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

A Study of the Structure of Butadiene Polymers by Means of Ozonolysis[1]

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One of the factors determining the intramolecular homogeneity of butadiene-type synthetic rubber is the extent to which the diene enters the polymer by 1,4-polymerization *versus* 1,2-addition. Another factor involves the arrangement of the two (or more) comonomers throughout the polymer chain; *i.e.*, whether there is a tendency toward bunching of one monomer unit or random alternation of the components within the molecule.

Much has been postulated about the correlation of the factors, particularly the first, with the rubber-like properties of the copolymers. It has been thought that the greater the regularity of the molecule through 1,4-polymerization of the butadiene, all other variables being unchanged, the more desirable would be the properties of the rubber. In order to test this supposition and to discover some of the features of the monomer distribution, an attempt has been made to degrade the butadiene–styrene copolymer by scission at the double bonds through ozonolysis.

This approach is by no means new. Harries[2] was the first to describe the method; Pummerer, Ebermayer and Gerlach[3] and Pummerer and Richtzenhain[4] have applied it to natural rubber; Alekseeva and Belitskaya[5] to a 1:1 butadiene–styrene copolymer; Hill, Lewis and Simonsen[6] to polybutadiene and to a butadiene–methyl methacrylate copolymer; Alekseeva[7] to a copolymer of butadiene and acrylonitrile and a mixed polymer of butadiene and methacrylonitrile; and Klebanskii and Vasil'eva[8] to polychloroprene. The present findings for the GR-S copolymer are similar to those of Alekseeva and Belitskaya[5] in regard to the nature of the products identified in the determination of total structure, although the butadiene–styrene ratio of 75–25 changes not only the proportions but also the nature of these products to some extent.

The diagram illustrates the fragments which might be expected from an oxidative ozonolysis of a portion of the GR-S molecule in which are found several of the many possible random arrangements. Each vinyl group from 1,2-polymerization of a butadiene molecule gives rise to a molecule of formic acid, and this should be the only volatile acid which appears in measurable quantities provided there is no oxidative degradation beyond the expected cleavage of the double bonds. Isolation and identification of the di- and polycarboxylic acids would complete the picture of the structure of the copolymer. Thus, where one 1,2-butadiene unit occurs between two 1,4-butadiene units (portion A), ozonization should produce butane-1,2,4-tricarboxylic acid; when a styrene unit occurs between two 1,4-butadiene units (portion B), β-phenyladipic acid should be formed; two contiguous 1,4-butadiene units (portion C) should lead to succinic acid; a portion (such as D) containing several adjacent 1,2-butadiene units should give a polybasic acid; alternation of styrene and 1,2-butadiene units (portion E) should lead to polybasic acids carrying phenyl groups as substituents. Obviously, the piling up of many 1,2-butadiene units and/or styrene units leads to acids of very complicated structures.

In the present study two samples of GR-S, one standard, G-1 (0.3% modifier), and one insoluble, G-23 (under-modified 0.15% modifier), have been ozonized in quantities sufficient to permit the isolation and identification of several of the di- and polybasic acids. In addition, the amount of formic acid produced by ozonization has been determined on a number of GR-S and related polymers.

Structure Determination

The ozone degradation procedure employed by Alekseeva and Belitskaya[5] for the examination of the structure of a bulk copolymer containing equal amounts of butadiene and styrene was followed, with some modifications, in the present investigation of GR-S. After ozonization and oxidative cleavage of the ozonide, the resulting acids were separated into volatile, water-soluble and water-insoluble fractions. Each portion was examined separately. The volatile acids were titrated with standard alkali and the acidity calculated as formic acid. In Table I are shown the quantities of formic acid obtained from 100 g. of each of the samples studied, together with the percentages of

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(2) Harries, "Untersuchungen über die natürlichen und künstlichen Kautscharten," Julius Springer, Berlin, 1919.

(3) Pummerer, Ebermayer and Gerlach, *Ber.*, **64B**, 809 (1931).

