tilled. The forerun and residue were discarded, and the center fractions combined and redistilled to give 2.2 g. of 6-oxo-8-methoxyoctanoic acid, b.p. 125–129.5° (1.3 mm.).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.57. Found: C, 57.4; H, 8.49.

Ethyl 6-Hydroxy-8-methoxyoctanoate (IX).—Solid sodium borohydride (0.4 g., 0.011 mole) was added in several portions to a solution of 5 g. (0.023 mole) of ethyl 6-oxo-8-methoxyoctanoate in 25 ml. of dry methanol. Heat was generated and the temperature rose to about 50°. The mixture was refluxed for 30 minutes, after which the methanol was removed by evaporation. Water (20 ml.) was added to the residue, and the mixture was heated for 30 minutes, and allowed to stand overnight. The organic layer was withdrawn and combined with three 10-ml. chloroform extracts of the aqueous phase. The organic solution was washed with 10 ml. of dilute sulfuric acid and two 10-ml. portions of water and dried over a mixture of sodium sulfate and sodium bicarbonate. The dried solution was filtered, and the chloroform evaporated to leave 5.1 g. of a yellow liquid which was fractionally distilled to give 2.1 g. (42%) of ethyl 6-hydroxy-8-methoxyoctanoate, b.p. 153–160° (13 mm.), $n^{25}D$ 1.4435.

Anal. Calcd. for $C_{11}H_{22}O_4$: C, 60.6; H, 10.1. Found: C, 60.6; H, 10.1.

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Organic Peroxides. XX. Peroxides from the Ozonization of Olefins in the Presence of Carbonium Ions

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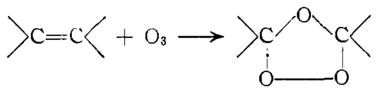
A countercurrent method for the efficient ozonization of olefins has been developed. Several olefins have been ozonized in *t*-butyl alcohol containing *t*-butylcarbonium ions. In several cases, especially with unsymmetrical olefins, two isomeric peroxides containing *t*-butoxy groups were identified from their decomposition products. Some of these products were identified as hydroperoxides containing *t*-butoxy groups. The simplest of these was *t*-butoxymethyl hydroperoxide which also was synthesized by an independent method. A mechanism has been proposed to account for the formation of the initial peroxides as well as those produced as their decomposition products. Since alkylidene peroxides were not isolated from the ozonization products of olefins in the presence of *t*-butylcarbonium ions, the zwitterions responsible for their formation were not produced during the ozonization. Several olefins were also ozonized in non-aqueous solvents and, with the exception of tetraphenylethylene, the yields of alkylidene peroxides were low indicating that the main products were the ozonides.

Introduction

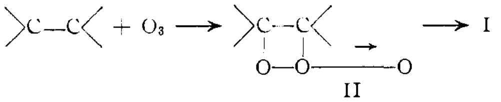
The direct attack of double bonds by ozone has been known for a long time, but in spite of the immense knowledge in this field only recently has the mechanism being elucidated. It is now known with certainty that ozone cleaves double bonds and through the researches of Rieche, *et al.*,[2] the structure of ozonides has been clarified. The simplest explanation of the ozonization of a double bond is illustrated by equation 1.



(1)

I-ozonide

However, it is very difficult to visualize under the extremely mild conditions of ozonization, how the double bond is completely cleaved and the above ozonide formed in one step. Staudinger[3] was the first to suggest that an unstable "molozonide" II is initially formed which rearranges to the more stable ozonide (I).

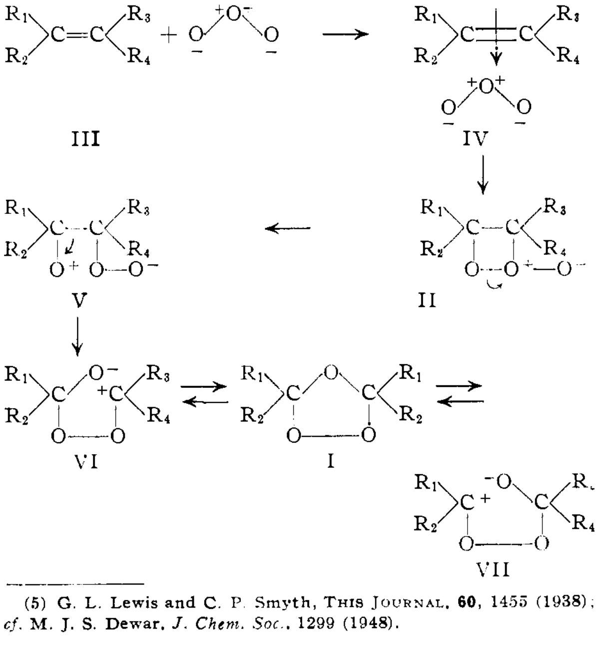


(2)

II

To explain this rearrangement Criegee[4] proposed that the molozonide undergoes an intramolecular change with the momentary formation of a positively polarized oxygen atom which abstracts the remaining two electrons from the carbon–carbon bond and rearranges into the neutral ozonide. The whole process of ozonization therefore may be viewed as an ionic reaction in which the ozonide acts as an electrophilic reagent.

