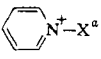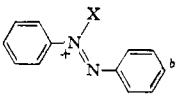clusion is consistent with the interpretations of the substituent effects given above and with the spectroscopic data to be reported elsewhere, although neither of these is capable of making a distinction between VII and VIII.

The difference in basicities of pyridine and its N-oxide is compared in Table VI with the difference between azobenzene and azoxybenzene, the latter of which may well be considered as an N-oxide of azobenzene. In both series the N-oxides are weaker bases by nearly the same amounts. This observation seems to suggest that the structure of the conjugate acids of the N-oxides is quite similar, and there seems to be no reason to doubt that the conjugate acid of pyridine N-oxide is N-hydroxypyridinium ion.[16] Consequently it

TABLE VI

COMPARISON OF pK BETWEEN PYRIDINE, AND ITS N-OXIDE, AND AZO- AND AZOXYBENZENE

X			Difference
H	5.29	−2.90[c]	8.19
OH	0.79	−6.45	7.24
Difference	4.50	3.55	

[a] In H_2O; cf. ref. 16, 5b.   [b] In 20% EtOH.   [c] Ref. 4b.

seems safe to conclude that azoxybenzenes are protonated at the oxygen atom.

(16) H. H. Jaffé, J. Am. Chem. Soc., **79**, 4445 (1955).

Ionic Reactions Occurring During Sulfuric Acid Catalyzed Alkylation. I. Alkylation of Isobutane with Butenes

BY J. E. HOFMANN AND A. SCHRIESHEIM
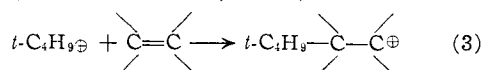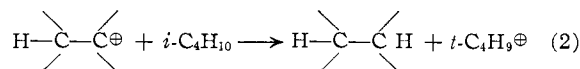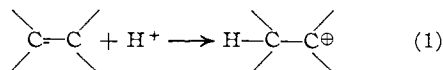
The sulfuric acid catalyzed alkylation between isobutane and butene-1, butene-2 and isobutylene was studied in continuous flow equipment. Product analyses were obtained as a function of time, and profound changes were found in hydrocarbon distribution. Initially, yields were low, but selectivity to trimethylpentanes was high. This was followed by an intermediate period of increasing yield but markedly reduced selectivity to trimethylpentanes. Finally, equilibrium experimental conditions were reached. Selectivity to trimethylpentane was again high and yields approached the theoretical. The results are interpreted by assuming the buildup of an isobutane solutizer or active hydride transfer agent in the acid phase.

Introduction

The acid catalyzed alkylation of olefins with isoparaffins was first described by Ipatieff.[1] This reaction is induced by a wide variety of catalysts, and it has been comprehensively reviewed by Kennedy[2] and Schmerling.[3] A careful study of the literature, however, shows that there is very little specific information concerning the role of the catalyst. Thus, it has been generally accepted that in protonic acids, as sulfuric, the olefin is protonated (step 1) to yield a carbonium ion that undergoes a

$$\searrow C = C \diagdown + H^+ \longrightarrow H - \searrow C - C \diagdown \oplus \quad (1)$$

$$H - \searrow C - C \diagdown \oplus + i\text{-}C_4H_{10} \longrightarrow H - \searrow C - C \diagdown H + t\text{-}C_4H_9 \oplus \quad (2)$$

$$t\text{-}C_4H_9 \oplus + \searrow C = C \diagdown \longrightarrow t\text{-}C_4H_9 - \searrow C - C \diagdown \oplus \quad (3)$$

$$t\text{-}C_4H_9 - \searrow C - C \diagdown \oplus + i\text{-}C_4H_{10} \longrightarrow$$

$$t\text{-}C_4H_9 \oplus + t\text{-}C_4H_9 - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - H \quad (4)$$
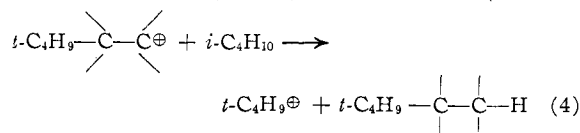
hydride exchange reaction[4,5] (step 2) with a mole-

cule of isobutane to generate the t-butyl cation. This cation then reacts with more olefin to form the alkylate ion (step 3), which may then undergo a second hydride transfer reaction to regenerate the chain-carrying t-butyl ion and produce the alkylate molecule.