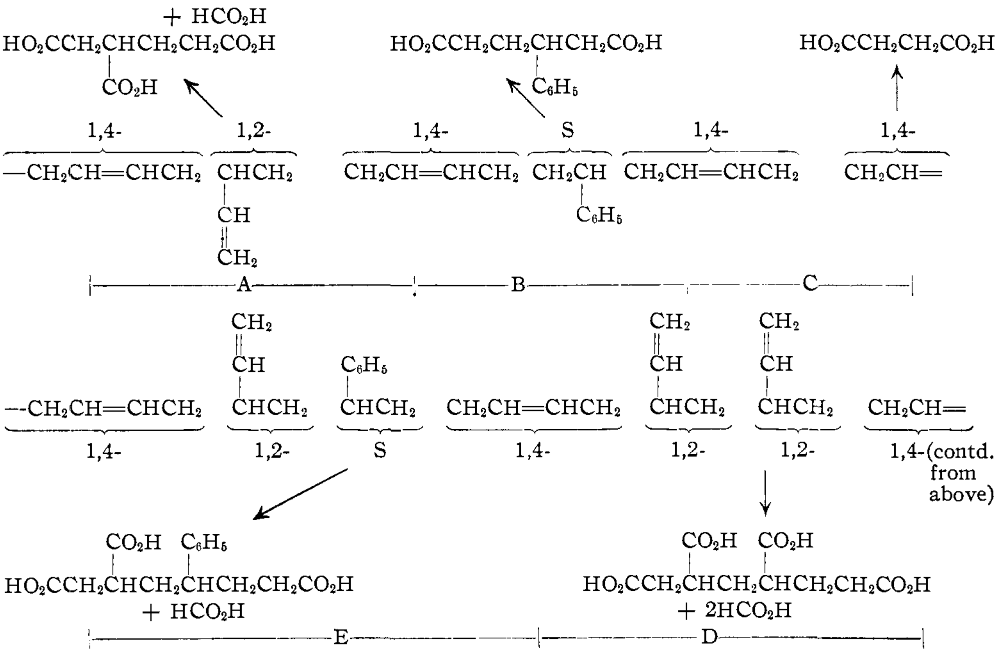
(4) Pummerer and Richtzenhain, *Rubber Chem. Tech.*, 11, 7 (1938).

(5) Alekseeva and Belitskaya, *ibid.*, **15**, 693 (1942); *J. Gen. Chem., U. S. S. R.*, **11**, 358 (1941).

(6) Hill, Lewis and Simonsen, *Trans. Faraday Soc.*, **35**, 1067, 1073 (1939).

(7) Alekseeva, *J. Gen. Chem. U. S. S. R.*, **9**, 1426 (1939); **11**, 353 (1941); *Rubber Chem. Tech.*, **15**, 698 (1942).

(8) Klebanskii and Vasil'eva, *J. prakt. Chem.*, **144**, 251 (1936); *Rubber Chem. Tech.*, **10**, 126 (1937).



butadiene accounted for in this manner. The values do not indicate any significant difference between samples G-1 and G-23.

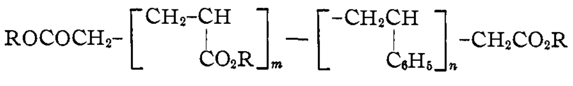
TABLE I

VOLATILE ACIDS FROM OZONIZATION

	G-1	G-23
Formic acid for 100 g. of rubber, g.	19.5	16.8
Butadiene equivalent, g.	23.0	19.8
Percentage of butadiene accounted for, assuming the rubber is 77% butadiene	29.9	25.7

Succinic acid was separated from the water-soluble acids by fractional crystallization. Then the remaining water-soluble acids were converted to their methyl esters, and the esters were subjected to distillation under reduced pressure. Table II shows the amounts of succinic acid and identified esters obtained from 100 g. of each of samples of G-1 and G-23, together with the amounts of butadiene and styrene accounted for.

