desiccator over calcium chloride, the pure light-yellow crystals melted at 252° dec.

Anal. Calcd. for $C_{12}H_{13}N_3O_8$: C, 44.04; H, 4.00; N, 12.84. Found (dried at 100° *in vacuo*): C, 44.25; H, 4.14; N, 12.65.

β-(3-Methoxy-4,6-dinitrophenyl)-D,L-alanine (50 mg.), derived from 3-methoxy-4,6-dinitrobenzaldehyde, was acetylated as described for β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine using one-third the quantities of sodium hydroxide, acetic anhydride and sulfuric acid. The crude product (50 mg., m.p. 205°) was purified from absolute ethanol; m.p. 212–213°. Found (dried at 79° *in vacuo*): C, 43.83; H, 3.98; N, 12.70.

N-Acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine Methyl Ester and N-Acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine Methyl Ester.—A solution of 50 mg. of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine in 2.5 ml. of pure dioxane was mixed with a dry ether solution of diazomethane, prepared[7] from 0.4 g. of N-nitrosomethylurea and 4 ml. of ether. After the solution had been kept at 26–27° for 16 hr., the solvent was evaporated to deposit a sirup which crystallized upon being stirred with ether. Purified by recrystallization as slightly yellow needles from aqueous methanol and dried in an evacuated desiccator over calcium chloride, the compound melted at 158–159°, yield 35 mg.

Anal. Calcd. for $C_{13}H_{15}N_3O_8$: C, 45.75; H, 4.43; N, 12.32. Found: C, 45.55; H, 4.54; N, 12.31.

The compound was prepared also by esterification of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine with the use of methanol and acetyl chloride.[5] To a solution prepared by adding 0.5 ml. of acetyl chloride to 5 ml. of methanol was added at 0° 43 mg. of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine. The solution was kept at 25° for 23 hr., and the solvent then was evaporated at 30° *in vacuo;* the sirup was taken up in methanol, the solvent was evaporated and the operation was repeated. The sirup was crystallized as needles from methanol and purification was completed by recrystallization from benzene; m.p. 157–158°, not depressed when the substance was mixed with crystals of the methyl ester prepared with the use of diazomethane.

The reaction of diazomethane with the isomer of N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine melting at 194–195° (N-acetyl-C)[1] gave N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester identical with the authentic compound obtained by the esterification of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine. A solution of 40 mg. of pure N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine (m.p. 194–195°) in 2 ml. of pure dioxane was treated with diazomethane as described for N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine; yield 28 mg., m.p. 157–158°. A mixed melting point with crystals of the methyl ester prepared from N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine showed no depression and the infrared spectra (solid potassium bromide disk method) of the compound from the two sources were identical. Found: C, 46.23; H, 4.43.

The reaction of diazomethane with N-acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine (38 mg.) was carried out as described for the similar reaction with N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine, using 0.3 g. of N-nitrosomethylurea, 3 ml. of ether and 2 ml. of dioxane. The product, after purification from methanol and drying in an evacuated desiccator over calcium chloride, melted at 172–173°, not depressed when mixed with crystals of the previously reported[1] isomer of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 172–173°. Found: C, 45.78; H, 4.39.

Acknowledgments.—Indebtedness is expressed to Dr. William C. Alford and his associates of the Analytical Laboratory of this Institute for the microanalyses, to Mr. William Jones for the infrared spectra, to Dr. E. L. May for the gift of purified aluminum isopropoxide and to Dr. S. Black and Dr. R. C. Greene for advice on the paper chromatography of one of the compounds.

BETHESDA 14, MARYLAND

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(7) W. E. Bachmann and W. S. Struve, in R. Adams, "Organic Reactions," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1942, p. 50.

[CONTRIBUTION FROM THE GENERAL LABORATORIES, U. S. RUBBER CO.]

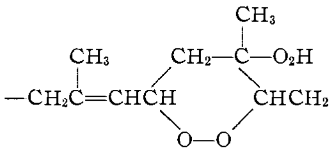
Chain Scission in the Oxidation of Hevea. IV. Low Molecular Weight Products from Dry Rubber

BY E. M. BEVILACQUA

RECEIVED DECEMBER 3, 1956

Estimates of yields of volatile products from the scission by oxygen of hevea rubber in latex[2] have been supplemented with measurements on dry rubber at 140°. The results make it possible to outline a mechanism for the scission reaction which accounts quantitatively for known products.

