

## Products of the Oxidation of Rubber. I. Compounds Boiling Lower than Water

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### Synopsis

Products of the oxidation of *cis*-polyisoprene boiling lower than water have been resolved and identified. They are: acetaldehyde, methyl formate, propionaldehyde, acetone, methanol, sylvan, methacrolein, ethanol, butanone, and butenone. Possible mechanisms for their origin are discussed.

Formulation of a mechanism for the reaction responsible for breaking the main hydrocarbon chain when rubber reacts with oxygen requires knowledge of the primary scission products. Previous attempts<sup>1-3</sup> have been based on a limited group of known products, including water, carbon dioxide,<sup>4</sup> acetaldehyde,<sup>5</sup> formic<sup>6</sup> and acetic<sup>7</sup> acids, and levulinaldehyde.<sup>8</sup> Levulinaldehyde has been considered to be a primary product. It is relatively readily oxidized to carbon dioxide and acetic acid, and these have been presumed to be derived from levulinaldehyde during the degradation of rubber. Formic acid is not observed to be a product of the further oxidation of levulinaldehyde and so may represent a second primary product. The ratios of acids and carbon dioxide observed when oxidation is carried out in latex<sup>1,7</sup> are consistent with a primary scission step giving one 5-carbon fragment (levulinaldehyde) and one 1-carbon fragment (formaldehyde or formic acid) as principal products. Thus, a reasonably self-consistent mechanism could be erected on the basis of the known products. However, previously available analytical methods were not competent to eliminate the possibility that other compounds are formed during oxidation.

The composition of the mixture of volatile oxidation products has now been studied by means of gas chromatography. Other compounds are formed in addition to those already known. Although the major products are those previously described, a complete description of the reactions leading to scission should account for the minor ones as well. Some of these are related to levulinaldehyde but others are not; they must result from independent reactions leading to chain breaking, without levulinaldehyde as a principal product.

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### Experimental

The analyses described in this report was made by using synthetic *cis*-polyisoprene as a raw material to avoid the possibility that trace constituents of the volatile mixture might arise from small amounts of nonrubber compounds present in raw natural rubber. Actually, the mixture of products obtained from isoprene rubber is not distinguishable from the mixture obtained from natural rubber by the analytical methods used.

Unvulcanized rubber has too low a viscosity to permit very extensive oxidation without excess distortion of the sample. Since high extents of oxidation are necessary to obtain sufficient low molecular weight material for analysis, rubber vulcanized with cumyl peroxide was used in this work. A few samples vulcanized with sulfur and accelerators have been used as well. The composition of the volatile products mixture from these is qualitatively similar to those obtained with peroxide vulcanizates, but with some differences.

Samples were oxidized with oxygen at atmospheric pressure in an apparatus which has been described.<sup>9</sup> Volatile products were collected in a U-shaped trap immersed in a Dry Ice-methanol mixture. The usual practice was to allow reaction to proceed until about 200 ml. of oxygen had been absorbed by a 2.5-3 g. sample of rubber. This gave between 50 and 100  $\mu$ l. of product, about 80% water. Some attempts were made to obtain larger samples at low extents of oxidation by using much larger rubber samples. This effort was discouraged by a combination of inhomogeneous oxidation and occasional explosions when the concentration of volatile materials in the vapor phase rose too high.

Samples of volatile product was transferred from the trap in which they were collected to small test tubes and stored frozen in Dry Ice until used. The products of several oxidations of 3 g. samples were usually combined. Chromatographic separations were made on an F&M Model 202B temperature programmed chromatograph with  $\frac{1}{4}$  in.  $\times$  10 ft. packed columns. A number of substrates were used. The most effective for materials boiling lower than water was bis( $\beta$ -methoxyethoxy)ethyl ether (TEGD).<sup>10</sup> This was used supported on 30-60 mesh Chromosorb P. An ethylene oxide-propylene oxide block copolymer (Pluronic P84)<sup>11</sup> was also used on occasion. This separates oxygen-containing compounds in the same order as TEGD but does not have the resolving power. compounds coming off the

individual fractions were made using larger samples. During the course of this work the sample size increased with experience until the latest separations were frequently made with up to 750  $\mu$ l. samples. The resolution of minor peaks sometimes appeared better with large samples than with small on the columns containing P84 as a substrate.

