1,4-Endoethylene-6,11-diketo-$\Delta^{4a(12a),6a(10a),7,9}$-dodecahydronaphthacene (XII).—A mixture of 2.0 g. (0.015 mole) of 2,3-dimethylenebicyclo[2.2.2]octane (II), 2.4 g. (0.015 mole) of 1,4-naphthoquinone, 0.1 g. of *p-t*-butylcatechol and 30 ml. of benzene was allowed to stand for 3 days at room temperature. The benzene was removed by evaporation and the residue was crystallized from cyclohexane to give 2.6 g. (59%) of a slightly impure adduct XII, m.p. 148–151°. Recrystallization from cyclohexane produced white flakes of analytically pure 1,4-endoethylene-6,11-diketo - $\Delta^{4a(12a),6a(10a),7,9}$ - dodecahydronaphthacene (XII), m.p. 150–151°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.29; H, 6.86.

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[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Autoxidation of 2,3-Dimethylbutadiene-1,3

BY FRED K. KAWAHARA

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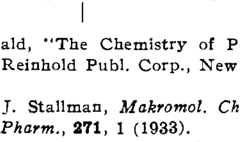
Autoxidation of 2,3-dimethylbutadiene-1,3 yields polymeric peroxides. The 1,2-addition of oxygen to 2,3-dimethylbutadiene-1,3 has been confirmed by the isolation of formaldehyde and isopropenyl methyl ketone. However, isolation of two additional volatile products, dimethyl glyoxal and α-isopropenylacrolein, points to a more complex reaction. Presence of dialkyl peroxidic linkages of at least two types is demonstrated by reductive cleavage. In addition, the presence of ether groups is shown in the polymeric peroxides, as well as that of carbonyls, hydroperoxides, acidic, ester and hydroxyl groups.

Introduction

An important problem in the storage of cracked gasoline is the development of undesirable polymeric material called gum. Gum formation is retarded through use of antioxidants and metal deactivators, and by proper choice of refining procedures. Valuable ways of further reducing gum might be discerned from the mechanism of formation and the structure of the polymeric gum.

Unfortunately, little is known about either. However, the catalytic action of oxygen on conjugated diolefins in gasoline is known to be an important factor in deterioration.[1] Structural studies of the peroxides formed by autoxidation of acyclic conjugated dienes have been limited because of the complexity of the products. Addition of oxygen to the double bonds has been assumed to occur at either the 1,2- or 1,4-position.[2] Only in the case of the cyclic diolefins has the 1,4-addition of oxygen to the diene system been structurally established; Hoch and Depke[3] have isolated 1,3-diols after the catalytic reduction of the polymeric peroxide of cyclopentadiene.

For reasons of convenience and availability, 2,3-dimethylbutadiene-1,3 has received particular attention. Bodendorf[2] hydrogenated the polymeric peroxide and identified formaldehyde among the cleavage products. Kern[4] thermally decomposed the same material and obtained, in addition to formaldehyde, isopropenyl methyl ketone. Isolation of these products led Kern to propose as the structure of the monomer of the polymeric peroxide of dimethylbutadiene



$$-\mathrm{O}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}-\overset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH_2}$$

A polymer of this monomer is formed by interpolymerization of oxygen with the diene at the 1,2-position.

An investigation of the products of the autoxidation of 2,3-dimethylbutadiene-1,3 has been carried out. One objective of the work was to determine whether 1,2-interpolymerization with oxygen was the sole mechanism or whether polymer was also formed by reaction at the 1,4-position, by carbon-to-carbon polymerization or by addition of RO· radicals to double bonds. A second objective was to isolate additional volatile products of the autoxidation and thus cast light upon the mechanism of polymer formation. The polymer was subjected to reductive procedures of varying severity to determine whether the peroxide linkages were of uniform strength, and thus of one type, or whether peroxide bonds of varying ease of reduction, and hence of different structure, were present. An additional aim was to determine the effect of different products of autoxidation upon the formation of others.