The polar nature of ozone has been established by Lewis and Smyth[5] who proposed that the middle oxygen atom is positively polarized, thus the structure most generally accepted for ozone is the obtuse-angled structure with the oxygen at the apex being positive. Under the influence of the polar ozone molecule a double bond is also polarized in such a manner that the π-electrons attach themselves to the positive oxygen atom of the ozone molecule. The mechanism of such a reaction may be illustrated as



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[1] Lucidol Research Associate 1952–1953.

[2] A. Rieche, R. Meister and H. Sauthoff, *Ann.*, **553**, 187 (1942).

[3] H. Staudinger, *Ber.*, **58**, 1088 (1925).

[4] R. Criegee, *Ann.*, **560**, 127 (1948); *cf.* J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949).

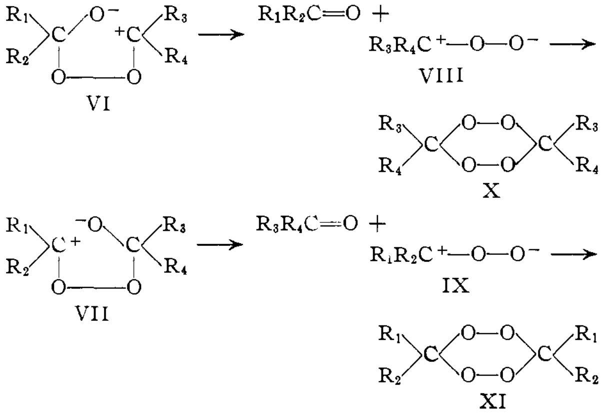
[5] G. L. Lewis and C. P. Smyth, THIS JOURNAL, **60**, 1455 (1938); *cf.* M. J. S. Dewar, *J. Chem. Soc.*, 1299 (1948).

TABLE I

ALKYLIDENE PEROXIDES FROM THE OZONIZATION OF OLEFINS

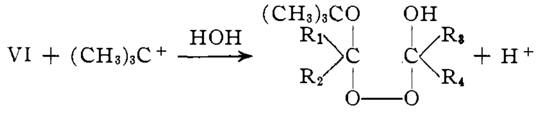
Olefin	Solvent	Temp. of ozonization, °C.	Peroxide	M.p., °C.	Yield, %
Tetramethylethylene	*n*-Pentane	−20	Diacetone	132–133	15.2
Isobutylene	*n*-Pentane	−50	Diacetone	131–132	20.0
Styrene[6b]	CCl_4	Room	Dibenzaldehyde	200 dec.	1.7
Stilbene[6b]	C_6H_6	Room	Dibenzaldehyde	200 dec.	9.6
α-Methylstyrene	*n*-Pentane	−20	Diacetophenone	182–183	13.0
2-Phenyl-3-methyl butene-2	*n*-Pentane	−50	Diacetone	132–133	10.7
1,1-Diphenylethylene[6b]	*n*-Hexane	Ice-salt	Dibenzophenone	206–208	5.8
1,1-Diphenylethylene	*n*-Pentane	−20	Dibenzophenone	206–208	15.1
1,1-Diphenylbutene-1[6b]	CCl_4	Room	Dibenzophenone	206–208	12.0
1,1-Diphenyl-2-acetoxyethene	*n*-Pentane	−20	Dibenzophenone	206–208	13.0
Triphenylethylene[6b]	CCl_4	Ice-salt	Mixture	184 dec.	...
Tetraphenylethylene[6a,6b]	CCl_4	0	Dibenzophenone	206–208	53–57
Tetraphenylethylene	CCl_4	0	Dibenzophenone	206–208	56
Tetraphenylethylene	Ethyl acetate	20	Dibenzophenone	200–205	20

All ionic intermediates are probably formed instantaneously with the zwitterions VI and VII existing in equilibrium with the neutral ozonide I. If there are no other ionic species present to combine with the zwitterions (VI or VII) either the *neutral* ozonide is formed or these ions decompose spontaneously into ketones or aldehydes and the zwitterions VIII and IX which dimerize to form the highly explosive alkylidene peroxides X and XI.

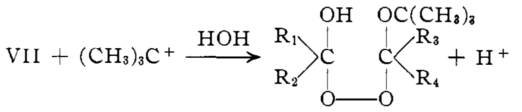


As a rule these peroxides are not the main products of ozonization and the amounts formed depend upon the solvent, the temperature of ozonization and the groups attached to the double bond.[6,7] Owing to their stability and relative insolubility in various solvents these peroxides can be isolated easily from ozonization reactions. Table I shows some of the yields of these peroxides isolated under various solvent and temperature conditions.

When ozonizations were carried out in the presence of carbonium ions neither the ozonides nor the alkylidene peroxides were formed but instead peroxides of the type XII and XIII have been isolated in good yields as the primary products. The formation of these peroxides can be accounted for by the assumption that carbonium ions react with the intermediate zwitterions (VI and VII). Using *t*-butylcarbonium ions this can be illustrated as



XII



XIII

Table II shows some of the peroxides isolated corresponding to structures XII or XIII. The presence of *t*-butyl groups was established by reduction of the peroxides with metallic sodium and isolation of *t*-butyl alcohol in the form of its 3,5-dinitrobenzoate. The corresponding ketones and/or aldehydes formed in this reaction also were identified and in some cases estimated quantitatively. In addition the presence of both the *t*-butyl ether group and the hydroxyl group as well as the peroxide group was identified by infrared spectra.