Some time ago Bolland and Hughes[1] deduced a structure (I) for the primary oxidation product of 1,5-dimethyl-1,5-dienes from the results of functional group analyses of partially oxidized squalene, oxidized under conditions of high chain length so that the primary product was obtained in high yield.



I

The significance of this result to the oxidation of hevea rubber was not known until quantitative estimates of the low molecular weight products of the oxidation of hevea in latex gave indirect evidence that a closely related structure must be formed in order to account for the observed products of the scission reaction.[2]

In latex the observed end-products, acetic acid, formic acid and carbon dioxide, are produced in stoichiometric ratios of 1:1:3. The yields relative to the production of new molecules by breaking the hydrocarbon chain show that six chain atoms appear as low molecular weight products at each scission.[3] A reasonable process involving six chain atoms in the scission reaction can be visualized readily by making use of a simple modification of the reaction mechanism postulated by Bolland and Hughes to account for I as a primary product. The important features of this mechanism are the ready addition of a peroxide radical to a double

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(1) J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

(2) E. M. Bevilacqua, THIS JOURNAL, **77**, 5394, 5396 (1955).

(3) E. M. Bevilacqua, *Rubber Age*, **80**, 271 (1956).

bond when a six-membered ring can be formed and the mobility of allylic radicals.[3]

The volatile compound of highest molecular weight previously identified with the oxidation of natural rubber is levulinaldehyde.[4] Although no clearcut evidence has been published for the direct formation of this material during oxidation with molecular oxygen, it generally has been assumed to be the product formed during aging of rubber which reacts with ammonia to give a compound which exhibits a positive "pyrrole" test. The present paper offers evidence supporting this belief and leading further to the conclusion that it is a direct intermediate in the scission reaction, which arises from the decomposition of a peroxide formed by the general process outlined by Bolland and Hughes.

Experimental

The molar ratio of volatile products from the oxidation of rubber to oxygen consumed is a function of temperature[2,3] approaching equivalence above 130°. In order to take advantage of this effect to obtain maximum yields of low molecular weight compounds, an apparatus was set up to permit experiments at elevated temperatures and to remove the volatile products from the reaction site as rapidly as possible.

In this apparatus the cell which contained the sample was mounted in a circulating air oven. The temperature was held constant to ±0.3°. In series with it were a trap immersed in a constant temperature bath and a gas circulating pump. The trap, outside the oven, was held at 0 or −80°, depending on what it was desired to collect. The pump, in the oven, was constructed according to the design of Cockett[5] modified only in that all moving parts in contact with the hot oxygen were of Teflon. A group of gas burets connected in parallel external to the cell were used to measure volume changes. They were surrounded by jackets in which water at 38° was circulated continuously during an experiment. All connections between parts not inside the oven or constant temperature baths were of capillary tubing to keep the volume subjected to uncontrolled temperature fluctuations as small as possible.

Pressure in the system was maintained constant during an experiment by periodic manual adjustment in which oil ("Hyvac" oil-93050) was added to the buret until a reference manometer containing a silicone oil (DC350) showed no head. The reference pressure was established in a sealed cell having nearly the same volume as the sample cell and mounted beside it in the oven. The volume of oil added was taken to be a direct measure of the volume of oxygen disappearing from the system by absorption in the sample. The oil, at 38°, absorbed oxygen at a negligible rate compared with the sample at 140°.

Low molecular weight products were recovered in the traps. The problem of quantitative recovery of very small amounts of products from large volumes of fast moving gas in one pass so that no product re-enters the oven, without raising the pressure drop in the apparatus, still has not been solved in a completely satisfactory way. However, the results indicate that nearly quantitative recovery of important products has been achieved. To trap acid gases two absorbers in series were used designed to give a high gas–liquid interface with a low resistance to flow. They were partially filled with standard alkali and held at 0° during a run. They were followed by a simple U-tube immersed in a Dry Ice–acetone-bath to remove water from the gas stream. In experiments in which it was attempted to estimate levulinaldehyde, this sequence of traps was replaced by a single small H-shaped trap cooled in a Dry Ice–acetone mixture.

Oxidized rubber samples were removed from the oven as soon as the desired amount of oxygen had been absorbed. They were cooled rapidly to room temperature in a stream of air or nitrogen, depending on how fast they absorbed oxygen. Intrinsic viscosities were determined in chloroform solution and molecular weights calculated on the basis of the relation determined by Carter, Scott and Magat,[6] as described previously.[2]

Results and Discussion

The first result using this apparatus was the observation that the condensate obtained in a trap held at −80° (from the gas stream passed over a sample in the oven at 140°) gave a strong positive test when heated with ammonium acetate, and the vapors were tested for pyrrole according to the procedure of Bruni.[4] The first few experiments were erratic and results depended on sample source and preparation. When a method for sample preparation was devised which gave consistently high yields of this product, as judged qualitatively, an effort was made to obtain quantitative determination.

