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Oxyfunctionalization of Hydrocarbons. 4.[1] FSO3H–SbF5, FSO3H, H2SO4, and HF Induced Electrophilic Oxygenation of Alkanes with Hydrogen Peroxide

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Abstract: The oxygenation of alkanes with hydrogen peroxide in the presence of FSO3H–SbF5, FSO3H, H2SO4, and HF was studied under typical electrophilic conditions. From the results obtained, it is concluded that the reactions proceed in strong acids via initial electrophilic hydroxylation of the appropriate σ bonds of the alkanes by the incipient hydroxyl cation, formed through protolytic cleavage of H_2O_2 through the hydroperoxonium ion $H_3O_2^+$.

In the preceding paper,[1] we reported the study of electrophilic oxygenation of alkanes with ozone in superacidic media. The reactions proceed via electrophilic oxygen insertion into the single σ bonds of the alkanes, effected by protonated ozone, i.e., O_3H^+, similar to such electrophilic reactions as hydrogen–deuterium exchange, protolysis,[2] chlorination (chlorolysis),[3] and nitration (nitrolysis)[4] of alkanes.

In a continuation of our studies on oxyfunctionalization of hydrocarbons, we extended our investigations to electrophilic hydroxylation of alkanes using hydrogen peroxide in strongly acidic media.

The acid-catalyzed reaction of hydrogen peroxide with alkanes was studied by Alder and Whiting.[5] They found 85% hydrogen peroxide with hydrogen fluoride–boron trifluoride to be an exceptionally powerful but unselective oxidant. For example, it reacted with cyclohexane at room temperature to cause extensive or even total oxidative decomposition of the substrate.

Frommer and Ullrich[6a] reported the hydroxylation of 2-methylbutane, methylcyclohexane, and n-pentane with 85% hydrogen peroxide in the presence of trifluoroacetic acid at 20 °C, giving 2-methyl-2-butanol, 1-methylcyclohexanol, and 2- and 3-pentanol, respectively, as major products. They suggested a nonionic transition state to be involved in the course of the reactions, such as

$$F_3C-C \underset{\underset{\displaystyle -C-H}{|}}{\overset{\displaystyle O\cdot}{\underset{\displaystyle O-O}{\diagup}}} \diagdown H$$
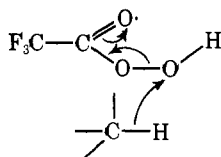
However, an ionic reaction path is also compatible with the results.

$$F_3C-C \overset{\displaystyle O}{\underset{\underset{\displaystyle -C-H}{|}}{\overset{\diagup}{O^+}}} -OH$$
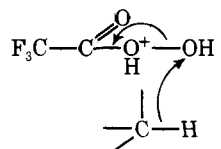
Hamilton has also observed that the CF_3CO_3H oxidation of cyclohexane and 1,2-dimethylcyclohexane to the corresponding alcohols occurs with retention of configuration.[6b]

We now wish to report the results of the reactions of alkanes with hydrogen peroxide (98%) in excess strong acid at various temperatures.
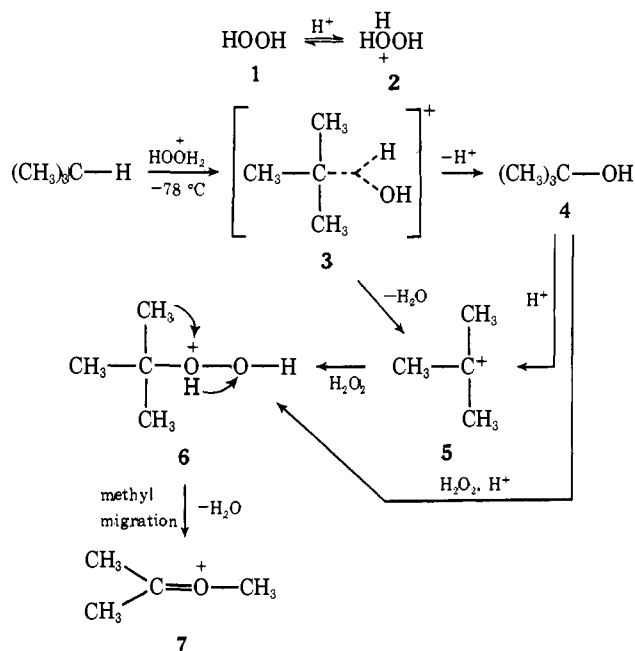
Results and Discussion

Reactions of Branched Chain Alkanes. The reactions of branched chain alkanes with hydrogen peroxide in magic acid (the equimolar mixture of FSO3H and SbF5)–SO2ClF solution were studied (by ^1H NMR spectroscopy) with various ratios of alkane and hydrogen peroxide, and at different temperatures. The results are summarized in Table I.

