

- Chem. Ber.*, **97**, 1811 (1964); **98**, 2339 (1965); (b) G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966).
- (12) J. J. Gajewski, *J. Am. Chem. Soc.*, **90**, 7178 (1968); **93**, 4450 (1971).
- (13) G. A. Doorakian, H. H. Freedman, R. F. Bryan, and H. P. Weber, *J. Am. Chem. Soc.*, **92**, 399 (1970).
- (14) (a) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, **91**, 6042 (1969); (b) M. J. S. Dewar and S. Kirschner, *ibid.*, **93**, 4290, 4291 (1971); (c) K. Hsu, R. J. Bunker, and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **94**, 5639 (1972); (d) K. Hsu, R. J. Bunker, and S. D. Peyerimhoff, *ibid.*, **94**, 5639 (1972); (e) M. J. S. Dewar and S. Kirschner, *ibid.*, **96**, 6809, (1974).
- (15) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
- (16) Consideration of overlap alone in the reversible cyclopropane ring opening via a propane-1,3-diyl intermediate where there is no possibility of a third rotation leads to the prediction that the observed stereospecificity<sup>17</sup> should be due to a disrotatory pathway. The very extensive calculations<sup>18</sup> predict a conrotatory pathway since hyperconjugative destabilization of the orbitally symmetric biradial apparently outweighs overlap considerations.
- (17) (a) J. A. Berson and L. D. Pedersen, *J. Am. Chem. Soc.*, **97**, 238 (1975); (b) J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *ibid.*, **97**, 240 (1975); **98**, 122 (1976).
- (18) (a) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968); (b) D. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 279 (1972); (c) P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972).

## Oxyfunctionalization of Hydrocarbons. 3.<sup>1a</sup> Superacid Catalyzed Oxygenation of Alkanes with Ozone Involving Protonated Ozone, O<sub>3</sub>H<sup>+</sup>

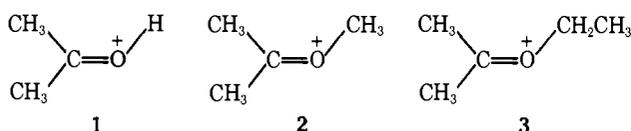
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**Abstract:** The reaction of ozone with a series of alkanes in superacid-SO<sub>2</sub>ClF solution has been investigated. Product analysis reveals that the reaction pathway involves oxygenation followed by a carbon to oxygen alkyl group migration analogous to the acid-catalyzed cleavage-rearrangement reaction of hydroperoxides. Mechanistic studies are consistent with electrophilic insertion into a  $\sigma$  bond by protonated ozone, O<sub>3</sub>H<sup>+</sup>.

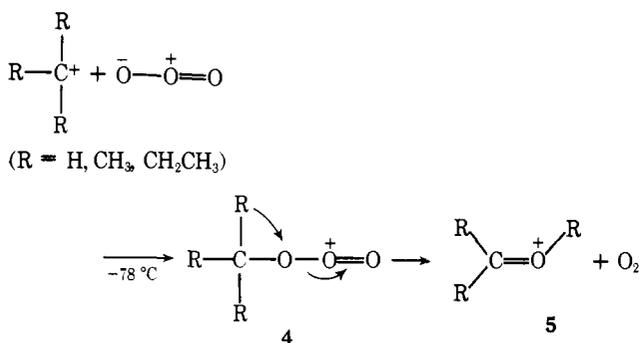
### Introduction

In the preceding paper of this series, we demonstrated the nucleophilic nature of ozone in its reactions with alkylcarbenium ions.<sup>1a</sup> In these reactions, 3–5% ozone in oxygen gas was bubbled through a solution of the alkylcarbenium ion, prepared from the corresponding alkyl halide in SO<sub>2</sub>ClF or SO<sub>2</sub> with FSO<sub>3</sub>H-SbF<sub>5</sub> (magic acid) or SbF<sub>5</sub> solutions.<sup>2</sup> NMR analyses of the ozonation products of the dimethylcarbenium ion, trimethylcarbenium ion, and dimethylethylcarbenium ion were consistent with the formation of protonated acetone (**1**), dimethylmethoxycarbenium ion (**2**), and dimethylethoxycarbenium ion (**3**), respectively.



The reactions can be described as shown in Scheme I. The oxygen eliminated from the intermediate trioxide (**4**) can be

Scheme I



considered to be in its singlet state as indicated, for example, in its ability to further oxidize products to the acetylium ion and subsequently to carbon dioxide. Such further oxidations as shown in control experiments could not be induced by ozone alone.

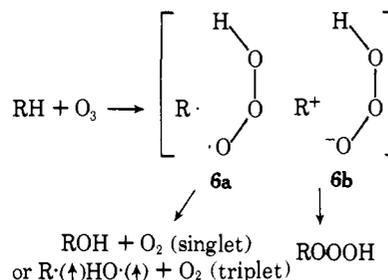
In continuation of our studies of oxyfunctionalization of hydrocarbons, we were interested in extending our investigation to the ozonation of alkanes in the presence of strong acids. We now wish to report the results of our studies of the electrophilic, magic acid catalyzed oxygenation of alkanes with ozone.