From reference to the diagram, it is seen that in order for the polymer chain to be cleaved by ozone, there must be present a butadiene molecule which has entered by 1,4-addition. Thus, the general formula for the esters derived from the cleavage products of a butadiene–styrene copolymer is



$$ROCOCH_2-\left[\begin{matrix}CH_2-CH\\ \quad | \\ \quad CO_2R\end{matrix}\right]_m-\left[\begin{matrix}-CH_2CH\\ \quad | \\ \quad C_6H_5\end{matrix}\right]_n-CH_2CO_2R$$

without regard to arrangement of internal units. Then tetramethyl hexane-1,x,y,6-tetracarboxylate would be represented by the above formula, where $m = 2$ and $n = 0$; and trimethyl x-phenylhexane-1,y,6-tricarboxylate would be represented by the same formula, where $m = 1$, and $n = 1$. These esters were only partially identified, so that the exact structural formulas are unknown. Obviously, several isomers are possible in each case. Alekseeva[7] isolated a hexane tetracarboxylic

TABLE II

COMPOUNDS FROM WATER-SOLUBLE ACIDS

Based on 100 g. of extracted rubber samples

	Compounds isolated	G-1 Wt., g.	G-1 Butadiene g.	G-1 Butadiene %	G-1 Styrene g.	G-1 Styrene %	G-23 Wt., g.	G-23 Butadiene g.	G-23 Butadiene %	G-23 Styrene g.	G-23 Styrene %
1	Succinic acid	37.05	16.93				30.64	14.02			
2	Dimethyl succinate	37.81	14.00				37.85	14.00			
	Total acid and ester		30.93	40.2				28.02	36.4		
3	Trimethyl butane-1,2,4-tricarboxylate	28.62	13.32	17.3			25.32	11.80	15.3		
4	Dimethyl β-phenyladipate	11.44	2.47	3.2	4.76	20.7	8.80	1.90	2.5	3.66	15.9
5	Tetramethyl hexane-1,x,y,6-tetracarboxylate	6.44	3.28	4.3			6.92	3.53	4.6		
6	Trimethyl x-phenylhexane-1,y,6-tricarboxylate	4.86	1.56	2.0	1.50	6.5	5.17	1.66	2.2	1.60	7.0
	Total		51.56	67.0	6.26	27.2		46.91	61.0	5.26	22.9

TABLE III

OZONIZATION OF POLYMERS

Sample	Description	Per cent. diene	Ozonization no.		
...	Natural rubber, crepe	100	11.8	9.5	8.6
G-1	GR-S, 75/25, 71% conversion	80[b]	19.3	19.1	
G-5	GR-S, 65/35, 81% conversion	81.4[c]	20.9		
RD-29	GR-S, at 110–130°	80[b]	17.1	18.0	
UI-111	GR-S, large amount of cetyl mercaptan modifier	80[b]	18.7		
UI-113	GR-S, ferricyanide initiated	80[b]	19.1	16.1	
RA-187	GR-S, latex treated with OEI (a mercaptan modifier)	75[a]	10.1	8.1	
UI-115	GR-S, acid-side	75[a]	13.4	14.3	
...	Unmilled standard GR-S	72[a]	22.2	18.3	
...	Same sample, cold-milled for 45 minutes	72	22.6	22.2	
RD-27	Polybutadiene, emulsion at 50°	100	19.4	20.7	
WB-407	Polybutadiene, emulsion at 110° for 30 minutes	100	12.0	11.8	
WB-16	Polybutadiene, sodium sand, 10°	100	22.8	22.2	
G-13	Polybutadiene, German, sodium catalyst (Buna-115)	100	38.5	42.2	
CKG-666P	Polybutadiene, Russian, sodium catalyst	100	42.8	40.5	
RD-931	Butadiene-*m*-chlorostyrene, 75:25	75[c]	12.6	11.8	
UI-121	Butadiene-vinylpyridine, 75:25	75[a]	13.9	12.7	
RD-578	Butadiene-β-vinylnaphthalene, 75:25	67.6[c]	19.5	17.7	17.9
UI-123	GR-N	72[a]	12.3	14.3	
...	Neoprene	100	5.8	7.0	3.4

[a] As charged. [b] Estimated. [c] Measured or known.

ester from the degradation of a butadiene–acrylonitrile copolymer, but it was believed that the secondary carboxyl groups were derived from acrylonitrile units. The complete structure of this ester was not determined either.