Experimental

Freshly distilled 2,3-dimethylbutadiene-1,3 (2.5 g.) was added to 100 ml. of *n*-heptane in a 450-ml. bottle. The *n*-heptane had been purified by treatment with acid and percolation through silica gel. The bottle was sealed and placed in dark storage at 110°F. for 28 days. After 14 days it was cooled to ice temperature and the air was changed before sealing again. Eighty such bottles were prepared for the study of three fractions: volatile products, heptane-soluble material and heptane-insoluble material.

Isolation and Identification of Volatile Products.—The volatile distillate obtained by distillation of total autoxidized product at 40° (20 mm.) with a nitrogen bubbler gave a positive peroxide test with glacial acetic acid and potassium iodide. Absence of peroxides in the aqueous extract of the volatile distillate was shown by a negative test with ferrous thiocyanate.[5]

Four volatile products were isolated and identified: formaldehyde, isopropenyl methyl ketone, α-isopropenylacrolein and dimethyl glyoxal. These compounds were identified by the melting points of the appropriate derivatives.[6]

Formaldehyde.—At the end of the storage period, four samples (originally totalling 10.0 g. of dimethylbutadiene) were combined and extracted with 100 ml. of water. The aqueous extract was then treated with a saturated solution of

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[1] R. H. Rosenwald, "The Chemistry of Petroleum Hydrocarbons," Coll. Vol. II, Reinhold Publ. Corp., New York, N. Y. 1955, p. 345.

[2] W. Kern and J. Stallman, *Makromol. Chem.*, **7**, 199 (1951); K. Bodendorf, *Arch. Pharm.*, **271**, 1 (1933).

[3] H. Hoch and F. Depke, *Ber.*, **84**, 349 (1951).

[4] W. Kern and A. R. Heinz, *Makrom. Chem.*, **16**, 81 (1955).

[5] R. F. Robey and H. K. Wise, *Anal. Chem.*, **17**, 425 (1945).

[6] Melting points were not corrected.

5,5-dimethyl-1,3-cyclohexanedione in water.[7] Fine white needles formed in 10 minutes. The crystals (0.119 g., m.p. 190–190.6°) were filtered off; when mixed with an authentic sample of formaldehyde dimethone (m.p. 190.3–191°), melting point was not lowered.

Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.9; H, 8.2. Found: C, 69.9; H, 8.2.

A second crop of crystals (0.226 g.) melted at 187–189°; a mixture with the known derivative melted at 188–190°.

Isopropenyl Methyl Ketone and α-Isopropenylacrolein.—Carbonyl compounds were isolated as derivatives of 2,4-dinitrophenylhydrazine. To two samples (originally 5.0 g. of dimethylbutadiene) were added 200 ml. of aldehyde-free ethyl alcohol, 3 g. of 2,4-dinitrophenylhydrazine and 4 ml. of concentrated hydrochloric acid. A mixture of solid dinitrophenylhydrazones separated. The reaction mixture was diluted with water and extracted with ether. Thus, the 2,4-dinitrophenylhydrazones were separated into ether-soluble and ether-insoluble portions.

Ether-soluble derivatives weighed 5.2 g. and were dissolved in 200 ml. of benzene and separated chromatographically. The column was packed with two parts of 100-mesh chromatographic-grade silicic acid to one part of Filter-Cel and wetted with hexane. A small amount of pure benzene was added, followed successively by the benzene solution of the ether-soluble 2,4-dinitrophenylhydrazones and 200 ml. of hexane. Development of the chromatogram was made with 4600 ml. of hexane containing 4% ether. Four principal bands were obtained and individually eluted with ether.

