The average yield of all of these esters was 85%.

ESTERS OF TRICHLOROMETHYL-*p*-CHLOROPHENYLCARBINOL

		M. p., °C.	Formula	Analyses for Cl, % Calcd.	Found
1	Acetate	120–121	$C_{10}H_8O_2Cl_4$	46.98	47.18
2	Propionate	71–72	$C_{11}H_{10}O_2Cl_4$	44.89	45.17
3	Benzoate	128–129	$C_{15}H_{10}O_2Cl_4$	38.98	38.87

The butyrate boils at 172–173° at 6 mm., d^{20}_{20} 1.331. The butyrate is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide. The other esters differ from this in that they are only sparingly soluble in ethyl and methyl alcohols.

A number of attempts were made to make these same esters of tribromomethyl-*p*-chlorophenylcarbinol using the same reagents and experimental conditions but the carbinol always came through unchanged. Attempts were also made to prepare the acetate by heating with acetyl chloride at 60–70° for three hours and the benzoate by heating with benzoic anhydride at 180–190° for five hours. The results here were also negative.

Summary

Trichloromethyl-*p*-chlorophenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied. The corresponding tribromo carbinol was prepared but it does not form these esters under the same experimental conditions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XV. Oxygen in Rubber

BY THOMAS MIDGLEY, JR., A. L. HENNE, A. F. SHEPARD AND MARY W. RENOLL

The harmful effects of oxygen on rubber have long been known, and the formation of peroxides during milling has been qualitatively demonstrated.[1] However, quantitative measurements of the oxygen have never been made, and the nature of the oxygen compounds has not been investigated.

Rubber frequently has been analyzed by combustion and the ratio of the carbon percentage to the hydrogen percentage has invariably been found to correspond closely to a $(C_5H_8)_n$ formula. However, it does not follow that such is the formula of rubber. In every instance, the total of the carbon and the hydrogen content has fallen short of 100%. The deficiency is very small, especially in the case of pure rubber, but it invariably exists. The best analyses available, those of the Bureau of Standards,[2] done on highly purified, and on recrystallized rubber, show a deficiency of 0.3%. This cannot be accounted for entirely by contamination of the samples, nor can the combustion be assumed to be that inaccurate. It is logical to regard this deficiency as the oxygen and nitrogen content of the sample.

In the present work, the quantity of oxygen present in rubber samples has been measured by means of the combustion method described by the Bureau of Standards; an effort has been made to determine the type of oxygen present and to study the progressive oxidation of rubber. The technique of the Bureau has been altered in only two details: (1) a Jena combustion tube was substituted for the Pyrex tube, to prevent sintering at the high temperature used to burn out the last traces of carbon; (2) weighings were improved to ±0.00002 g.

Procedure

Sol rubber was prepared and purified by fractional precipitation[3] until it contained only 0.007 ± 0.0003% of nitrogen by Nessler titration. A sample of this rubber was analyzed by combustion to determine the H/C ratio and the oxygen and nitrogen content by deficiency. Another sample of the same specimen was treated with methylmagnesium iodide and the resulting methane measured to determine the amount of active hydrogen. The amount of carboxylic or ketonic groups present was investigated by treating a third sample with thionylmagnesium iodide, purifying the reaction product and analyzing it for sulfur.[4] The data are listed in Tables I and II together with the results of the same methods used on purified sodium rubber and on the degraded products of both.

Discussion of the Results

The striking fact shown by the tables is that pure synthetic rubber is oxygen free, while natu-

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(1) Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

(2) Smith, Saylor and Wing, *Bur. Standards J. Research*, **10**, 479–92 (1933).

(3) Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

(4) Midgley, Henne, Shepard and Renoll, *ibid.*, **56**, 1325 (1934).

TABLE I

ANALYSIS OF RUBBER BY COMBUSTION

	H	C	H/C
Calcd. for $(C_5H_8)_n$, %	H, 11.84	C, 88.16	H/C = 0.13436
Synthetic rubber, found	11.82, 11.83 and 11.83	88.17, 88.17 and 88.17	.1342
Natural rubber, found	11.86 and 11.86	88.07 and 88.07	.1346

Basis of Calculation: C = 12.0048, H = 1.0081 and O = 16.0000.

Note: The samples of natural rubber contained 0.007% N.