TABLE II

OZONIZATION OF CERTAIN OLEFINS IN THE PRESENCE OF *t*-BUTYLCARBONIUM IONS

Olefin	Yield of peroxide in % per mole of O_3 used	Peroxide isolated	Active oxygen (O), % Calcd.	Found
2-Methylbutene-2	45.0	$C_9H_{20}O_4$	8.33	7.20
Tetramethylethylene	57.0	$C_{10}H_{22}O_4$	7.76	8.0
Styrene	92.0	$C_{12}H_{18}O_4$	7.08	7.11
α-Methylstyrene	86.0	$C_{13}H_{20}O_4$	6.67	6.60
1,1-Diphenylethylene	100.0	$C_{18}H_{22}O_4$	5.33	5.19
D-Limonene (one —C=C—)	85.7	$C_{14}H_{26}O_4$	6.20	5.50
p-Menthene-$\Delta^{4,(8)}$	68.0	$C_{14}H_{28}O_4$	6.16	6.0

That the zwitterions VIII and IX were not produced under these conditions is shown by the fact that no derivatives of *t*-butylhydroperoxide were isolated but instead the *t*-butyl group was found attached to the oxygen of one of the hydroxyl groups.[7] Furthermore, when ozonization was carried out in a non-aqueous solvent (chloroform), then the reaction mixture treated with carbonium ions in *t*-butyl alcohol, the usual yield of alkylidene peroxides was obtained indicating that these

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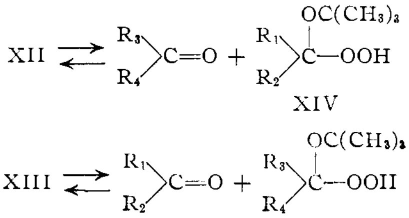
(6) (a) E. P. Kohler and N. K. Richtmyer, THIS JOURNAL, **52**, 2042 (1930); C. S. Marvel and V. Nichols, *ibid.*, **60**, 1455 (1938); *J. Org. Chem.*, **6**, 296 (1941).

(7) R. Criegee and G. Lohaus, *Ann.*, **538**, 6 (1953).

peroxides, if formed, are not affected by the presence of carbonium ions. We have found also that alkylidene peroxides are stable even in boiling dilute sulfuric acid.

Peroxides of the type XII and XIII may be considered as either hemiperketals or hemiperacetals depending on the groups originally attached to the double bond, and therefore are expected to lose easily aldehydes or ketones and go over to more stable peroxides of the type XIV or XV. This is especially true if the original peroxides are subjected to a high vacuum at room or higher temperatures. Thus from 1,1-diphenylethylene two distinct peroxides were obtained: a volatile peroxide identified as *t*-butoxymethyl hydroperoxide (XVI) and a nonvolatile peroxide identified as diphenyl *t*-butoxymethyl hydroperoxide (XVII). These results seem to indicate that both peroxides XII and XIII are formed during the reaction and when the mixture is subjected to a high vacuum one loses formaldehyde and the other benzophenone. Both of these products were found among the decomposition products. Furthermore, it is very difficult at present, from these results, to state that ozone adds to the double bond in accordance with the Markownikoff's rule. Table III shows some of the peroxides produced by the slow dissociation of the primary peroxides shown in Table II.



$$\mathrm{XII} \rightleftarrows \begin{matrix}R_3\\R_4\end{matrix}\!>\!C{=}O + \begin{matrix}R_1\\R_2\end{matrix}\!>\!\overset{OC(CH_3)_3}{\overset{|}{C}}\text{—}OOH$$

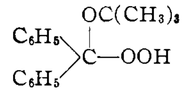
XIV

$$\mathrm{XIII} \rightleftarrows \begin{matrix}R_1\\R_2\end{matrix}\!>\!C{=}O + \begin{matrix}R_3\\R_4\end{matrix}\!>\!\overset{OC(CH_3)_3}{\overset{|}{C}}\text{—}OOH$$

XV

$(CH_3)_3COCH_2OOH$

XVI

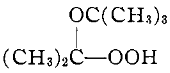
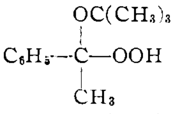
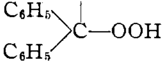
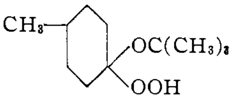


$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!\overset{OC(CH_3)_3}{\overset{|}{C}}\text{—}OOH$$

XVII

TABLE III

SECONDARY PEROXIDES OBTAINED FROM THE DECOMPOSITION OF PRIMARY PEROXIDES

Peroxide	n^{25}_D	Active oxygen (O), % Calcd.	Found
 $(CH_3)_2\overset{OC(CH_3)_3}{\overset{\mid}{C}}\text{—}OOH$	1.4250	10.8	11.1
$(CH_3)_3COCH_2OOH$	1.4131	13.32	13.8
 $C_6H_5\text{—}\underset{\underset{CH_3}{\mid}}{\overset{\overset{OC(CH_3)_3}{\mid}}{C}}\text{—}OOH$	1.5024	7.6	7.9
 $\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\!\overset{OC(CH_3)_3}{\overset{\mid}{C}}\text{—}OOH$	1.5534	5.88	5.83
	....	7.9	8.0

In all of the above peroxides the *t*-butoxy and hydroperoxy groups were shown to be present by infrared spectra and by degradation experiments. In one case, *t*-butoxymethylhydroperoxide, the peroxide was synthesized by an independent procedure and its properties compared with those of the peroxide obtained from ozonization reactions as well as with those of its isomer, *t*-butylhydroxymethyl peroxide.[8] The properties of the two isomeric peroxides are given in Table IV for comparison.

