Ionic Reactions Occurring in Sulfuric Acid. III. The Sulfuric Acid-Catalyzed Self-Alkylation of Isobutane with C_3–C_6 Olefins

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Quantitative data have been obtained for the acid-catalyzed self-alkylation of isobutane with branched and normal olefins ranging from propene to hexenes. It has been found that self-alkylation increases with both increasing molecular weight and branching of the olefin. At least two mechanistic schemes are required to interpret the data. The first, a classical protonation–hydride transfer sequence predominates with *n*-olefins while an alkylation–fission sequence is preferred for isoolefins.

The abnormal reaction of isobutane with certain olefins, particularly C_{5+} branched olefins, has been known for almost as long as the alkylation reaction itself.[1] The over-all reaction involves the combination of 2 moles of the isoparaffin and thus came to be known as "self-alkylation" (reaction 1) or hydrogen transfer.

$$2i\text{-}C_4H_{10} + C_nH_{2n} \longrightarrow i\text{-}C_8H_{18} + C_nH_{2n+2} \qquad (1)$$

With isobutane as the isoparaffin, the octanes formed are similar to that observed when isobutene is employed as the reactant olefin.

The mechanism for self-alkylation has been explained in terms of familiar carbonium reactions.[2] The olefin is protonated (reaction 2) and the resulting carbonium

$$C_nH_{2n} + H^+ \rightleftharpoons C_nH^+_{2n+1} \qquad (2)$$

is saturated by hydride transfer with the isoparaffin (reaction 3). The *t*-butyl cation is in equilibrium with

$$C_nH^+_{2n+1} + i\text{-}C_4H_{10} \longrightarrow C_nH_{2n+2} + t\text{-}C_4H_9^+ \qquad (3)$$

isobutylene (reaction 4), and the isobutylene thus

$$t\text{-}C_4H_9^+ \rightleftharpoons H^+ + i\text{-}C_4H_8 \qquad (4)$$

formed is alkylated to form the trimethylpentyl cation (reaction 5).

$$t\text{-}C_4H_9^+ + i\text{-}C_4H_8 \longrightarrow (CH_3)_3CCH_2\overset{+}{C}(CH_3)_2 \qquad (5)$$

Despite the general knowledge available, only limited quantitative data have appeared in the literature. McAllister[1] presents evidence that self-alkylation increases with molecular weight and increased branching, while Schmerling[3] reports on the reaction between propylene and isobutane using aluminum chloride monomethanolate as the catalyst. Such data are of interest from both a process point of view as well as from mechanistic considerations. Process wise, product quality will certainly be a function of the degree of self-alkylation while mechanistically it is important to compare observed results with the reaction scheme described previously. This paper discusses quantitative data for olefins ranging from C_3 through C_6 (including C_4-olefins).

Experimental

All experiments were carried out in a 1-l. magnetically agitated autoclave. Isobutane (3.8 moles) and 220 g. of concentrated (97.7 wt. %) sulfuric acid were charged to the autoclave. Approximately 2 wt. % acid sludge was added to minimize any inducation period.[4] After equilibrating the autoclave at 10°, 0.35 mole of olefin was added continuously over a 2-hr. period. At the end of this period, the total of the hydrocarbon phase was sampled and analyzed by gas chromatography using a Perkin-Elmer Model 154 gas chromatograph equipped with a 21-ft. column of Dow Corning (DC-200) silicone oil at 75°.

Concentrated sulfuric acid from American Cyanamide and Matheson research grade isobutane were employed throughout this study. Phillips pure grade olefins were used in all cases except for propylene which was Matheson C.P. grade.

Results

Alkylate compositions on a pentane and higher basis are shown in Table I for each of the olefins studied. Moles of C_8 and moles of saturated paraffin of the same carbon number as the reactant olefin were calculated from the total hydrocarbon composition as determined by the gas chromatographic analysis. The degree of self-alkylation, as determined by octane formation, as a function of carbon number of the reactant olefin is shown in Fig. 1. Figure 2 contains a comparison of octane formation with the amount of olefin that was saturated to a paraffin at the same carbon number.