The water-insoluble acids were converted to their methyl esters, but neither they nor the remainder of the esters of the water-soluble acids could be fractionated or otherwise separated for characterization. Analysis and refractive index measurements of some unidentified distillates, coupled with the knowledge of the identity of certain esters isolated by earlier workers, led to the tentative identification of these small portions as octane pentacarboxylic ester ($m = 3$, $n = 0$), phenyloctane tetracarboxylic ester ($m = 2$, $n = 1$), diphenylsuberic ester ($m = 0$, $n = 2$), and fumaric ester. The latter might have resulted from the dehydration of malic acid which arose from the introduction of a hydroxyl group *alpha* to a double bond of a 1,4-butadiene unit. None of these compounds represented appreciable fractions of the total butadiene units; however, the supposed dimethyl diphenylsuberate was equivalent to 14.5% of the styrene in sample G-1 and 26.2% of that in sample G-23. It is natural to predict that the higher-boiling residues would contain large numbers of benzene rings and correspondingly large fractions of the styrene. It is not surprising, therefore, that much of the styrene was unaccounted for.

The slight differences in the amounts of esters of water-soluble acids obtained from samples G-1 and G-23 are perhaps not significant; however, the larger amounts of water-insoluble acids found in the degradation of G-23 may be an indication of a structural difference in the two rubbers. Whether this fact is a result of, or is coincidental with the difference in the amounts of modifier used cannot be determined from available data.

Determination of Terminal Vinyl Groups

In an effort to determine structural differences between butadiene copolymers prepared under varying experimental conditions, a study has been attempted to show the proportions of butadiene which have entered the polymer molecule by 1,2- and 1,4-addition. The determination of the volatile products, formic acid and formaldehyde, from ozonolysis of the terminal vinyl groups should give a measure of the extent of 1,2-addition. Chloroform solutions of the polymers were treated with ozonized oxygen and decomposed by steam distillation. The products of distillation were oxidized by means of alkaline mercuric acetate, according to the method of Reid and Weihe,[9] to give carbon dioxide (after acidification) which was absorbed and weighed. The results could be made quite reproducible, although not necessarily accurate in the absolute sense. For this reason, the apparent percentage of 1,2-polymerization has been given the less specific title of "ozonization number."

"Ozonization numbers" for a variety of polymers are listed in Table III. These values are considerably lower than the results reported recently by Yakubchik, Vasil'iev and Zhabina[10] for the vinyl content of several polybutadienes and copolymers of butadiene and styrene. After we had completed our work, it was found that our analytical procedure did not account for all of the

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(9) Reid and Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

(10) Yakubchik, Vasil'iev and Zhabina, *J. Applied Chem., U. S. S. R.*, **17**, 107 (1944); *Rubber Chem. Tech.*, **18**, 780 (1945).

available formaldehyde and formic acid. It would appear that in some cases our "ozonization numbers" should be increased by almost 70%. The possibility also exists that ozone may have attacked the polymers at linkages other than the double bonds which would lead to abnormal amounts of formaldehyde and formic acid. For these reasons the actual error in the method is unknown and may vary from case to case.

However, since all polymers were treated under comparable conditions, the relationships which have been shown to exist between the different types of butadiene polymers may be of some qualitative importance. If the relative values shown in Table III are representative of the fraction of butadiene which has polymerized in the 1,2-manner, it is evident that few changes in the emulsion system are successful in reducing this type of polymerization.

Experimental

I. Structure Determination

A. **Sample G-1.**—The rubber sample G-1 used in this investigation was made by the United States Rubber Company in Detroit, Michigan. It was prepared by the standard process except that it was coagulated by means of carbon dioxide. Other specifications for this sample were as follows: conversion 71.4%; benzene insoluble, trace; intrinsic viscosity 1.97.

Sixty grams of shredded G-1 was extracted in four portions of 15 g. each in a Soxhlet extractor for twenty-eight hours. The extraction medium was the toluene–ethanol azeotrope consisting of 20.2 parts of toluene to 47.3 parts of ethanol by volume (b. p. 76.7°). The extracted material was dried in a vacuum desiccator containing calcium chloride and paraffin. After drying to constant weight, each portion weighed 13.7 g.; the total weight of extracted rubber was 54.8 g. Each 13.7-g. portion was dissolved in 500–600 ml. of dry chloroform, and each solution was divided into four approximately equal parts for ozonization. A stream of oxygen containing about 2% of ozone was passed through each sample for seven to eight hours at a rate of 110–120 ml. per minute. This time was approximately 25% longer than was necessary for a 10% potassium iodide solution to indicate that some ozone was passing unabsorbed through the rubber solution. During the ozonization a small amount of insoluble material precipitated, while the color of the solution changed from brown to yellow. After ozonization, each series of four small samples was recombined for subsequent treatment.

