

perature for 3 days.<sup>25</sup> The almost colorless solution was boiled briefly to expel the last traces of diazomethane, dried over anhydrous magnesium sulfate, and filtered. After removal of the solvent on a rotary evaporator, the residue was distilled through a short column to yield 8.97 g (0.058 mole) of methyl 2,3-diazabicyclo[3.2.0]hept-2-ene-1-carboxylate: bp 66° (0.20 mm),  $n_D^{20}$  1.4750,  $\lambda_{\max}$  322 m $\mu$  ( $\epsilon$  216).<sup>25</sup> The product showed infrared absorptions at 5.75 (saturated ester) and 6.51  $\mu$  (N=N) and no evidence of olefinic absorption. The nmr spectrum consisted of a partially overlapping one-proton singlet at  $\tau$  5.44 and a one-proton doublet at 5.52, a three-proton singlet at 6.42, and three complex multiplets centered at 7.27, 7.88, and 8.63, with relative areas of 2:2:1.

*Anal.* Calcd for  $C_7H_{10}O_2N_2$ : C, 54.53; H, 6.54; N, 18.17. Found: C, 54.56; H, 6.57; N, 18.34.

**Pyrolysis of Methyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1-carboxylate (28).**—A 1.54-g (0.010 mole) sample of 28 was pyrolyzed at 155° (90 mm) and the volatile products were collected in a cooled receiver. After 2 hr 1.12 g (89%) of colorless liquid, bp ca. 110°, had been collected and only a small black residue remained in the pyrolysis flask. A component with the same vpc retention time as authentic 2 accounted for about 30% of the six-component mixture. No column gave sufficient separation to allow preparative separation and the mixture was not further characterized.

**Photolysis of Methyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1-carboxylate (28).**—A solution of 3.38 g (0.022 mole) of 28 in 900 ml of dry pentane was irradiated with a 450-w Hanovia lamp in a Pyrex vessel until the pyrazoline absorption at 322 m $\mu$  could no longer be detected (5.5 hr). The solvent was then removed on a rotary evaporator and the residue was distilled through a short column to give 2.67 g (82.5%) of colorless liquid, bp 72–77° (34 mm). This consisted of four main components by vpc [10-ft 15% diethylene glycol succinate (DEGS) on Chromosorb P, 115°] in the ratio 9:15:23:53. The third and fourth components were separated from the first two on a 15 ft  $\times$   $\frac{3}{8}$  in. column of 25% DEGS on Chromosorb P at 120°. The major component was shown to be 2 by direct comparison with an authentic sample.

The third component, bp 78° (40 mm),  $n_D^{20}$  1.4612,  $\lambda_{\max}$  227 m $\mu$  ( $\epsilon$  12,300), was identified as methyl 2-methylcyclobutene-1-carboxylate (29). Its infrared spectrum showed strong absorptions at 5.81 (conjugated ester) and 6.00  $\mu$  (C=C).<sup>26</sup> The nmr

(25) T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).

(26) Reference 24, p 36.

spectrum of 29 consisted of a three-proton singlet at  $\tau$  6.36, a four-proton multiplet centered at 7.6 (ring methylenes), and an apparent octuplet (three protons,  $J = 1$  cps) at 8.02.<sup>27</sup>

*Anal.* Calcd for  $C_7H_{10}O_2$ : C, 66.64; H, 7.99. Found: C, 66.47; H, 7.96.

**Reduction of *cis*-Cyclobutane-1,2-dicarboxylic Anhydride (9).**<sup>17</sup>—A solution of 1.26 g (0.010 mole) of 9 in 70 ml of reagent ethyl acetate was hydrogenated over 0.630 g of prereduced platinum oxide at 26° (745 mm). After 12 hr 601 ml (0.024 mole) of hydrogen had been consumed and the rate of hydrogen uptake had slowed to less than 1 ml/hr. The solution was filtered through Celite, and the solvent was removed at reduced pressure. The residue was taken up in ether and treated with cold, ethereal diazomethane until a yellow color persisted. Excess diazomethane was removed by brief boiling, and the ether was distilled off. Distillation of the residue gave 132 mg of pure methyl *cis*-2-methylcyclobutane-1-carboxylate (30), bp 62° (30 mm), and 556 mg of a 1:5 mixture of 30 and 12, bp 96–101° (8 mm). Lactone 12 was collected by preparative vpc (SE 30 column) and identified by comparison with an authentic sample. The nmr spectrum of 30 consisted of a three-proton singlet at  $\tau$  6.39, a three-proton doublet ( $J = 6.5$  cps,  $CHCH_3$ ) at 8.99, and a broad six-proton envelope extending from 6.54 to 8.58.