Discussion

Figure 1 shows the trend of self-alkylation with increasing molecular weight and is similar to what has been observed in the past.[1] That is, self-alkylation increases with increasing molecular weight and increased branching of the olefin. The data presented for the C_4-olefins, 1-butene and isobutylene, were obtained during studies of the alkylation of C^{14}-labeled olefins.[5] Experimentally, these data were obtained under slightly different conditions, principally continuous *vs.* batch operation, but the over-all conditions were close enough to make a reasonable comparison.

For simplicity, data interpretation can be broken into two separate categories:

Effect of Molecular Weight.—It is clear from Fig. 1 that self-alkylation increases with increasing carbon number for both the normal and branched olefins. If one adopts as a mechanism for self-alkylation the reactions previously outlined (reactions 2–5), then one step must be favored as the olefin molecular weight increases. Within a given series, *i.e.*, branched or normal, it is not likely that the rate of protonation (reaction 2) or equilibrium would change markedly from olefin to olefin. Likewise, relative rates of hydride transfer (reaction 3) should not vary appreciably for a given series. Since the mechanism, particularly with regard

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[1] S. H. McAllister, J. Anderson, S. A. Ballard, and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941).

[2] L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, p. 375.

[3] L. Schmerling, *J. Am. Chem. Soc.*, **68**, 275 (1946).

[4] J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 953 (1962).

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

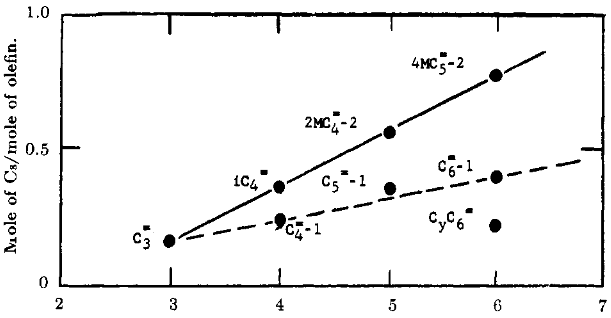


Fig. 1.—Effect of molecular weight.

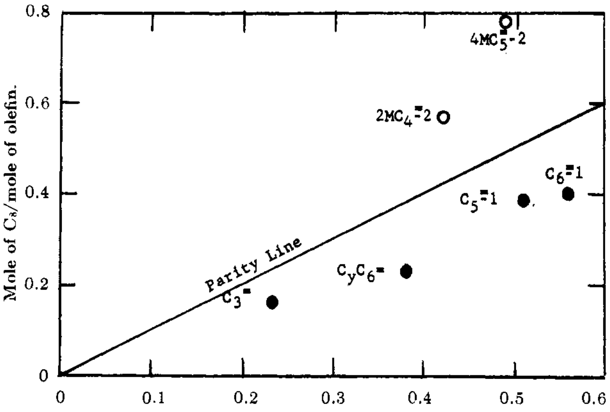
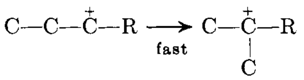


Fig. 2.—Comparison of C_8 formation with olefin saturation (the saturated paraffin having the same carbon number as the reactant olefin).

to normal olefins, appears to be proper, it is apparent that some other phenomenon must be operative. This could be physical and involve more rapid extraction of the higher molecular species into the hydrocarbon phase. However, any rigorous explanation at this time would be premature.

Effect of Branching.—Comparison of branched *vs.* normal olefins is somewhat more obvious. Protonation of a branched olefin leads to a tertiary carbonium ion as compared to a secondary ion for a normal olefin. The enhanced stability of tertiary ions drives protonation (reaction 2) to the right, and this in turn leads to more self-alkylation *via* the subsequent steps. An interesting point that must also be considered in this comparison is the fact that the product from self-alkylation of normal olefins is always predominantly the corresponding isoparaffin. For instance, from Table I it can be seen that isopentane is formed from 1-pentene, 2- and 3-methylpentane from 1-hexene, and a large amount of methylcyclopentane from cyclohexene. This has been observed in the past[3] and most likely arises because a secondary ion, once formed, rapidly rearranges to a more stable tertiary ion (reaction 6).



$$\text{C—C—}\overset{+}{\text{C}}\text{—R} \xrightarrow[\text{fast}]{} \text{C—}\underset{\substack{|\\ \text{C}}}{\overset{+}{\text{C}}}\text{—R} \qquad (6)$$

This still leaves the rate at which the original normal olefin is protonated at the limiting factor which differentiates between normal and isoolefins.