The chloroform was removed from the solution of the ozonide under reduced pressure at room temperature. The ozonide remained as a clear, very viscous liquid. It was cleaved by treatment with 300 ml. of 3% hydrogen peroxide for three to four hours. During this treatment the mixture was warmed first on a water-bath and then gradually brought to the temperature of boiling water. Nearly all of the decomposition product went into solution and only a small amount of a waxy, insoluble material remained.

The solution was removed by decantation and the solid was washed with a small amount of water. The original solution and washings were combined and subjected to distillation under diminished pressure. The distillation flask was heated in a water-bath at 35–50° and the receiver was cooled in a ice–salt mixture. The distillate was made up to a volume of 1000 ml. with distilled water and a 50-ml. aliquot was withdrawn for titration. The volume of alkali required for each of the 13.7-g. samples of rubber was approximately the same. The acidity was calculated as formic acid and in this way it was found that the 54.8 g. of rubber produced 10.7 g. of formic acid.

The residues from the four distillations were combined and dried to constant weight in a vacuum desiccator. There was obtained 83.5 g. of non-volatile, water-soluble acids. Fractional crystallization of this mixture of acids yielded 20.3 g. of succinic acid; m. p. 180–182° (uncor.); neut. equiv. 60 (calcd. for $C_4H_6O_4$: 59). The remainder of the water-soluble acids was esterified with methyl alcohol containing about 8% of hydrogen chloride. The reaction mixture was worked up in the usual manner; the unesterified acids were recovered and treated again with methanolic hydrogen chloride. In all, 59 g. of methyl esters was obtained.

The esters were distilled through a Podbielniak-type column (5 × 455 mm.) at a pressure of 3–5 mm. The distillation was carried out slowly and at a uniform rate; the distillate was collected in portions of 0.5 to 1.0 g. each. The cumulative yield of distillate was plotted against the refractive index, and the fractions were determined from the resulting curve in the usual way. The following table shows the fractions obtained up to a bath temperature of 210°.

TABLE IV

	Compounds	Wt., g.	n^{20}_D
1	Dimethyl succinate	20.73	1.4192
2	Dimethyl fumarate (?)	1.20	
3	Trimethyl butane-1,2,4-tricarboxylate	15.68	1.4446
4	Dimethyl β-phenyladipate	6.27	1.4972
5	Residue	12.0	

Fraction 1 was shown to be dimethyl succinate by its index of refraction (Bruhl[11] reported n^{20}_D 1.4198), its saponification equivalent and by hydrolysis to succinic acid.

Anal. Calcd. for $C_6H_{10}O_4$: sap. equiv., 73.1. Found: sap. equiv., 73.2.

Fraction 2, obtained in a small amount and impure state only, is believed to contain dimethyl fumarate. It was unsaturated to bromine in carbon tetrachloride, but the bromine addition compound could not be isolated.

Fraction 3 was identified as trimethyl butane-1,2,4-tricarboxylate.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.90; sapn. equiv., 77.3. Found: C, 52.07; H, 6.91; sapn. equiv., 77.5.

Acid hydrolysis of a portion of this fraction produced a water-soluble, solid acid which crystallized from acetone as beautiful white prisms, m. p. 119–121° (Hill, Lewis and Simonsen[6] reported the melting point of butane-1,2,4-tricarboxylic acid as 116–120°, Haworth and King[12] as 120–121° and Kay and Perkin[13] as 116–118°).

Anal. Calcd. for $C_7H_{10}O_6$: neut. equiv., 63.3. Found: neut. equiv., 63.6.

Analytical evidence indicated that Fraction 4 was dimethyl β-phenyladipate.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.20; H, 7.20; sapn. equiv., 125. Found: C, 66.29; H, 7.18; sapn. equiv., 123.

Acid hydrolysis of a small amount of this material produced a solid acid. After recrystallization from water, it was obtained in the form of white plates, m. p. 147–148° (Manske[14] gave the melting point of β phenyladipic acid as 146° and Price and Karabinos[15] have reported the melting point to be 147–148°). A mixed melting point determination with a known sample of β-phenyladipic acid showed no depression.