As neither hydrogen peroxide nor magic acid–SO2ClF alone, under the reaction conditions employed, led to any reaction products, it is considered that the reactions proceed via electrophilic hydroxylation of the C–H bond of alkanes with protonated hydrogen peroxide (2), yielding the hydroxycarbenium ion (3), which cleaves to give either alcohol (4) or carbenium ion (5). Since 1 mol of isobutane required 2 mol of hydrogen peroxide to complete the reaction to oxonium ion 3, 4 or 5 seem to react with excess hydrogen peroxide, giving tert-butyl hydroperoxide (6). The strong acid induced rearrangement and cleavage of 6 results in very rapid formation of the dimethylmethoxy carbenium ion (7). A similar rearrangement of tertiary alkyl hydroperoxides in strong sulfuric acid was previously shown to occur by Deno and co-workers.[7] The path of the reaction is depicted in Scheme I.

Under the reaction conditions employed the intermediacy of tert-butyl alcohol (4), tert-butyl cation (5), and/or hydroperoxide (6) could not be directly observed because of high reactivity of all these species with acidic hydrogen peroxide. Indeed, when a solution of tert-butyl alcohol was treated with hydrogen peroxide in magic acid–SO2ClF at −78 °C, immediate quantitative formation of 7 was observed.

When the reaction was carried out at room temperature by means of passing isobutane into magic acid (excess)–hydrogen peroxide solution, the formation of methyl alcohol (9), methyl acetate (11), and some dimethylmethoxy carbenium ion (7), together with dimeric acetone peroxide (1,1,4,4-tetramethyl-2,3,4,5-tetraoxacyclohexane, 10) was observed. Formation of 10 was confirmed by a comparison of spectra in
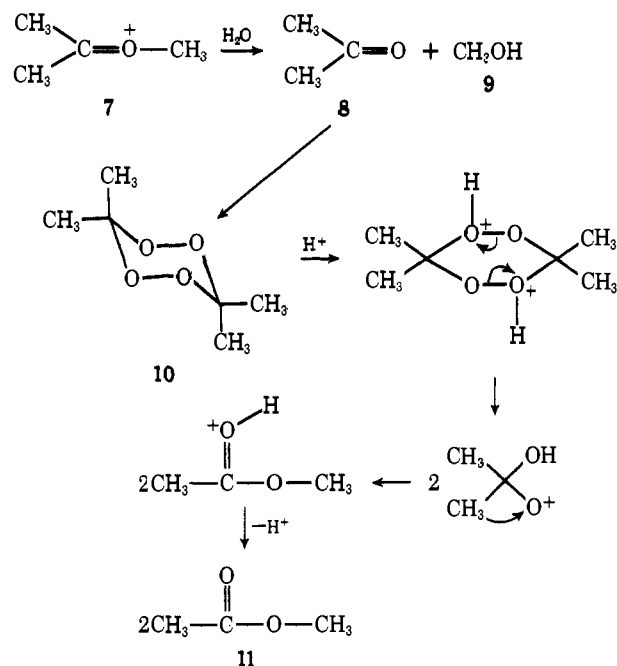
Scheme I

HOOH $\underset{}{\overset{H^+}{\rightleftharpoons}}$ HOOH$_+$H

1   2

$(CH_3)_3C$—H $\xrightarrow[-78\ ^\circ C]{\overset{+}{HOOH_2}}$ $\left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdots\overset{H}{\underset{OH}{\diagdown}} \right]^+$ $\xrightarrow{-H^+}$ $(CH_3)_3C$—OH

3   4

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{C}}}-\overset{}{\underset{H}{O}}-O-H$ $\xleftarrow[H_2O_2]{}$ $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{C}}}$ $\xleftarrow[]{H^+}$

6   5

H_2O_2, H^+

methyl migration $\Big\downarrow -H_2O$

$\underset{CH_3}{\overset{CH_3}{\diagup}}C\overset{+}{=}O$—$CH_3$

7

strong acid between an authentic sample synthesized by the method of Criegee et al.[8] as well as Sanderson et al.[9] and the reaction products (see Experimental Section).

In magic acid-SO$_2$ClF solution, the hydrolysis of **7** giving acetone (**8**) and methanol (**9**) did not take place at low temperature, because water is deactivated by protonation, but did at above 0 °C. Acetone in excess acid-hydrogen peroxide solution did not show reaction at −78 °C; however, by raising the temperature to −60 °C new ^{1}H NMR signals, attributable to the axial and equatorial methyl groups in dimeric acetone peroxide (**10**), appeared and, at −20 °C, conversion of acetone to this compound was almost complete. On allowing the solution to stand at room temperature, the formation of methyl acetate (**11**) was observed.

These results clearly show that products observed can be rationalized as arising from hydrolysis of **7** and from Baeyer–Villiger oxidation of **8** via **10**, as shown in Scheme II.