### Results and Discussion

In the reactions of propane, isobutane, and isopentane with ozone in magic acid-SO<sub>2</sub>ClF solution at -78 °C, the same products were obtained as from the reactions of the corresponding stable alkylcarbenium ions with ozone,<sup>1a</sup> that is **1**, **2**, and **3** in yields of 20, 45, and 40%, respectively.

It has been reported that the first step in the ozonation of alkanes has some characteristics of a radical reaction and some of an insertion reaction.<sup>3</sup> The most recent study<sup>4</sup> on the ozonation of alkanes still leaves considerable doubt as to the nature of the initial intermediate (**6**) depicted in Scheme II.

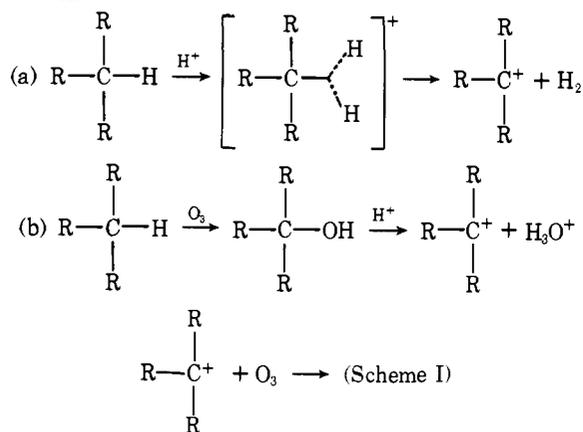
Scheme II



Varkony, Pars, and Mazur<sup>4a</sup> proposed formation of an ozone-hydrocarbon complex, followed by electrophilic oxygen insertion into a C-H bond, whereas Hellmann and Hamilton<sup>4b</sup> favor as the major contributing form **6a** since this would readily give O-O bond cleavage leading to formation of the observed products. Contributions from **6b**, which would give the trioxide, were considered not to be significant since experiments by Whiting<sup>5</sup> showed no evidence for a trioxide intermediate in alkane ozonation under the conditions where the trioxide formed in isopropyl alcohol oxidation is readily detected.

For the reactions under our present experimental conditions it is possible to postulate formation of an alkylcarbenium ion via protolysis of the alkane<sup>6</sup> prior to the ozone quenching of that ion, as shown in Scheme III(a). Alkylcarbenium ions may also be generated via initial oxidation of the alkane to an al-

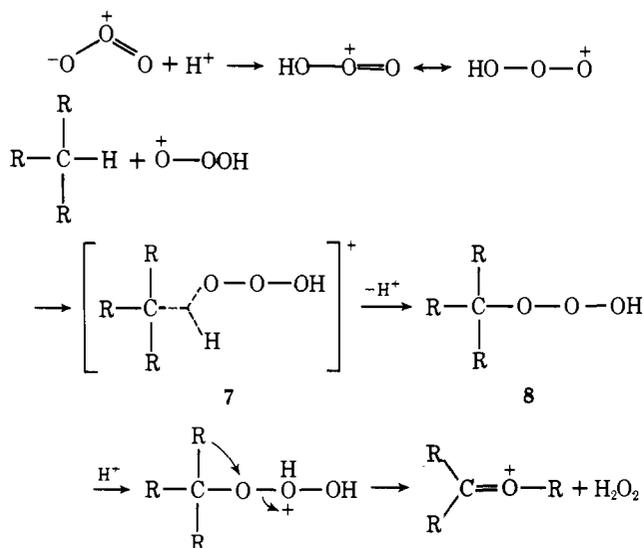
Scheme III



cohol, followed by protonation and dehydration as shown in Scheme III(b), since there have been a number of reports of ozone reacting with alkanes yielding alcohols and ketones.<sup>4,5,7</sup> In both cases, intermediate alkylcarbenium ions then would undergo nucleophilic reaction with ozone to give **4** as in Scheme I.

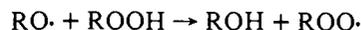
However, one may also postulate another path for these reactions, namely electrophilic attack by protonated ozone on the alkanes, resulting in oxygen insertion into a single bond, as shown in Scheme IV. Since ozone has a strong 1,3-dipole<sup>8a</sup> or at least strong polarizability, even if a singlet biradical structure is also feasible,<sup>8b</sup> it would be expected to readily

Scheme IV



protonate in superacids in an analogous manner of alkylation of ozone by alkylcarbenium ions. Protonated ozone,  $\text{O}_3\text{H}^+$ , once formed should have much higher affinity (i.e., a more powerful electrophile) for  $\sigma$ -donor single bonds in alkanes than neutral ozone and would thus be expected to initiate ozonolysis of alkanes in a similar manner to nitrolysis by the nitronium ion  $\text{NO}_2^+$ <sup>9</sup> and chlorolysis by the incipient chloronium ion  $\text{Cl}^+$ <sup>10</sup> or the more generally studied protolysis by<sup>6</sup> superacids.

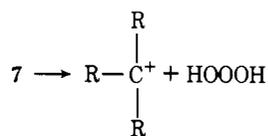
Loss of a proton from **7** yields the neutral hydrotrioxide **8**. Such neutral trioxides have been proposed as intermediates in the decomposition of tertiary alkyl hydroperoxides with lead tetraacetate<sup>11</sup>



and in the ozonation of ethers,<sup>12</sup> aldehydes,<sup>13</sup> and alcohols.<sup>14</sup>

More recently Bartlett and Laha<sup>15</sup> isolated crystalline trioxides, stable below  $-30^\circ\text{C}$ , by ozonolysis of *tert*-butyl hydroperoxide, the sodium salt of *tert*-butyl hydroperoxide, or the sodium salt of cumyl hydroperoxide.