Preliminary identification of compounds boiling lower than water was made by comparison of retention times with those of known compounds. Ketones and aldehydes were further identified by comparison of x-ray patterns of derivatives, mostly 2,4-dinitrophenylhydrazones, with those of authentic specimens. Most of the samples which were identified were also confirmed by comparison of infrared spectra with authentic samples. A Connecticut Instrument Company trap with a microcell having a 2  $\mu$ l. cavity was used to collect small fractions for infrared examination. In some trials samples were collected first in a Hamilton fraction collector and transferred to the microcell. In our experience a good spectrum could be obtained only if several microliters of material were available when either of these traps was used. In later work it was found possible to obtain reasonably satisfactory spectra with as little as 0.5  $\mu$ l. by trapping the component directly into solution instead of condensing it as the free material. For this purpose the exit port of the chromatograph was modified with a male joint to which a hypodermic needle could be affixed. The stream through the needle was bubbled through a small amount of carbon disulfide, cooled in a Dry Ice-methanol mixture. Quite high recoveries were obtained in this way. The reactions with reagents for preparation of derivatives were carried out in a similar way by bubbling the gas stream through an appropriate reagent solution.

For compounds boiling below water, little difficulty was encountered from contamination of a peak through condensation in cooler parts of the apparatus. Where necessary to avoid contamination, a clean needle was used for each peak.

Some constituents were confirmed by comparison of their retention times on two columns of quite different retention characteristics. For these experiments the samples of effluent were trapped in ether. The ether solutions were injected for the second run in the usual way by a cooled syringe.

## Results

Typical chromatograms are illustrated in Figures 1 and 2. Figure 1a is a chromatogram obtained on a P84 column, showing the constituents which have been observed thus far, except that peaks 9 and 10 overlap on this substrate. The peaks boiling below the boiling point of water are numbered in accordance with the order in which they separate on a TEGD column, those boiling higher than water are numbered according to their appearance in this chromatogram. Figure 1b illustrates the high resolution obtained on a TEGD column. Figure 2 illustrates that the procedure for trapping and rerunning constituents gives satisfactory collection of effluent materials.

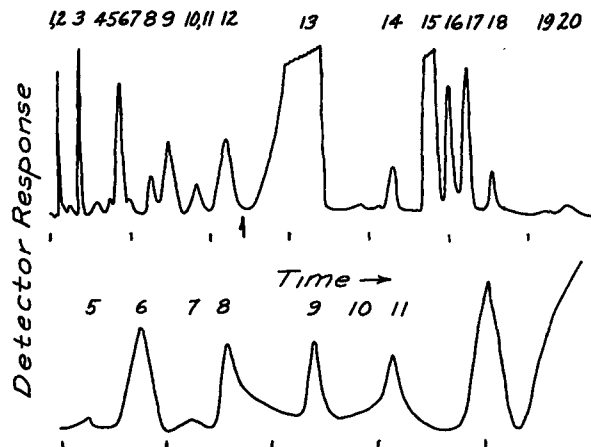


Fig. 1. Typical chromatograms. (a) (upper curve) 45  $\mu$ l. sample, column Pluronic P84, He flow 30 ml./min. 45° to arrow then at 4.2°/min. to 160° and hold, trace starts at injection time, intervals 12 min. (b) (lower curve) 100  $\mu$ l. sample; column TEGD, He flow 30 ml./min. 50° to 50 min. then at 4.2°/min. to 70° and hold, Trace starts at 30 min., intervals 12 min.

