[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

OXIDATIVE HYDROLYSIS OF THE OZONIDES OF POLYBUTADIENES. III. UNEXPECTED CLEAVAGE PRODUCTS[1,2]

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The isolation of 1,2,3-propanetricarboxylic acid as a product of oxidative ozonolysis of polybutadiene and of 4-vinylcyclohexene[2] has again emphasized the fact that the cleavage of an olefin by ozone and hydrogen peroxide does not always yield the expected products. In all of the chromatographic separations of the acids from the cleavage of polybutadienes, a considerable amount of acidic material which was obviously not completely oxidized has been found in the early part of the separation. The present work was undertaken to learn what these partially oxidized products were and to see if any of them might be precursors of the 1,2,3-propanetricarboxylic acid.

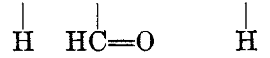
After ozonization and oxidative decomposition of the ozonides, the resulting material was separated into volatile and non-volatile fractions. The volatile portion was titrated with standard alkali and the acidity calculated as formic acid. This acid material is a mixture of at least three acids; however, the relative amounts were not determined and the calculation was made as formic acid which is the major constituent.

The non-volatile acids were separated by use of a modification of the partition chromatographic technique reported by Marvel and Rands (1). A graph of the separation achieved is shown in Figure 1. Acids represented by peaks V and VII were identified as succinic and 1,2,4-butanetricarboxylic acids respectively. Peak III was identified as acetic acid by isolation and by preparing the *p*-nitrobenzyl derivative.

It was discovered that aldehydic substances were present in both the non-volatile and volatile portions. Peak II (Figure 1) was found to represent β-formylpropionic acid (Formula I). This was established by isolating the substance in question and identifying it as its 2,4-dinitrophenylhydrazone. From the fraction represented by peak I in Figure 1, a 2,4-dinitrophenylhydrazone was isolated which analytical data indicate to be the tris-derivative of β-formyladipaldehyde (Formula II). Also from this same fraction, was isolated the 2,4-dinitrophenylhydrazone of levulinic acid.

$HO_2CCH_2CH_2CHO$

I



$$O{=}\underset{H}{C}CH_2\underset{HC{=}O}{CH}CH_2CH_2\underset{H}{C}{=}O$$

II

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

[2] This is the third paper on oxidative hydrolysis of the ozonides of polymers and copolymers of butadiene. For the second see Marvel, Schilling, Shields, Bluestein, Irwin, Sheth, and Honig, *J. Org. Chem.*, **16**, preceding article.

On treating a portion of the volatile fraction with 2,4-dinitrophenylhydrazine a mixture of 2,4-dinitrophenylhydrazones was obtained which was separated chromatographically. From this mixture derivatives of acetaldehyde, acetone, β-formylpropionic acid, and a substance corresponding to the tris-derivative of β-formyladipaldehyde were separated and identified.

It was also observed that during the oxidative decomposition of the ozonide carbon dioxide was liberated which is further evidence that some of the fragments isolated must be secondary oxidation products of the original structure.

β-Formylpropionic acid and β-formyladipaldehyde can readily be explained as incompletely oxidized cleavage products which should have been converted to succinic acid and 1,2,4-butanetricarboxylic acid, respectively. The formation of acetic acid, acetaldehyde, acetone, and levulinic acid from the known units in a polybutadiene structure is difficult to explain. These products can be explained on the assumption that some rearrangement of the external double bond occurs (III to V) during the course of polymerization.

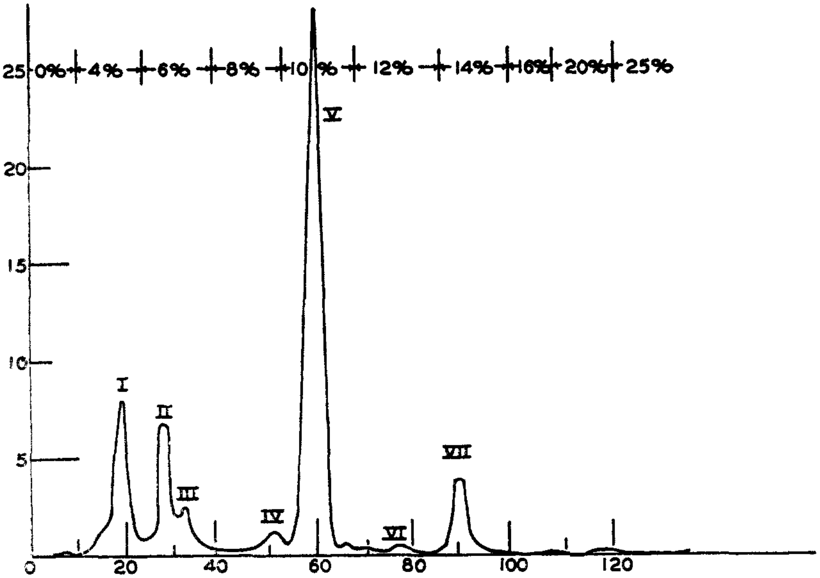
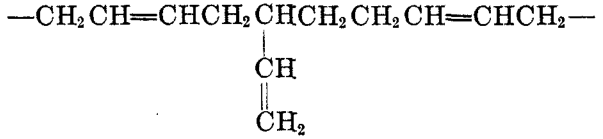
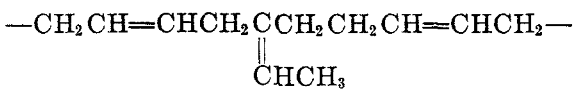