The two bands most strongly adsorbed contained brown, gummy material from which no crystalline products could be isolated. From the remaining two bands, red crystalline compounds were obtained. The first, 1.02 g., was 1-(2,4-dinitrophenyl)-3,4-dimethyl-4,5-dihydropyrazole—the cyclization product of the dinitrophenylhydrazone of isopropenyl methyl ketone. After crystallization from a mixture of ethyl alcohol and ethyl acetate, it melted at 189–189.5° (reported[8] m.p. 190–191°).

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.0; H, 4.6; N, 21.2. Found: C, 50.1; H, 4.4; N, 20.7. Absorption maxima in alcohol: 249, 360.5 mμ.

The second band, 0.275 g., was the 2,4-dinitrophenylhydrazone of α-isopropenylacrolein. After recrystallization from a mixture of ethyl alcohol and ethyl acetate, it melted at 195–195.5°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.2; H, 4.4; N, 20.3. Found: C, 51.9; H, 4.7; N, 20.1. Absorption maxima in alcohol: 258, 293, 381 mμ.

Dimethyl Glyoxal.—Treatment of a portion of the ether-insoluble dinitrophenylhydrazone with alcoholic potassium hydroxide gave a blue color test indicating the presence of a dicarbonyl compound.[9] The crude dinitrophenylhydrazone was treated with 1 ml. of acetone, 5 ml. of ethanol and 2 drops of concentrated hydrochloric acid. This mixture was refluxed 5 minutes, filtered hot and washed twice with hot ethyl alcohol. The remaining insoluble material was crystallized from nitrobenzene. The product, 70.1 mg., melted above 305°.

Anal. Calcd. for $C_{16}H_{14}N_8O_8$: C, 43.1; H, 3.2; N, 25.1. Found: C, 42.6; H, 2.9; N, 24.9.

Analysis of the Heptane-soluble Material.—At the end of the storage period, the heptane-soluble material from 30 samples (originally 75.0 g. of dimethylbutadiene) was decanted and the solvent was removed under vacuum in a nitrogen atmosphere. The heptane-soluble residue, 10.61 g., was then separated into water-soluble and water-insoluble parts by solution in 150 ml. of ether and extraction with four 50-ml. portions of water.

Water-soluble Part.—The water-soluble part weighed 1.81 g. It contained no acidic, aldehydic or peroxidic groups. A test for glycols was positive.[10] This mixture was separated by paper chromatography in which equal parts of ethanol, *n*-butanol and water were used as developer.[11] Presence of three different glycols was indicated by three distinct bands when the chromatogram was treated with ammoniacal silver nitrate solution.

Water-insoluble Part.—The water-insoluble part, dissolved in ether, was extracted with 5% aqueous sodium carbonate solution. Acidic material recovered weighed 1.63 g. The dried neutral components, 7.15 g., had the following properties.

Anal. Calcd. for $(C_6H_{10}O_2)_n$: C, 63.1; H, 8.8. Found: C, 65.4; H, 9.4; mol. wt., ebullioscopic in benzene, 316 ± 10; hydroperoxide value, 0.775 meq. per g.[12]; carbonyl value,[13] 3.60 meq. per g.; acid number, 0.08 meq. per g.; ester number, 2.08 meq. per g.; hydroxyl number, 3.09 meq. per g.

Of the neutral material, 3.69 g. was hydrogenated to reduce hydroperoxides and double bonds. Hydrogenation was carried out in ethanol with freshly prepared platinum dioxide as catalyst. The hydrogenation equivalent was 1302. After the catalyst was removed by filtration, the alcohol was distilled from the filtrate at 50° (12 mm.). The product, 3.28 g., was free of hydroperoxides by the starch-iodide test. Increase in carbonyl value of the hydrogenated product from 3.6 to 4.45 meq. per gram indicated cleavage of unstable dialkyl peroxides.

The hydrogenated product, 3.08 g., was then treated with aluminum isopropoxide to reduce all carbonyl groups.[14] Inorganic material was hydrolyzed with cold dilute hydrochloric acid. Esters were then saponified with 0.5 *N* alcoholic potassium hydroxide solution and the resulting mixture was acidified to congo red with 1 *N* hydrochloric acid solution. The organic material was taken up in ether. Removal of the ether left 2.00 g. of carbonyl-free product having a hydroxyl number of 4.27 meq. per g. and an acid number of 0.63 meq. per g.