It was assumed that the material is levulinaldehyde; no good quantitative test for this aldehyde is known. Although optical methods for carbonyl compounds based on the formation of the dinitrophenylhydrazone have been reported in the literature to give good results in the concentration range encountered here, they will not differentiate between aldehydes, and in our hands the results for other carbonyl compounds have not been nearly as satisfactory as could be desired at low concentrations. Since no other low molecular weight methyl ketone is suspected to be a probable product from the oxidation of rubber under our conditions, it was attempted to apply the iodoform reaction[7] for the quantitative estimation of levulinaldehyde in the volatile material collected in the trap. When this was done the results shown in Table I were obtained. In this and the other tables and figures in this report where units are not specified they are moles per 10^5 grams of rubber. Plotting the values of methyl ketone against "cuts" from this table we obtain Fig. 1. It is evident that a linear correlation exists between volatile methyl ketone, presumably levulinaldehyde, and cuts of the hydrocarbon chain, and that they are formed in amounts of the same order of magnitude. This observation immediately permits closing a gap in the mechanism originally advanced for the reaction by which oxygen severs the hydrocarbon chain,[2] in which the nature of the five carbon fragment from which low molecular weight products are formed was entirely

TABLE I

VOLATILE METHYL KETONE PRODUCED

(All units moles/10^5 grams rubber)

Oxygen absorbed	Cuts	Methyl ketone
6.0	1.2	0.19
12.0	1.6	.32
14.0	1.4	.37
17.5	1.8	.39
20.0	1.6	.64
23.8	2.2	.75
28.0	1.9	.65
36.6	2.9	.94

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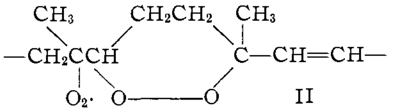
(4) This is reviewed by Dufraisse in "The Chemistry and Technology of Rubber," C. C. Davis and J. T. Blake, eds., Reinhold Publishing Corp., New York, N. Y., 1937, Ch. XIII.

(5) A. H. Cockett, *Nature*, **176**, 768 (1955).

(6) W. C. Carter, R. L. Scott and M. Magat, THIS JOURNAL, **68**, 1480 (1946).

(7) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd Ed., Vol. III, D. Van Nostrand Co., Inc., New York, N. Y., 1953, p. 263.

hypothetical. Levulinaldehyde clearly can be the source of both the acetic acid and the carbon dioxide found in the experiments in which rubber was oxidized in latex. The complete mechanism has been outlined elsewhere[3]; it gives a satisfactory explanation for all the known low molecular weight products of the oxidation of rubber, although details of certain steps still need to be worked out. It requires that each scission be accompanied by the loss of six carbon atoms from the hydrocarbon chain, the key intermediate having a structure of the form


II

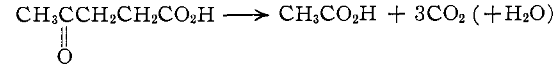
Upon scission the entire material in the six-membered ring of the peroxide dissociates from the chain, giving as the first stable product levulinaldehyde. When the rubber is oxidized as latex, the aldehyde is trapped in the aqueous phase and rapidly oxidized to CO_2 and acetic acid.[2] Although this step has not been demonstrated experimentally, the readily available levulinic acid does undergo rapid oxidation in dilute aqueous ammonia solution under the same conditions as were used in the latex experiments, giving the theoretical yields of carbon dioxide and acetic acid.

Results of typical experiments are given in Table II. In these the acid[8] (98.1% levulinic acid by titration) was oxidized at 90° as a 0.227 *N* solution in 2% ammonia containing a small amount of added copper. The apparatus and procedure have been described.[2] Acetic acid was identified by its volatility and characteristic odor and confirmed by partition chromatography on silica and by X-ray comparison of its silver salt with an authentic specimen.[9] These results correspond to substantially quantitative oxidation of the acid

TABLE II

PRODUCTS OF LEVULINIC ACID OXIDATION

Oxygen consumed (mmoles)	Produced CO_2 (mmoles)	Produced acid (meq.)	$\frac{CO_2}{acid}$
..	6.59	2.41	2.75
12.6	7.92	2.42	3.28



$$CH_3\underset{\overset{\|}{O}}{C}CH_2CH_2CO_2H \longrightarrow CH_3CO_2H + 3CO_2\ (+H_2O)$$

No other acids were identified among the products of these experiments, although the oxidation presumably must involve others as intermediates.