General Mechanistic Considerations.—Although the mechanism outlined in reactions 2–5 explains the normal products of self-alkylation, it does not allow for by-product formation. (By-products are defined as those hydrocarbons that have carbon numbers other than the carbon number of the olefin, a C_8, or the normal alkylation product of the olefin and isobutane.) Alkylation of the normal olefins leads to only a small amount of by-products and does not require additional interpretation. However, during alkylation of the two isoolefins, a relatively large amount of by-products are formed (isohexanes from the methylbutene; isopentane and isoheptanes from the methylpentene). Explanation of these materials requires additional reactions, and these in turn have direct bearing on the mechanism of self-alkylation.

If, during β-fission, only fragments of C_4 and larger can be formed, then formation of a C_6 from isobutane and a C_5-olefin must arise from a C_{10} or larger. Likewise, formation of C_5 and C_7 compounds from isobutane and a C_6-olefin requires at least some C_{11} or higher as intermediates. Formation of these higher molecular weight intermediates requires olefin dimerization or at least two successive alkylation steps. The rapid rate at which isobutylene tends to polymerize and undergo nonselective cracking was noted during our tracer studies.[5] A similar alkylation–fission sequence has been demonstrated during the sulfuric acid-catalyzed isomerization of isoparaffins.[6] Rapid dimerization of a C_5-olefin leads to a C_{10}, which in turn can crack to fragments of C_6 and C_4 or C_5 and C_5. In the latter case, differentiation between the classical mechanism for self-alkylation and this mechanism is impossible. However, if both the normal and isoolefins were initially dimerized, one can expect similar nonselective cracking patterns. Since only the isoolefins show a large amount of by-product formation, it is likely that they are also the only ones that participate in the alkylation–fission scheme[7] to any great extent.

By material balance and mass action, the buildup of higher molecular weight intermediates followed by nonselective fission must be accompanied by the formation of isobutylene and subsequently octanes (as long as isobutane is in large excess). This is illustrated graphically in Fig. 2. The normal olefins and cyclohexene all fall below the parity line, while the two isoolefins are above the line. Below the line is indicative of less than 1 mole of C_8 for each mole of saturated paraffin of the same carbon number as the olefin. Since isobutylene itself would not be alkylated to C_8 with 100% selectivity, this situation could arise from reaction sequence 2–5 accompanied by the normal alkylation of isobutylene with about 70% selectivity. A point above the line requires that more octanes be formed than saturated paraffins of the same carbon number as the reactant olefin. For the isoolefins, this is a consequence of the aforementioned by-product formation. Reaction 7 is presented as one possible example of reaction

$$2C_6H_{12} + 5i\text{-}C_4H_{10} \longrightarrow 2C_5H_{12} + C_6H_{14} + 2C_8H_{18} \qquad (7)$$

stoichiometry which yields 2 moles of C_8 for each mole of C_6-olefin that is saturated to a C_6-paraffin.

This is only one of a number of over-all equations that could be written and each will require several addition and fission reactions. However, as long as by-products between C_5 and C_7 are formed, there will

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[6] G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 729 (1963).

[7] In this sense, alkylation could be the addition of *t*-butyl cation to an olefin or the addition of protonated olefin to another olefin, *i.e.*, olefin dimerization.