TABLE IV

PROPERTIES OF ISOMERIC PEROXIDES

Peroxide	$(CH_3)_3COCH_2OOH$		$(CH_3)_3COOCH_2OH$	
B.p., °C. (mm.)	33–31 (4)		52–53 (8)	
n_D (*t*, °C.)	1.4131 (25)		1.4130 (24)	
	Calcd.	Found	Calcd.	Found
Carbon, %	49.98	49.62	49.98	51.5
Hydrogen, %	10.07	10.19	10.07	10.9
Active oxygen	13.32	12.97	13.32	13.3
Reacn. with KI + H^+	Fast		Slow	
Decompn. with ^-OH to liberate H_2	Fast		Slow	
Reacn. with $PbAc_4$	Fast		Slow	
Stability to Fe^{++}	Decompn. rapid		Decompn. very slow	

Method of Ozonization

In the study of the ozonization of various unsaturated compounds in a homogeneous system using *t*-butylcarbonium ions, *t*-butyl alcohol was chosen as the solvent after preliminary studies indicated that this solvent is relatively stable to ozone. In order to increase the efficiency of utilization of ozone in our reactions, a countercurrent circulating system was designed and constructed as shown in Fig. 1. This is made up of two independent circulatory systems. One consists of a circulating pump A and a copper coil B which is immersed in a bath which is usually kept at 0° but may be anywhere between room temperature and −70°, depending upon the temperature desired for the ozonization. The liquid (ethylene glycol, or any other suitable liquid) circulates around the reaction chamber C, then through a column D filled with glass beads to increase the surface, then back to pump A. This gives a very efficient cooling system. The other circulating system is composed of a solid glass piston E machined to fit into a block of Teflon F which is not attacked by ozone. The piston E is attached to an eccentric G which is operated by a motor of variable speed. On the other side of the Teflon block is a ground glass joint which is sealed as shown to two ground glass valves H and H′. The product to be ozonized is dissolved in *t*-butyl alcohol containing enough sulfuric acid to produce one mole of *t*-butylcarbonium ions per double bond present in the compound to be ozonized. The mixture is placed in the flask I which can be refrigerated if necessary and from which it is pumped and circulated through the column and the reaction chamber. Ozone from the ozonizer enters the reaction chamber through the tube K and passes upward through the column as the liquid mixture flows downward. The liquid in the U tube L prevents the ozone from flowing in the opposite direction and thereby avoids excessive contact of ozone with the peroxides. The stopcock J serves as a convenient outlet for withdrawing samples for the study of the course of ozonization.

The ozonizer was of the type published by Henne and Perilstein[9] except that instead of a single ozonizer tube four tubes were connected in series. The efficiency of such a multiple ozonizer was about 7% which is slightly more than twice that of an ordinary commercial ozonizer. A fairly constant flow of dry oxygen through the ozonizer was maintained at all times, and the ozone produced per unit time was determined quantitatively at the beginning and at the end of each reaction in order to estimate the total ozone used and compare it with the total amount of peroxides formed.

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[8] F. H. Dickey, F. F. Rust and W. E. Vaughan, THIS JOURNAL, 71, 1432 (1949).

[9] A. L. Henne and W. L. Perilstein, *ibid.*, 65, 2183 (1943).

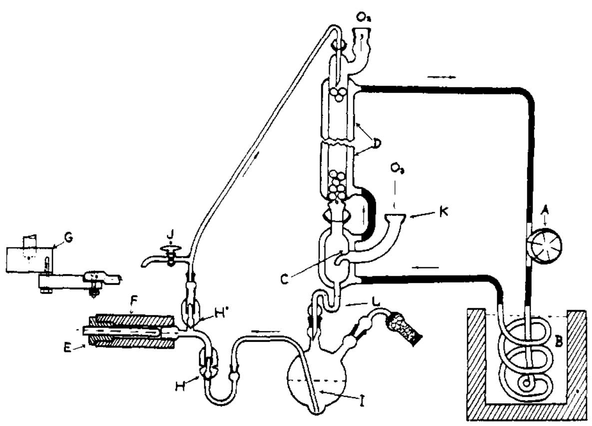

Fig. 1.—Countercurrent ozonization apparatus.

Figure 2 shows the total amount of peroxides formed as estimated iodometrically and plotted against the time of ozonization. The curve shown is for tetramethylethylene and is typical for all olefins studied except that the time necessary to reach maximum peroxide concentration is different for different olefins. It may be seen that during the first three hours of ozonization the peroxide formation is directly proportional to the time of ozonization indicating that the formation of peroxides is much faster than their decomposition. However, after three hours ozone begins to come out and slow decomposition sets in. Usually the reaction was stopped either after the maximum concentration of peroxides was reached or when the exit gases began to show the presence of ozone as indicated by starch–potassium iodide test.

Experimental

The active oxygen of all peroxides described in this paper was estimated by the methods described by Kokatnur and Jelling[10] and Wagner, *et al.*[11] Pure *n*-pentane was found by Greenwood and Wolkowich[12] to be inert to ozone at low temperatures and when this solvent[13] was used in the present work it was purified by saturating a large volume of it at 0° with ozone until the solution acquired a definite bluish color. Dry oxygen then was passed through the solution to remove the excess ozone and the mixture passed through a column of silica gel until the pentane passing through was free from peroxides, ozonides and other oxygenated products. *n*-Pentane purified by this method was found completely stable to ozone below $-20°$. Other solvents mentioned in Table I were of the purest quality obtainable.