Anal. Calcd. for $C_{12}H_{14}O_4$: neut. equiv., 110.5. Found: neut. equiv., 111.

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[11] Bruhl, *J. prakt. Chem.*, [2] **50**, 140 (1894).

[12] Haworth and King, *J. Chem. Soc.*, **105**, 1342 (1914).

[13] Kay and Perkin, *ibid.*, **89**, 1640 (1906).

[14] Manske, THIS JOURNAL, **53**, 1104 (1931).

[15] Price and Karabinos, *ibid.*, **62**, 1159 (1940).

The residue from the above-mentioned distillation was subjected to distillation under the low pressure obtained with a mercury vapor diffusion pump. The separation of these high-boiling esters was not good; in no case was an analytically pure sample obtained. Table V shows the fractions obtained:

TABLE V

	Compound	Wt., g.	$n^{20}D$
1	Tetramethyl hexane-1,x,y-6-tetracarboxylate	3.53	1.4643
2	Trimethyl x-phenylhexane-1,y,6-tricarboxylate	2.66	1.4963
3	Uncharacterized	2.72	
4	Residue	1.50	

The center portion of Fraction 1 gave the following analytical values:

Anal. Calcd. for $C_{14}H_{22}O_8$: C, 52.83; H, 6.91; sapn. equiv., 79.5. Found: C, 54.90; H, 6.52; sapn. equiv., 82.0.

Acid hydrolysis of this substance produced a viscous, brown, water-soluble liquid. After standing for several days, the liquid deposited a small amount of a tan colored powder. Recrystallization from acetone yielded white prisms; m. p. 116–132° with decomposition. This substance was extremely soluble in water; alcohol and acetone and insoluble in ether, benzene and petroleum ether.

Anal. Calcd. for $C_{10}H_{14}O_8$: C, 45.80; H, 5.34; neut. equiv., 65.5. Found: C, 46.83; H, 5.93; neut. equiv., 74.5.

Hexane-1,3,4,6-tetracarboxylic acid has been reported by Silberrad[16] and Sell and Easterfield[17] to melt at 215° with decomposition. Its dimethyl ester, prepared by Sell and Jackson,[18] melted at 133°. Ingold and Shoppe[19] have stated the melting point of hexane-1,2,4,6-tetracarboxylic acid to be 206–207°.

A center portion of Fraction 2 gave the data:

Anal. Calcd. for $C_{18}H_{24}O_6$: C, 64.29; H, 7.14; sapn. equiv., 112. Found: C, 61.73; H, 6.53; sapn. equiv., 106.

No solid compound could be isolated from the acid hydrolysis of this fraction.

The uncharacterized distillate was redistilled and collected in small portions of 0.25–0.30 g. Values of the refractive indices of these portions were relatively high and varied from 1.4905 for the first portion to 1.5049 for the last. Carbon and hydrogen analyses paralleled these changes and varied from 59.67 and 6.97% to 61.00 and 7.02%, respectively. A center portion had a molecular weight of 375 and a saponification equivalent of 95; calculated for pentamethyl octanepentacarboxylate: C, 53.47; H, 6.93; molecular weight, 404; saponification equivalent, 80.8; calculated for tetramethyl phenyloctanetetracarboxylate: C, 62.56; H, 7.11; molecular weight, 422; saponification equivalent, 105.5.

The water-insoluble acids (6.3 g.), which were completely soluble in aqueous sodium carbonate, were esterified with a large excess of dry methanol containing 7 to 8% of hydrogen chloride in a manner identical with that employed for the water-soluble acids. The resulting esters (5.05 g.) were distilled from a bulb with a low side-arm using a mercury vapor pump. The distillate weighed 3.10 g. It was redistilled and the product was collected in small portions of 0.35–0.50 g. Plotting the refractive indices of these small fractions against the cumulative weight of the product gave a smooth curve with no breaks. The refractive index ($n^{20}D$) varied from 1.4960 to 1.5320. All portions were viscous, yellow colored liquids and the viscosity increased from fraction to fraction. The following analytical data were obtained from a center portion: C, 68.79; H, 7.40; molecular weight, 343; saponification equivalent, 160. Analytical data for dimethyl diphenylsuberate, $C_{22}H_{26}O_4$, are: C, 74.58; H, 7.34; molecular weight, 354; saponification equivalent, 177.