In a classic series of papers, Beeck, et al.,[6] showed that hydride transfer does, indeed, occur on the tertiary C–H bond of isobutane. The results of these investigations when coupled with previous research[2,3] tended to support the assumption that the acid serves merely to initiate the reaction by protonation of the olefin and to provide an ionic media for the reaction to take place. Certain inconsistencies in this interpretation developed during our general research program on acid catalysis,[7]

(1) V. N. Ipatieff, "Catalytic Reactions of High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, pp. 673-701.

(2) R. M. Kennedy, "Catalysts," Vol. 6, Reinhold Publ. Corp., New York, N. Y., 1958, pp. 1-41.

(3) L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publ. Corp., New York, N. Y., 1955, pp. 363-408.

(4) P. D. Bartlett, F. E. Condon and A. Schneider, J. Am. Chem. Soc., **66**, 1531 (1944).

(5) N. C. Deno, H. J. Peterson and G. S. Saines, Chem. Revs., **60**, No. 1, 7 (1960).

(6) O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, J. Chem. Phys., **17**, 418 (1949); J. Am. Chem. Soc., **73**, 5741 (1951); **74**, 3299 (1952).

(7) G. M. Kramer and A. Schriesheim, J. Phys. Chem., **66**, in press (1962). Unpublished work from this Laboratory by Dr. G. M. Kramer indicated rather clearly that alkylate is not formed when fresh sulfuric acid is contacted with isobutane and isobutylene for short contact times. This work was carried out by mixing hydrocarbon and fresh acid in a mixing tee and then rapidly quenching the emulsion with caustic. Analysis of the low boiling fraction indicated complete conversion of the olefin but no significant quantity of higher boiling saturated hydrocarbons could be found. A small yield of 2,4,4-trimethylpentene-1 was detected and also a fairly large amount of unsaturated material boiling in the C_{12} and higher range was formed. Clearly, this was the result of olefin dimer and trimerization with no significant amount of hydride transfer between isobutane and the higher molecular weight ionic fragments.
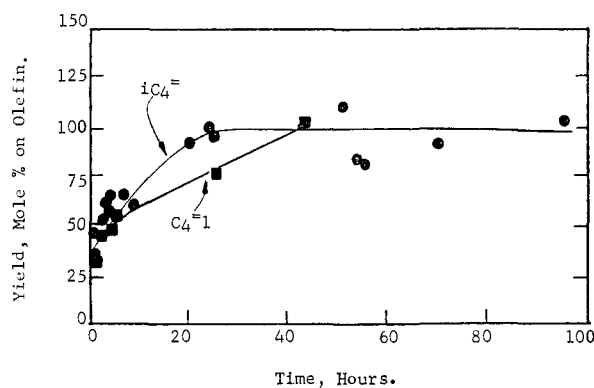
Fig. 1.

and we therefore initiated a study that was devoted to an attempt to elucidate the role of the acid medium in the alkylation reaction. It was also felt that such a study would have wide implications to the general field of acid-catalyzed reactions occurring in sulfuric acid.

Previous research work on both the alkylation reaction and the role of sulfuric acid had invariably been carried out in static equipment in which the acid was contacted with the isoparaffin and olefin and the entire mixture analyzed at the end of the reaction. However, there was some indication that an induction period existed for the alkylation reaction during the batch studies.[8] Since the catalytic nature of the acid was under study, the approach adopted in this investigation was to utilize flow equipment in which the reaction could be followed as a function of time, and, in particular, to obtain initial reaction products. Two series of experiments were carried out. One used C^{14}-tagged olefins and the other did not. This paper is concerned with the acid-catalyzed alkylation reaction using non-tagged molecules. A subsequent paper will describe our research results using the tagged compounds.