Ozonization of Isobutylene in *n*-Pentane.—A solution of isobutylene (6 g.) in 50 cc. of purified *n*-pentane (see above) was ozonized at $-50°$ for six hours by the bubbling method. A considerable amount of formaldehyde was evolved and some of it polymerized in the exit tube. A crystalline solid (1.6 g.) separated out from the solution and was removed by filtration. This solid had a m.p. of 131–132° and was identified as diacetone peroxide.[14,15] The ozonide was not isolated in this case.

Ozonization of Tetramethylethylene in *n*-Pentane.—A solution of tetramethylethylene (15 g., b.p. 72–74°, $n^{25}D$ 1.4068) in 500 cc. of purified pentane was ozonized by the countercurrent method (Fig. 1) for six hours at $-20°$. The reaction was stopped and a solid, diacetone peroxide (1 g., m.p. 132–133°), was removed by filtration. The filtrate was concentrated under reduced pressure to about 50 cc., whereby an additional 1 g. of diacetone peroxide was separated from the solution. The remaining solution was subjected to a vacuum (2 mm.) distillation at room temperature whereby a viscous residue (10.9 g.) was obtained which failed to crystallize by any known means. Upon heating it exploded violently. This proved to be the ozonide of tetramethylethylene.

Anal. Calcd. for $C_6H_{12}O_6$: active oxygen (O), 12.12. Found: (O), 12.14.

Another sample (5 g.) of tetramethylethylene was ozonized at 0° in chloroform (100 cc.) by the bubbling method until the solution acquired a bluish color. The excess ozone was removed by bubbling oxygen through the solution and the cold solution was added slowly with stirring to a cold (0°) solution of *t*-butyl alcohol (50 cc.) containing 5 g. of 70% sulfuric acid. Stirring was continued for three hours longer, then 250 cc. of ether was added and the mixture thoroughly shaken with excess solid magnesium carbonate containing 40% magnesium oxide to neutralize the sulfuric acid present in the solution. The mixture then was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. A residue (3.5 g.) was obtained which was dissolved in a small amount of pentane and the solution allowed to stand at $-8°$ overnight. A crystalline solid (0.5 g.) separated out, m.p. 132–133°, and proved to be diacetone peroxide.

Since this peroxide was isolated from the above mixture, a pure sample of it was allowed to stand for some time in a solution of *t*-butyl alcohol and 70% sulfuric acid. When the mixture was worked up the peroxide was recovered completely unchanged. Even when it was heated in dilute sulfuric acid there was no apparent reaction and the peroxide was recovered unchanged.

Ozonization of Tetramethylethylene in the Presence of *t*-Butylcarbonium Ions.—To a solution of *t*-butyl alcohol (200 cc.) containing 14.3 g. of 70% sulfuric acid was added 16.8 g. of tetramethylethylene and the mixture ozonized countercurrently in an apparatus shown in Fig. 1 for five hours at a temperature of about 15° and at the rate of 0.02 mole of ozone per hour.[16] Small samples were withdrawn every half-hour and the peroxide determined iodometrically. The results are plotted in Fig. 2.

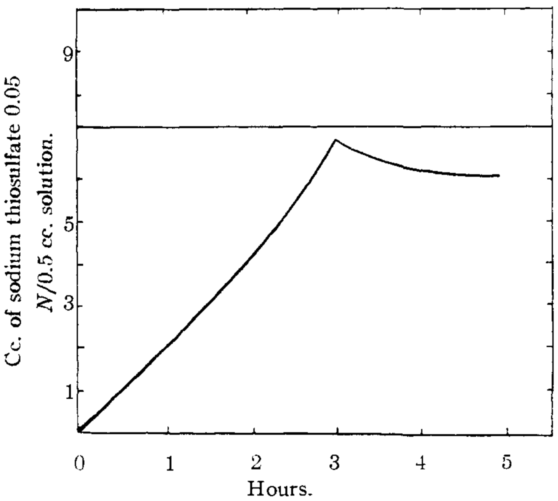

Fig. 2.—Rate of peroxide formation in ozonizations in the presence of carbonium ions.

The reaction mixture was then washed out of the apparatus with 200 cc. of ether and to the resulting mixture was added 10 cc. of water and excess magnesium carbonate containing about 40% magnesium oxide. The mixture was thoroughly shaken to remove all the sulfuric acid, then filtered and dried over magnesium sulfate. The mixture was then filtered and most of the solvent removed at room temperature in a stream of nitrogen under reduced pressure (20 mm.), but the last traces were removed at 0° in a vacuum of 1–2 mm. using a Dry Ice trap between the oil-pump and the distilling flask. The residue usually was subjected to

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[10] V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

[11] C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 979 (1947).

[12] F. L. Greenwood and M. G. Wolkowich, *J. Org. Chem.*, **17**, 1551 (1952).

[13] Phillips Petroleum Co. pure grade.

[14] A. Baeyer and V. Villiger, *Ber.*, **33**, 860 (1900).

[15] W. Dilthey, M. Inckel and H. Stephan *J. prakt. Chem.*, **154**, 219 (1940).