B. Sample G-23.—The rubber sample G-23 used in this study was made by the United States Rubber Company at Naugatuck, Connecticut. It was prepared by the standard process, except that only 0.15% of modifier was employed. Tests in this Laboratory have shown that this sample is less than 30% soluble in benzene.

Apparently because of the low solubility in chloroform, samples of G-23 required about 50% longer for ozonization than like samples of G-1. At the end of the ozonization periods, the polymer had dissolved completely, however. The other procedures were the same as those employed for G-1. Very similar curves (refractive index *vs.* cumulative yield) and identical degradation products were obtained at all stages. For these reasons the experimental results for G-23 are presented in table form only.

TABLE VI

Rubber, g.	80.0
After extraction, g.	74.4
Volatile acids (calcd. as formic acid), g.	12.5
Water-soluble acids, g.	103.6
Succinic acid from water-soluble acids, g.	22.8
Esters from remainder of water-soluble acids, g.	76.1
Water-insoluble acids, g.	12.5
Esters from water-insoluble acids, g.	11.27

TABLE VII

ESTERS FROM WATER-SOLUBLE ACIDS

	Ester	Wt., g.
1	Dimethyl succinate	28.16
2	Dimethyl fumarate (?)	2.1
3	Trimethyl butane-1,2,4-tricarboxylate	18.84
4	Dimethyl β-phenyladipate	6.55
5	Tetramethyl hexane-1,x,y,6-tetracarboxylate	5.15
6	Trimethyl x-phenylhexane-1,y,6-tricarboxylate	3.85
7	Uncharacterized	4.59
8	Residue	3.5

TABLE VIII

ESTERS FROM WATER-INSOLUBLE ACIDS

	Ester	Wt., g.
1	Distillate	7.63
2	Residue	2.1

II. Measurement of Terminal Vinyl Groups

The rubber sample was torn into small pieces and extracted with the ethanol–toluene azeotrope. After drying under reduced pressure, the sample was dissolved in purified chloroform and a small amount of the solution was evaporated to determine the rubber concentration. An aliquot part was withdrawn and treated with ozonized oxygen for two and one-half hours at a rate of approximately 125 ml. per minute. The concentration of ozone was about 4%.

At the end of the ozonization period, the solvent was removed by means of an aspirator at a temperature of about 40°. Distilled water was added to the dry ozonide and the mixture was subjected to steam distillation. The distillate was then analyzed for formic acid and formaldehyde by the method of Reid and Weihe.[9] The amount of carbon dioxide obtained was used for the calculation of the "ozonization numbers" given in Table III.

Acknowledgment.—The authors wish to thank Professor Carl S. Marvel for his constant inter-

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[16] Silberrad, *J. Chem. Soc.*, **85**, 611 (1904).

[17] Sell and Easterfield, *ibid.*, **65**, 828 (1894).

[18] Sell and Jackson, *ibid.*, **75**, 507 (1899).

[19] Ingold and Shoppe, *ibid.*, 1912 (1926).

est and many helpful suggestions offered during the course of this investigation.

Summary

1. Two samples of the GR-S copolymer of butadiene and styrene have been degraded by means of ozonolysis. A number of fragments have been isolated and identified so that an approximate idea of the structures of the copolymers has been obtained.

2. A series of butadiene copolymers has been treated with ozone in an attempt to determine the extent to which the butadiene has polymerized by 1,2-addition in contrast to 1,4-addition. Although the analytical procedure employed afforded only relative values, referred to as "ozonization numbers," the results indicate that the manner in which the butadiene molecule enters the growing copolymer chain is not greatly influenced by experimental conditions.