**Reduction of Methyl 2-Methylcyclobutene-1-carboxylate (29).**—A solution of 126 mg (0.001 mole) of 29 in 10 ml of acetone was hydrogenated over 20 mg of prereduced 5% palladium on carbon. Hydrogen uptake ceased abruptly after 22 min with 25.3 ml (1.01 equiv) of hydrogen being consumed. After an additional 10 min the solution was filtered through Celite and concentrated to give 111 mg of 30, identical with an authentic sample by infrared spectroscopy and vpc retention times on two different columns.

**Registry No.**—9, 7687-27-6; 12, 7687-28-7; 13, *trans* isomer, 7695-32-1; 13, *cis* isomer, 7687-29-8; 14, 7687-30-1; 15, 7690-92-8; 26, 7687-31-2; 27, 7687-32-3; 28, 7687-33-4; 29, 7687-34-5; 30, 7687-35-6.

(27) It is well known (J. D. Roberts, "Nuclear Magnetic Resonance, Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 54, 103) that the nmr spectrum of cyclobutene consists of two singlets. Similarly J. Shabtai and E. Gel-Av [*J. Org. Chem.*, **28**, 2893 (1963)] have shown that the methylene protons of 1-methylcyclobutene are unsplit. However, we have observed that the methylene protons of 5 appear as a typical  $A_2X_2$  pattern of two triplets ( $J = 3$  cps) with fine structure, centered at  $\tau$  7.30 and 7.56. The vinyl proton appeared as a multiplet at  $\tau$  3.23.

## The Reaction of 2,3,4-Trimethylpentane in Concentrated Sulfuric Acid

G. M. KRAMER

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

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The effect of acidity on the reaction of 2,3,4-trimethylpentane in sulfuric acid has been investigated using tritiated acid. The reaction after an induction period appears to follow a second-order dependence on proton activity. The initial reaction leads to the formation of butyl ions and butylene in the acid. The product distributions provide evidence for an initially homogeneous reaction which acquires considerable heterogeneous character as reaction proceeds.

The behavior of paraffins in concentrated sulfuric acid has been studied extensively and is known to be quite complex. Difficulties in interpreting results arise for many reasons. Among these are the facts that the systems are heterogeneous, that an initiation process appears necessary for reaction, that the distinction between initiation and reaction rates as well as the dependence of each upon acid strength is not well understood, and that the nature of the reaction intermediates is not universally agreed upon.

This paper is primarily concerned with the relationship between reaction rate and acid strength. This investigation has been carried out with tracer tech-

niques using tritiated acid. The relationship obtained is similar to that found by Beeck, Otvos, Stevenson, and Wagner<sup>1</sup> for hydrogen-exchange reactions of isobutane in sulfuric acid, but different from one reported by Roebuck and Evering,<sup>2</sup> with a different paraffin. In addition, some qualitative and quantitative information pointing to paraffin oxidation as an initiating step and evidence for the occurrence of reaction at two sites (bulk acid and interface) have been obtained.

(1) O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

(2) A. K. Roebuck and B. L. Evering, *J. Am. Chem. Soc.*, **75**, 1631 (1953).

### Experimental Section

The reaction of 2,3,4-trimethylpentane with sulfuric acid containing tracer quantities of  $T_2O$  was studied under well-mixed conditions at  $25^\circ$ . Experiments were run by adding 1 ml of the paraffin to 1 ml of acid in a small vial. The vial was inserted into a mechanical shaker, "Wig-L-Bug," and agitated for the required time. The acid was rapidly frozen out of the emulsion by contacting the vial with Dry Ice and a small sample of hydrocarbon was withdrawn for analysis on a radio assaying gas chromatograph.<sup>3</sup>

Data suitable for kinetic analyses were obtained by thawing the frozen acid without agitation in a  $25^\circ$  bath before mixing for the next reaction period. The acid has a radioactivity of roughly 1 mcurie/g. Its strength was varied from about 89 to 98.5 w %.

Commercially available acid to which water or oleum was added was used for all the tracer studies. To be sure that an initiator was not present in the acid, however, several experiments were run with nontritiated acid which had been distilled and collected under a nitrogen atmosphere. The acid was handled in a drybox and yielded the same conversions as were obtained with commercial acid under less stringent conditions.

