The product then was chromatographed[11] on a 30-inch column of 60–200 mesh silica gel. Absolute ethanol was used as eluent. Collection of the aromatic fraction was begun when the effluent reached $n^{20}\text{D}$ 1.4752; collected 2.2 g.

(b) Oxidation.—The product of the preceding step was oxidized by refluxing for 20 hours with 15 g. of potassium permanganate dissolved in 230 ml. of water. Five ml. of methyl alcohol was then added to remove the last traces of permanganate. The reaction mixture was filtered hot and the cake of manganese dioxide washed with 200 ml. of hot distilled water. The solution was evaporated to *ca.* 50 ml. and the hot solution acidified with concentrated hydrochloric acid and cooled in an ice-bath. The precipitate was filtered on a sintered glass funnel, washed with ice-water, air-dried, and then transferred to a desiccator; m.p. 121–121.5° (cor.).

The yield was not determined on the active run since some ethanol was mixed with the toluene after chromatographing. Exploratory experiments using 3.0 g. of toluene gave 60% yield.

(c) Decarboxylation.—Decarboxylation of the benzoic acid obtained in the preceding step was carried out according to the procedure outlined by Calvin, *et al.*,[12] using 0.8 g. of copper chromite catalyst and 10 ml. of redistilled quinoline. A nitrogen sweep carried the benzene into a Dry Ice trap and the carbon dioxide evolved was collected in sodium hydroxide, precipitated as barium carbonate, and assayed. The benzene recovered had $n^{20}\text{D}$ −1.5011, yield 75–80%.

A portion of the benzene was burned and the carbon dioxide converted to infinitely thick barium carbonate samples, which were then assayed. It was found that 31% of the radioactive carbon was in the benzene ring and 69% on the methyl group.

In the experiment where *sec*-butyl bromide was a chain initiator only 2% of the radioactive carbon was present in the ring.

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[11] B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

[12] Reference 9, page 229.

[CONTRIBUTION NO. 147 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Scission in the Oxidation of Hevea. I

BY E. M. BEVILACQUA

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The efficiency of chain scission of raw hevea by molecular oxygen increases rapidly with increase in temperature, to a limiting value of about 6.2 molecules of oxygen per bond broken. This value is close to the theoretical for destruction of one isoprene unit per bond broken, which leads to the inference that the higher efficiencies which have been reported for oxidation of vulcanized rubber may be the result of scission at the points of cross-linking.

Introduction

The essential role of oxygen in the reduction of viscosity of unvulcanized rubber during mastication is well known in a qualitative way, but there is little quantitative information about the efficiency with which it is used in this process. A recent study of the low temperature breakdown of hevea by Pike and Watson[1] clearly suggests that the efficiency (measured in terms of scissions of the hydrocarbon chain per mole of oxygen absorbed) is high under conditions where mechanical rupture of carbon to carbon bonds is important. At elevated temperatures (above about 120°) the viscosity of hevea has fallen sufficiently so that mechanical rupture is no longer effective and mastication serves only to mix the rubber and to expose continuously fresh surfaces to air. Measurements of the efficiency of oxidation on films thin enough so that oxygen diffusion does not affect the results should therefore be satisfactory to determine the efficiency of oxidative scission under practical milling conditions.

It is not possible to make such measurements with ordinary forms of rubber without some preliminary degradation of the hydrocarbon, either accompanying solution in a solvent or during milling to produce a thin sheet. The USF rubber process[2] affords a particularly convenient source of undegraded rubber, which has been used in this investigation.

Experimental

USF type rubber was prepared by a slight modification of the published procedure.[2] Normal latex, preserved with 0.4% formaldehyde by weight, was diluted with distilled water to give a calculated ash content in the final rubber equal to that of commercial USF. After adjustment of the *pH* to 3.8 to 4.0 with formic acid, the mixture was allowed to cream for 24 hours. The cream was separated from the clear serum and spread on glass to give a final film of the desired thickness after drying. All the films used were less than 0.01 cm. thick. Films were wrapped in desized glass cloth for oxidation.

Oxidations were carried out at a constant pressure of one atmosphere of oxygen in a simple apparatus consisting of a large test-tube mounted in a circulating air oven. The test-tube was connected by capillary glass tubing to a reference manometer and a manually operated gas buret maintained at 30°. The reference manometers were connected to a reservoir of air at constant temperature to eliminate the effect of variations in atmospheric pressure. Lumps of barium oxide were mounted in the oxidation cells during an experiment to absorb evolved water and acid.

Cells containing the samples were evacuated with a mechanical pump, allowed to reach the oven temperature, then filled with oxygen preheated to the operating temperature. Oxygen consumed was measured with the gas buret by periodic adjustment to the reference pressure. During an experiment samples were removed from the oven after the desired amount of oxygen had been absorbed and cooled rapidly to room temperature. Intrinsic viscosities of the oxidized rubbers were determined in benzene solution.