In the experiment described here the yield from the oxidation of dry rubber of approximately one-third mole of methyl ketone per mole of scissions is presumably a measure of the efficiency with which levulinaldehyde was removed from the reaction zone before it could undergo further oxidation. If this is so, the low molecular weight acids found as products of latex oxidation should also appear in this experiment, and if quantitative recovery can be obtained it should be possible to calculate roughly the amounts which will be found: One scission is equivalent to one levulinaldehyde plus one formaldehyde which yield as the completely oxidized end products three CO_2 plus one acetic acid from the first aldehyde and one formic acid from the second. Since one-third of the levulinaldehyde is removed as such, the final yields of CO_2 and volatile acids should be

$CO_2 \approx 2/3 \times 3 = 2$ moles/mole scissions

Volatile acid $\approx 2/3 \times 1 + 1 = 1.7$ moles/mole scissions

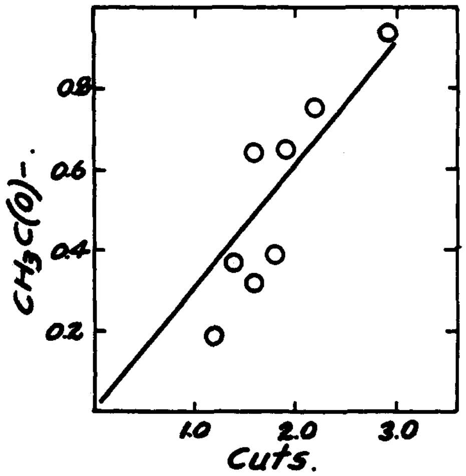


Fig. 1.—Volatile methyl ketone (levulinaldehyde) formed during oxidation of rubber at 140°.

Experimental results of such determinations are assembled in Table III for the same type of rubber sample which was used to obtain the results of Table I. When the data of Table III are plotted for comparison with predicted values based on the calculations in the preceding paragraph, the yields of CO_2 and volatile acid are of the expected order of magnitude, although the scatter of the points for CO_2 is undesirably high and the acid yields are somewhat low. Although we can attribute part of the scatter to simple experimental error in separating and measuring the very small quantities of acids obtained from the necessarily small samples of rubber, the results shown in the next Fig. 2 and 3 indicate that fairly good precision can be obtained and some of the differences between prediction and experimental results are real and must be accounted for. The data presented in Fig. 1 and in Table III were obtained by the oxidation of rubber which was coagulated on a form from whole latex and then leached with boiling water for 2 hr. Data

TABLE III

ACIDS FORMED DURING OXIDATION

(Rubber leached with water)

Oxygen absorbed	Cuts	CO_2	Volatile acid
4.0	0.6	1.2	1.0
8.0	1.2	3.6	0.8
12.0	0.8	2.9	0.8
16.8	1.0	4.4	1.3
24.1	1.9	7.4	1.6
25.0	(2.0)	8.8	1.0
31.2	3.2	4.0	1.6
31.7	2.3	2.9	2.0
39.6	4.1	4.0	2.4
45.0	(3.3)	6.3	1.7

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[8] Supplied by the Quaker Oats Co.

[9] F. W. Mathews, *et al.*, *Ind. Eng. Chem.*, **22**, 514 (1950).

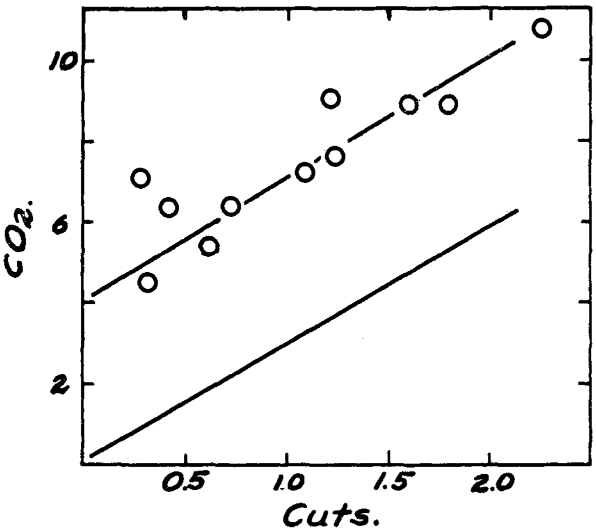

Fig. 2.—Yield of CO_2 from unleached rubber; solid line in Figs 2 and 3 has slope calculated in text.