In this paper it will be shown that the acid undergoes marked changes during the course of the alkylation reaction. These changes, in turn, affect product distribution and the entire process may be interpreted on the basis of a series of ionic reactions, occurring in the acid phase, that produce either an isobutane solutizer, or, more probably, an efficient hydride transfer intermediate.

Experimental

Experimental work was carried out in a small continuous flow reactor. The flow plan for this unit is described below
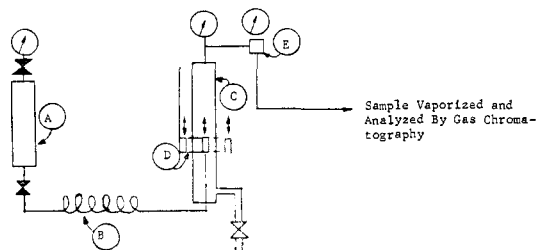
where A is Reactant charge cylinder containing a mixture of isobutane and olefin, B the capillary tubing for flow con-

(8) T. D. Stewart and W. H. Calkins, J. Am. Chem. Soc., 70, 1006 (1948).

trol, C the glass reaction tube (over-all length 20 cm., inside diameter 1.2 cm.), D the reciprocating magnet for mixing (length of stroke 6 cm.) and E the back pressure regulator.

A typical experiment is performed in the following manner. After purging the entire system with nitrogen, fresh 98 wt. % sulfuric acid is charged to the reaction tube C to a level about 6 cm. above the top of the hydrocarbon feed tube so that it completely fills the reaction zone. Hydrocarbon flow and mixing is then commenced. The hydrocarbon-acid emulsion is disengaged in the top of the reaction tube and the hydrocarbon is then depressured and vaporized by heating to 150°. The feed is a premixed olefin-isobutane blend with a mole ratio of iC_4H_{10}/C_4H_8 of approximately 15/1. The feed is charged at an olefin space velocity of 0.02–0.05 volume of olefin/hour/volume of catalyst. The total hydrocarbon sample is periodically analyzed on a Perkin–Elmer model 154B gas chromatograph. The chromatograph column is 21 feet of Dow Corning Silicone oil (DC-200) supported on firebrick. The initial acid charge remains in the reactor for the duration of the experiment, and a titration of the acid is obtained at the end of each run.

One experiment was carried out in a 1-liter continuous stirred autoclave. Experimental procedures were essentially the same as the flow equipment except that reactor acid was withdrawn periodically and fresh 98% acid was added in order to maintain a constant acidity. Experimental conditions for this run were: 10°, 50 p.s.i.g., 96 wt.% H_2SO_4, 7/1 mole ratio of isobutane to butylene in the reaction mixture, and 60 vol. % acid in the reactor emulsion.

Hydrocarbon reagents used in this study were Matheson research grade isobutane and Matheson C.P. grade olefins. The H_2SO_4 was 98% carboy acid from American Cyanamid Co. This acid analyzed 97.7 wt. % H_2SO_4. 2,5-Dimethylhexadiene-1,5 was obtained from the Aldrich Chemical Co.

Results

The most striking feature of the results is the marked changes in both the yield of product and in product distribution with time. Figure 1 shows that a minimum of 20 hours was required before experimental equilibrium yields of alkylate were obtained. Initial yields for isobutane/butylene mixtures were only about 30 mole % on olefin compared to about 100 mole % at experimental equilibrium. Product yields in the isobutane–butene-1 system were initially lower than the $iC_4/iC_4^=$ system but seemed to asymptote at the same level.