The trimethylpentane utilized, Phillips 99 mol % minimum, was treated with 85%  $H_2SO_4$  or 96%  $H_2SO_4$  for a very short time, washed with water, and dried and stored over a 13X molecular sieve. When treated with 96% acid noticeable reaction occurred and the 2,3,4-trimethylpentane was redistilled before storage over the molecular sieve.

Sulfur dioxide was determined by potassium iodate titration after passing a nitrogen stream through the sulfuric acid solution into a scrubber containing a starch and potassium iodide solution. The titration assembly was that supplied by the H. W. Dietert Co., Detroit, Mich., with their Varitemp Combustion Furnace No. 3420.

### Results

The reaction of 2,3,4-trimethylpentane (2,3,4-TMP) is preceded by an induction period over the entire acidity range studied. This period is inversely related to acidity being barely noticeable in 98% acid and lasting for minutes in 90% acid. After the induction period the reaction appears to be first order in trimethylpentane. First-order rate constants obtained from log weight per cent 2,3,4-TMP vs. time plots as a function of acidity are given in Table I. A graph of the log of these rate constants vs. the  $H_0$  acidity function has a slope of nearly 2 suggesting a second order dependence on proton activity (Figure 1).

TABLE I

REACTION RATE CONSTANTS AS A FUNCTION OF ACIDITY

Acidity, wt %	$-H_0^a$	$k_{2,3,4-TMP}$ , sec <sup>-1</sup>
88.92	8.72	$1.77 \times 10^{-6}$
90.64	9.05	$1.05 \times 10^{-5}$
92.36	9.35	$5.08 \times 10^{-5}$
94.17	9.70	$1.95 \times 10^{-4}$
96.06	10.05	$1.26 \times 10^{-3}$
97.78	10.40	$5.00 \times 10^{-3}$
98.53	10.58	$7.81 \times 10^{-3}$

<sup>a</sup> M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

Samples of acid were withdrawn for  $SO_2$  determination from several runs at a given acidity at various intervals after the induction period. Sulfur dioxide formation appears to occur rapidly at first and then subsides. The extent and rate of formation are dependent on acidity and temperature and will be treated in a separate publication.<sup>4</sup> However, it may

(3) A. Y. Mottlau, *Anal. Chem.*, **33**, 293 (1961).

(4) Submitted for publication.

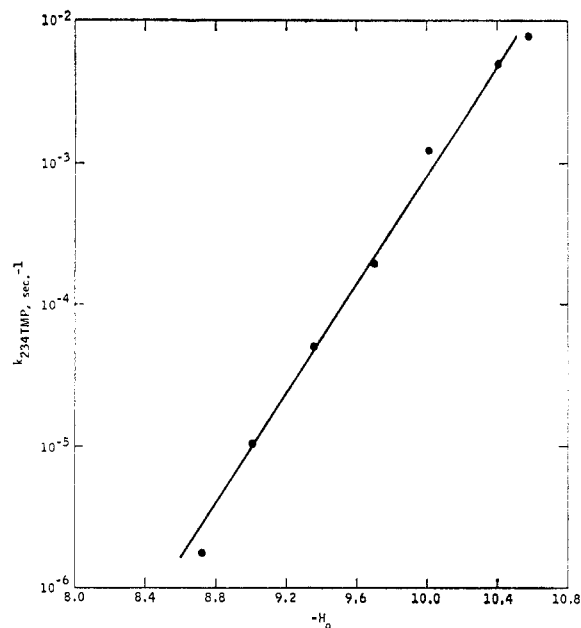


Figure 1.—First-order rate constants for the reaction of 2,3,4-trimethylpentane in concentrated sulfuric acid.

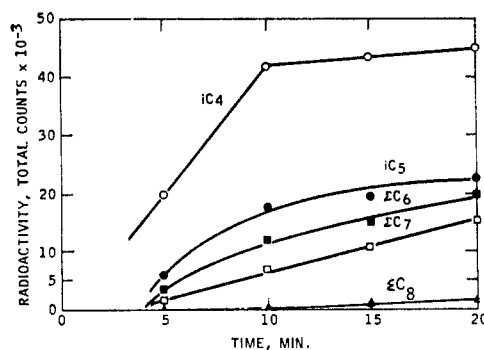


Figure 2.—Reaction products obtained from 2,3,4-trimethylpentane in  $H_2SO_4$  at 94%.