Scheme II

$\underset{CH_3}{\overset{CH_3}{\diagup}}C\overset{+}{=}O$—$CH_3$ $\xrightarrow{H_2O}$ $\underset{CH_3}{\overset{CH_3}{\diagup}}C=O$ + CH_3OH

7   8   9

$CH_3-\overset{\overset{CH_3}{|}}{\underset{}{C}}\overset{O-O}{\underset{O-O}{\diagdown\diagup}}\overset{}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

10

$\xrightarrow{H^+}$ $\underset{CH_3}{\overset{CH_3}{\diagup}}\overset{O^+-O}{\underset{O-O^+}{\diagdown\diagup}}\underset{CH_3}{\overset{CH_3}{\diagdown}}$

$2CH_3-\overset{\overset{+O}{\parallel}}{\underset{}{C}}-O-CH_3$ $\xleftarrow{}$ 2 $\underset{CH_3}{\overset{CH_3}{\diagup}}\overset{OH}{\underset{O^+}{\diagdown}}$

$\Big\downarrow -H^+$

$2CH_3-\overset{\overset{O}{\parallel}}{\underset{}{C}}-O-CH_3$

11

Table I. Products of Reaction of Branched Chain Alkanes with H$_2$O$_2$ in Magic Acid–SO$_2$ClF solution[a]

Alkane	Alkane, mmol	H$_2$O$_2$, mmol	Temp,[b] °C	Major products[c]
C C-C-C H	2	2	−78 ~−20	$(CH_3)_2C=\overset{+}{O}CH_3{}^d$
	2	4	−78 ~−20	$(CH_3)_2C=\overset{+}{O}CH_3{}^e$
	2	6	−78 ~−20	$(CH_3)_2C=\overset{+}{O}CH_3{}^e$
	2	6	20[h]	$(CH_3)_2C=\overset{+}{O}CH_3$ (trace), DAP^f (25%), CH$_3$OH (50%), CH$_3$COCH$_3$ (25%)^g
C C-C-C-C H	2	3	−78 ~−20	$(CH_3)_2C=\overset{+}{O}CH_2CH_3$, $(CH_3)_2\overset{+}{C}CH_2CH_3{}^i$
	2	6	−78 ~−20	$(CH_3)_2C=\overset{+}{O}CH_2CH_3{}^e$
C C-C-C-C-C H	2	3	−78 ~−20	$CH_3CH_2C(CH_3)=\overset{+}{O}CH_2CH_3$, $CH_3CH_2\overset{+}{C}(CH_3)CH_2CH_3{}^i$
	2	6	−78 ~−20	$(CH_3CH_2)C(CH_3)\overset{+}{O}CH_2CH_3{}^e$
C-C C-C-C-C-C H	2	3	−78 ~−20	$(CH_3CH_2)_2C=\overset{+}{O}CH_2CH_3$, $(CH_3CH_2)_2\overset{+}{C}CH_2CH_3{}^i$
	2	6	−78 ~−20	$(CH_3CH_2)_2C=\overset{+}{O}CH_2CH_3{}^e$
C C C-C-C-C C H	2	4	−78	$(CH_3)_2C=\overset{+}{O}CH_3$ (50%), $(CH_3)_2C=\overset{+}{O}H$ (50%)^g
	2	6	−40	$(CH_3)_2C=\overset{+}{O}CH_3$ (50%), DAP^f (50%)

^{a} All experiments except for room temperature reactions were carried out using magic acid (1 ml)–SO$_2$ClF (1 ml) solution at −78 °C. The resultant solutions were transferred to a precooled ^{1}H NMR tube for analysis. ^{b} ^{1}H NMR probe temperature. ^{c} Product assignments were made by comparison with previously reported data.[11] ^{d} No other products could be detected except for unreacted alkane. ^{e} Almost 100% conversion. ^{f} Dimeric acetone peroxide. ^{g} The ratio of these products can be determined by using the characteristic ^{1}H NMR chemical shift of methyl groups in these compounds which showed separate singlet signals. ^{h} 0.1 mol of isobutane was passed through a magic acid (3 ml)–H$_2$O$_2$ (6 mmol) solution at a flow rate of 15 ml/min, The reaction was continuously cooled by water because of exothermic reaction. ^{i} The ratio of oxonium and alkyl carbenium ion produced was about 50:50.

We are presently further investigating the behavior of cyclic peroxides, including dimeric acetone peroxide in various acid media together with the Baeyer–Villiger type of oxidation for various methyl alkyl ketones, and will report these results separately.[10] It should be, however, pointed out that Deno[7] first observed the Baeyer–Villiger oxidation of methyl ketones with H$_2$SO$_5$ in H$_2$SO$_4$.

Isopentane, 3-methylpentane, and 3-ethylpentane also gave the corresponding expected oxonium ions, i.e., dimethylethoxy carbenium ion, methylethylethoxy carbenium ion, and diethylethoxy carbenium ion, together with the corresponding alkyl carbenium ions, i.e., dimethylethyl carbenium ion, methyldiethyl carbenium ion, and triethyl carbenium ion, respectively.