[16] Although oxygen was passed through the ozonizer at fairly constant rate, the rate of ozone formation was determined at the beginning and at the end of each experiment in order to estimate the total ozone used. Usually the rate of ozone formation remained constant during each experiment.

the latter conditions for several hours or until the active oxygen analysis remained constant. A yield of about 57% of the peroxide was obtained based on the ozone used.

Anal. Calcd. for $C_{10}H_{22}O_4$ (type XII or XIII): active oxygen (O), 7.76. Found: (O), 8.00.

When the above peroxide was subjected to a high vacuum (10^{-2} mm.) at 25–30° for several hours, slow decomposition took place with the evolution of acetone and another more stable peroxide was obtained, $n^{25}D$ 1.4250.

Anal. Calcd. for $C_7H_{16}O_3$ (XIV or XV): (O), 10.8. Found: (O), 11.1.

Ozonization of 2-Methylbutene-2 in the Presence of *t*-Butylcarbonium Ions.—To a solution of 200 cc. of *t*-butyl alcohol containing 12.5 g. of 80% sulfuric acid was added 14 g. of 2-methylbutene-2 and the mixture ozonized countercurrently (Fig. 1) for four hours at the rate of 0.022 mole of ozone per hour. The mixture was worked up in the same manner as in the previous case. A yield of 45% of the peroxide was obtained based on the ozone used.

Anal. Calcd. for $C_9H_{20}O_4$ (XII or XIII): (O), 8.33. Found: (O), 7.2.

Ozonization of α-Methylstyrene in *n*-Pentane.—A solution of α-methylstyrene (10 g.) and purified *n*-pentane (50 cc.) was ozonized at −20° by the bubbling method for four hours. Considerable gaseous formaldehyde was evolved during the ozonization. The solvent then was removed and the residue crystallized from hot glacial acetic acid. Diacetophenone peroxide (1.5 g., 13%) was obtained, m.p. 182–183°.[15,17] Like diacetone peroxide this peroxide is inert to various reagents including sulfur dioxide. Attempts to increase the yield of this peroxide by carrying out the ozonization in various solvents including water emulsions were not successful.

Ozonization of α-Methylstyrene in the Presence of *t*-Butylcarbonium Ions.—A solution of *t*-butyl alcohol (200 cc.) containing 12.5 g. of 80% sulfuric acid and 13 g. of α-methylstyrene was ozonized at 15–17° by the countercurrent method for four hours at the rate of about 0.022 mole of ozone per hour. The product was then worked up as in the previous cases whereby a viscous non-volatile residue (86% based on ozone used) was obtained; $n^{27}D$ 1.4936.

Anal. Calcd. for $C_{13}H_{20}O_4$ (XII or XIII): C, 64.97; H, 8.39; (O), 6.67. Found: C, 64.37; H, 8.51; (O), 6.60.

The viscous residue failed to crystallize by any methods tried and yielded *no* trace of diacetophenone peroxide.

In order to determine the structure of this peroxide a weighed sample was heated at 50° while sulfur dioxide was passed through the mixture to reduce the peroxide and to remove any formaldehyde formed during the reaction. The acetophenone formed then was determined by precipitating its 2,4-dinitrophenylhydrazone, m.p. 237–237.5°. On the basis of structure XII or XIII, the acetophenone formed should correspond to 50%; found, 53.2%.

In another experiment the peroxide was decomposed with metallic sodium following the method of Milas and Surgenor[18] and the alcohol formed distilled and identified by preparing its 3,5-dinitrobenzoate m.p. 142°. A mixed m.p. with an authentic sample prepared from *t*-butyl alcohol gave no depression showing definitely that the original peroxide contained *t*-butoxy groups.

When another sample of the peroxide was treated with ferrous sulfate and the mixture steam distilled, the first portion of the distillate gave a yellow 2,4-dinitrophenylhydrazone, m.p. 159–161°. A mixed m.p. with an authentic sample of 2,4-dinitrophenylhydrazone of formaldehyde gave no depression showing again that the original peroxide contained hydroxymethylene groups.

A larger sample of the peroxide was then steam distilled in the presence of small amounts of sulfuric acid. The distillate contained acetophenone and *t*-butyl alcohol but no formaldehyde. The aqueous solution in the distilling flask contained the same total active oxygen content as the original sample of the peroxide. Furthermore, the peroxide remaining in the flask was not hydrogen peroxide since it failed to give a positive test with a clean silver foil. The sulfuric acid was then removed by adding excess barium carbonate and the mixture filtered. When the water was removed under reduced pressure, a white solid separated out which melted at 40–43°. This was recrystallyzed from ether, m.p. 60–62°, identified as dihydroxydimethylene peroxide.[19] This peroxide was synthesized by an independent method (see below) and the synthetic product compared with that isolated from the ozonization of α-methylstyrene; the two were identical.