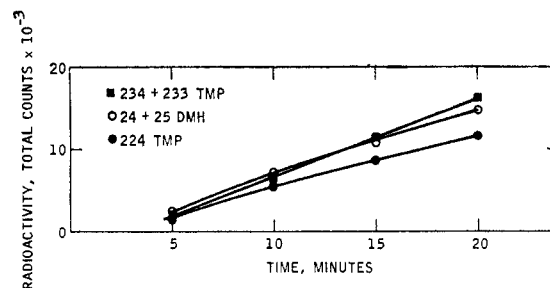


Figure 3.—Reaction products obtained from 2,3,4-trimethylpentane in  $H_2SO_4$  at 94.2%.

be noted that about 100 ppm  $SO_2$  ( $C = 2.86 \times 10^{-3}$  mole/l.) forms during the induction period. This corresponds to the oxidation of about 0.04% of the trimethylpentane.

The first saturated hydrocarbon formed in the reaction of 2,3,4-trimethylpentane with  $H_2SO_4$  is isobutane. This is illustrated in Figures 2, 3, 4, and 5 in which the radioactivity in the  $C_4$ - $C_8$  products is plotted as a function of time. Figures 2 and 3 pertain to 94% and Figures 4 and 5 are for 98.5% acid. The  $C_5$ ,  $C_6$ , and  $C_7$  products as well as all the  $C_8$  products from after isobutane. The initial formation of isobutane is common to the reaction over the 89–98% acidity range.

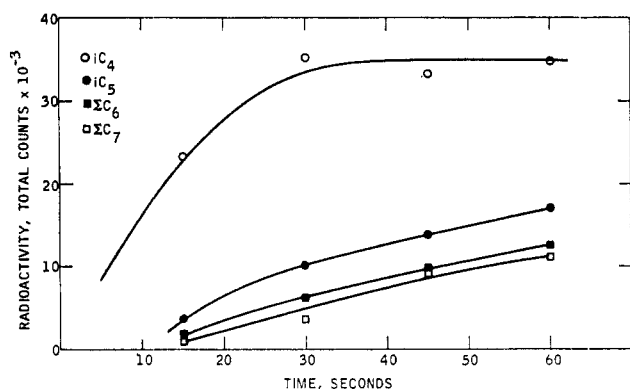


Figure 4.—Reaction products obtained from 2,3,4-trimethylpentane in  $\text{HTSO}_4$  at 98.5%.

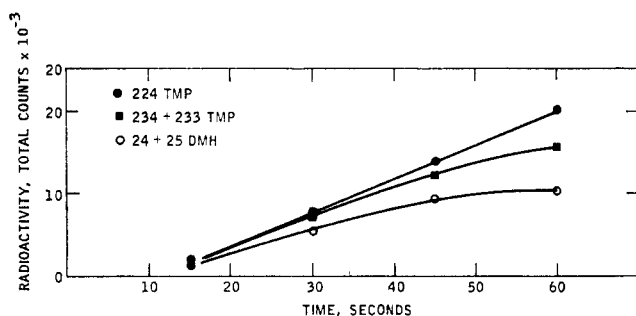


Figure 5.—Reaction products obtained from 2,3,4-trimethylpentane in  $\text{HTSO}_4$  at 98.5%.

The  $\text{C}_8$  hydrocarbons initially contain a high percentage of dimethylhexanes and a dimethylhexane to trimethylpentane ratio greater than 0.5:1. This ratio decreases with increasing conversions and it is tabulated in Table II.

2,3,4-TMP convn, wt %	DMH/TMP
94.17% $\text{H}_2\text{SO}_4$	
3.2	0.62/1
9.5	0.58/1
12.0	0.55/1
20.3	0.53/1
98.53% $\text{H}_2\text{SO}_4$	
6.0	0.33/1
11.7	0.37/1
14.2	0.36/1
27.0	0.31/1

<sup>a</sup> Typical alkylate, DMH/TMP = 0.15/1.