The formation of alkyl carbenium ion in the case of these alkanes is interesting, since the trimethyl carbenium ion is not formed in the case of isobutane under the same conditions.

2,2,3-Trimethylbutane did not give the expected dimethyl-tert-butoxy carbenium ion, but gave dimethylmethoxy carbenium ion (**7**) and protonated acetone. This can be explained by the expected oxonium ion undergoing cleavage-rearrangement to form acetone and tert-butyl alcohol, giving trimethyl carbenium ion which in turn readily reacted with hy-

Table II. Products of Reaction of Branched Chain Alkanes with H_2O_2 in FSO_3H Solution[a]

Alkane	Alkane, mmol	H_2O_2, mmol	Temp,[b] °C	Reaction time, min[c]	Conversion of alkane, %	Products
C C-C-C H	2	4	−78	30	10	$(CH_3)_2C=\overset{+}{O}CH_3$ (100%)
	2	4	−10	30	40	$(CH_3)_2C=\overset{+}{O}CH_3$ (90%), CH_3OH (5%), $(CH_3)_2C=O$ (5%)
	2	4	RT	3 h	100	$(CH_3)_2C=\overset{+}{O}CH_3$ (30%), CH_3OH (35%), $(CH_3)_2C=O$ (35%)
	2	6	−78	30	25	$(CH_3)_2C=\overset{+}{O}CH_3$ (100%)
	2	6	−40	20	80	$(CH_3)_2C=\overset{+}{O}CH_3$ (100%)
	2	6	−20	60	100	$(CH_3)_2C=\overset{+}{O}CH_3$ (70%), CH_3OH (20%), DAP[d] (10%)
	2	6	RT	60	100	$(CH_3)_2=\overset{+}{O}CH_3$ (10%), CH_3OH (35%), DAP[d] (10%), CH_3COOCH_3 (30%), CH_3COOH (15%)
	2	10	−78	30	5	$(CH_3)_2C=\overset{+}{O}CH_3$ (100%)
	2	10	−60	30	60	$(CH_3)_2C=\overset{+}{O}CH_3$ (40%), CH_3OH (40%), DAP[d] (20%)
	2	10	−40	30	100	CH_3OH (70%), DAP[d] (30%)
	2	20	−78	30	Tr	CH_3OH (70%), DAP[d] (30%)
	2	20	−60	30	10	CH_3OH (70%), DAP[d] (30%)
	2	20	−40	30	40	CH_3OH (70%), DAP[d] (30%)
	2	20	0	60	100	CH_3OH (40%), CH_3COOH (20%), CH_3COOCH_3 (30%), DAP[d] (10%)
C C-C-C-C[e] H	2	4	−78	30		$(CH_3)_2C=\overset{+}{O}CH_2CH_3$ (100%)
	2	4	−40	60		$(CH_3)_2C=O$ (50%), CH_3CH_2OH (50%)
	2	4	RT	60		$(CH_3)_2C=O$ (50%), CH_3CH_2OH (50%)
	2	6	−78	30		$(CH_3)_2C=\overset{+}{O}CH_2CH_3$ (70%), CH_3CH_2OH (20%), DAP[d] (10%)
	2	6	−60	30		$(CH_3)_2C=\overset{+}{O}CH_2CH_3$ (25%), CH_3CH_2OH (50%), DAP[d] (25%)
	2	6	RT	60		CH_3OH (20%), CH_3CH_2OH (50%), CH_3COOCH_3 (10%), CH_3COOH (20%)
C C-C-C-C-C[e] H	2	4	−78	30		$CH_3CH_2C(CH_3)=\overset{+}{O}CH_2CH_3$, CH_3CH_2OH[f,g]
	2	4	−40	30		CH_3CH_2OH, CH_3COOH, $CH_3COOCH_2CH_3$[f,g]
C-C C-C-C-C-C[e]	2	4	−78	30		$(CH_3CH_2)_2C=OCH_2CH_3$, CH_3CH_2OH[f,g]
	2	4	−40	30		$CH_3CH_2COOCH_2CH_3$ (50%), CH_3CH_2OH (50%)
C C C-C-C-C[e] C H	2	6	−40	30		CH_3OH (50%), DAP[d] (50%)

[a] Reaction procedures and analysis of products were similar to the case of the magic acid–SO_2ClF reactions. [b] ^1H NMR probe temperature. [c] Time of the sample kept at given temperature before analysis. [d] Dimeric acetone peroxide. [e] Because of complex reaction mixture, conversion could not be ascertained. [f] Because of complex reaction mixture, product distributions could not be clearly determined. [g] Yet unidentified by-products were also observed.