Dihydroxydimethylene Peroxide.—To 200 cc. of an aqueous solution containing 17 g. of hydrogen peroxide (0.5 mole) and 10 g. of sulfuric acid (1.0 mole) was added slowly at 0° with vigorous stirring 30 g. of trioxymethylene (1.0 mole). Stirring was continued overnight at room temperature whereby all of the trioxymethylene had gone into solution. To this solution then was added slowly 20 g. (1.0 mole) of barium carbonate and the barium sulfate precipitated removed by filtration through 10 g. of Celite analytical filter. To remove the excess barium ions from the aqueous solution, the filtrate was passed through a column filled with Amberlite type of cationic exchange resin. The aqueous solution was then concentrated in vacuum to about 80% strength which is safe to handle (Note: This peroxide in the crystalline state is dangerously explosive and should be handled with great care!). To obtain the crystalline peroxide, the water from a small sample of the 80% solution was completely removed and the solid obtained recrystallized from ether, m.p. 63–64°; mixed m.p. with the peroxide obtained from α-methylstyrene gave no depression.

When a sample of the original peroxide (XII or XIII) was subjected to a high vacuum (10^{-2} mm.) at 30°, it decomposed into two peroxides: one volatile peroxide which was condensed together with acetophenone in a Dry Ice trap, and a non-volatile peroxide residue. On reductive decomposition the volatile peroxide yielded *t*-butyl alcohol and formaldehyde, while the non-volatile peroxide yielded *t*-butyl alcohol and no formaldehyde. The non-volatile peroxide was obtained as a gum and failed to crystallize; $n^{25}D$ 1.5024.

Anal. Calcd. for $C_{12}H_{18}O_3$ (XIV): (O), 7.6; acetophenone, 57.1. Found: (O), 7.9; acetophenone, 55.6.

Since lead tetraacetate caused rapid decomposition with both peroxides, it was concluded that they were hydroperoxides. It was not possible to obtain the volatile peroxide in the pure state but it was suspected to be the unknown *t*-butoxymethyl hydroperoxide and its synthesis therefore was undertaken by an independent method in order to establish its properties and structure.

***t*-Butoxymethyl Hydroperoxide.**—A solution of dihydroxydimethylene peroxide was prepared as directed above and without removing the sulfuric acid, the solution was concentrated at 40° under reduced pressure (20 mm.) to a volume of 95 cc. To this solution was then added 80 cc. of *t*-butyl alcohol and 200 cc. of ethyl ether and the mixture cooled to 0°. The water was removed by adding 60 g. of anhydrous magnesium sulfate with stirring. The mixture was allowed to stand at room temperature for two hours, filtered and the ether removed in vacuum. The residue (80 g.; (O), 8.4%) then was added dropwise with stirring to a cold (0°) mixture of *t*-butyl alcohol (55 g.) and 70% sulfuric acid (100 g.). Stirring was continued for three hours at room temperature, then 60 g. of magnesium carbonate was added and the mixture extracted with four 100-cc. portions of ethyl ether. The ether extracts were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The residue then was fractionated in vacuum and the fraction (4 g.) boiling at 31–33° (4 mm.) collected and analyzed. The analysis and properties of this peroxide are recorded in Table IV and compared with those of the isomeric peroxide.

These results seem to indicate that the original peroxide obtained by the ozonization of α-methylstyrene in the presence of *t*-butylcarbonium ions is a mixture of two peroxides of the type XII and XIII.

Ozonization of 1,1-Diphenylethylene in *n*-Pentane.—1,1-Diphenylethylene was prepared according to Allen and Converse.[20] A solution of 1,1-diphenylethylene (12 g.) and 50 cc. of purified *n*-pentane was ozonized at −20° for three hours by the bubbling method. The solvent then was removed in vacuum and the residue washed several times with

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(17) C. Harries, *Ann.*, **390**, 265 (1912).

(18) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

(19) H. Wieland and A. Wingler, *Ann.*, **431**, 301 (1923).

(20) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 226.

ethanol then recrystallized from a 50–50 benzene–ethyl acetate mixture; yield of dibenzophenone peroxide 2 g. (15.1%), m.p. 206–208° (*cf.* ref. 6).

Ozonization of 1,1-Diphenylethylene in the Presence of *t*-Butylcarbonium Ions.—To a solution of *t*-butyl alcohol (100 cc.) containing 6.8 g. of 80% sulfuric acid was added 10 g. of 1,1-diphenylethylene and the mixture ozonized at 16–17° for two hours and 40 minutes by the countercurrent method at the rate of 0.0138 mole of ozone per hour. The product was worked up as in the previous cases and a yield of 100% of the crude peroxide was obtained based on the ozone used. After pumping for several hours at 0° and at 1 mm. pressure, the highly viscous residue failed to yield any crystals by any method tried.

Anal. Calcd. for $C_{18}H_{22}O_4$ (XII or XIII): (O), 5.33. Found: (O), 5.19.

That this peroxide is also a mixture of two isomeric peroxides was shown by the separation and identification of their decomposition products. A sample of the peroxide was subjected at 30° to a prolonged vacuum (2 mm.) distillation and the low-boiling products collected in two traps, one at −78° and the other at liquid nitrogen temperature. All of the product was collected in the first trap. This was allowed to warm to room temperature and a slow stream of dry nitrogen was passed over the condensate and through a reagent solution of 2,4-dinitrophenylhydrazine. A precipitate was obtained from the latter which was recrystallized from aqueous ethanol, m.p. 165–167°. This was identical with the 2,4-dinitrophenylhydrazone of formaldehyde, m.p. 167°.

The remaining condensate in the trap was then subjected to a vacuum (2 mm.) at 0° for several hours and analyzed.

Anal. Calcd. for $C_5H_{12}O_3$: (O), 13.33. Found: (O), 13.8.