Product distribution also changes during the initial equilibration period, and these data are shown in Figs. 2 and 3. For all three of the butene
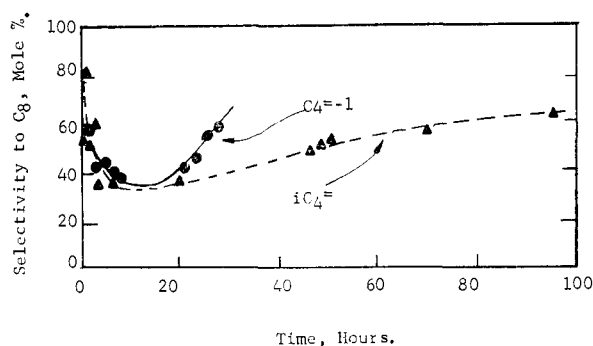

Fig. 2.

isomers, it was found that the initial pentane and heavier products contained primarily octanes. However, there was a rapid change in selectivity, and after 10 hours the product contained only about 35 mole % octanes. After this time interval, there was another change in selectivity and the octanes increased. The rate of change was faster for butene-1 than isobutylene. The distribution

among the octane isomers was also changing with time in a similar manner (Fig. 3), and initial products from butene-1, butene-2 and isobutylene were primarily trimethylpentanes. Dimethylhexanes build up in the octane fraction as the reaction progresses, and the trimethylpentane/dimethylhexane ratio goes through a minimum at about the same time as the selectivity to C_8 also goes through a minimum (Fig. 2).

Product analyses obtained from the 1-liter continuous autoclave show the same trend as was observed in the small flow unit. In this case, the reactants consisted of isobutane and a mixture of butylenes having the following analysis on a mole % basis.

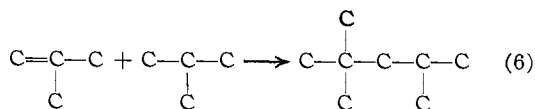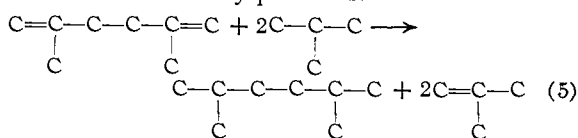|			
C_3	1.9	i-$C_4^=$	1.2
i-C_4	70.8	$C_4^=$-1	3.0
n-C_4	14.5	$C_4^=$-2	7.6
		C_5	0.9

Figure 4 shows the selectivity to octanes and the ratio of trimethylpentane to dimethylhexane in the octane fraction. Both the selectivity and the trimethylpentane/dimethylhexane ratio go through a minimum at about hour 15, and about 40 hours is required before alkylate is formed at equilibrium conditions.

The diolefin, 2,5-dimethylhexadiene-1,5, was also alkylated in flow equipment with isobutane in order to help interpret reaction data, and this reaction led to several interesting products. The primary reaction was that of self-alkylation. Self-alkylation involves the transfer of hydrogen from isobutane to

PRODUCT DISTRIBUTION FROM ALKYLATION OF 2,5-DI-
METHYLHEXADIENE-1,5 WITH ISOBUTANE

Compound	Mole %	Compound	Mole %
i-C_5	14	3,4-DMC$_6$	1
2,3-DMC$_4$, 2 + 3-MC$_5$	6	C$_9$	10
2,3 + 2,4-DMC$_5$	4	C$_{10}$ + C$_{11}$	2
2,2,4-TMC$_5$	13	C$_{12}$	6
2,4 + 2,5-DMC$_6$, 2,2,3-TMC$_5$	32	C$_8$-Naphthenes	Trace
2,3,4-TMC$_5$	3		
2,3,3-TMC$_5$, 2,3-DMC$_6$	9		

the diolefin and subsequent alkylation of isobutylene to form trimethylpentanes.

$$C=C-C-C-C=C + 2C-C-C \longrightarrow$$
$$\underset{C}{|} \qquad \underset{C}{|} \qquad \underset{C}{|}$$

$$C-C-C-C-C-C + 2C=C-C \quad (5)$$
$$\underset{C}{|} \qquad \underset{C}{|} \qquad \underset{C}{|}$$

$$C=C-C + C-C-C \longrightarrow C-\underset{C}{\overset{C}{|}}-C-C-C \quad (6)$$
$$\underset{C}{|} \qquad \underset{C}{|} \qquad \underset{C}{|} \quad \underset{C}{|}$$

Self-alkylation is well known for the reaction between isobutane and C_5^+ olefins and has been observed many times in the presence of sulfuric acid.[8-11] In addition to formation of self-alkylation products, C_{12} and higher hydrocarbons were observed in fair concentration, and traces of C_8-naphthenes were