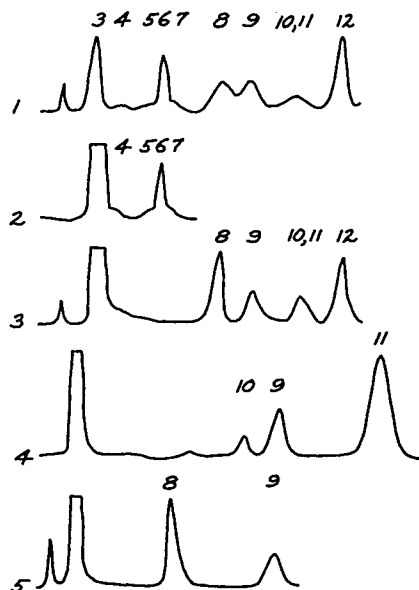


Fig. 2. Sequential separations. Trace 1: first run on P84, peaks 4-7 caught in ether in trap 1, peaks 8-12 in trap 2. Trace 2: Rerun of trap 1. Trace 3: Rerun of trap 2. Trace 4: Rerun of combined peaks 10, 11 on CET. Trace 5: Rerun of peak 8 on CET. The relative positions of alcohols and ketones are markedly shifted relative to their positions on P84.

TABLE I  
Identity of Peaks in Figure 1<sup>a</sup>

Compound	Observed on				Dinitro- phenyl- hydrazone	Infra- red	Other
	CEG	P84	TEGD	CET			
1 CO	—	+	+	—	—	—	—
2 CO <sub>2</sub>	+	+	+	+	—	—	—
3 Acetalde- hyde	+	+	+	+	+	—	b, c, d
4 Methyl formate	+	+	+	—	—	+	—
5 Propional- dehyde	+	+	+	—	+	+	—
6 Acetone	+?	+	+	+	+	+	°
7 Methyl ace- tate (?)	—	+	+	+	—	—	Boils ca. 60°C.
8 Methanol	?	+	+	+	—	+	—
8a Sylvan	—	+	+	—	+	+	—
9 Methacro- lein	+?	+	+	—	+	+	b, c
10 Ethanol	+?	+	+	+	—	+?	—
11 Butanone	?	+	+	+	+	+	—
12 Butenone	+	+	+	+	+	+	d
13 Water	+	+	+	+	—	—	—
14 —	?	+	—	—	+	—	—
15 Acetic acid	+	+	—	—	—	—	—
16 Formic acid	+	+	—	—	—	—	—
17 Levulinal- dehyde	+	+	—	—	+	—	b, d
18 —	?	+	—	—	—	—	—
19 —	?	+	—	—	—	—	—
20 —	?	+	—	—	+	—	—

<sup>a</sup> A plus (+) indicates a positive result; +? indicates two constituents occur together. A minus (—) indicates either a negative result or analysis not tried. Boiling points are estimated from retention times on P84.

<sup>b</sup> Diphenylethylene diamine, +.

<sup>c</sup> Fuchsine reagent, +.

<sup>d</sup> Iodoform, +.

The peaks which are numbered in Figures 1 and 2 are listed in Table I together with their identifications and other characterizing information where these are known. Comments on the identifications are given here.

**Peaks 1 and 2, Carbon Monoxide and Carbon Dioxide.** Carbon dioxide is known to be a product of the reaction and also is potentially a contaminant because samples are stored in solid carbon dioxide. The carbon monoxide arises from decarbonylation of formic acid in the injection port.

**Peak 2a, Unknown.** This peak has been observed only with the P84 column and when large samples were run. It may be formaldehyde, which usually is not observed because of condensation in the column.

**Peak 3, Acetaldehyde.** Acetaldehyde was originally suspected as a constituent of the volatile product mixture from the oxidation of natural rubber as a result of experiments in which it was oxidized to the acid with silver oxide.<sup>5</sup> It was tentatively identified in early work with a CEG column on the basis of retention time and carbonyl reactivity. The 2,4-dinitrophenylhydrazone has been prepared directly from the column using both natural rubber and isoprene rubber as starting material. The compound is too volatile to be trapped readily for infrared examination.

**Peak 4, Methyl Formate.** Material from repeated runs was trapped together. Identification was by position on the chromatogram and the infrared spectrum.