To demonstrate the presence of more-stable peroxides, the carbonyl-free product was hydrogenated over platinum catalyst in glacial acetic acid. Its hydrogenation equivalent was 1087. The dried product, 1.86 g., gave a positive carbonyl test with 2,4-dinitrophenylhydrazine. Together with the absorption of hydrogen, it indicated cleavage of dialkyl peroxides.

To cleave the most-stable peroxides in one step, 1.68 g. of the polymer that had been hydrogenated in alcohol and rendered carbonyl-free by reduction with aluminum isopropoxide was further reduced. The polymer was dissolved in purified tetrahydrofuran and treated with excess lithium aluminum hydride for 8 hr.[15] Excess hydride was then decomposed with ethyl alcohol, the solvent was removed under vacuum and the residue was acidified to congo red with 3 *N* sulfuric acid. Careful extraction of the acidified mixture with ether yielded 1.24 g. of product. It had a hydroxyl number of 8.67 meq. per g., an increase from 4.27 meq. per g. Molecular weight of the product was 144 ± 8. Treatment with lithium aluminum hydride thus cleaved material of 316 molecular weight to a product of 144 molecular weight by breaking dialkyl peroxide bonds and converting them to hydroxyl groups. Infrared absorption spectra of the reduced heptane-soluble polymer showed a band at 9.12 μ. Such a band indicates the presence of either a secondary alcohol or an ether linkage. No alkyl peroxide bands in region of 5.5 to 5.6 μ were found.

Anal. Found: C, 61.70; H, 10.26.

Analysis of Heptane-insoluble Material.—After decantation of the heptane-soluble material, 4.82 g. of heptane-insoluble material remained in the 30 bottles. It was similarly separated into water-soluble and water-insoluble parts.

Water-soluble Part.—Extraction of the heptane-insoluble material with water yielded 1.08 g. of water-soluble components. The aqueous extract gave a positive test for glycols.[10] A portion of the extract was subjected to paper chromatography; treatment of the chromatogram with ammoniacal silver nitrate solution indicated the presence of two glycols.

Water-insoluble Portion.—To remove acids, the water-insoluble material was dissolved in ether and extracted with

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[7] D. Vorlander, *Z. Anal. Chem.*, **77**, 247 (1929).

[8] G. Morgan and C. F. Griffith, *J. Chem. Soc.*, 841 (1937).

[9] H. H. Strain, THIS JOURNAL, **57**, 758 (1935).

[10] F. Feigl, "Spot Tests," Elsevier Publishing Co., Houston, Texas, 1954, p. 130.

[11] L. Hough, *Nature*, **165**, 400 (1950).

[12] D. C. Walker and H. S. Conway, *Anal. Chem.*, **25**, 923 (1953).

[13] Determined after reduction of hydroperoxides with ferrous ions in dilute hydrochloric acid; modified oximation method was used. D. M. Smith and J. Mitchell, Jr., *Anal. Chem.*, **22**, 750 (1950).

[14] A. L. Wilds, "Organic Reactions," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 203.

[15] M. Matic and D. A. Sutton, *J. Chem. Soc.*, 2679 (1952).

5% aqueous sodium carbonate. Acidification of the aqueous extract gave 0.92 g. of organic acids. The neutral water-insoluble material, weighing 2.82 g., was soluble in ethanol but only slightly soluble in ether; peroxide number, 0.74 meq. per g.; carbonyl number, 4.6 meq. per g.; hydroxyl number, 0.22 meq. per g.; mol. wt., ebullioscopic in acetone, 367 ± 10.

Anal. Found: C, 62.3; H, 8.7.