URBANA, ILLINOIS RECEIVED JUNE 19, 1946

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, UNIVERSITY OF FLORIDA]

Rate of the Thermal Isomerization of α-Pinene in the Liquid Phase[1]

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In a previous article[3] the authors reported the results of their investigation of the reactions resulting from heating α-pinene in the liquid phase within the temperature range 189.5–285°. It was shown that dipentene (*dl*-limonene) and *allo*-ocimene are formed by simultaneous side reactions from the α-pinene and that the *allo*-ocimene in turn yields α-pyronene, β-pyronene and a dimer. It was observed that the optical rotations of the small amounts of unreacted α-pinene, which were sometimes recovered, had decreased markedly, thus indicating a partial racemization of the substrate. Formulas for all the compounds involved are given in the previous paper.[3] A full list of references is given in the earlier paper.[3]

Measurement of the rates of the individual reactions involved in this isomerization would determine whether the reactions are all of the expected first order or whether certain obscure effects complicate the process. In the present paper the measurements of the rates of racemization of α-pinene and its simultaneous isomerization to dipentene and *allo*-ocimene are reported. The data were obtained for the temperatures 189.5 and 204.5°. At these temperatures the reactions proceed slowly enough to permit the measurements to be made with a satisfactory degree of accuracy.

Experimental

Preparation and Purification of Reactants.—*d*-α-Pinene from wood turpentine and *l*-α-pinene from gum turpentine[4] were used in the investigation of the thermal isomerization reactions. For additional studies of the racemization of α-pinene, 300 g. of *l*-α-pinene of high optical rotation were obtained by refluxing pure *l*-β-pinene with 1% of its weight of oxalic acid[5] for several hours and then distilling off the lower boiling product from the reaction mixture.

The spiral screen type of fractional distillation column, previously described,[6] was used to purify all of these materials. The products had the physical properties attributed to α-pinene of very high purity.[7] α-Pinene prepared from wood turpentine: b. p. (20 mm.) 52.3°; α^{25}_D (2 dm.) +57.52° to +58.26°; n^{25}_D 1.4631–1.4632. α-Pinene prepared from gum turpentine: b. p. (20 mm.) 52.2°; α^{25}_D (2 dm.) −6.49°; n^{25}_D 1.4631; d^{25}_4 0.8542. α-Pinene from β-pinene: b. p. (20 mm.) 52.3°; α^{25}_D (2 dm.) −80.75; n^{25}_D 1.4631; d^{25}_4 0.8541.

Apparatus and Procedure.—Ninty-four cc. (80 g.) portions of freshly distilled α-pinene were sealed in tubes and heated in the constant temperature oil-bath, previously described,[3] to effect the isomerization. The temperatures at which the tubes were heated, 189.5 and 204.5°, were determined by means of a thermometer calibrated by the U. S. Bureau of Standards (reading directly to 0.1°). A Beckmann thermometer placed in the bath showed an average variation of ±0.03° and a maximum variation of ±0.04° at each temperature. It also indicated that the average temperature of the bath did not drift during the course of the heating of the tubes.

The volume of liquid in each sealed tube was so large that it was necessary to determine the time required for the liquid to come to the temperature of the bath. The rates of heating and cooling of the substrate were measured by means of a sealed tube containing the requisite amount of liquid and an enclosed thermometer. This was done by placing the tube in the oil-bath for different lengths of time and observing the temperature of the enclosed thermometer. The tube was allowed to cool to room temperature between each determination. Whenever the sealed tubes were placed in the bath for these tests and for all other experiments an additional 250-watt blade heater was turned on during the interval that the tube was being heated to temperature in order to counteract the cooling of the oil-bath by the cold tube. Five minutes after immersion the sealed tube containing 94 cc. (80 g.) of α-pinene was within 15° of the temperature of the oil-bath. However, the final temperature was not reached for another six or seven minutes. As an approximate correction, the time of heating of the α-pinene tubes was recorded as starting eight minutes after the tubes were immersed in the oil-bath. This correction is of no significance for tubes heated more than twelve hours.

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(1) The material included in this paper is based upon an abstract of a dissertation presented to the Graduate Council of the University of Florida in partial fulfilment for the degree of Doctor of Philosophy, May, 1943.

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(3) Fuguitt and Hawkins, THIS JOURNAL, **67**, 242 (1945).

(4) Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

(5) Bain, private communication.

(6) Stallcup, Fuguitt and Hawkins, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 503 (1942).

(7) Fuguitt, Stallcup and Hawkins, THIS JOURNAL, **64**, 2978 (1942).