FIG. 1. NO. 1044—60.5% CONV. OXIDIZED 3% H_2O_2 10 HRS. AT 85°C. ON LARGE COLUMN



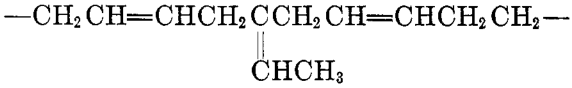
$$-\mathrm{CH_2CH{=}CHCH_2}\underset{\substack{| \\ \mathrm{CH} \\ \| \\ \mathrm{CH_2}}}{\mathrm{C}}\mathrm{HCH_2CH_2CH{=}CHCH_2}-$$

III



$$-\mathrm{CH_2CH{=}CHCH_2}\underset{\substack{\| \\ \mathrm{CHCH_3}}}{\mathrm{C}}\mathrm{CH_2CH_2CH{=}CHCH_2}-$$

IV



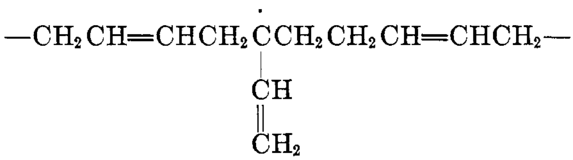
$$-CH_2CH{=}CHCH_2\underset{\underset{\displaystyle CHCH_3}{\|}}{C}CH_2CH{=}CHCH_2CH_2-$$

V

Acetic acid and acetaldehyde may then come from the ethylidene group in the rearranged unit. Levulinic acid could also be formed from this unit through decarboxylation of β-ketoadipic acid.

If further double bond shifts of an allylic nature occur in unit IV it would be possible to account for the formation of acetone. Thus, unit V could readily yield acetonedicarboxylic acid which would decarboxylate to give acetone.

These rearrangements would not be expected unless some chain transfer reactions are occurring during the course of polymerization which result in removal of an allylic hydrogen atom with the formation of a fairly stable allyl radical



$$-CH_2CH{=}CHCH_2\underset{\underset{\underset{\underset{\displaystyle CH_2}{\|}}{\displaystyle CH}}{|}}{\overset{\cdot}{C}}CH_2CH_2CH{=}CHCH_2-$$

VI

(VI) which could then either grow side chains by addition of butadiene units or rearrange and pick up hydrogen again to give new stable structural units. Perhaps the formation of these unexpected cleavage products can also be explained by assuming the breakdown of the ozonized polymer by ozone and hydrogen peroxide in some unorthodox manner. However, if we assume intermediate allyl free radicals in the polymers, all of the other rearrangements needed to account for the oxidation products isolated are reasonable.

In addition to these products, the dinitrophenylhydrazones of some other carbonyl compounds were isolated but not identified. No direct precursor of 1,2,3-propanetricarboxylic acid was found.

EXPERIMENTAL

Purification of polymer. Ten grams of polybutadiene[2] (Paper II, Table I, 1044, 60.5% conversion) was dissolved in 750 ml. of thiophene-free benzene. The resulting solution was poured slowly with vigorous stirring into 1500 ml. of approximately 0.2% ethanolic phenyl-β-naphthylamine. The precipitated rubber was washed with 200 ml. of the dilute phenyl-β-naphthylamine solution. This was repeated two additional times and after the third precipitation the polymer was broken in small pieces and dried under a pressure of less than 10 mm. overnight.

Ozonization. The dry, purified polymer (6 g.) was dissolved in 900 ml. of chloroform. After cooling the resulting solution to −5 to 0° in an ice-salt mixture, a stream of oxygen containing 2% ozone was passed through the solution until two 20-ml. portions of 5% potassium iodide successively turned red. The time of ozonization was about 6.5 hours.