This peroxide responded to all qualitative tests (Table IV) of *t*-butoxymethyl hydroperoxide. In addition, an infrared spectrum showed the presence of characteristic bands at 11.9 μ (-OOH), 9.4 μ (C-O-C), a doublet at 7.25 and 7.30 μ [-C(CH$_3$)$_3$] and at 3.2 μ (associated -OH).

The non-volatile residue from the above distillation was extracted several times with pentane to remove the benzophenone, then subjected to a high vacuum (1 mm.) at 30° until it gave a constant analysis for active oxygen; n^{25}D 1.5534.

Anal. Calcd. for $C_{17}H_{20}O_3$: (O), 5.88. Found: (O), 5.83.

The presence of the hydroperoxy group was established by its rapid decomposition with lead tetraacetate.

Ozonization of Styrene in the Presence of *t*-Butylcarbonium Ions.—To a solution of *t*-butyl alcohol (200 cc.) and 6.1 g. of 80% sulfuric acid was added 5.2 g. of freshly distilled styrene and the mixture ozonized at 15–17° by the countercurrent method for two hours at the rate of 0.02 mole of ozone per hour. The product was isolated in the usual manner and analyzed. A yield of 92% was obtained based on the ozone used.

Anal. Calcd. for $C_{12}H_{12}O_4$ (XII or XIII): (O), 7.08. Found: (O), 7.11.

Ozonization of D-Limonene in the Presence of *t*-Butylcarbonium Ions.—To a solution of *t*-butyl alcohol (200 cc.) and 12.5 g. of 80% sulfuric acid was added 13.5 g. of D-limonene and the mixture ozonized at 15–17° by the countercurrent method for three hours at the rate of 0.028 mole of ozone per hour. The product then was isolated as in the previous cases and analyzed. A yield of 85.7% was obtained based on the ozone used.

Anal. Calcd. for $C_{14}H_{26}O_4$ (XII or XIII): (O), 6.20. Found: (O), 5.50.

Ozonization of *p*-Menthene-$\Delta^{4,(8)}$ in the Presence of *t*-Butylcarbonium Ions.—To a solution of *t*-butyl alcohol (200 cc.) and 12.5 g. of 80% sulfuric acid was added 13.8 g. of *p*-methene-$\Delta^{4,(8)}$[21] and the mixture ozonized at 15–17° countercurrently at the rate of 0.022 mole of ozone per hour. The product was isolated in the usual manner; yield 68% based on the ozone used.

Anal. Calcd. for $C_{14}H_{28}O_4$ (XII or XIII): (O), 6.16. Found: (O), 6.00.

A sample of this peroxide was subjected at 30° to a high vacuum (10^{-3} mm.) for several hours and the residue again analyzed.

Anal. Calcd. for $C_{11}H_{12}O_3$: (O), 7.9; active hydrogen, 1.00. Found: (O), 8.0; active hydrogen, 0.95.

Ozonization of 2-Phenyl-3-methylbutene-2 in *n*-Pentane.—A solution of 16.7 g. of 2-phenyl-3-methylbutene-2 (b.p. 188–189°, n^{25}D 1.15120) and 100 cc. of purified *n*-pentane was ozonized for four hours at −50° by the bubbling method. The solution then was concentrated in vacuum to 30 cc. and allowed to stand at 0° for two days. A crystalline solid (0.9 g., 10.7%) separated, m.p. 128–129°; this was recrystallized once from pentane; m.p. 132–133°, mixed m.p. with diacetone peroxide gave no depression. It may be significant that no diacetophenone peroxide was isolated in spite of the fact that it is much less soluble in pentane than diacetone peroxide.

Ozonization of 1,1-Diphenyl-2-acetoxyethane in *n*-Pentane.—1,1-Diphenyl-2-acetoxyethene was prepared from diphenylacetaldehyde[22] by the method of Tiffeneau[23]; m.p. 56–58°. A solution of 5.3 g. of 1,1-diphenyl-2-acetoxyethene and 50 cc. of purified *n*-pentane was ozonized at −20° for four hours by the bubbling method. The solvent then was removed under reduced pressure and the residue extracted several times with ethanol to remove the benzophenone. The peroxide then was recrystallized from a 50–50 benzene–ethyl acetate mixture; yield 13%, m.p. 206–208°.

Ozonization of Tetraphenylethylene in Carbon Tetrachloride.—Tetraphenylethylene was prepared by the method of Norris, Thomas and Brown[24]; m.p. 226–227°. A sample (10 g.) of this hydrocarbon was ozonized in carbon tetrachloride (200 cc.) at 0° for four hours by the bubbling method. The solvent then was removed under reduced pressure and the residue recrystallized from benzene; yield 56%, m.p. 206–208°. This was identified as dibenzophenone peroxide.

Another sample of tetraphenylethylene was ozonized in ethyl acetate at 20°. A yield of 20% of crude dibenzophenone peroxide was isolated from this solution.

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[21] This hydrocarbon was prepared by the dehydration of *p*-methanol-8 with oxalic acid; b.p. 170–174°; n^{25}D 1.4544; lit. b.p. 172–174°; n^{21}D 1.4568.

[22] S. Daniloff and E. Venus-Danilova, *Ber.*, **59**, 1041 (1922).

[23] M. Tiffeneau, *Compt. rend.*, **150**, 1183 (1910).

[24] J. F. Norris, R. Thomas and D. M. Brown, *Ber.*, **43**, 2958 (1910).