Molecular weights were calculated from the relationship between intrinsic viscosity and number average molecular weight reported by Carter, Scott and Magat.[3] Use of this relation involves the implicit assumption that the ratio of number average to viscosity average molecular weight does not change materially during oxidation.

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[1] W. F. Watson, *Trans. Inst. Rubber Ind.*, **29**, 32 (1953); M. Pike and W. F. Watson, *J. Polym. Sci.*, **9**, 229 (1952).

[2] J. McGavack, C. E. Linscott and J. W. Haefele, *Ind. Eng. Chem.*, **34**, 1335 (1942).

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

Discussion

Results of one experiment are shown in Table I and results of measurements at three temperatures in Table II.

TABLE I

OXIDATION OF USF RUBBER AT 130°

Time in oven, min.	Oxygen absorbed, mmoles/100 g.	"Gel," %	[η]	Moles oxygen / Moles scissions
..	0	7	9.08	..
10	1.06	4	2.88	5.6
30	2.50	6	2.82	12.5
40	3.47	3	2.21	11.3
48	4.25	8	1.94	10.8
68	6.36	6	1.60	12.2
			Mean	10.5

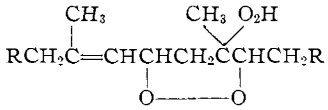
TABLE II

EFFICIENCY OF CHAIN SCISSION BY OXYGEN

Temp., °C.	130	130	130	140	150
Moles oxygen / Moles scissions	10.5	11.4	11.3	6.2	6.3

Published estimates of the efficiency of chain scission during oxidation of raw hevea have been based largely on experiments at low temperature where oxidative scission may be expected to be relatively inefficient.[4] Tobolsky, Metz and Mesrobian[5] have shown that the efficiency of scission should, and does, increase as the rate of oxidation increases, as has also been found here. The measurements of Tobolsky and co-workers were made with vulcanized rubbers; they observed a higher limiting efficiency than was found for raw hevea in this work. When oxidation was carried out at the maximum rate at a given temperature, very nearly one scission of the hydrocarbon chain was found, per mole of oxygen absorbed.

The only published work which affords a guide for an attempt to formulate a reaction scheme which would explain the observed efficiencies is that of Bolland and Hughes[6] on the primary oxidation product of squalene, a low molecular weight model for rubber. They have shown that this hydroperoxide contains four atoms of oxygen and suggest that the structure which predominates in the product is of the form



$$\mathrm{RCH_2\overset{CH_3}{C}{=}CHCHCH_2\overset{CH_3\ O_2H}{C}CHCH_2R'}$$

Investigation of the oxidation of rubber in latex[7] has given evidence that one isoprene unit is destroyed for every chain scission. If it is assumed that the hevea hydroperoxide has the same structure as that found for squalene, a plausible reaction sequence may be envisioned, which yields the observed low molecular weight products of the scission reaction: carbon dioxide, acetic acid and formic acid. This scheme requires six moles of oxygen per mole of chain scissions, which is close to the amount observed in the present work at the higher temperatures.

If the interpretation of hydrocarbon scission given here and in the following paper[7] is correct, some alternative or additional mechanism must exist to give the high efficiencies observed by Tobolsky, Metz and Mesrobian. Since the reaction of oxygen with the rubber hydrocarbon itself would not be expected to be greatly modified by oxidation under low stress, an obvious possibility exists that direct attack at the points of cross-linking is important in the vulcanized rubber.[8]

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[4] E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 125 (1943); J. McGavack and E. M. Bevilacqua, *Ind. Eng. Chem.*, **43**, 475 (1951); L. Bateman, *Trans. Inst. Rubber Ind.*, **26**, 246 (1950).

[5] A. V. Tobolsky, D. J. Metz and R. B. Mesrobian, THIS JOURNAL, **72**, 1942 (1950).

[6] J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

[7] E. M. Bevilacqua, THIS JOURNAL, **77**, 5396 (1955).

[8] It has been pointed out that this discussion ignores the effect of possible cross-linking during oxidation. There is, at present, no published evidence which would permit a satisfactory estimate of the importance of a cross-linking reaction during the oxidation of hevea. It is well known that oxidized rubber becomes cross-linked in the absence of oxygen and that vulcanizates become resinified on severe oxidation, but the nature of these changes is undetermined. Using a disazodicarboxylate as the curing agent, Metz and Mesrobian (*J. Polymer Sci.*, **11**, 83 (1953)) have determined the change in modulus of well characterized simple hevea vulcanizates when oxidized, both relaxed and under stress. As nearly as can be estimated from their data, presented graphically, scission efficiency was the same within experimental error, whether calculated from stress relaxation or modulus change, up to about 8 hours (at 80°). At this time the samples had absorbed roughly 100 millimoles of oxygen per hundred grams, most of which is involved in reactions other than scission. This is about ten times the maximum amount absorbed by the rubber in the experiments reported here. It is probable that oxygen-induced cross-linking occurs through secondary reactions which, in hevea, are suppressed at high oxygen concentrations, unless so much oxygen has been combined with the rubber that substantial changes in the hydrocarbon have occurred.