The Oxidation of Paraffins in Sulfuric Acid

G. M. KRAMER

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

Received September 29, 1966

Branched paraffins have been found to undergo moderately long-chain reactions in concentrated sulfuric acid after an induction period during which oxidation occurs. The chain lengths decrease as conversion proceeds. The small amount of oxidation observed is attributed essentially entirely to the initial reaction of the paraffin and not to secondary reactions of product olefins.

Carbonium ion theory provides a convenient basis for the discussion of an enormous range of reactions. The behavior of branched paraffins in concentrated sulfuric acid in particular has been the subject of numerous investigations which lend themselves readily to this theory. Still, little quantitative information is available dealing with the initiation process by which the ions form and its relation to observed reactivity.

In a previous paper,[1] and in agreement with others,[2,3] it has been noted that 2,3,4-trimethylpentane reacts in sulfuric acid after an induction period during which sulfur dioxide is formed. The reaction follows a second-order dependence on acidity which can be rationalized by assuming that a steady-state carbonium ion concentration, depending in part on oxidation of the paraffin by a species like HSO_3^+, is reached. While the nature of the oxidizing species is still in doubt, evidence has been developed to show that oxidation precedes a carbonium ion chain reaction of considerable length. The oxidation process appears to have a low activation energy and the length of the carbonium ion chain dwindles with time. Data have also been obtained which indicate that oxidation which is found is essentially due to reaction of the paraffins and not in any substantial amount to secondary oxidation of olefins or other by-products of the initial reaction.

Experimental Section

The oxidation of a series of paraffins was studied under two slightly different reaction conditions. Under condition A, equal volumes of hydrocarbon and acid were vigorously contacted for variable lengths of time in a "Wig-L-Bug" shaking apparatus. The initial temperature was 25 ± 2° and it increased by 2.5°/min under typical reaction conditions. These experiments are considered to be pseudo-adiabatic.

In the second series of experiments (B) a chilled air stream was used to maintain an average temperature in the reactor of 21 ± 2°. The temperature was measured with a flexible thermocouple immersed in the reactor during actual runs.

The reactor was a 5-cc vial containing 1.5 cc of H_2SO_4 and 1.5 cc of hydrocarbon. After reaction the vial was cooled, a portion of the hydrocarbon layer was taken for gas chromatographic analysis, and the remaining hydrocarbon and acid layers were analyzed for total sulfur dioxide content. The latter was determined by standard iodine–sodium thiosulfate titration procedures using chloroform to provide a sharp end point. Reactions were generally run in triplicate or quadruplicate with repetitive blanks interspersed among them.

Research grade paraffins which were treated with 80% H_2SO_4, and washed, distilled, and stored over molecular sieves to remove possible unsaturated contaminants were used in all the experiments. Sulfuric acid of the desired strength was prepared by adding water or oleum to standard 96% H_2SO_4 and was determined by NaOH titration.

Results and Discussion

In Table I are summarized the extent of oxidation and conversion observed for a series of oxidation experiments under pseudo-adiabatic (A) and pseudo-isothermal (B) conditions.

TABLE I

OXIDATION AND CONVERSION OF BRANCHED, SATURATED HYDROCARBONS IN 98.5% SULFURIC ACID

	Condn, 2 min			
	Pseudo-adiabatic, $T = 27.5 \pm 2°$		Pseudo-isothermal, $T = 21 \pm 2°$	
Compound	SO_2, ppm[a]	Convn, %[b]	SO_2, ppm	Convn, %
3-Methylpentane			17	<1
2-Methylpentane			17	<1
2,4-Dimethylpentane	25	1	17	<1
2,3,4-Trimethylpentane	⩾80	21	23	7.0
2,2,4-Trimethylpentane	59	6.6	33	0.7
2,3-Dimethylbutane	50			
Methylcyclopentane	29		23	

[a] In the acid. [b] Conversion is based on the extent of isomerization or cracking of the paraffin.

The conversion figures are based on the extent of isomerization and cracking of the paraffins, neglecting the oxidation reaction which would only make a minor contribution to the term. For example, the formation of 23 ppm of SO_2 in the acid upon reaction with 2,3,4-trimethylpentane corresponds to only 0.01% oxidation. If we assume that oxidation does in fact lead to the formation of carbonium ions which initiate isomerization, polymerization, and cracking reactions, then it is evident that long-chain reactions propagated by hydride transfer from isoparaffins to the ions are in effect. The data suggest that oxidation of the more highly branched paraffins occurs more readily than that of the less branched paraffins. In addition, the difference in oxidation under the pseudo-adiabatic and isothermal conditions indicates a fairly low activation energy of ~6 to 10 kcal/mole for this reaction.