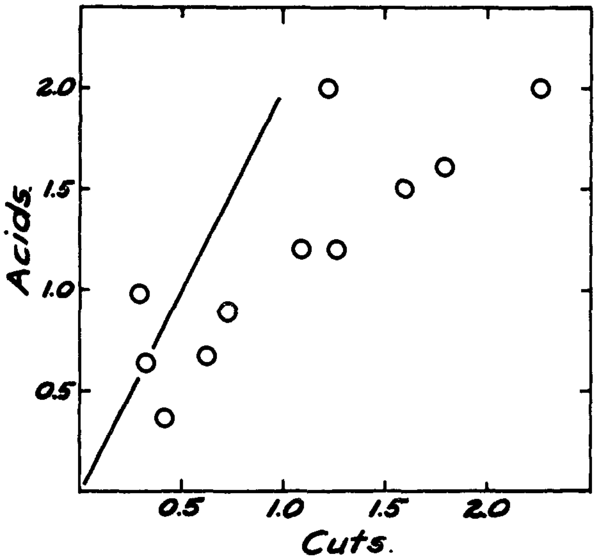

Fig. 3.—Yield of volatile acids same samples as Fig. 2.

in the following two figures were obtained using unleached samples (Table IV). In these figures the solid lines have theoretical slopes. It is apparent that spuriously high yields of carbon dioxide are formed, probably resulting from the thermal instability of serum acids present in the unleached rubber. Presumably the scatter of the CO_2 results in Table III is attributable to incomplete removal of acids in the leaching process. On the other hand, the yields of volatile acids in this experiment are reasonably self consistent and about the same as in the previous one.

TABLE IV

ACIDS FORMED DURING OXIDATION

(Rubber dried on form)

Oxygen	Cuts	CO_2	Volatile acid
3.15	0.29	7.1	0.98
5.77	.42	6.4	.36
6.30	.32	4.5	.64
8.65	.62	5.4	.67
9.45	.73	6.4	.89
12.60	1.09	7.2	1.2
15.7	1.26	7.6	1.2
15.7	1.21	9.1	2.0
18.9	1.80	8.9	1.6
22.1	2.26	10.8	2.0
23.6	1.60	8.9	1.5

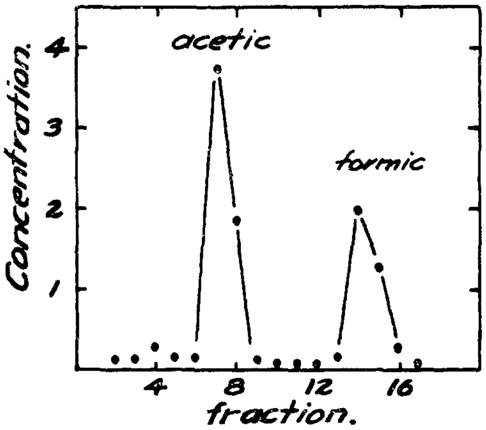

Fig. 4.—Separation of volatile acids on silica column; areas under peaks are proportional to concentrations.

Our calculations are based on the assumption that all the formic acid normally produced when latex is oxidized is formed in the present experiment also and that only the acetic acid yield is lowered by sweeping out the cell with gas. When the mixture of volatile acids actually obtained was analyzed by separation on a silica column, it was found that acetic acid is present in concentrations which are equal to or greater than that of formic acid (Fig. 4). The material which still remains to be accounted for, therefore, is formic acid or a precursor thereof.

Several explanations have been considered for the low apparent yield of formic acid, which has not been resolved experimentally. If formic acid were rapidly oxidized, CO_2 yields should be consistently high. This is not definitely excluded by our data but appears unlikely. If a non-acid intermediate (presumably formaldehyde) were distilled from the reaction cell, yields would be low. Formaldehyde has been found in the distillate, but it accounts for only about 10% of the missing formic acid. The results of end-group determinations[10] suggest that under the conditions used in these experiments about half the carbon from which formic acid is derived during oxidation of latex remains with the polymer, rather than appearing as a volatile product.

In summary, the results reported here, together with those reported previously, show that there is no significant change in the mechanism of degradation of rubber by oxygen over a wide temperature range. The over-all mechanism appears to be well established and able to account for the variations in product ratios caused by changing experimental conditions. Only the details of the final steps in the scission process remain to be clarified.[11]

PASSAIC, N. J.

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(10) E. M. Bevilacqua, to be published.

(11) A report of this work was presented at a meeting of the Rubber Division of the American Chemical Society, September 20, 1956.