Table III. Products of Reaction of Branched Chain Alkanes with H_2O_2 in HF Solution[a]

Alkane	Alkane, mmol	H_2O_2, mmol	Reaction temp, °C	Reaction time, min	Conversion[b] of alkane, %	Products
C C-C-C H	2	4	−50	60		$(CH_3)_2C=\overset{+}{O}CH_3$
	2	4	−10	30		$(CH_3)_2C=O$ (50%), CH_3OH (50%)
	2	6	−40	30		DAP[c] (50%), CH_3OH (50%)
	2	6	−20	30	~100	DAP[c] (10%), CH_3COOCH_3 (20%), CH_3COOH (10%), CH_3OH (60%)
C C-C-C-C H	2	6	−40	30		DAP[c] (50%), CH_3CH_2OH (50%)
C-C C-C-C-C-C H	2	6	−40	30		$(CH_3CH_2)_2C=O$ (20%), CH_3CH_2OH (50%), $CH_3CH_2COOCH_2CH_3$ (30%)
C C C-C-C-C C H	2	6	−10	60	~100	CH_3OH (50%), CH_3COOCH_3 (25%), CH_3COOH (25%)

[a] Reaction procedures and analysis of products were similar to those in magic acid. [b] Because of poor miscibility of alkane with HF accurate conversions could not be observed in most systems. [c] Dimeric acetone peroxide.

drogen peroxide to give the dimethylmethoxy carbenium ion (7).[11c] When the reaction was carried out with excess hydrogen peroxide at −40 °C, the formation of dimeric acetone peroxide was again observed.

The reaction of alkanes with hydrogen peroxide in the presence of acids weaker than magic acid, such as FSO_3H, HF, and H_2SO_4 (96%), was also studied. The results are summarized in Tables II, III, and IV.

Table IV. Products of Reaction of Branched Chain Alkanes with H_2O_2 in H_2SO_4 Solution[a]

Alkane	Alkane, mmol	H_2O_2, mmol	Reaction temp, °C	Reaction time, min	Conversion of alkane, %	Products
$\begin{smallmatrix}C\\ \mid \\ C{-}C{-}C\\ \mid \\ H\end{smallmatrix}$[b]	100	10	−20		0	
	100	10	0		Tr	CH_3OH (70%), CH_3COOH[d] (30%)
	100	10	RT		15[c]	CH_3OH (70%), CH_3COOH[d] (30%)
$\begin{smallmatrix}C\\ \mid \\ C{-}C{-}C{-}C\\ \mid \\ H\end{smallmatrix}$	2	4	−10	30	Tr	$(CH_3)_2C{=}O$ (50%), CH_3CH_2OH (50%)
	2	6	0	30	Tr	CH_3COOCH_3 (50%), CH_3CH_2OH[e,f] (50%)
	2	6	RT	30	~20	CH_3CH_2OH[e] (40%), CH_3OH (20%), CH_3COOCH_3 (20%), CH_3COOH[f] (20%)
	2	6	40	10	~20	CH_3OH (33%), CH_3CH_2OH[e] (33%), CH_3COOH[f] (33%)
$\begin{smallmatrix}C & \;C\\ \mid & \mid \\ C{-}C{-}C{-}C\\ \mid & \mid \\ C & H\end{smallmatrix}$	2	6	0	60	~20	CH_3OH (50%), CH_3COOH (30%), $(CH_3)_3COSO_3H$[f] (20%)
	2	6	40	60	~20	CH_3OH (60%), CH_3COOH[d] (40%)

[a] Reaction procedures and analysis of products were similar to those in magic acid solutions. [b] 0.1 mol of isobutane was passed through the acid solution at flow rate of 15 ml/min. [c] Based on H_2O_2. [d] Trace of tert-butyl sulfate was also observed. [e] Together with ethyl sulfate. [f] Unidentified products were also observed.

Table V. Products of Reaction of Straight Chain Alkanes with H_2O_2 in Strong Acids

Acid	Alkane[a]	Amount of H_2O_2, mmol	Reaction temp, °C	Products[c]
MA	CH_4	6	−20	NR
MA	CH_4	6	0 ~ RT	CH_3OH
FSO_3H	CH_4	6	60	CH_3OH
$MA{-}SO_2ClF$[b]	CH_3CH_3	6	−60	NR
	CH_3CH_3	6	−40	CH_3CH_2OH
	$CH_3CH_2CH_3$	6	−78	$(CH_3)_2CHOH$ (40%), $(CH_3)_2C{=}O$ (60%)
	$CH_3CH_2CH_3$	6	−60	$(CH_3)_2CHOH$ (30%), $(CH_3)_2C{=}O$ (70%)
	$CH_3CH_2CH_3$	6	−40	$(CH_3)_2CHOH$ (10%), $(CH_3)_2C{=}O$ (40%), DAP (50%)
FSO_3H	$CH_3CH_2CH_3$	6	−78	$(CH_3)_2CHOH$
	$CH_3CH_2CH_3$	6	−60	DAP
	$CH_3CH_2CH_3$	6	−40	CH_3OH (20%), CH_3COOH (20%), CH_3COOCH_3 (60%)
H_2SO_4	$CH_3CH_2CH_3$	6	0	$(CH_3)_2CHOH$ (50%), CH_3COOH (30%), CH_3OH (20%)
$MA{-}SO_2ClF$[b]	$CH_3CH_2CH_2CH_3$	2	−78	$CH_3CH_2CHOHCH_3$
	$CH_3CH_2CH_2CH_3$	2	−50	$CH_3CH_2CHOHCH_3$, $(CH_3)_3C^+$
	$CH_3CH_2CH_2CH_3$	6	−60	$(CH_3)_2C{=}OCH_3$