**Peak 5, Propionaldehyde.** This was collected in same runs as peak 4. Infrared identification as aldehyde was confirmed by means of the dinitrophenylhydrazone.

**Peak 6, Acetone.** Acetone was first suspected from examination of the infrared spectra of a peak obtained on a CEG column, in which it occurs mixed with methacrolein and methanol. It is separated from both of these on P84 and TEGD columns. Infrared spectra and derivative x-ray patterns prepared from a P84 column correspond to acetone. One preparation of the 2,4-dinitrophenylhydrazone from a different column gave a derivative which was crystalline but did not correspond to a known pattern.

**Peak 7.** This peak is suspected to represent methyl acetate on the basis of position on the chromatogram. No satisfactory spectrum has been obtained.

**Peak 8, Methanol.** Methanol was identified on the basis of its retention time on several columns. It was confirmed by trapping from a TEGD column and rerunning on CET and XF1150. Infrared confirmation was obtained by combining the material collected from the separation of a total of 1 g. of original volatile product and trapping it into carbon disulfide.

**Peak 8a, Sylvan.** This peak was overlooked during most of the study. It was finally observed when an abrupt change in temperature at peak 8 caused it to appear distinctly. Infrared spectrum, retention time, and dinitrophenylhydrazone all conform to 2-methylfuran.

**Peak 9, Methacrolein.** Methacrolein was first identified tentatively from the infrared spectrum of a fraction trapped off a CEG column. It was confirmed by preparation of the crystalline 2,4-dinitrophenylhydrazone. Further analysis of the spectrum by R. R. Hampton led to the suggestion that acetone and methanol were also present. This led to a search for improved substrates, ending with the discovery that good resolution could be obtained on TEGD and P84.

**Peak 10, Ethanol.** This peak was tentatively identified on the basis of a mixture of peaks 10 and 11 trapped directly from a TEGD column and confirmed by rerunning on a CEG (Fig. 2). Sufficient material has not yet been collected to confirm by derivative preparation.

**Peak 11, Butanone.** Butanone was originally identified from its infrared spectrum in the mixture with Peak 10. It was not possible to obtain a

derivative directly from the column when single samples of 100  $\mu$ l. of material were used. A 2,4-dinitrophenylhydrazone was finally obtained by the same procedure used for methanol.

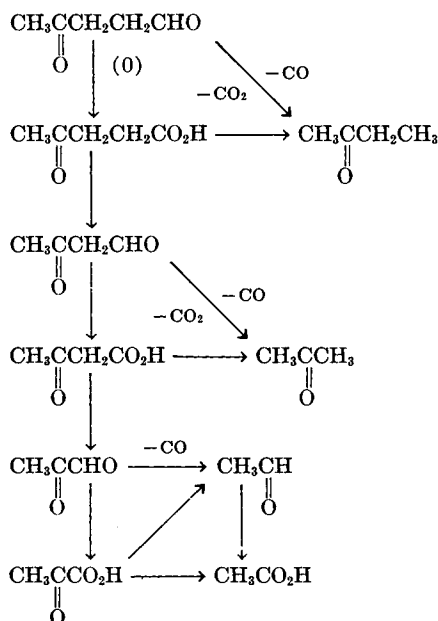
**Peak 12, Butenone.** As described in the discussion, butenone was predicted to be a constituent of the product mixture as soon as methacrolein was identified. Peak 12 was tentatively identified as butenone on the basis of its retention time on TEGD. A confirmatory infrared spectrum has been obtained. The 2,4-dinitrophenylhydrazone has been prepared directly from the column, but it has not proved possible to obtain a crystalline derivative.

Identification of higher boiling constituents is still under way. Those known from earlier work are identified in Table I.