The product was observed to be darker and more viscous than the heptane-soluble material. Stepwise hydrogenation of the neutral material, first in absolute ethyl alcohol and then in glacial acetic acid, indicated that peroxide bonds differing in stability were present.

Discussion

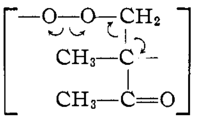
One-third to one-half of the dimethylbutadiene was accounted for

Monomeric cleavage products	8.5–12.5%
dimethyl glyoxal	Trace
formaldehyde	0.5%
isopropenyl methyl ketone	6–8%
α-isopropenylacrolein	2–4%
Heptane-soluble products	14–30%
acids	2.2%
glycols	2.4%
polymeric peroxides	9.6%
Heptane-insoluble products	5–9%
acids	1.2%
glycols	1.4%
polymeric peroxides	3.8%

The balance of the material was unreacted 2,3-dimethylbutadiene-1,3. Presumably, oxidation longer than 28 days would have given somewhat higher yields.

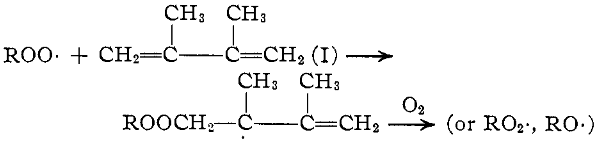
Two previously isolated products, formaldehyde and isopropenyl methyl ketone, led to the conclusion that the polymeric peroxide forms by interpolymerization of oxygen with the conjugated diene at the 1,2-position. The isolation of formaldehyde and isopropenyl methyl ketone from the autoxidation reaction mixture supports this view.

Additional information leading to a more complex picture of the autoxidation process has been obtained. Isolation of trace amounts of dimethyl glyoxal shows that a small part of the polymeric peroxide forms by the 1,2-addition of oxygen to isopropenyl methyl ketone. Dimethyl glyoxal is a fission fragment resulting from the decomposition of peroxide of the structure



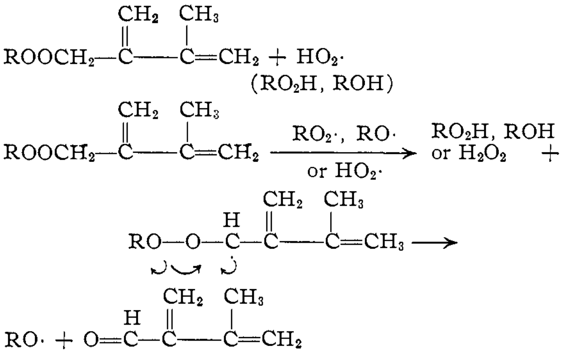
$$\left[\begin{array}{l} \mathrm{-O-O-CH_2} \\ \quad\ \mathrm{CH_3-\overset{|}{C}-} \\ \quad\ \mathrm{CH_3-\overset{|}{C}{=}O} \end{array}\right]$$

Isolation of α-isopropenylacrolein points to another reaction occurring during autoxidation. Formation of this unsaturated aldehyde is best explained by the direct attack of a peroxy radical upon the double bond of 2,3-dimethylbutadiene-1,3, followed by decomposition of the diene peroxide



$$\mathrm{ROO\cdot} + \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2\ (I)} \longrightarrow$$

$$\mathrm{ROOCH_2{-}\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2} \xrightarrow{O_2} (\text{or } \mathrm{RO_2\cdot},\ \mathrm{RO\cdot})$$



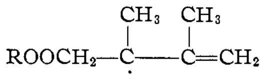
$$\mathrm{ROOCH_2{-}\overset{CH_2}{\overset{\|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2} + \mathrm{HO_2\cdot}\quad (\mathrm{RO_2H,\ ROH})$$

$$\mathrm{ROOCH_2{-}\overset{CH_2}{\overset{\|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2} \xrightarrow[\text{or } \mathrm{HO_2\cdot}]{\mathrm{RO_2\cdot},\ \mathrm{RO\cdot}} \begin{array}{l}\mathrm{RO_2H,\ ROH} \\ \text{or } \mathrm{H_2O_2}\end{array} +$$

$$\mathrm{RO{-}O{-}\overset{H}{C}{-}\overset{CH_2}{\overset{\|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_3} \longrightarrow$$