In the pseudo-isothermal experiments, additional SO_2 formation was not detected after 2 min with any of the hydrocarbons. This could be due either to the formation of an inhibitor or to the fact that hydride transfer from the paraffins to carbonium ions in the acid becomes a dominating competing reaction.

Continual oxidation and SO_2 formation are, however, readily detected in prolonged pseudo-adiabatic experiments. The relationship between the extent of oxidation and conversion for 3-methylpentane, 2,4-dimethylpentane, and 2,3,4-trimethylpentane is shown in Figure 1. In every case it is clear that conversion is preceded by a small amount of oxidation. Long-chain conversion processes, the chain length of which may be estimated from the slopes in Figure 1, then follow. The

---

(1) G. M. Kramer, *J. Org. Chem.*, **32**, 920 (1967).

(2) R. L. Burwell and G. S. Gordon, *J. Am. Chem. Soc.*, **70**, 3128 (1948).

(3) G. S. Gordon and R. L. Burwell, *ibid.*, **71**, 2355 (1949).

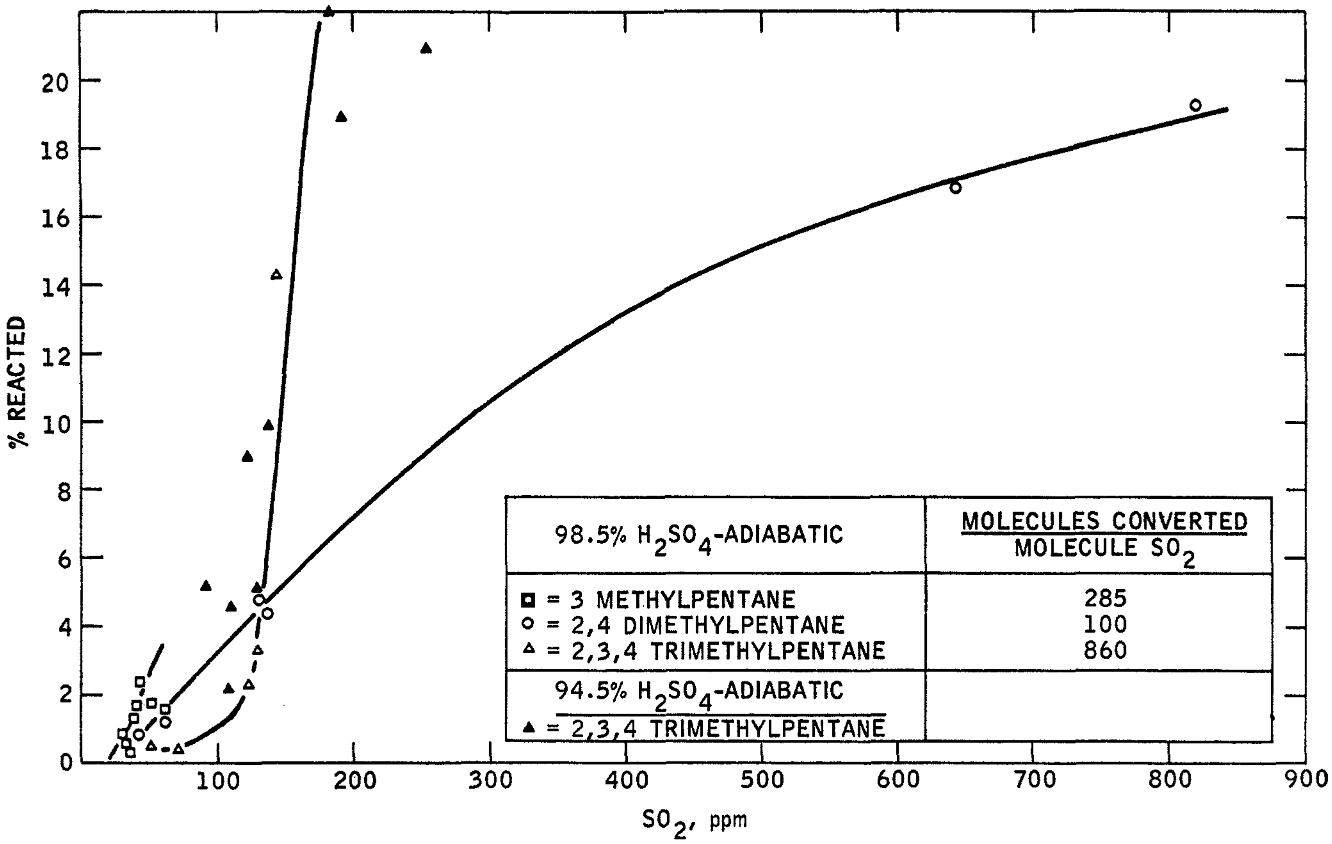

Figure 1.—Oxidation initiates long-chain processes.