Hydrolysis: With 3% hydrogen peroxide. The chloroform was removed under reduced pressure at room temperature. To the residual ozonides was added 120 ml. of 3% hydrogen peroxide and the mixture was heated in a bath at 85° for ten hours. After cooling, the excess hydrogen peroxide was decomposed by adding approximately 160 mg. of platinum oxide catalyst (2) and warming in a bath at 80° for one hour. The solution was filtered and evaporated to dryness at room temperature under a pressure of less than 2 mm.; the volatile portions were collected in a trap cooled in Dry Ice-carbon tetrachloride and later the carbonyl compounds in this were separated and identified. The residue, which weighted 11 g., was dissolved in distilled water to give a solution containing 250 mg. of solid per milliliter of solution and this solution was used for the chromatographic separations.

Separation of products. To 426 g. of silicic acid contained in a large mortar was gradually added 200 ml. of distilled water. After each addition of water the mixture was thoroughly ground with a pestle. Distilled chloroform (1800 ml.) then was added slowly with mixing and the whole worked into a smooth slurry. This was poured into a glass tube, 68 x 6.5 cm. (internal diameter), constricted at the bottom and so shaped at the top that a size 3 stopper could carry the pressure inlet tube. The excess chloroform was removed until the surface of the column was firm but not dry.

The aqueous solution of acids (15 ml., approximately 3.75 g. of solids) obtained from the hydrolysis of the ozonide with hydrogen peroxide was thoroughly mixed with 30 g. of silicic acid. A slurry was made by adding 200 ml. of distilled chloroform and this was added to the top of the large column through a funnel, constructed of such a length that its lower end came to within a few millimeters of the surface. The slurry was then poured slowly into the funnel and finally washed through with 50 ml. of chloroform. The excess chloroform of the acid layer was removed under pressure and a wad of cotton was placed upon the top of the column. Development was then started and the eluant was collected in 125-ml. portions. Five-milliliter aliquots were titrated in order to determine when an acid was being eluted from the column.

The developing solutions used were as follows:

800 ml. of 100% $CHCl_3$
2000 ml. of 96% $CHCl_3$— 4% C_2H_5OH[a]
2000 ml. of 94% $CHCl_3$— 6% C_2H_5OH[a]
2000 ml. of 92% $CHCl_3$— 8% C_2H_5OH[a]
2000 ml. of 90% $CHCl_3$—10% C_2H_5OH[a]
2500 ml. of 88% $CHCl_3$—12% C_2H_5OH[a]
2000 ml. of 86% $CHCl_3$—14% C_2H_5OH[a]
1000 ml. of 84% $CHCl_3$—16% C_2H_5OH[a]
2000 ml. of 80% $CHCl_3$—20% C_2H_5OH[a]
500 ml. of 75% $CHCl_3$—25% C_2H_5OH[a]

[a] Per cent by volume.

In order to isolate the acids, the portions (I to VII), as discerned from the graph (Figure 1), were separated and the solvents removed under a vacuum at room temperature.

Portions I and II proved to be mainly carbonyl compounds and were treated with 2,4-dinitrophenylhydrazine.

Portion III was acidic and a portion was treated with *p*-nitrobenzyl chloride as described by Shriner and Fuson (3) to give the *p*-nitrobenzyl ester. About 10 mg. of white crystals, m.p. 71–74°, were obtained. Recrystallization from alcohol gave m.p. 74.5–75.5° and a mixture of these crystals with authentic *p*-nitrobenzyl acetate melted at 75–76°.

Portion IV contained carbonyl groups but was not present in sufficient amount to identify.

Portion V was succinic acid, m.p. 184–186°. A mixture with authentic succinic acid melted at 187–188.5°.

Portion VI was too small to identify but did give a 2,4-dinitrophenylhydrazone showing it was a carbonyl derivative.

Portion VII proved to be 1,2,4-butanetricarboxylic acid, m.p. 123–124°. A mixture with an authentic specimen of this acid gave no depression in melting point.

Identification of carbonyl compounds. The carbonyl compounds in portions I and II and in the trap used to collect volatile material in the early evaporations were converted to 2,4-dinitrophenylhydrazones by the procedure of Iddles and Jackson (4).

Portion I. The material from portion I gave a mixture of 2,4-dinitrophenylhydrazones. When this mixture was treated with chloroform, one very insoluble component was separated from the mixture. On recrystallization from nitrobenzene it gave orange needles, m.p. 277–278° with decomposition.

Anal. Calc'd for $C_{25}H_{22}N_{12}O_{12}$: C, 43.93; H, 3.39; N, 24.59.
Found: C, 43.69; H, 3.14; N, 24.68.

This thus appears to be the 2,4-dinitrophenylhydrazone of the unknown trialdehyde corresponding to 1,2,4-butanetricarboxylic acid.