### Origin of Constituents

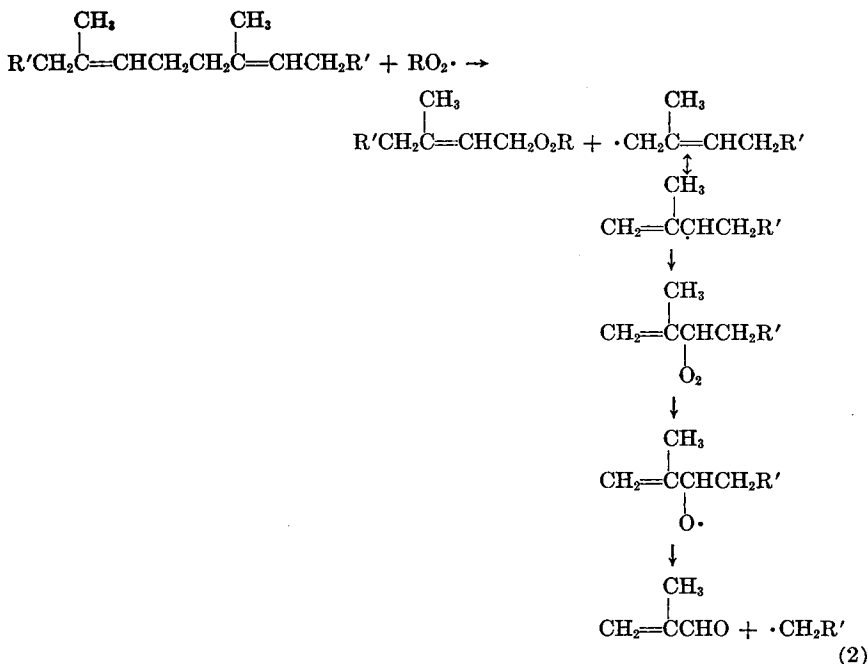
All of the constituents identified in Table I are believed to be products of the oxidation of hydrocarbon and none artifacts of sample preparation. The only two likely to be introduced accidentally are methanol and acetone, both of which have been used for the preliminary extraction before vacuum drying. Comparisons have been made by using samples extracted before drying either with methanol or with acetone. The relative sizes of chromatographic peaks for the two constituents are not appreciably affected by the choice of solvent. It is therefore considered unlikely that traces of solvent not removed by the drying procedure are the source of either of these constituents.

Tentative explanations for the origin of levulinialdehyde and acetic and formic acids have been made previously. No intermediates attrib-

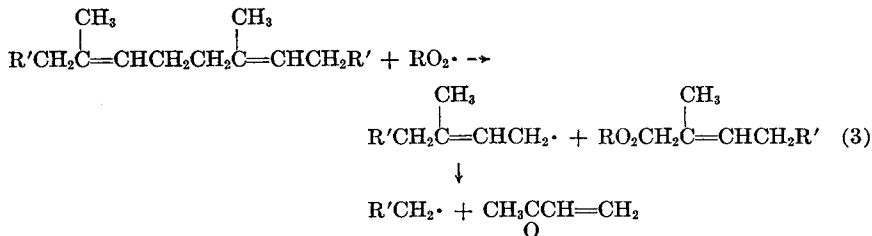


unable to further oxidation of the five-carbon keto aldehyde have been identified previously. It is suggested that acetaldehyde, acetone, and butanone are all such intermediates related as shown in the scheme of eq. (1).

Methacrolein and butenone cannot be readily formulated as oxidation products of other known intermediates. Methacrolein particularly, which retains the angular methyl group, must arise from an independent reaction. At high extents of oxidation the yields of these compounds are high enough relative to levulin aldehyde to suggest that they result from a single initial attack on the hydrocarbon chain. If so, they would appear to be evidence for chain scission as an alternative to a propagation step in polyisoprene oxidation; they may represent the result of a radical exchange process not observed in previous work. The reaction sequence which led to the suggestion that butenone is a product is based on this possibility.