(8) S. H. McAllister, *et al.*, *J. Org. Chem.*, **6**, 647 (1941).
(9) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1778 (1945).
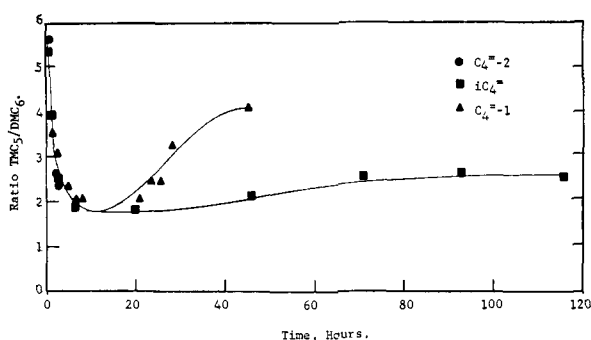(10) *Ibid.*, **68**, 275 (1946).
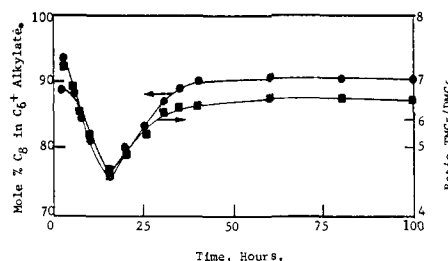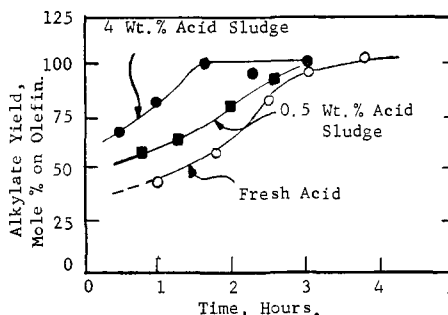(11) J. E. Hofmann, to be published.

Fig. 3.

Fig. 4.

Fig. 5.

also found to be present. The predominant C_8-naphthene was 1,1,3-trimethylcyclopentane.

Finally, pre-addition of the hydrocarbons liberated by hydrolysis of sulfuric acid that had been used as an alkylation medium resulted in an increase in the initial yield. Figure 5 compares the yield from fresh acid with that obtained at two levels of such pre-addition, 0.5 and 4.0 wt. % based on initial acid charge.
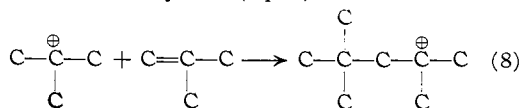
Discussion of Results

In order to interpret these findings, it will be necessary to explain the marked changes in the yield and selectivity that occur during the initial course of the reaction. A discussion of this is most easily accomplished by dealing with only one olefin, isobutylene. After the mechanism has been developed, it can be expanded readily to include other olefins.
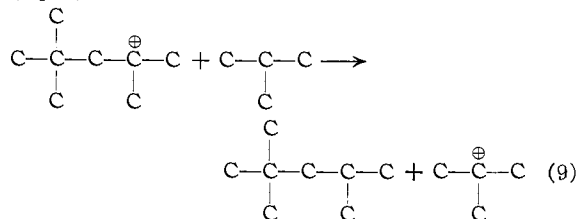
The formation of initial products in less than theoretical yield suggests that isobutane is not entering the reaction and that the predominant reaction is protonation of the olefin (eq. 7),
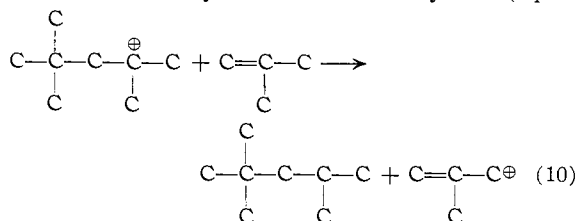
$$C=C-C + H_2SO_4 \longrightarrow C-\overset{\oplus}{C}-C + HSO_4^- \quad (7)$$
$$\underset{C}{|} \qquad\qquad\qquad\quad \underset{C}{|}$$
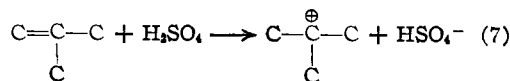
followed by addition of the *t*-butyl cation to another molecule of isobutylene (eq. 8).