The chloroform-soluble 2,4-dinitrophenylhydrazones from portion I were separated by chromatography. A column was prepared from a thorough mixture of 100 g. of silicic acid (Mallinckrodt Analytical Reagent Grade) and 50 g. of "Celite" tightly packed in a 36-mm. diameter glass tube. The column height was about 235 mm. The top of the column was protected by a circle of filter paper. The column was thoroughly wet with redistilled high-boiling petroleum ether (about 250 ml.) and then a small amount of the dinitrophenylhydrazone mixture (about 0.1 g.) in 10–20 ml. of chloroform was added to the column. The column was washed with about 50 ml. of high-boiling petroleum ether and then developed under a positive pressure of about 20 mm. of mercury with the following solutions: First, 500 ml. of 4% (by volume) dry ethyl ether in high-boiling petroleum ether; second, 500 ml. of 6% dry ether in high-boiling petroleum ether; third, 1000–1500 ml. of 10% dry ether in high-boiling petroleum ether; fourth, 500 ml. of 2% dry ether in chloroform; and finally 500–1000 ml. of 5% dry ether in chloroform. The exact amount of solvents depended on the bands developed and the bands could either be washed through the column or the column could be extruded and sectioned.

From this mixture three distinct bands appeared although the two smaller bands could not be identified. The major band gave a deep red color in methanolic potassium hydroxide solution. After recrystallization from aqueous ethanol it gave yellow-orange needles, m.p. 185–188°. This melting point is below that of the levulinic acid derivative (206.5°) but in the range to be expected after this derivative is repeatedly recrystallized from alcohol according to Cowley and Schuette (5) who state that partial esterification occurs. A mixture of the above material with an authentic specimen of the 2,4-dinitrophenylhydrazone of levulinic acid recrystallized in the same manner from alcohol melted at 189–191°. Portion I was characterized by the strong sweetish odor characteristic of a solution of levulinic acid.

Anal. Calc'd for $C_{11}H_{13}N_4O_6$: C, 44.45; H, 4.41; N, 18.85.
Found: C, 44.11; H, 4.38; N, 18.35.

Portion II. Portion II from the chromatographic separation was converted to the 2,4-dinitrophenylhydrazone. The derivative was orange but gave a red color in methanolic potassium hydroxide solution. Recrystallization from chloroform-acetone mixture gave orange-yellow plates, m.p. 200.5° with decomposition. An authentic specimen of β-formylpropionic acid, prepared by the method of Dakin (6) gave a 2,4-dinitrophenylhydrazone, m.p. 197–198° (with decomposition), and the mixture with the unknown melted at 197–198.5°.

Anal. Calc'd for $C_{10}H_{10}N_4O_6$: C, 42.56; H, 3.54; N, 19.85.
Found: C, 42.78; H, 3.51; N, 19.99.

Identification of carbonyl compounds in volatile fractions. The mixture of carbonyl compounds obtained in the trap on evaporating the aqueous solution of acids was converted to 2,4-dinitrophenylhydrazones and these were also separated on the column of silicic acid and Celite. Seven bands were evident in the separation but most of these contained very small amounts of material and were not identified.

From band 2 about 20 mg. of yellow-orange needles was obtained. After recrystallization from high-boiling petroleum ether these melted at 125–126° and their melting point was not depressed when mixed with an authentic specimen of acetone 2,4-dinitrophenylhydrazone.

Band 3 gave about 40 mg. of orange needles which after recrystallization from a mixture of benzene and high-boiling petroleum ether melted at 146–148°.

Anal. Calc'd for $C_8H_8N_4O_4$: C, 42.86; H, 3.60; N, 24.99.

Found: C, 43.13; H, 4.00; N, 24.77.

This analysis indicated the material was the derivative of acetaldehyde which is reported to melt at 168° when recrystallized from alcohol (6). However, an authentic specimen of the acetaldehyde derivative recrystallized from benzene melted at 149° (7) and when mixed with the unknown material the melting point was 147–149°.

Band 4 gave 10 mg. of orange-yellow needles which melted at 113–114° after recrystallization from high-boiling petroleum ether.

Anal. Found: C, 46.94; H, 4.70; N, 18.63.

The material in band 4 was also isolated from one of the non-volatile portions but the compound was not identified.

Band 5 contained only a trace of material and band 6 gave a very few mg. of the derivative of β-formylpropionic acid.

Band 7 gave some of the derivative of levulinic acid.

SUMMARY

The oxidative cleavage of the ozonides of an emulsion polybutadiene (60.5% conversion) with 3% hydrogen peroxide has produced small amounts of acetic acid, acetaldehyde, acetone, levulinic acid, β-formylpropionic acid, and the trialdehyde corresponding to 1,2,4-butanetricarboxylic acid in addition to the expected formic acid, succinic acid, and 1,2,4-butanetricarboxylic acid.

The β-formylpropionic acid and the trialdehyde are due to incomplete oxidation of the cleavage products of the ozonides. The formation of acetaldehyde, acetic acid, acetone, and levulinic acid can be explained by the assumption that some rearrangement of the double bonds in the polymer occurs. This may indicate the formation of allyl free radicals by chain transfer during polymerization.

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