Another possible cleavage path for transition-state **7** would give alkylcarbenium ion and hydrogen trioxide:



Hydrogen trioxide is reported, although extremely unstable, decomposing into water and oxygen.<sup>16</sup>

The question of which mechanism(s) is operative will be discussed subsequently with reference to the experimental results of the ozonation of specific alkanes in strong acid media.

**Branched Alkanes. Isobutane and Related Isoalkanes.** A stream of  $\lesssim 10\%$  ozone containing oxygen was passed through a solution of isobutane in  $\text{SO}_2\text{ClF}-\text{SbF}_5-\text{FSO}_3\text{H}$  solution held at  $-78^\circ\text{N}$ . Upon introduction of ozone, the colorless solution immediately turned a brown color.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the resultant solution were consistent with formation of the dimethylmethoxycarbenium ion (**2**) in 45% yield together with trace amounts of the acylium ion,  $\text{CH}_3\text{CO}^+$ .

Similar treatment of isopentane, 3-methylpentane, and 3-ethylpentane resulted in formation of carboxonium ions having the skeletal structure of **5** as the major product. The results of our experiments are summarized in Table I.

The data concerning isobutane and isoalkanes would seem to indicate that they could be in accord with either of the reaction pathways shown in Scheme III and Scheme IV. However, it should be noted that the rate of formation of the dimethylmethoxycarbenium ion from isobutane was remarkably faster than that of trimethylcarbenium ion from isobutane in the absence of ozone under the same conditions. Indeed, a solution of isobutane in excess magic acid- $\text{SO}_2\text{ClF}$  solution kept standing at  $-78^\circ\text{C}$  for 5 h showed only trace amounts of the trimethylcarbenium ion. Passage of a stream of oxygen gas through the solution for ten times longer than in case of ozonation experiments showed no effect. It was only when ozone was introduced into the system that rapid reaction took place.

On the other hand, *tert*-butyl alcohol itself in magic acid- $\text{SO}_2\text{ClF}$  solution gave readily and quantitatively the trimethylcarbenium ion even at  $-78^\circ\text{C}$  and in the presence of ozone under the same conditions gave the dimethylmethoxycarbenium ion.

Although, in our experiments, isobutane did not give any oxidation products in the absence of magic acid under the same

Table I. Products of Reaction of Alkanes with Ozone in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2\text{ClF}$  Solution<sup>a</sup>

Alkane	Reaction temp, °C	Major reaction products <sup>b,c</sup>
$\text{CH}_4$	-50 <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}^e$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3^f$
$\text{CH}_3\text{CH}_3$	-78 <sup>a</sup>	$\text{CH}_3\text{C}(\text{H})=\overset{+}{\text{O}}\text{H}g, i$
	R.T. <sup>d</sup>	same <sup>g</sup>
$\text{CH}_3\text{CH}_2\text{CH}_3$	-78	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}h, i$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}^i$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-78	$\text{CH}_3\text{C}(\text{H})=\overset{+}{\text{O}}\text{CH}_2\text{CH}_3,$ $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\overset{+}{\text{O}}\text{H}i, j$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3^i$
$(\text{CH}_3)_3\text{CH}$	-78	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3^k$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-78	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_2\text{CH}_3,$ $(\text{CH}_3\text{CH}_2)_2\text{C}=\overset{+}{\text{O}}\text{H}^l$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3^i$
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	-78	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_2\text{CH}_3^m$
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$	-78	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}(\text{CH}_3)_2,$ $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}^i, n$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}(\text{CH}_3)_2,$ $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}^n, o$
$(\text{CH}_3\text{CH}_2)_2\text{CHCH}_3$	-78	$\text{C}_2\text{H}_5(\text{CH}_3)\text{C}=\overset{+}{\text{O}}\text{C}_2\text{H}_5, p$
$(\text{CH}_3\text{CH}_2)_2\text{CHCH}_2\text{CH}_3$	-78	$(\text{CH}_3\text{CH}_2)_2\text{C}=\overset{+}{\text{O}}\text{CH}_2\text{CH}_3, p$
$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$	-78	$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{C}=\overset{+}{\text{O}}\text{CH}_3,$ $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{H}^q, i$
	R.T. <sup>d</sup>	$(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3^k$