$$C-\overset{\oplus}{\underset{\underset{C}{|}}{C}}-C \ + \ C=C-\underset{\underset{C}{|}}{C} \longrightarrow C-\underset{\underset{C}{|}}{C}-C-\overset{\oplus}{\underset{\underset{C}{|}}{C}}-C \quad (8)$$
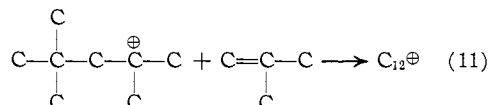
The resulting isoöctyl ion can now undergo several reactions: abstraction of a hydride from isobutane (eq. 9)

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\oplus}{C}-C \ + \ C-\underset{\underset{C}{|}}{C}-C \longrightarrow$$

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-C-C \ + \ C-\overset{\oplus}{\underset{\underset{C}{|}}{C}}-C \quad (9)$$

abstraction of hydride from isobutylene (eq. 10)

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\oplus}{C}-C \ + \ C=C-C \longrightarrow$$

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-C-C \ + \ C=C-C^{\oplus} \quad (10)$$

addition to another molecule of isobutylene (eq. 11)

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{\oplus}{\underset{\underset{C}{|}}{C}}-C \ + \ C=C-C \longrightarrow C_{12}^{\oplus} \quad (11)$$
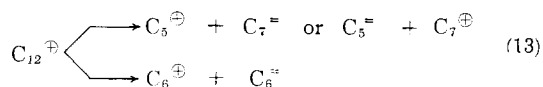
At low isobutane concentration, reactions 10 and 11 predominate and the initial product observed is expected to be largely trimethylpentane (from reaction 10). Such a situation clearly holds from Figs. 2, 3 and 4.

The intermediates found in steps 10 and 11 are, however, highly reactive and are expected to react rapidly and form more stable compounds. For example, the allylic ion formed in reaction 10 may add to isobutylene and produce the carbon skeleton of 2,5-dimethylhexane (eq. 12).

$$C=C-C^{\oplus} \ + \ C=C-\underset{\underset{C}{|}}{C} \longrightarrow C=C-C-C-\overset{\oplus}{\underset{\underset{C}{|}}{C}}-C \quad (12)$$
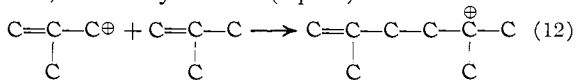
2,5-Dimethylhexadiene-1,5 can be transformed to a dimethylhexane *via* hydrogen transfer so that reaction 12 and subsequent hydrogen transfer reactions can easily account for the shift in distribution from a high ratio of trimethylpentane to dimethylhexanes to a low ratio.

Similarly, scission of the $C_{12}^{\oplus}$ formed in reaction 11 leads to the precursors of pentanes, hexanes and heptanes.[12] Saturation of the ionic fragments of step 13 by hydride transfer and of the olefins by protonation and hydride transfer would result in the increase in the low

$$C_{12}^{\oplus} \overset{\longrightarrow C_5{}^{\oplus} \ + \ C_7{}^= \ \text{or} \ C_5{}^= \ + \ C_7{}^{\oplus}}{\underset{\longrightarrow C_6{}^{\oplus} \ + \ C_6{}^=}{\bigg\langle}} \quad (13)$$
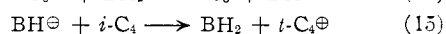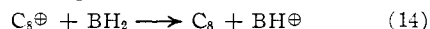
(12) A. Schneider and R. J. Kennedy, *J. Am. Chem. Soc.*, **73**, 5013 (1951); **74**, 2553 (1952).

boiling hydrocarbons observed in the continuous experiments. Data from this Laboratory using C^{14}-radio tracers have established that $C_{12}^{\oplus}$ is the intermediate in the production of $C_5{}^-$, $C_6{}^-$, and C_7-fragments.[13]