[a] In the case of methane, ethane, and propane using H_2SO_4, 1 mol of alkane was passed through the H_2O_2−acid solution at the flow rate of 15 ml/min. [b] Magic acid−SO_2ClF (1:1) mole solution. [c] In the case of magic acid system, conversion was almost 100% except for methane and ethane reactions. In another system, no attempt was made to calculate the conversion.

The products formed in the reaction using FSO_3H were almost identical with those formed in magic acid. Some of the differences observed were lower conversion rate of alkanes and increased formation of products due to hydrolysis of oxonium ions or esters compared to those under the same reaction conditions in magic acid system. These are due to the lowering of acidity of the solutions which causes the enhanced nucleophilic activity of water (the hydronium ion is increasingly in equilibrium with unprotonated water).

This tendency was increased, as expected, when the reactions were carried out in the presence of hydrogen fluoride or sulfuric acid. A temperature of at least −40 °C or above was needed for hydrogen fluoride and −10 °C or above for sulfuric acid to induce the reaction of alkanes with hydrogen peroxide. There was observed a constant relationship of the ratio of reaction products. For example, depending on the acids used, isobutane gave methyl alcohol and acetic acid in 2:1 mole ratio at −10 °C or at room temperature, isopentane gave methyl alcohol, ethyl alcohol, and acetic acid in the molar ratio of 1:1:1 at 40 °C, and 2,2,3-trimethylbutane, under the same reaction conditions, gave methyl alcohol and acetic acid in the molar ratio of 3:2. We particularly want to emphasize the results of the reactions in hydrogen fluoride which gave the same reaction products and thus indicate the same reaction pattern as reactions with the other strong acids, in spite of the fact that hydrogen fluoride cannot form a peracid. This suggests that the oxidation reactions using hydrogen peroxide in strong acids are indeed due to protonated hydrogen peroxide, i.e., $H_3O_2^+$, as peracids, such as Caro's acid, cannot be formed in HF or its conjugate acids, such as $HF-SbF_5$ or $HF-BF_3$, which also yield similar products. Further, it should be pointed out that both magic acid and fluorosulfuric acid, in the low temperature range, show only protonation of water (to the hydronium ion) and no evidence of any hydrolysis. Hydrogen peroxide being a thousand times weaker nucleophile than water would, therefore, be even less expected to form peracids (i.e., Caro's acid). The effective hydroxylating agent consequently is considered to be the hydroperoxonium ion, $H_3O_2^+$. The direct observation of the latter in superacidic systems as a static species (similar to the H_3O^+ ion) was not possible due to rapid hydrogen exchange with the solvent systems, involving probably the diprotonated ion

$$H{-}\overset{+}{\underset{H}{O}}{-}\overset{+}{\underset{H}{O}}{-}H$$
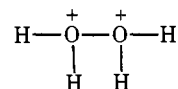
Products formed in the reaction of tertiary isoalkanes with hydrogen peroxide in strong acid solutions can be summarized as follows.

$$R_1{-}\overset{R_2}{\underset{H}{C}}{-}R_3 \longrightarrow R_1COOH + R_2OH + R_3OH$$