<sup>a</sup> In all experiments, a 3–4 mol excess of ozone to alkanes was used. Conversion of alkanes was almost 100% in all cases, except for methane and ethane. For equal amounts of ozone and alkane, 30% conversion of propane, 45% of isobutane, and 40% of isopentane were observed. <sup>b</sup> Assignments of product were made by comparison of their NMR spectra with previously reported data; see: G. A. Olah, D. H. O'Brien, and M. Caline, *J. Am. Chem. Soc.*, 89, 3582, 3586 (1967); G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc.*, 96, 884 (1974); G. A. Olah, D. G. Parker, N. Yoneda, and F. Pelizza, *J. Am. Chem. Soc.*, 98, 2245 (1976). <sup>c</sup> Product analysis indicated the formation of  $\text{CO}_2$  in most reactions, as well as formation of minor unidentified by-products. Major products represent at least 70%, frequently up to 90%, of all products. <sup>d</sup> A mixture of 4 mol excess ozone and alkane was passed through magic acid- $\text{SO}_2\text{ClF}$ . For room temperature reactions neat magic acid was used. <sup>e</sup> Some 2 was also observed. <sup>f</sup> Some 1 was also observed. <sup>g</sup> Some 1, 2, and  $\text{CH}_3\text{C}^+=\text{O}$  were also observed. <sup>h</sup> 2 and  $\text{CH}_3\text{C}^+=\text{O}$  were also observed as minor products. <sup>i</sup> Other unidentified products were also formed. <sup>j</sup> 2 and 1 were also formed. <sup>k</sup> Almost 100%. <sup>l</sup> Protonated ketones,  $\text{R}_2\text{C}=\text{O}^+-\text{H}$ , were also observed. <sup>m</sup> Some 1 and  $\text{CH}_3\text{C}^+=\text{O}$  were observed. <sup>n</sup> By raising the temperature of the solution an increase of 1 was observed. <sup>o</sup> Some  $\text{CH}_3(\text{H})\text{C}=\text{O}^+-\text{H}$  and 2 were also found. <sup>p</sup> Formation of some  $\text{R}(\text{R}')-\text{C}=\text{O}^+-\text{H}$  was also observed. <sup>q</sup> Ratio of these products was 50:50.

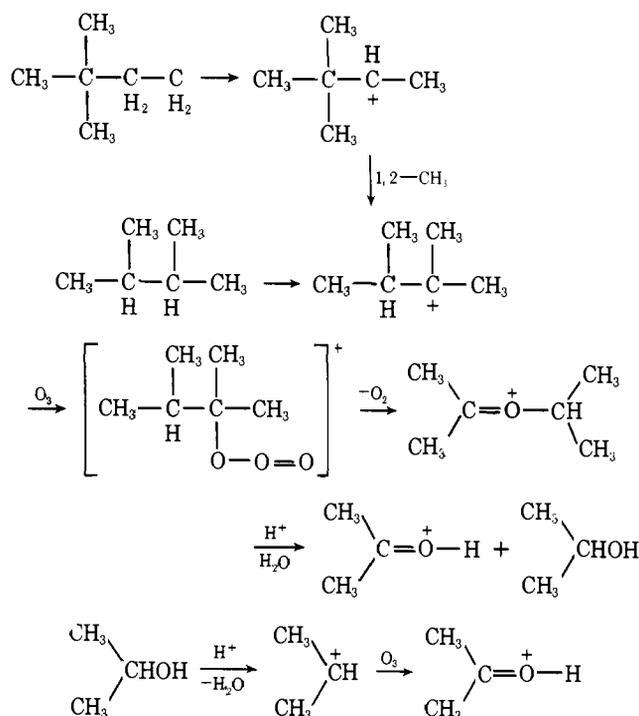
low-temperature ozonation conditions, we have not been able to definitely determine whether formation of intermediate oxidation products, such as alcohols, plays any role in the ozonation of alkanes in magic acid. There is, however, no experimental indication that for reactions proceeding via the intermediacy of carbenium ions initial oxidation of the alkanes to alcohols is important. This oxidation, indeed, was found to be extremely slow in the acidic media studied.

The results of ozonolysis for isoalkanes in magic acid can also be explained as being due to electrophilic insertion by

protonated ozone into tertiary C-H bond of the alkanes. Attempts to directly observe protonated ozone, i.e.,  $\text{O}_3\text{H}^+$  by  $^1\text{H}$  NMR spectroscopy, were inconclusive because of difficulty in differentiating between the chemical shift of  $\text{O}_3\text{H}^+$  and  $\text{H}_3\text{O}^+$ .

In principle, it should be possible to distinguish between the electrophilic insertion (Scheme IV) and the nucleophilic reaction with  $\text{O}_3$  (Scheme III), since, in the former, hydrogen peroxide is formed while the latter gives oxygen as the cleavage-rearrangement product of the intermediate trioxide **4**. Analysis of the final reaction solution for hydrogen peroxide proved negative. However, it is known that hydrogen peroxide reacts readily not only with ozone,<sup>17</sup> but also with alkylcarbenium ions and with alkanes in acid solutions.<sup>18</sup> Therefore, hydrogen peroxide formed in the reaction of alkanes with ozone in magic acid- $\text{SO}_2\text{ClF}$  solution would certainly react further by one or more of the above mentioned reactions. (We are reporting our studies of the oxygenation of alkanes with hydrogen peroxide in strong acids in detail in the following paper of this series.)

**2,2-Dimethylbutane and 2,3-dimethylbutane** in magic acid solution both gave the same distribution of products, namely 60% of dimethylisopropoxycarbenium ion (**9**), 35% of protonated acetone, and some acetylium ion  $\text{CH}_3\text{CO}^+$ , upon treatment with ozone at  $-78^\circ\text{C}$ . This clearly demonstrates the intermediacy of alkylcarbenium ions in these reactions, viz:



**Straight Chain Alkanes. Ethane and Propane.** Under the same ozonation conditions (magic acid in  $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ ), ethane gave protonated acetaldehyde as the major reaction product, together with formation of some acetone, dimethylmethoxycarbenium ion, acetylium ion,<sup>19</sup> and some yet unidentified minor by-products.