Following this period of change in selectivity and lowering of the TMC_5/DMC_6 ratio, it was observed that the TMC_5/DMC_6 ratio once again increased. The only reasonable interpretation of this phenomenon is that, with time, isobutane becomes available and the hydride transfer between isobutane and trimethylpentyl cation (reaction 9) now predominates over reactions 10 and 11. At this point, the over-all mechanism is consistent with the classical chain reaction proposed for the alkylation of isobutane with olefins and the reaction proceeds according to eq. 1–4.

The significant question raised by this mechanism is: "How is the isobutane made available and why is it not available in fresh sulfuric acid?" While conclusive data on this point are lacking, the following considerations appear to be reasonable. The initial time period is accompanied by a darkening of the sulfuric acid due to the formation of unsaturated hydrocarbons. Meager information on the composition of these hydrocarbons indicates that they consist primarily of cyclic unsaturated material, most probably cyclic dienes. The fact that pre-addition of such material (Fig. 5) increases initial yields indicates that this material is an important part of the catalyst and must be present before isobutane enters the reaction. It is proposed that these unsaturated compounds serve either to increase the solubility of isobutane in the acid, or that the unsaturates actually take part as intermediates in the hydride transfer reactions. Thus, if B represents such an unsaturated molecule and BH_2 a partially hydrogenated form, the following reactions could be postulated.

$$C_8^{\oplus} \ + \ BH_2 \longrightarrow C_8 \ + \ BH^{\oplus} \quad (14)$$

$$BH^{\ominus} \ + \ i\text{-}C_4 \longrightarrow BH_2 \ + \ t\text{-}C_4^{\oplus} \quad (15)$$

This mechanism merely inserts these compounds as intermediates in the over-all hydride transfer reaction 9.

A spent sulfuric acid alkylation catalyst, containing the sludge, was contacted for three hours with pure isobutane at 10°. The resulting hydrocarbon layer was found to contain about 1% of saturated material boiling higher than butane.

$C_8{}^+$, mol. %		$C_9{}^+$, mol. %	
Pentanes	2	Dimethylhexanes	10
Hexanes	2	Nonanes	3
Heptanes	2	Decanes	5
Trimethylpentanes	63	Dimethylcyclopentanes	13

These could only have come about by hydride exchange reactions similar to the one depicted in eq. 15. When a similar experiment was carried out with fresh H_2SO_4, no heavy hydrocarbons were formed. While insufficient evidence is available to determine exactly which of the two roles is most important, it would certainly appear reasonable to assign either the isobutane solutizer or the hydride transfer intermediate role to the unsaturated material. We believe that the facts point toward

(13) J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 957 (1962).

the latter role. Regardless of the interpretation, however, the inescapable conclusion is reached that "no alkylation occurs between isobutane and an olefin in sulfuric acid until this isobutane 'activator' has built up."

The question of how these materials are produced is of some importance and evidence is available on how they are formed. Traces of trimethylcyclopentanes were produced during the alkylation of 2,5-dimethyl hexadiene-1,5 with isobutane and these naphthenes undoubtedly arose from the intramolecular alkylation of the unsaturated cation I.
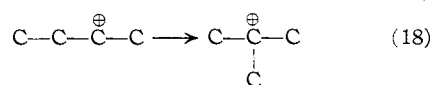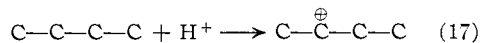
$$\text{(16)}$$

I   II
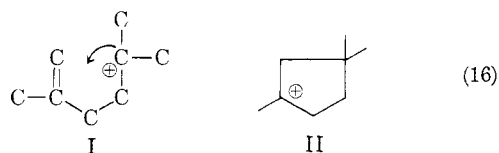
Hydride exchange between isobutane and molecule II would lead to 1,1,3-trimethylcyclopentane while dehydrogenation by hydrogen transfer would lead to the cyclic diene. Similar mechanisms have been postulated for the production of high molecular weight unsaturates in Friedel–Crafts reactions.[14]