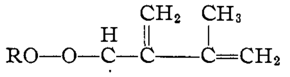
$$\mathrm{RO\cdot} + \mathrm{O{=}\overset{H}{C}{-}\overset{CH_2}{\overset{\|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2}$$

Recent work shows that *t*-butyl peroxy radicals readily add to the terminal carbon atom of 1-olefins to yield *t*-butyl alkenyl-2 peroxides.[16] Similarly, the peroxy radical adds to the terminal carbon atom of dimethylbutadiene. The radical



$$\mathrm{ROOCH_2{-}\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2}$$

may lose a hydrogen atom by disproportionation with another radical (R—O₂· or R—O·) as well as with oxygen. Thus, the double bond of the dimethylbutadiene moiety is shifted to the α-position. A free radical attack upon alkyl alkenyl-2 peroxide at its most reactive point will yield the



$$\mathrm{RO{-}O{-}\underset{\cdot}{\overset{H}{C}}{-}\overset{CH_2}{\overset{\|}{C}}{-\!-}\overset{CH_3}{\overset{|}{C}}{=}CH_2}$$

radical which will decompose readily to the α-isopropenylacrolein and RO· radical.

To demonstrate the presence of dialkyl peroxide linkages in the heptane-soluble material, it was treated with lithium aluminum hydride to reduce all peroxides to alcohols. When applied to a sample of the material freed of hydroperoxides, carbonyl groups, esters and epoxides, this treatment increased the hydroxyl number from 4.27 to 8.67 meq. per g. The increase can only result from reduction of peroxides to alcohols.

The presence of ether linkages in the heptane-soluble polymeric peroxide was shown by an oxygen balance on the material treated with lithium aluminum hydride. The reduced material contained 17.5 meq. of oxygen per gram. The hydroxyl and acid groups account for 8.67 and 1.2 meq., respectively. The difference, 7.63 meq., is due to the oxygen in ether linkages, the presence of which was indicated by infrared absorption. Such ether linkages are formed by the addition to double bonds of alkoxy radicals derived from the decomposition of hydroperoxides or peroxides. The elemental analyses show that the final product contains monomer units of six carbon atoms averaging one hydroxyl and one ether group per unit. The molecular weight of 144 indicates a mixture of monomers and dimers of such units.

Presence in the heptane-soluble material of dialkyl peroxides of varying degrees of stability was shown by stepwise hydrogenation. The polymer was first hydrogenated over platinum in ethanol to reduce olefins and hydroperoxides and to cleave the

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(16) M. S. Kharasch, P. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