Propane, however, gave mainly protonated acetone (**11**) (90%), together with some protonated acetaldehyde (**9**) and acetylium ion. These products, excluding the acetylium ion,<sup>19</sup> can be derived from the alkylcarbenium ions which can be formed by the protolysis of the alkanes, followed by nucleophilic attack of ozone, as shown in Scheme V.

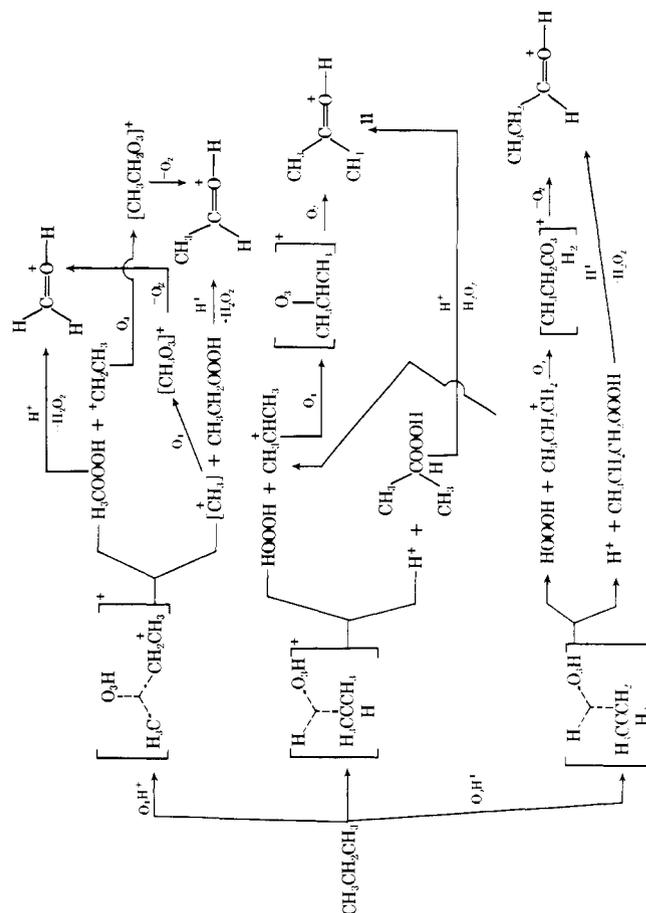
The product distributions obtained in both cases, however, are not in accord with those predicted based on the protolytic reactivity order of single bonds in alkanes, i.e.,  $\text{R}_3\text{C}-\text{H} > \text{C}-\text{C}$



Table II. Products of Reaction of Alkanes with Ozone in Various Acid-SO<sub>2</sub>ClF Solutions<sup>a</sup>

Alkane	Acid	Reaction temp, °C	Major reaction products <sup>b</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	FSO <sub>3</sub> H	R.T.	(CH <sub>3</sub> ) <sub>2</sub> C=O <sup>c</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>3</sub>	FSO <sub>3</sub> H	60	same
	FSO <sub>3</sub> H	-78 <sup>e</sup>	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	FSO <sub>3</sub> H	R.T.	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub> , (CH <sub>3</sub> ) <sub>2</sub> C=O <sup>g</sup> and CH <sub>3</sub> OH <sup>g</sup>
	FSO <sub>3</sub> H	60	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub> , (CH <sub>3</sub> ) <sub>2</sub> C=O <sup>g</sup> and CH <sub>3</sub> OH <sup>g</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	FSO <sub>3</sub> H	-78	CH <sub>3</sub> (H)C=OCH <sub>2</sub> CH <sub>3</sub> , CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> )=O, (CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub> <sup>f</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	FSO <sub>3</sub> H	-78	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>2</sub> CH <sub>3</sub> <sup>f</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>	FSO <sub>3</sub> H	-78	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>2</sub> CH <sub>3</sub> <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> CHCH(CH <sub>3</sub> )CH <sub>2</sub>	FSO <sub>3</sub> H	-78	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub> , (CH <sub>3</sub> ) <sub>2</sub> C=O <sup>d,g</sup>
	FSO <sub>3</sub> H	-78	(CH <sub>3</sub> ) <sub>2</sub> C=OCH <sub>3</sub> <sup>d</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>3</sub>	BF <sub>3</sub> -HF <sup>h</sup>	-78	same <sup>d</sup>
	HF	-78	same <sup>d</sup>
	H <sub>2</sub> SO <sub>4</sub>	-10	(CH <sub>3</sub> ) <sub>2</sub> C=O, CH <sub>3</sub> OH
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	60	CH <sub>3</sub> CH <sub>2</sub> (CH <sub>2</sub> )C=O <sup>f</sup>
	FSO <sub>3</sub> H	60	(CH <sub>3</sub> ) <sub>2</sub> C=O <sup>f</sup>