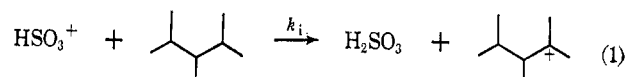
### Discussion

An adequate explanation for the behavior of 2,3,4-trimethylpentane in sulfuric acid should at least provide a qualitative mechanistic rationale for an induction period and a kinetic law of the type  $R = k[2,3,4\text{-TMP}]h_0^2$ . A plausible mechanism which could account for the results assumes the buildup of an essentially steady-state concentration of carbonium ion intermediates. These propagate the reaction of 2,3,4-TMP by hydride abstraction to form 2,3,4-TMP<sup>+</sup> ions. The intermediates are initially formed by oxidation of the paraffin, possibly by  $\text{HSO}_3^+$ , and reach a steady-state concentration as a variety of terminating

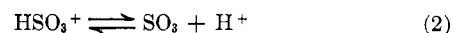
reactions become increasingly important. The initial carbonium ion concentration can be shown to depend on the square of the acidity function of oxidation by  $\text{HSO}_3^+$  and termination by sulfonation of olefins with  $\text{SO}_3$  obtains.

The induction period would be a natural consequence of this mechanism and would be a period during which reduction of sulfuric acid to  $\text{SO}_2$  would be most pronounced. As the intermediate ion concentration builds up the rate becomes increasingly dependent on hydride transfer to these intermediates rather than on the reducing agent in the acid. The oxidation rate itself will also tend to decrease as oxidation occurs because of the formation of water and consequent lowering of the  $\text{HSO}_3^+$  concentration.

A second-order dependence of rate on acidity may be derived as follows. Initiation (eq 1) is assumed to require attack of  $\text{HSO}_3^+$  on the paraffin.  $\text{HSO}_3^+$  should



be in equilibrium with  $\text{SO}_3$  (eq 2) so that the rate of



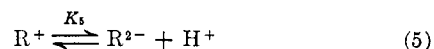
initiation will be given by

$$R_i = \frac{k_i a_{2,3,4\text{-TMP}} a_{\text{HSO}_3^+}}{K_2} \quad (3)$$

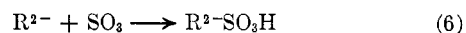
Assuming that this reaction takes place in the acid phase and no diffusional limitations exist, it will be zero order in 2,3,4-TMP since the latter is present in sufficient excess to keep the acid saturated, *i.e.*

$$R_i = \frac{k_i' a_{\text{SO}_3} a_{\text{H}^+}}{K_2} \quad (4)$$

All carbonium ions in the acid are assumed to exist in equilibrium with their corresponding olefins (eq 5).



They are assumed to disappear upon sulfonation by  $\text{SO}_3$  (eq 6) to form an unsaturated sulfonic acid. The



rate of termination is then

$$R_t = k_t a_{\text{R}^{2+}} = a_{\text{SO}_3} = \frac{k_i a_{\text{R}^+} K_3 a_{\text{SO}_3}}{a_{\text{H}^+}} \quad (7)$$

Equating the rates of initiation and termination, and solving for the carbonium ion activity yields

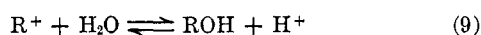
$$a_{\text{R}^+} = \frac{k_i'}{k_t K_2 K_3} a_{\text{H}^+}^2 \quad (8)$$

Thus, if the propagation rate involving hydride transfer to carbonium ions significantly exceeds the oxidation rate the reaction would sensibly follow the square of the proton activity. Moreover, if this reaction is an interfacial reaction, it will depend on the 2,3,4-TMP concentration in the emulsion.

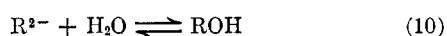
The proposed mechanism rationalizes a rate law of the type  $R = k[2,3,4\text{-TMP}]h_0^2$  which will satisfy the data. It must be considered quite tentative, however, in view of the large number of assumptions and simplifications which have been made. The most serious in our view is that the carbonium ion concentration is limited by sulfonation of the olefins with which they

are in equilibrium (eq 6). At low ion concentrations this approximation may not be bad, but at high ion plus olefin concentrations, polymerization and allylic hydride transfer certainly become competing reactions. Probably less objectionable is the suggestion that  $\text{HSO}_3^+$  is the oxidizing agent, although other species such as  $\text{H}_3\text{SO}_4^+$  or  $\text{H}_2\text{SO}_4$  may also oxidize paraffins.