apparent chain lengths, *L*, of molecules reacted per initiator formed is 285 for 3-methylpentane, 100 for 2,4-dimethylpentane, and 860 for 2,3,4-trimethylpentane. It is interesting to note that the relationship between oxidation and chain length found in 98.5% acid is essentially the same as that obtained in 94.5% acid, although the oxidation rate is much faster in the stronger acid.

The estimated *L* values are for "forward" reactions only and are therefore lower than the true chain lengths. Still, it is clear that the initial oxidation leads to the formation of intermediates which participate in fairly long chain processes. It is, however, difficult to obtain quantitative comparison of the reactivity of the individual paraffins. For example, the apparent conversions after little oxidation lie in the order 3-methylpentane > 2,4-dimethylpentane > 2,3,4-trimethylpentane, but the order clearly changes with time. Further, this measure of reactivity is incompatible with the ease of oxidation order, 2,3,4-trimethylpentane > 3-methylpentane = 2,4-dimethylpentane as in Table I.

An additional problem inherent in comparing the reactivity of trimethylpentanes with the methylpentanes and dimethylpentanes is that the trimethylpentyl cations appear to readily rearrange and cleave to *t*-butyl cations and isobutylene.[1,4] The cleavage reaction, at least at low conversions in strong acid, thus leads to a very much higher intermediate concentration than is obtainable from the hexanes and heptanes.

A characteristic feature of the oxidation–conversion curves is that the chain length severely diminishes with time. To some extent this may be due to the drop in acidity accompanying the oxidation process. That this is not the sole factor, however, is indicated by the similar curves with 2,3,4-trimethylpentane in 98.5 and 94.5% acid. It seems more likely that the drop in chain length is due to the formation of an inhibitor.

Concerning the formation of SO_2, one may raise the question of whether it arises solely by reduction of the acid by the paraffins, or in part by subsequent reaction of the initial products, as is shown in eq 1–3, where

$$RH + HSO_3^+ \longrightarrow R^+ + H_2O + SO_2 \qquad (1)$$

$$R^+ \rightleftharpoons R\colon + H^+ \qquad (2)$$

$$R\colon + HSO_3^+ \longrightarrow R^+ + H_2O + SO_2 \qquad (3)$$

HSO_3^+ is postulated as the oxidizing species. This possibility was tested in a series of isothermal experiments in which 2-methyl-2-butene in varying amounts was added to 98.5% acid. Reaction times varied from 0.05 to 30 min. In all cases (Table II), a small, fairly

Table II

Oxidation of 2-Methyl-2-butene in 98.5% Sulfuric Acid (2 Min, Pseudo-Isothermal, 21 ± 2°)

Time, min	Concn, mole/l.	SO_2 in acid, ppm
0.05	0.012	8.8 ± 3
2	0.120	
	0.012	13.5 ± 3
	0.0065	
5	0.120	13.3 + 3
30	0.120	9.0 ± 3
5	0.060[a]	46

[a] Added in five equal increments at 1-min intervals.

---

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

reproducible amount of SO_2 was formed. The experiments show that oxidation occurs immediately upon contact of the olefin with the acid and not after the olefin is adsorbed. This being the case, it should be possible to obtain more oxidation by a very slow or stepwise addition of olefin to the acid. This was found in an experiment in which five stepwide additions of olefin increased the SO_2 yield four- to fivefold.

A plausible explanation of these results is that the olefin is oxidized at the surface of the acid as it is being adsorbed, but once adsorbed it is converted to a form which is not easily oxidized. We believe that the inert form is mainly that of the *t*-amyl cation although other processes such as sulfonation or the extensive rearrangements leading to cyclopentadienyl ions, as proposed by Deno,[5] could also lead to a relatively stable species.

Registry No.—Sulfuric acid, 7664-93-9; 3-methylpentane, 96-14-0; 2-methylpentane, 107-83-5; 2,4-dimethylpentane, 108-08-7; 2,3,4-trimethylpentane, 565-75-3; 2,2,4-trimethylpentane, 540-84-1; 2,3-dimethylbutane, 79-29-8; methylcyclopentane, 96-37-7; 2-methyl-2-butene, 513-35-9.

Acknowledgment.—We wish to thank the Esso Research and Engineering Co., for permission to publish these results, and Dr. J. P. Kennedy, for his helpful comments.