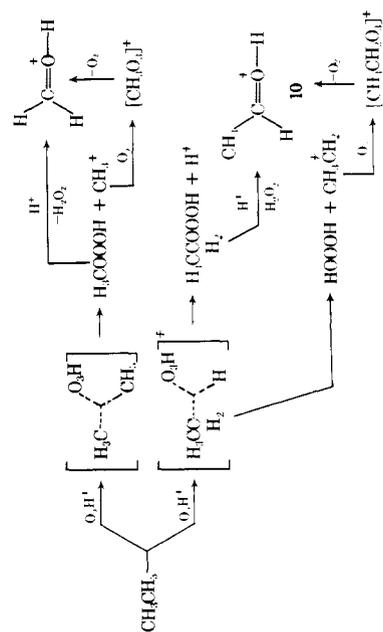
<sup>a</sup> In all experiments excess acid was used. In the reactions carried out above a temperature of -10 °C, the mixture of ozone (in O<sub>2</sub>) and alkane was passed through the neat acid. <sup>b</sup> Product assignments were made as described in Table I. Major products represent at least 70%, frequently up to 90%, of all products. <sup>c</sup> Small amounts of (CH<sub>3</sub>)<sub>2</sub>C=OCH<sub>3</sub> and CH<sub>3</sub>OH and some unknown by-products were also found. <sup>d</sup> With negligible amounts of by-products found. <sup>e</sup> In case of using equimolar amount of ozone and alkane at -78 °C, 6% conversion and at -30 °C, 40% conversion was obtained respectively. <sup>f</sup> Some yet unidentified by-products were also found. <sup>g</sup> The ratio of these products is 50:50. <sup>h</sup> The mixture of BF<sub>3</sub> and ozone-oxygen gas was bubbled through the solution of alkane in HF-SO<sub>2</sub>ClF.



from the reaction of ozone with the secondary butyl cation which can be derived from the protolysis of secondary C-H bonds in butane or dehydration of the secondary alcohol which would be an initial oxidation product of butane. However, attempts to prepare the secondary butyl cation from butane or 2-butanol in the absence of ozone under the same conditions were not successful. Besides unreacted butane and protonated *sec*-butyl alcohol, respectively, only the trimethylcarbenium ion could be observed at -50 °C. Consequently, even if the initial product of oxidation of butane were 2-butanol, it would finally give the dimethylmethoxycarbenium ion. 2-Butanol, under similar reaction conditions at -78 °C, showed no reaction with ozone, but as the temperature was raised above -50 °C reaction did occur, yielding the dimethylmethoxycarbenium ion.

The oxygenation of secondary C-H bonds in butane with O<sub>3</sub>H<sup>+</sup> which may have precedence over reaction with C-C bonds (because of probable steric effects) can give **13** and **14** as the major products. However, in sharp contrast to isobutane, and other isoalkanes, it should be noted that in order to form the dimethylmethoxycarbenium ion, even though it is a minor product, skeletal rearrangements involving methyl and hydrogen migration must have occurred in the course of reaction. In fact, when the reaction was carried out at room temperature, the major product was the ion **2**, strongly indicating in this case

Scheme VI



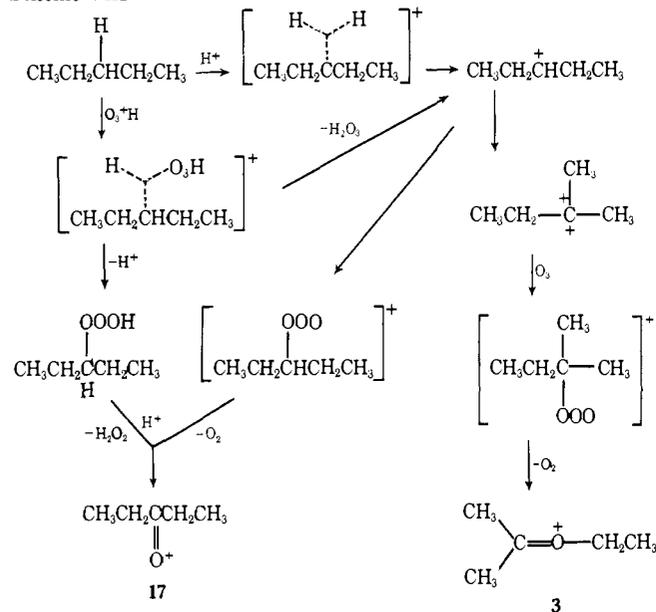


the formation of alkylcarbenium ion prior to reaction with ozone.

We feel these data conclusively show that, in the oxygenation with  $O_3H^+$ , the transition-states **15** and **16** can cleave losing hydrogen trioxide to give the incipient primary or the secondary butyl cations, followed by rearrangement to the trimethylcarbenium ion via methyl (hydrogen) migration.

Pentane when treated with ozone in magic acid- $SO_2ClF$  at  $-78^\circ C$  gave a more complex reaction mixture as indicated by the  $^1H$  NMR spectrum of the resultant solution. In this case, however, the dimethylethoxycarbenium ion **3** was one of the major products. This result indicates significant skeletal rearrangement of the linear molecule had occurred even at  $-78^\circ C$ , giving rise to the product **3** as shown in Scheme VIII.

Scheme VIII



It is known that the dimethylethylcarbenium ion may be derived from pentane in magic acid solution at  $-30^\circ C$ .<sup>20</sup> However, again it must be pointed out that the rate of its formation is very slow at  $-78^\circ C$ , i.e., under present experimental conditions.