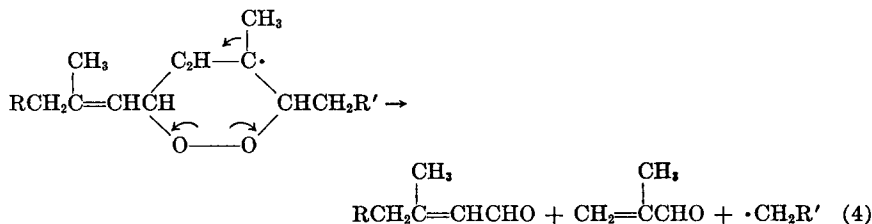


Since the asymmetry about the bond joining the two methylene groups would not be expected to lead to reaction exclusively at one of the two carbon atoms of the pair the alternative sequence must also be considered:

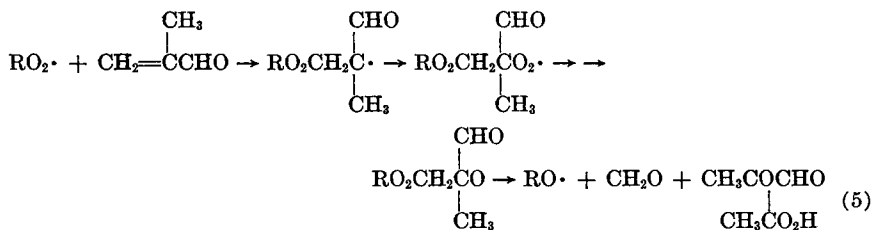




This scheme thus predicts the formation of two constituents of the product mixture in approximately equimolecular amounts, as is found with peroxide vulcanizates. However, the possibility of alternative formulations to account for these compounds must be considered. None has been found for methyl vinyl ketone but a reaction involving a cyclic peroxidic intermediate could account for methacrolein:



We have speculated that methacrolein and methyl vinyl ketone might be intermediates leading to formic acid, for which no fully satisfactory scheme has yet been developed. Recalling the reactions written by Mayo to account for the oxidation of styrene, with the production of formaldehyde and benzaldehyde as principal primary products, we may formulate similar schemes for methacrolein and butenone:



This scheme predicts the same products from butenone. A few experiments have been made to see if these compounds are readily oxidized to give formic and acetic acids by oxidizing them in dilute aqueous solution. This has been done previously with levulinic acid and with levulinolaldehyde. Starting with methacrolein very complex mixtures are obtained, including some formic and acetic acids. Starting with butenone a high yield of a single component, believed to be the cyclic dimer, was obtained under the conditions used.

With CEG as a substrate, no significant difference in composition of the low molecular weight products of oxidation of sulfur and of peroxide vulcanizates was observed.<sup>12</sup> The ratio of acids to other constituents appeared to be low, in agreement with evidence that acid yields are low from accelerated sulfur vulcanizates. With the improved resolution obtained using P84 specific differences in the amounts of minor constituents have been found. Peaks 12 (butenone) and 18 are much larger from the mixture of oxidation products derived from a peroxide vulcanizate. Peak 18 contains two components, one is present in small amount or missing entirely from the oxidation products of the sulfur vulcanizate.

All samples were thoroughly extracted and dried before they were oxidized; it is unlikely that volatile residues from the curative are present when peroxide vulcanizates are used. The simplicity of the vulcanization reaction<sup>13</sup> makes it unlikely that addition of fragments of peroxide to the rubber is responsible for the additional material in the volatile products. The differences may be attributable to the nature of the crosslinking.

### References

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### Résumé

Les produits d'oxydation du *cis*-polyisoprène, bouillant plus bas que l'eau, sont séparés et identifiés. Ce sont: l'acétyldéhyde, le formiate de méthyle, l'acétone, le méthanol, le sylvane, la méthacroléine, l'éthanol, la butanone et la buténone. On discute les divers mécanismes possibles.

### Zusammenfassung

Die Oxydationsprodukte von *cis*-Polyisopren mit niedrigerem Siedepunkt als Wasser wurden getrennt und identifiziert. Diese sind: Acetaldehyd, Methylformiat, Propionaldehyd, Aceton, Methanol, Sylvan, Methacrolein, Äthanol, Butanon, und Butenon. Mögliche Mechanismen für ihre Bildung werden diskutiert.

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