(R_1, R_2, R_3 = methyl or ethyl)
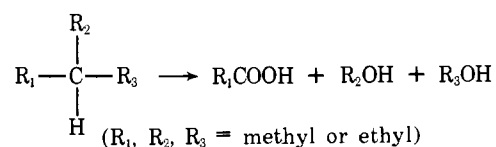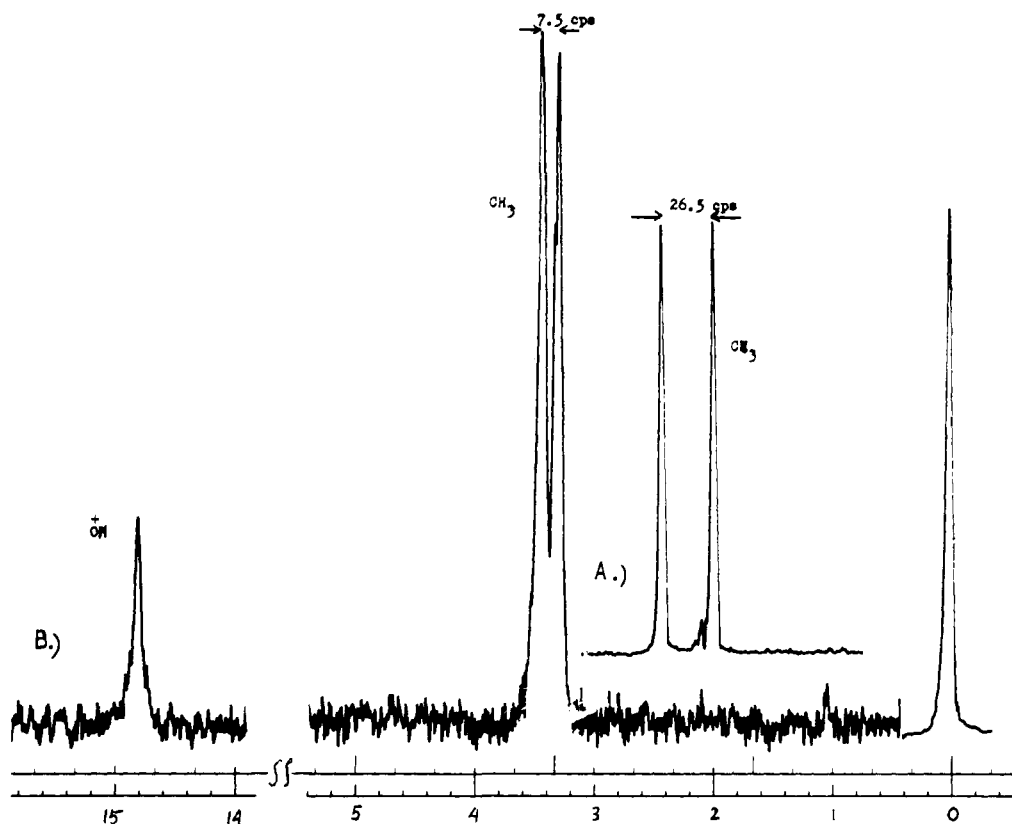
Figure 1. ¹H NMR spectra of dimeric acetone peroxide. (A) In $CDCl_3$ at −20 °C. (B) In FSO_3H at −100 °C.
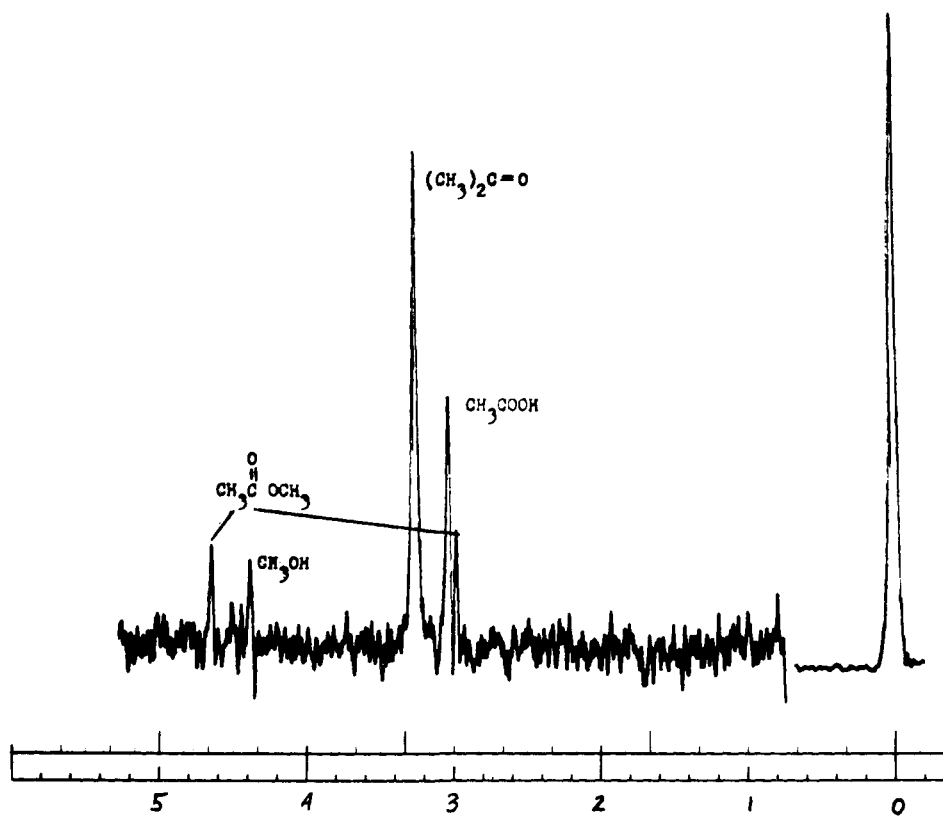
Figure 2. ¹H NMR spectrum after keeping solution B of Figure 1 at 10 °C for 1 h and cooling back to −20 °C.

$$R_1—\underset{\underset{H}{|}}{\overset{\overset{R_2}{|}}{C}}—R_3 \longrightarrow CH_3COOH + 2CH_3OH + R_1COOH + R_2OH$$

(R_1, R_2 = methyl or ethyl; R_3 = *tert*-butyl)
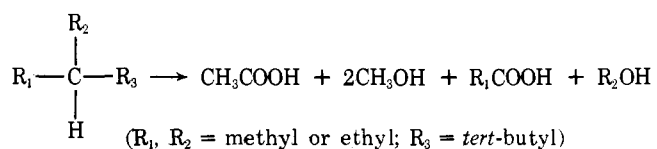
Straight-Chain Alkanes. Under the same reaction conditions employed as in the case of branched-chain alkanes, straight-chain alkanes such as ethane, propane, butane, and even methane gave related oxygenation products. The results are summarized in Table V.