The other major identified product in the reaction was protonated diethyl ketone (**17**), which could arise from direct nucleophilic attack by ozone on the diethylcarbenium ion or by electrophilic oxygenation by  $O_3H^+$  at the secondary C-H bond in pentane as shown in Scheme VIII.

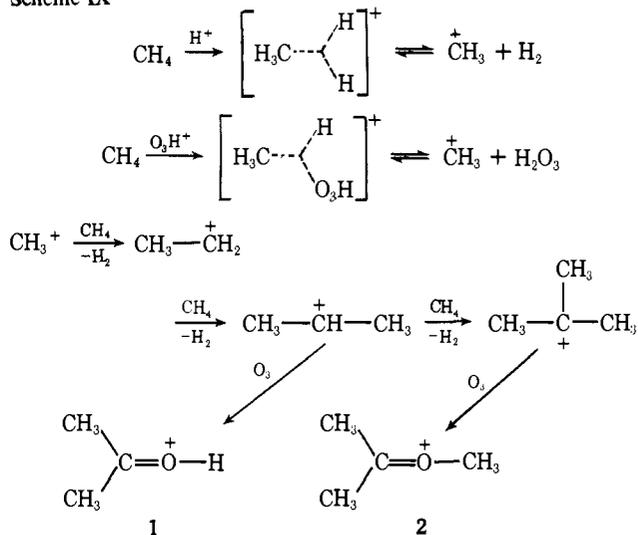
**Methane.** Further evidence for initial electrophilic attack by  $O_3H^+$  comes from the reaction of methane with ozone in magic acid.

When a mixture of methane and ozone (1:1 molar ratio of  $CH_4/O_3$ ) was passed through magic acid- $SO_2ClF$  solution at  $-50^\circ C$  or through neat magic acid at room temperature, the major reaction product was protonated acetone (**1**) at  $-50^\circ C$  and dimethylmethoxycarbenium ion (**2**) at room temperature, respectively. No formaldehyde could be detected in  $^1H$  NMR spectroscopic analysis of products.

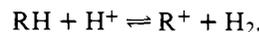
The data indicate the reaction to be almost exclusively nucleophilic oxygenation by ozone (or  $H_2O_2$  or  $H_2O_3$ ) of the alkylcarbenium ions which arise from the oligo-condensation of methane as shown in Scheme IX.

We have previously reported that methane can undergo oligomerization in magic acid solution, giving ethane, propane, isobutane, and higher alkanes through the corresponding carbocations.<sup>20</sup> However, it is required for this reaction with a reasonable rate to have a relatively high temperature ( $\geq 60$

Scheme IX



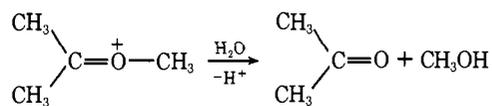
$^\circ C$ ). Indeed, when a stream of methane was passed through a magic acid solution in  $-SO_2ClF$  at a flow rate of 10 ml/min at  $-30^\circ C$  for 48 h, only a trace amount of the trimethylcarbenium ion could be detected in the resultant solution. Since we obtained significant amounts of oxygenated products in the presence of ozone under the same conditions with a reaction time of 6 h, we consequently feel formation of alkylcarbenium ion from methane should be a consequence of the electrophilic attack of  $^+O_3H$  of the C-H bonds of methane. Alternatively it could be visualized that the protolytic formation of carbenium ions in the absence of ozone is slow because of the unfavorable equilibrium



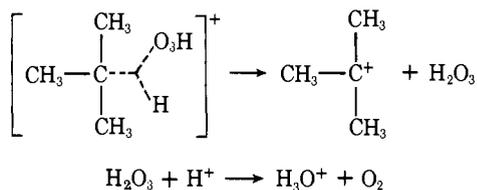
This equilibrium, however, in our experience does not show any significance at low concentrations and atmospheric pressure of  $H_2$ .

**Reaction of Alkanes with Ozone in  $HF-BF_3$ ,  $FSO_3H$ ,  $HF$ , and  $H_2SO_4$ .** To provide further evidence in support of the ozonization reaction via  $O_3H^+$ , we also studied the reaction of alkanes with ozone in the presence of acids weaker than magic acid, such as  $HF-BF_3$ ,  $FSO_3H$ ,  $HF$ , and  $H_2SO_4$ , which themselves, at the temperatures indicated, do not react with any of the alkanes to give carbenium ions. Ozonolysis of alkanes in these acids yields products identical with those formed, as discussed previously, in magic acid. We feel, consequently, that these results further prove that the reactions involve electrophilic oxygenation by  $O_3H^+$  of the alkanes.

The yield of dimethylmethoxycarbenium ion (**2**) was, however, low (5-10%) in the reaction of isobutane with ozone in these acid systems, diluted with  $-SO_2ClF$  at  $-78^\circ C$ . Ozone in the presence of these acids obviously acts as a weaker agent than in the presence of magic acid. Another feature of the reactions is an increase of products such as acetone and methanol which can be derived from hydrolysis of the intermediate ion **2**, upon increasing the reaction temperature.