---

(5) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 132 (1964).

The Cleavage of Sulfides and Sulfones by Alkali Metals in Liquid Amines. III. The Cleavage of Alkyl Cycloalkyl and Dicycloalkyl Sulfides and Sulfones by Lithium in Methylamine[1a]

WILLIAM E. TRUCE AND FORREST J. FRANK

Department of Chemistry, Purdue University, Lafayette, Indiana

Received January 10, 1967

A series of *n*-alkyl cycloalkyl sulfides and sulfones and a dicycloalkyl sulfide and sulfone was treated with lithium in methylamine, and the direction of cleavage was determined. The sulfide cleavages may be rationalized in terms of a radical process, whereas sulfone cleavages seem to reflect appreciable carbanion character.

Metal in amine solutions have been employed for the cleavage of many organic compounds, and mechanisms have been proposed involving one-electron (radical) and two-electron transfer (carbanion) processes.[2] Cleavage of ethers with sodium in ammonia has been explained by a carbanion mechanism,[2,3] whereas cleavage of tetraalkylammonium halides has been postulated to involve a gradation of mechanisms in which tertiary and secondary groups cleave as radicals, and primary groups cleave as carbanions.[4] Sulfides are cleaved by calcium hexaammine to give products whose formation can be rationalized on the basis of radical or carbanion processes.[5] Of the systems used for cleaving sulfides and sulfones.[5-8] the most general one was found to be lithium in methylamine, producing a hydrocarbon and a mercaptan or sulfinic acid, respectively, in good yields.[7] Alkyl aryl sulfide cleavages by this system were accounted for in terms of radical processes.[8] On the other hand, dialkyl sulfide fission was explained on the basis of a gradation of mechanisms, *e.g.*, the cleavage of *n*-butyl *sec*-butyl sulfide yields equal amounts of *n*- and *sec*-butyl mercaptans, and the proposal was made that some factor other than radical or carbanion stability was involved.[8] In the present work, cleavage has been extended to a series of alkyl cycloalkyl sulfides and their corresponding sulfones and a dicycloalkyl sulfide and its sulfone.

Results

The sulfides shown below (I–IV) were prepared by nucleophilic displacement by mercaptide on a halide or tosylate. Cleavage was accomplished by dropwise addition of lithium dissolved in methylamine to a solution of sulfide in methylamine at the boiling point of the solvent (−7°).[7] After cleavage, the mercaptan fraction was isolated, and its composition was determined by vpc. Details and results of the cleavages are shown in Table I.

$\mathrm{R^A{-}S^B{-}CH(CH_2)_{n-1}}$

I, $R = C_6H_{11}$; $n = 5$
II, $R = n\text{-}C_7H_{15}$; $n = 5$
III, $R = n\text{-}C_7H_{15}$; $n = 6$
IV, $R = n\text{-}C_7H_{15}$; $n = 4$

Cyclohexyl cyclopentyl sulfide (I) cleaved chiefly at bond B (79%), whereas the amount of fission at bond B increased to 87% for cyclopentyl *n*-heptyl sulfide (II). Cyclohexyl *n*-heptyl sulfide (III) showed only a slight preference for bond-B breakage (56%), and the direction of cleavage shifted to bond A (62%) for cyclobutyl *n*-heptyl sulfide (IV).

The corresponding sulfones listed below were prepared by oxidation of the sulfides, and cleaved in the same manner as the sulfides except that the work-up differed. The sulfinic acid fraction was difficult to analyze; therefore the hydrocarbon fraction was analyzed by vpc, and the yield was determined by addition of an internal standard. Since a liquid cyclobutyl portion was desired for vpc analysis, a methyl group was placed in the 3 position of the cyclobutane ring,

---

(1) (a) Abstracted from the Ph.D. Thesis of F. J. F. (b) To whom inquires should be directed at Illinois Wesleyan University, Bloomington, Ill.

(2) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(3) F. J. Sowa, *et al.*, *J. Am. Chem. Soc.*, **59**, 603, 1488 (1937); **60**, 94 (1938).

(4) E. Grovenstein and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

(5) J. Van Schooten, J. Knotnerus, H. Boer, and Ph. M. Duinker, *Rec. Trav. Chim.*, **77**, 935 (1958).

(6) (a) F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); (b) R. C. Krug and S. Tocker, *J. Org. Chem.* **20**, 1 (1955); (c) G. K. Hughes and E. P. O. Thompson, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 269 (1949).

(7) W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

(8) W. E. Truce and J. J. Breiter, *ibid.*, **84**, 1621 (1962).