TABLE I

ALKYLATE COMPOSITIONS

	Experiment					
	1	2	3	4	5	6
Alkylate composition, mole %	Propylene	2-Methyl-2-butene	1-Pentene	4-Methyl-2-pentene	1-Hexene	Cyclohexene
Isopentane	3.1	36.2	31.6	22.4	8.3	1.3
n-Pentane	...	...	2.3	...	...	...
2,3-Dimethylbutane	2.4	5.7	1.2	3.3	0.7	1.2
2-Methylpentane	...	...	...	14.9	24.1	...
3-Methylpentane	...	1.3	0.1	4.5	12.8	...
n-Hexane	...	...	...	...	1.8	...
2,4-Dimethylpentane	21.9	1.5	0.5	2.1	1.0	...
2,3-Dimethylpentane, 2-methylhexane	52.2	1.8	0.2	3.5	0.3	...
Methylcyclopentane	...	...	...	...	...	30.5
Cyclohexane	...	...	...	...	...	...
2,2,4-Trimethylpentane	11.4	23.6	14.8	18.1	16.9	15.3
2,2,3-Trimethylpentane, 2,4- + 2,5-dimethylhexane	0.6	5.3	1.9	4.7	1.7	1.8
2,3,3- + 2,3,4-Trimethylpentane, 2,3-dimethylhexane	8.4	18.8	8.9	12.7	10.0	13.1
C_9	...	5.9	38.2	9.3	...	...
C_{10}	...	...	...	4.5	22.4	13.4[a]
Mole of paraffin[b]/mole of olefin	0.23	0.42	0.51	0.49	0.56	0.38
Mole of C_8/mole of olefin	0.16	0.57	0.38	0.78	0.40	0.23

[a] Possibly contains alkylated naphthenes. [b] Saturated paraffin having the same carbon number as the reactant olefin.

be an increase in octane formation. Since paraffins with the same carbon number as the reactant olefin are also formed by the alkylation–fission scheme, it is impossible to say how much is formed by this mechanism as compared to straight self-alkylation. It is clear, however, that considerably more alkylation–fission occurs with the isoolefins than with the normal olefins.

It is apparent from the preceding discussion that all the reaction products can be explained on the basis of classical carbonium ion reactions. However, the specific mechanistic route will depend to a large degree upon the reactant olefin. With normal olefins, the straight self-alkylation mechanism (reactions 2–5) appears to predominate. A normal hexene is particularly illustrative of this because alternative mechanisms would predict the formation of fairly large amounts of non-C_6 products. With isoolefins, an alkylation–fission sequence becomes increasingly important. This is borne out by the observed nonselectivity of the reactions with both the methylbutene and the methylpentene. Unfortunately, the general complexity makes it impossible to assess just how much of each mechanism is applicable to the different olefins.

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Identification of the Disultone from Sulfuryl Chloride and 1-Propanol

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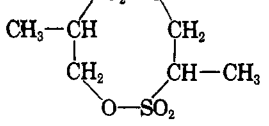
The crystalline product from the reaction of sulfuryl chloride with 1-propanol is assigned structure II on degradative and spectroscopic evidence. The mode of its formation is rationalized.

In 1952 Manecke[2] reported that sulfuryl chloride treatment of 1-propanol led to an eight-membered cyclic product to which he assigned structure I. Analytical and molecular weight data established the formula as $C_6H_{12}O_6S_2$, but it does not appear that alternate structures for the disultone were considered. Although hydrolytic and degradative reactions were reported, the structures of such products were not confirmed.

We have reinvestigated this reaction and established that the product is actually 4,8-dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-tetraoxide (II).[3] Repetition of Manecke's procedure afforded the same material in an over-all yield of 3% (the yield was not reported originally); modifications increased the yield



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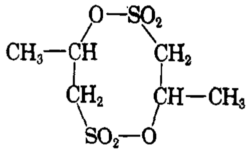

II

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(1)(a) To whom inquiries should be addressed at Williams College; (b) based in part on the Honors theses of B.A.H., Jr. (1962), and C.W.N. (1960), Williams College; (c) Iowa State University.

(2) G. Manecke, *Chem. Ber.*, **85**, 160 (1952).

(3) The correct structure was originally proposed to us by Professor W. von E. Doering; his interest and encouragement in this work are gratefully acknowledged.