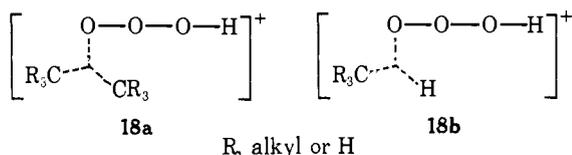
Since there is little water present in the system at the outset of the reaction, it must be formed as the reaction proceeds. A probable source of water would be hydrogen trioxide<sup>16</sup> formed from cleavage of the pentacoordinated carbonium ion in the hydrogen-abstraction step:



That hydrolysis of carboxonium ions is not significant in magic acid solution is due to the fact that water is completely protonated, deactivating it as a nucleophile.

### Conclusions

We have investigated the electrophilic oxygenation of alkanes with ozone in magic acid- (or HF-BF<sub>3</sub>, FSO<sub>3</sub>H, HF, and H<sub>2</sub>SO<sub>4</sub>) SO<sub>2</sub>ClF solutions at temperatures of -78 °C to room temperature. Our primary mechanistic interest in this study was focused on the question of whether ozone plays the role of a nucleophilic or electrophilic reagent in the reaction. From the results obtained it seems reasonable to conclude that the reactions are those of an electrophilic insertion into the single  $\sigma$  bonds of the alkane, effected by protonated ozone, i.e., O<sub>3</sub>H<sup>+</sup>, similarly to such electrophilic reactions as protolysis, chlorolysis, and nitrolysis of alkanes. We consider, when postulating protonated ozone as an obviously more powerful electrophile than neutral ozone, that the hydrocarbon-ozone complex transition state will be represented by the pentacoordinated ions **18a** and **18b**:



(The concept of pentacoordinated carbonium ion formation, with subsequent cleavage to trivalent carbenium ions and hydrogen trioxide or alkyl hydrotrioxide, satisfactorily explains the results of saturated hydrocarbon reactions with ozone in the presence of strong acid media.

### Experimental Section

**Materials.** All the alkanes were commercially available and of highest purity and were used without further purification. SbF<sub>5</sub> and FSO<sub>3</sub>H were used after distillation. The ozone generator was a Welsbach T-816 which yielded 3-15% ozone at a rate of 0.2 ~ 0.5 l/min<sup>-1</sup> oxygen gas flow.

**Reaction Apparatus.** The reaction apparatus was constructed of glass, except when using HF, and was provided with suitable gas inlet and outlets for sampling and introduction of reagents. When using HF the reaction vessel and inlets were made out of Teflon.

**Ozonolysis.** The solution of alkane (~5-10 mmol) and acid (~10-60 mmol) in SO<sub>2</sub>ClF was placed in the reaction vessel at the reaction temperature. Then ozone (~5-50 mmol) contained in an O<sub>2</sub> stream was passed through the solution. For higher temperatures (above room temperature), the mixture of alkane and ozone was passed through the neat acid. After addition of excess ozone, the solution was subjected to analysis by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The experimental conditions and analytical methods used were similar to those used and described in our preceding work.<sup>1a</sup>

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### References and Notes

- (1) (a) Part 2: G. A. Olah, N. Yoneda, and D. G. Parker, *J. Am. Chem. Soc.*, **98**, 2251 (1976); (b) Postdoctoral fellows.
- (2) See for example, G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973).
- (3) G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15, 1968.
- (4) (a) H. Varkony, S. Pašš, and Y. Mazur, *J. Chem. Soc., Chem. Commun.*, 437 (1974); (b) T. M. Hellman and G. A. Hamilton, *J. Am. Chem. Soc.*, **96**, 1530 (1974).
- (5) M. C. Whiting, A. J. N. Bolt, and J. H. Parrish, *Adv. Chem. Ser.*, **No. 77**, 4 (1968).
- (6) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 4960 (1973).
- (7) D. G. Williamson and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **92**, 2949 (1970).
- (8) (a) R. Trambarulo, S. N. Ghosh, C. A. Barrus, and W. Gordy, *J. Chem. Phys.*, **24**, 851 (1953); (b) W. R. Wadt and W. A. Goddard, III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
- (9) G. A. Olah, A. Germain, H. C. Lin, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 2928 (1975).
- (10) G. A. Olah, R. Renner, P. Schilling, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 7686 (1973).
- (11) (a) P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, **88**, 3288 (1966); (b) P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).
- (12) R. E. Erickson, R. T. Hansen, and J. Harkins, *J. Am. Chem. Soc.*, **90**, 6777 (1968).
- (13) H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).
- (14) (a) R. W. Murray, W. C. Cumma, Jr., and J. W. P. Lin, *J. Am. Chem. Soc.*, **92**, 3205 (1970); (b) F. E. Stary, D. E. Emge, and R. W. Murray, *ibid.*, **96**, 5671 (1974).
- (15) P. D. Bartlett and M. Laha, *Isr. J. Chem.*, **10**, 101 (1972).
- (16) G. Czapski and B. H. J. B. elski, *J. Phys. Chem.*, **67**, 2180 (1963); **72**, 3836 (1968).
- (17) H. Taube and W. C. Bray, *J. Am. Chem. Soc.*, **62**, 3357 (1940).
- (18) G. A. Olah, N. Yoneda, and D. G. Parker, *J. Am. Chem. Soc.*, in press.
- (19) The further oxidation products, acetylum ion and CO<sub>2</sub>, were observed in a number of reactions studied. We have previously shown that such secondary oxidations are not induced by ozone (ref 1a).
- (20) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Am. Chem. Soc.*, **93**, 1251 (1971).