Methane, when reacted with hydrogen peroxide–magic acid above 0 °C, gave mainly methyl alcohol. Similar results were obtained using hydrogen peroxide–FSO_3H at 60 °C. Ethane with hydrogen peroxide–magic acid at −40 °C gave ethyl alcohol.

The reaction of propane with hydrogen peroxide took place more easily than that of methane or ethane and yielded isopropyl alcohol as the initial oxidation product. By raising temperature, isopropyl alcohol gave acetone, which underwent further oxidation with hydrogen peroxide, giving dimeric acetone peroxide, methyl acetate, methyl alcohol, and acetic acid, as shown previously. The related reaction of butane with hydrogen peroxide in magic acid at −78 °C gave sec-butyl alcohol. By raising the temperature, sec-butyl alcohol was converted into trimethylcarbenium ion. When excess hydrogen peroxide was used in the reaction, dimethylmethoxy carbenium ion was obtained, formed by the reaction of H_2O_2 with the tert-butyl cation via subsequent cleavage–rearrangement reaction of the intermediate tert-butyl hydroperoxide (as reported previously).

From the products obtained in the reactions, the relative order of reactivity of single bonds in alkanes toward $O_2H_3^+$ can be given as $R_3C–H > R_2HC–H > RH_2C–H > C–C$. This order is in accord with that of observed for electrophilic insertion of protonated ozone, O_3H^+, into the single σ bonds of alkanes.

Conclusions

The electrophilic oxygenation of alkanes with hydrogen peroxide in acid solution was studied. The results can be best explained by initial insertion of the incipient hydroxyl cation ^+OH, formed from protonated hydrogen peroxide, $H_3O_2^+$, into the σ bonds in alkanes, through pentacoordinated carbonium ions.

Experimental Section

Materials. All the alkanes used were of commercially available highest purity. They were used without further purification. SbF_5 and FSO_3H were twice distilled. Hydrogen peroxide (98%) was obtained from the FMC Corp.

Dimeric acetone peroxide (DAP) was prepared according to Criegee's method.[8] Tetramethylethylene in pentane solution was ozonized at −78 °C, using a Welsbach Model T ozonator. The white, solid product was filtered and washed with acetone. The ^1H NMR spectrum of the purified material in $CDCl_3$ was identical with the published spectrum.[12]

In Figure 1, ^1H NMR spectra of dimeric acetone peroxide in $CDCl_3$ at −20 °C and in FSO_3H at −100 °C are shown. Dimeric acetone peroxide can be detected as the protonated species in FSO_3H at −100 °C. At −60 °C, the signal of the acidic peroxide at δ 14.7 disappeared, although no change of signals at δ 3.4 was observed.

In FSO_3H, dimeric acetone peroxide can be best considered to be protonated and to have a more planar form as compared with the chair form[12] of the neutral dimeric peroxide in $CDCl_3$. Thus chemical shift differences between the axial and equatorial methyl groups will be lower in FSO_3H solution. However, the effect of protonation causes a net downfield shift for both groups.

By raising the temperature to −30 °C, formation of acetone was observed, while at 0 °C the formation of methyl acetate, methyl alcohol, and acetic acid was observed as shown in Figure 2.

General Procedure of Oxygenation. A solution (or mixture) of the appropriate alkane (2 mmol) in 2–3 ml of superacid–SO_2ClF was placed into a 15-ml glass reaction vessel, which was well stirred by a Vortex mixer while kept at −78 °C (dry ice–acetone). Hydrogen peroxide, 98% (2–20 mmol), cooled to −5 °C was then added by pipet very carefully into the well-stirred acid solution. In the case of HF, a Teflon reaction tube (15 ml) was used. Due to the danger of explosion, extreme caution should be exercised during the reaction procedure. All work was carried out in a well-shielded fume hood, protected with strong safety shields. The reaction mixtures were then reacted at the temperatures and times specified in the tables. The resulting solutions were directly analyzed (without attempts to isolate products) by ^1H NMR spectroscopy.

The experimental conditions and ^1H NMR analytical methods used were similar to those used and described in our preceding papers.[1,11c] For positive identification of products, solutions with known compositions were made up in the same solvent systems and compared with those of the reaction mixtures.

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