degree of mixture dispersion would be to construct Arrhenius plots (i.e. ln k vs 1/T) showing the effect of reaction temperature on the specific reaction rate at constant mixing power

and then cross-plot the data in the form of ln k as a function of

mixing power at constant temperature. The resulting family of curves

should adequately describe the effect of mixing and graphically show

the presence or absence of a transition region. The slope of the line

obtained when ln k is plotted as a function of 1/T will be indicative of

the controlling resistance since temperature has large effect on the rate

of chemical reactions whereas it has little effect on mass transfer rates.

For example, a line with a slope close to zero would definitely indicate

a diffusion controlled reaction.

One industrially promising aspect of the study of the sulfuric acid

catalyzed alkylation reaction is the possible effect of an induction period

before the reaction can begin. If an induction period is required, the

use of pre-contactors to contact isobutane and sulfuric acid before

charging the isobutane to the reactor could result in achieving a con-

siderable reduction in reactor size. This aspect of the problem should

certainly be investigated since it could result in rather large savings

in the investment required for new alkylation units and provide an in-

expensive solution for refiners with alkylation units that are reactor

limited.

It would also be of interest to study the effect of prolonged con-

tact with sulfuric acid of one of the reaction products, say 2,2,4-

trimethylpentane. Analysis of the hydrocarbon phase both before and

at time intervals during contact would provide information on the re-

versibility of the reaction and/or possible degradation reactions.

A possible method of slowing the reaction down, other than by lowering the reaction temperature, might be through the use of dilution techniques. In any event, the effect on the reaction of the addition of normal butane to the reacting mixture should be investigated. The effect of diluting the sulfuric acid with water to provide a less concentrated, and possibly less active catalyst phase should also be investigated.

A comprehensive study of the reaction along the lines outlined above should help fill the voids, apparent from the survey of the literature, that exist on the engineering of process.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The results of the experimental work of the liquid phase sulfuric acid catalyzed reaction, the data of Abrams and Kyhn on the hydrofluoric acid catalyzed reaction, and the data of Frey on the gas phase uncatalyzed reaction all indicate, under favorable conditions, that the reaction between olefins and isobutane is relatively rapid. For the acid catalyzed reactions, utilization of olefins is realized within a matter of seconds.

From the available data it would appear that commercial alkylation reactors have been oversized. It is possible that the contact time between acid and hydrocarbon in some reactors is sufficient to cause a loss in product quality and quantity from various degradation reactions.

It is obvious that the acid catalyzed reactions are complex, with alkylation, polymerization, depolymerization, isomerization, hydrogenation and dehydrogenation reactions all taking place simultaneously. A very extensive study would be required to determine the various reaction rates before accurate equations could be derived.

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APPENDIX A

LIST OF NOMENCLATURE

A — frequency factor $ft^3/(lb.\ mole)\ (sec)$ or $cm^3/(gm.\ mole)\ (sec)$

E_o — activation energy at absolute zero, Btu/lb. mole or cal/gm. mole

E — experimental activation energy, Btu/lb. mole

F — function

h — Planck's constant, 6.624×10^{-27} erg. sec.

k — specific reaction rate, same units as A

k^t — Boltzman's constant, 1.88×10^{-6} erg/^{o}K

$\ln$ — logarithm to the base e

m — constant

n_a — moles of component A present at any time

n_b — moles of component B present at any time

n_c — moles of component C present at any time

n_t — total number of moles present at any time

n_{ao} — moles of component A present initially

n_{bo} — moles of component B present initially

P — pressure, psia

Q_a^o — total partition function per cc for component A

Q_b^o — total partition function per cc for component B

Q^o — total partition function per cc for the activated complex

r — reaction rate, moles/(sec) (ft^3)