Expansion of this mechanism to include the other butylenes is obvious. For example, it is well known

(14) A. Schriesheim and S. Khoobiar, "Proceedings of the International Catalyst Society," Paris, 1960.

that in sulfuric acid the alkylate products from butene-1 and butene-2 are nearly identical.[15] This is explained on the basis of a rapid isomerization equilibration between the two. At normal reaction temperatures, 0–20°, equilibrium favors butene-2 by a factor of about 10 to 1. Hence, it can be assumed that regardless of whether the reactant is butene-1 or -2, it is the alkylation of butene-2 that is under consideration. The initial step in the alkylation of butene-2 is protonation (step 17) followed by rearrangement to the more stable tertiary carbonium ion (step 18). Data obtained at this Laboratory, to be published shortly,[11,13] clearly demonstrate these two steps.

$$\text{C—C—C—C} + \text{H}^+ \longrightarrow \text{C—}\overset{\oplus}{\text{C}}\text{—C—C} \quad \text{(17)}$$

$$\text{C—C—}\overset{\oplus}{\text{C}}\text{—C} \longrightarrow \text{C—}\overset{\oplus}{\underset{\text{C}}{\text{C}}}\text{—C} \quad \text{(18)}$$

The exact extent of this isomerization is unknown. The present argument requires that it only occurs to a sufficient extent to initiate the reaction. The reaction path after step 18 is identical to the mechanism outlined for isobutylene.

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(15) S. F. Birch, et al., Ind. Eng. Chem., **31**, 884 (1939); **31**, 1079 (1939).

Ionic Reactions Occurring During Sulfuric Acid Catalyzed Alkylation. II. Alkylation of Isobutane with C14-Labeled Butenes

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The sulfuric acid catalyzed alkylation of isobutane with C14-labeled butylenes was studied in continuous flow equipment. Product analyses and C14-distribution determinations were obtained for the initial products and for the products formed at steady-state conditions. It was found that initial product stemmed primarily from olefin polymerization reactions, while at steady-state the predominant reaction was direct alkylation. In addition, a considerable difference in reactivity between butene-1 and isobutylene was observed with isobutylene having a greater tendency to polymerize. Radioactive carbon distributions show that the formation of fragments smaller than octanes proceed via the scission of a $C_{12}^{\oplus}$ intermediate. It is concluded that the transition from initial product to steady-state occurs as a result of a buildup of an isobutane solutizer or active hydride transfer agent.

Introduction

The acid catalyzed isoparaffin–olefin alkylation reaction has been the subject of considerable study since first described by Ipatieff[1] and has been the subject of comprehensive reviews by Kennedy[2] and Schmerling.[3] However, formulation of a detailed mechanism for the reaction has been based upon indirect evidence. For instance, in the low temperature acid-catalyzed reaction between isobutane and butylenes, no direct evidence is available on the mechanism of formation of fragments such as pentanes, hexanes and heptanes.

(1) V. N. Ipatieff, "Catalytic Reactions of High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, pp. 673-701.

(2) R. M. Kennedy, "Catalysis," Vol. 6, Reinhold Publ. Corp., New York, N. Y., 1958, pp. 1-41.

(3) L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publ. Corp., New York, N. Y., 1955, pp. 363-408.

In addition to this lack of knowledge, certain peculiarities have arisen in the reaction mechanism[4,5] when comparing fresh with equilibrium or "steady-state" sulfuric acid catalyst. In this case, "steady-state" acid is defined as that which has been in use for a length of time sufficient to produce a product of constant composition. In order to study the whole reaction in more detail, a study was made of the alkylation of isobutane with radio-labeled butenes. The C14-content of all the products could be followed and these data would lead to more direct information regarding the detailed mechanism of the alkylation reaction. Previous studies[4] also dictated that because the acid does change with

(4) J. E. Hofmann and A. Schriesheim, J. Am. Chem. Soc., **84**, 953 (1962).

(5) T. D. Stewart and W. H. Calkins, ibid., **70**, 1006 (1948).