We have chosen to correlate our data with the aid of the  $H_0$  acidity function and have thus assumed that sulfur trioxide and low molecular weight olefins behave as typical Hammett bases in concentrated sulfuric acid. The latter hypothesis was advanced by Deno<sup>5,6</sup> who reasoned that isobutylene ought to follow the same acidity function as dienes in sulfuric acid. The dienes appear to follow  $H_0$  rather than  $H_R$  or  $H_{R'}$ , indicating that they are in equilibrium with alkenyl cations having the activity coefficient behavior of Hammett indicators. If in the above derivation it is assumed that carbonium ion equilibria follow  $H_R$  rather than  $H_0$ , it can also be shown that  $a_{R^+}$  is proportional to  $a_{H^+}^2$ . Thus by replacing eq 5 with the equilibrium



and introducing



into eq 7, one may obtain eq 11.

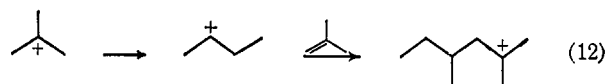
$$a_{R^+} = \frac{k_1'K_{10}}{k_2K_9} a_{H^+}^2 \quad (11)$$

These results appear to contrast with a previous study of 3-methylpentane isomerization in sulfuric acid for which a 0.6th-order dependence of rate on acidity was reported.<sup>2</sup> However, no distinction between the oxidation rate and the subsequent isomerization rate was made in that study. In addition, the rate constants were based upon conversion after 1 hr and do not correspond to the maximum rates obtained which makes comparison with the present results difficult.

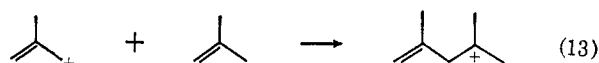
The formation of radioactive isobutane as the initial saturated product rather than 2,3,4- or any other trimethylpentane has several mechanistic implications. It suggests that once a 2,3,4-trimethylpentyl ion forms it rearranges to a 2,2,4-trimethylpentyl ion which undergoes  $\beta$  scission to form a *t*-butyl ion and isobutylene. This sequence of reactions is evidently faster than hydride transfer from 2,3,4-trimethylpentane to either the 2,3,4- or 2,2,4-trimethylpentyl ion. As a result the butyl ion and butylene concentration in the acid steadily rises until homogeneous alkylation begins. The secondary products initially observed thus should represent the "homogeneous" sulfuric acid alkylation product distribution. This product composition dif-

fers markedly from normal sulfuric acid alkylate, (Table II).

The "homogeneous" alkylate has relatively high concentrations of light hydrocarbons, ( $C_5$ - $C_7$ ) and dimethylhexanes. Possible routes to the  $C_5$ - $C_7$  compounds through  $C_{12}^+$  intermediates arising either by the addition of butyl ions to octenes or octyl ions to butene have recently been reconsidered.<sup>7</sup> The dimethylhexanes probably arise either from the isomerization of *t*-butyl ion to a secondary butyl ion followed by its alkylation with another isobutylene (eq 12), or



by the addition of isobutenyl cations to isobutylene (eq 13), followed by multiple protonation and hydride



abstraction.<sup>8,9</sup> The major point derived from this is that the product from the *in situ* reaction of *t*-butyl ion and isobutylene is unlike the product obtained in the conventional alkylation of isobutane with isobutylene. As the ion concentration increases in the acid, the homogeneous product should look less and less like conventional alkylate because of mass law effects favoring homogeneous ion-olefin reaction. The composition of the recovered hydrocarbons, however, shifts in the direction of conventional alkylate as the 2,3,4-trimethylpentane reaction proceeds. This is consistent with a change from a purely homogeneous reaction to one which begins to occur at a second site. The shift in the dimethylhexyl/trimethylpentyl ratio with time is thus evidence for a heterogeneous hydride transfer becoming dominant in this reaction.

In summary, the reaction of 2,3,4-trimethylpentane with sulfuric acid has been found to depend on the square of the proton activity. The reaction appears to be initiated by an oxidation step during which sulfur dioxide and carbonium ions form. The ions initially formed yield a homogeneous reaction product which differs from that formed later on in several respects. This is taken as evidence for a change in the reaction site from the bulk acid to the acid-hydrocarbon interface.

**Registry No.**—2,3,4-Trimethylpentane, 565-75-3.

**Acknowledgment.**—I wish to thank the Esso Research and Engineering Co. for permission to publish this work.

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

(8) Unpublished data of G. M. Kramer. The addition of *t*-butyl chloride to sulfuric acid results in the formation of isobutane. This suggests that allylic hydride transfer from isobutylene is occurring.

(9) J. E. Hofmann, *J. Org. Chem.*, **29**, 3627 (1964).

(5) N. C. Deno, *Prog. Phys. Org. Chem.*, **2**, 137, 161 (1964).

(6) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).