R — universal gas constant, consistent units

T   -   temperature, $^{\circ}$K or $^{\circ}$R

V   -   volume, ft^3 or cm^3
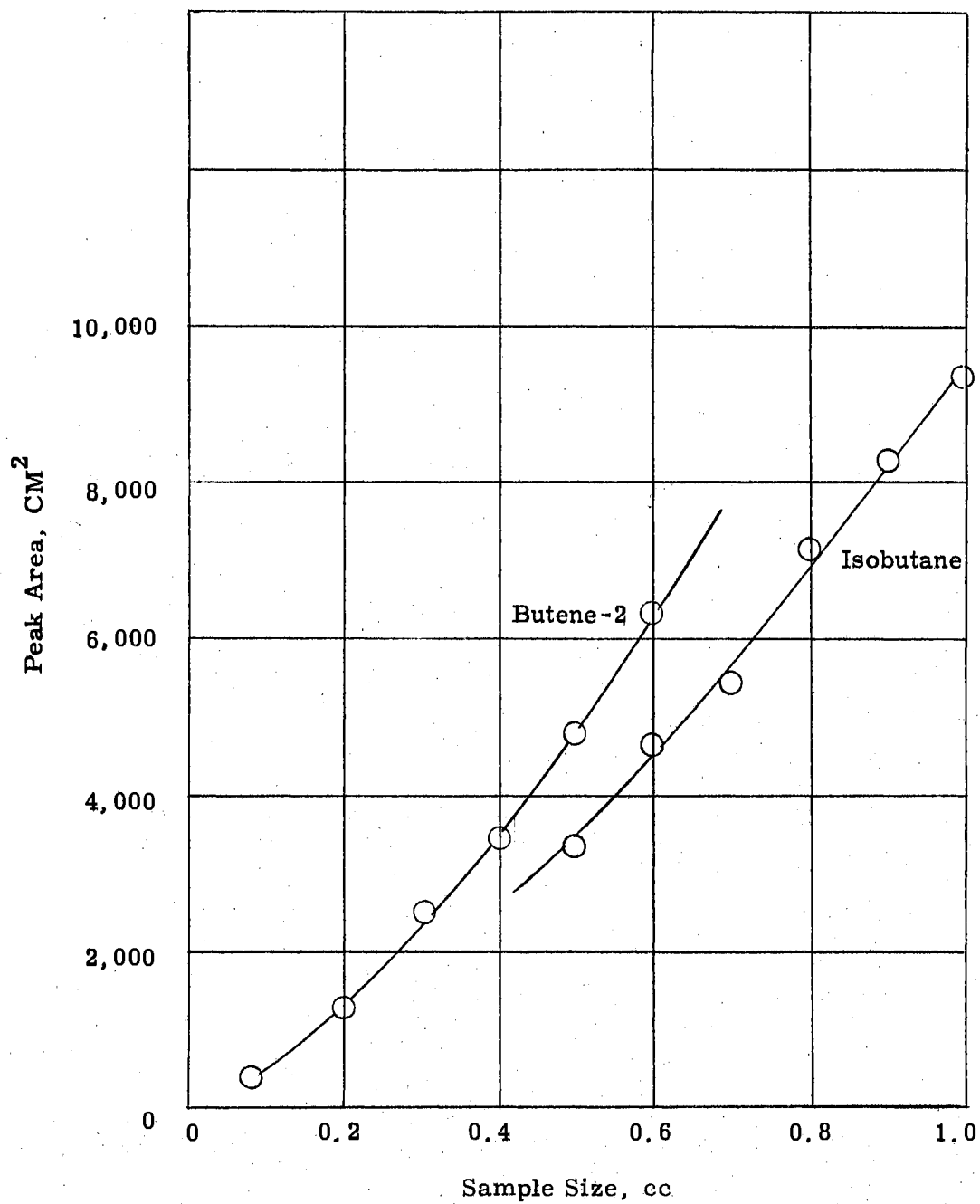
θ   -   time, seconds

APPENDIX B

Fig. 3. Chromatograph Calibration Curves
for Isobutane and Butene-2

APPENDIX C

SAMPLE CALCULATIONS

Estimation of Activation Energy and Frequency
Factor from the Data of Frey

The Arrhenius equation (Equation (3-18)) can be written in the form

$$\ln k = \ln A - \frac{E}{RT} \quad . \tag{C-1}$$

Values of the specific reaction rate must be available at two different temperatures. Denote the specific reaction rate at T_1 by k_1 and at T_2 by k_2. Assume that the experimental activation energy E is independent of temperature and pressure, and that the frequency factor is independent of temperature but proportional to the square of the pressure. The assumptions concerning temperature independence are, of course, valid only over narrow temperature ranges. Then

$$\ln k_1 = \ln A_1 - \frac{E}{RT_1} \tag{C-2}$$

and

$$\ln k_2 = \ln \left(\frac{P_2}{P_1} \right)^2 A_1 - \frac{E}{RT_2} \tag{C-3}$$

$$= \ln A_1 + 2 \ln \left(\frac{P_2}{P_1} \right) - \frac{E}{RT_2} \tag{C-4}$$

placing k_2 on the same pressure base as k_1. Subtracting Equation (C-4) from Equation (C-2) gives

$$\ln \frac{k_1}{k_2} = \frac{E\,(T_1 - T_2)}{R\,T_1 T_2} - 2\,\ln\left(\frac{P_2}{P_1}\right) \quad . \tag{C-5}$$

Rearranging Equation (C-5)

$$\ln \frac{k_1}{k_2} + 2\,\ln \frac{P_2}{P_1} = \frac{E\,(T_1 - T_2)}{R\,T_1 T_2} \quad . \tag{C-6}$$

Equation (C-6) can be solved for the activation energy E, since all other terms in the equation are known. The calculated value of E can then be used in either Equation (C-2) or Equation (C-3) to solve for the frequency factor, A, based on the pressure applicable to k_1.