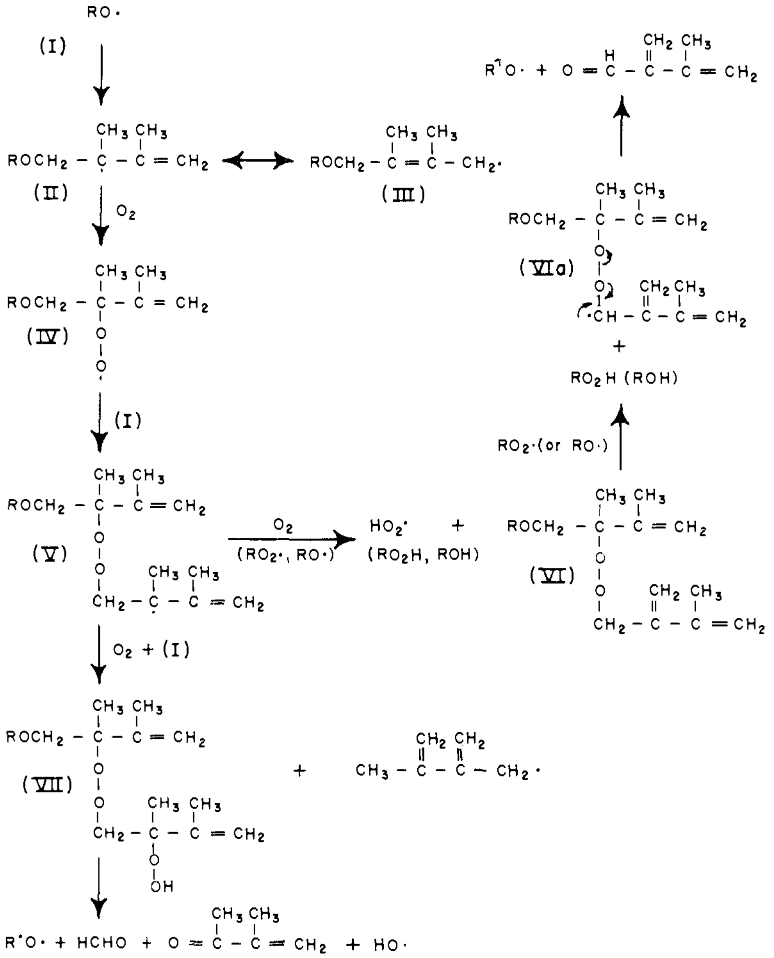

Fig. 1.—Scheme for the autoxidation of 2,3-dimethylbutadiene-1,3.

less-stable dialkyl peroxides to aldehydes. Formation of aldehydes was shown by the 23% increase in carbonyl content. These carbonyl groups were reduced with aluminum isopropoxide. The carbonyl-free product was then reduced over platinum in glacial acetic acid. Under these more drastic conditions, more stable dialkyl peroxides were cleaved and more carbonyl groups were formed. Thus, the peroxide bonds have at least two different degrees of stability.

The heptane-insoluble material is a product of the heptane-soluble polymeric peroxide. The insoluble material appears after the formation of the soluble peroxides. Peroxidation of such soluble polymeric peroxides leads to a more-polar polymer, which is insoluble in hydrocarbon solvents.

Several questions remain unanswered. No evidence for 1,4-addition of oxygen has been obtained; the 2,3-dimethylmaleic dialdehyde-1,4 that would indicate this type of addition has not been found.[17] Further work should determine the extent of carbon–carbon polymerization in the autoxidation reaction. The origin of the alkoxy radicals—whether simple dialkyl peroxide, cyclic peroxide, or hydroperoxide—also remains undetermined.

This experimental work suggests the reaction scheme for the autoxidation of dimethylbutadiene shown in Fig. 1. The peroxide formed from 2,3-dimethylbutadiene-1,3 during the initial stage of autoxidation serves as an initiator when decomposed to the alkoxy radical. This radical adds to the conjugated diene to yield either radical II or III. An ether linkage is thus formed.[18] Oxygen adds to II in the 1,2-position, although 1,4-addition may also occur. The addition of the peroxy radical IV to another diene, followed by oxygen attack, may result in chain termination and lead to product VI. Decomposition of the intermediate VIa, formed by a free radical attack upon the α-methylenic hydrogen of VI, will yield α-isopropenylacrolein. The chain may also be terminated by further addition of oxygen, followed by hydroperoxide formation. Product VII thus contains an ether linkage, a dialkyl peroxidic bond and a labile hydroperoxidic group. Decomposition will yield formaldehyde, isopropenyl methyl ketone and free radical fragments that will initiate new chain reactions.

WHITING, INDIANA

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[17] The absence of 2,3-dimethylbutanediol-1,4, which would provide evidence for 1,4-addition was not established; closer study of the diols produced by reduction of larger amounts of heptane-soluble polymeric peroxides might reveal its presence.

[18] M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).