Using the specific reaction rates calculated from Frey's data we have

$$k_1 = 0.058$$

$$k_2 = 0.0585$$

$$T_1 = 1400^\circ \text{ R}$$

$$T_2 = 1428^\circ \text{ R}$$

$$P_1 = 4500 \text{ psia}$$

$$P_2 = 2500 \text{ psia}$$

$$\ln \frac{0.058}{0.0585} + 2\,\ln \frac{2500}{4500} = \frac{28\,E}{(1.987)(1400)(1428)} \quad . \tag{C-7}$$

Solving for E

$$E = 168,000 \text{ Btu/lb. mole}$$

Solving for A

$$A = k_1\,e^{\frac{E}{RT}}$$

$$= 9.85\,(10^{24}) \quad . \tag{C-8}$$

Estimation of Specific Reaction Rates Using
Absolute Reaction Rate Theory

Hirschfelder (26) states that the activation energy for a four

atom reaction of the type $AB + CD = AC + BD$ the activation energy is

approximately 28% of the energies of the bonds being broken.

Considering the over-all reaction of isobutane with butene-2,

two bonds are broken, a carbon-hydrogen bond and one-half of a

carbon-carbon double bond. The bond energies involved are approxi-

mately 98 Kcal./gm. mole for the carbon-hydrogen bond and 62 Kcal./

gm. mole for one-half of the carbon-carbon double bond.(28).

The estimated activation energy is, therefore

$$E = 0.28 (98 + 62) = 45 \text{ Kcal./gm. mole} \qquad . \qquad (C-9)$$

Frost and Pearson (24) have calculated order of magnitude

values per degree of freedom for the translational, rotational, and vi-

brational partition functions. The values are presented below in

Table IX. For a detailed discussion of the assumptions made to ob-

tain these values, the reader should refer to page 84 of Frost and

Pearson.

TABLE IX

APPROXIMATE VALUES OF PARTITION FUNCTIONS
PER DEGREE OF FREEDOM

	Designation	Order of Magnitude
Translation	f_t	$10^8 - 10^9$
Rotation	f_r	$10^1 - 10^2$
Vibration	f_v	$10^0 - 10^1$

Consider a bimolecular reaction between two polyatomic molecules A and B of n_A and n_B atoms, respectively, and non-linear. The necessary partition function can be represented by

$$Q_A^o = f_t^3 \ f_r^3 \ f_v^{3n_a-6} \tag{C-10}$$

$$Q_B^o = f_t^3 \ f_r^3 \ f_v^{3n_b-6} \tag{C-11}$$

$$Q_\ddagger^o = f_t^3 \ f_r^3 \ f_v^{3n_a + 3n_b - 7} \ . \tag{C-12}$$

$Q_\ddagger^o$ has one less vibrational degree of freedom because of reaction. Substituting Equations (C-10), (C-11), and (C-12) into Equation (3-19) and assuming that all f_t's, f_r's and f_v's are equal since they represent only order of magnitude, we obtain

$$k \doteq \frac{k'T}{h} \cdot \frac{f_v^5}{f_t^3 \ f_r^3} \ e^{-\frac{E_o}{RT}} \ . \tag{C-13}$$

Assuming values of f_t, f_r, and f_v from Table IX that force Equation (C-13) to give the same order of magnitude value for a specific reaction rate as that calculated from Frey's data, and including conversion factors to convert from the units cc/(gm. mole) (sec) to the units of ft^3/(lb. mole) (sec) we have

$$k \doteq 2.01 \ (10^8) \ T \ e^{-\frac{E_o}{RT}} \ . \tag{C-14}$$

Substituting the value of E from Equation (C-9) and the value of R in energy units into Equation (C-14) gives

$$k \doteq 2.01 \, (10^8) \, T \, e^{-\frac{2263}{T}} \, . \qquad \text{(C-15)}$$

Substituting $T = 1400^{\circ}$ R into Equation (C-15) gives

$$k = 3.6 \times 10^{-2} \, ft^3/(lb. \ mole) \, (sec) \quad . \qquad \text{(C-16)}$$

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