TABLE II

NATURAL RUBBER (SOL RUBBER)

(Nitrogen content = 0.007%)

Material	Analyses, % Ash	C	H	H/C	Oxygen content measured by Combustion	Active H	Mol. wt. cryoscopy
Original	0.01	88.07	11.86	0.1346	0.06	0.028	∞
Milled 1.5 hours	.065	87.71	11.79	.1344	.44	.095	∞
Degraded 1 day	.02	87.58	11.75	.1342	.65	.16	∞
Degraded 7 days	.02	82.45	11.05	.1340	6.48	1.51	4400
SYNTHETIC RUBBER							
Original	0.00	88.17	11.83	0.1342	0.00	0.00	∞
Degraded 1 day	.01	88.14	11.83	.1342	.02	.00	∞
Degraded 11 days	.01	85.43	11.47	.1343	3.09	.91	∞
Degraded 18 days	.03	84.73	11.34	.1338	3.90	1.49	8100
Degraded 31 days	.00	79.40	10.60	.1335	10.00	2.88	4300

ral rubber purified to the same extent by the same procedure contains oxygen; this oxygen is associated with an appreciable amount of active hydrogen while CO groups or oxygen of a peroxide nature are practically absent. Consequently, the experimental results may be interpreted as establishing the presence of an hydroxyl group in what has heretofore been called a hydrocarbon.

In view of the fact that oxygen is measured by deficiency, and its order of magnitude is very small, it is proper to question the significance of the experimental results.

First, may not the deficiency, as determined by the combustion, be purely an experimental error in the case of undegraded rubber?

This objection is refuted by the fact that a sample of sodium rubber has been repeatedly analyzed in the same apparatus and manner to give zero deficiency within the probable limits of experimental error.

Second, may not all of the oxygen found in undegraded rubber be attributed to an unremoved impurity?

Such an assumption is refuted by the fact that purified natural rubber gels when it is treated with a Grignard reagent; this is a test for combined oxygen in rubber, as previously shown.[5]

Third, could the combined oxygen be the result of slight degradation during fractionation? This is unlikely because synthetic rubber, which degrades quite easily, was subjected to the same method of purification, yet remained free of oxygen.

Fourth, is the combined oxygen a natural part of the rubber molecule or is it the result of slight oxidation between the time the latex left the tree and the time fractionation started?

The present results are only conclusive for the particular sample used. This sample was taken from the center of a bale of sprayed latex rubber and showed no visible signs of oxidation such as could be seen at the surface of the bale. Similar samples had been investigated previously by fractionation and no evidence of degradation had been found. It is probable, therefore, that the combined oxygen is a part of the rubber molecule occurring in nature.

Irrespective of its origin or significance, combined oxygen has been demonstrated to be present in the natural rubber investigated.

Quantitative Value of the Data

No quantitative significance is attached to any minor variation of the data except for the original undegraded sample of natural rubber and the oxygen-free synthetic; hence, this part of the discussion is confined to these two.

The values selected for the atomic weights of hydrogen and carbon are important and affect the results. The latest reported values by Aston,

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(5) Midgley, Henne and Shepard, THIS JOURNAL, 56, 1156 (1934).

namely, 1.0081 for hydrogen and 12.0048 for carbon, have been used in the calculations.

The deficiency of the natural rubber analysis is determined as 0.06%. This value includes the combined oxygen of the rubber and all the oxygen and nitrogen of the impurities present. The samples contained 0.007% of nitrogen. Previous experience with the fractionation of rubber has shown that the nitrogen impurities which are soluble in benzene and alcohol mixtures are easily eliminated but that an insoluble nitrogenous material collects in a gel phase. By degenerating the gel rubber this impurity may be collected. It contains two atoms of oxygen for each atom of nitrogen and behaves as an amino acid. It is almost certain that this impurity is the source of the nitrogen found, hence the total nitrogen and oxygen external from the rubber molecule itself becomes 0.023%. This leaves the combined oxygen as 0.042%.

The results of the treatment with thionyl Grignard were of no significance. The method is no more accurate than the values obtained. And even though these values were other than experimental error, they still would not represent any more oxygen than that available for this reaction in the nitrogen impurity. If there is any ketone, aldehyde or carboxyl oxygen present in the original L. S. rubber, this investigation fails to disclose it.

The hydroxyl oxygen, as disclosed by active hydrogen measurements, is more reliable. This method gives closely checking results. Blanks indicate a high accuracy for acids but a slightly low value for alcohols. If allowance is made for the active hydrogen present in the nitrogen impurity, considered as an amino acid, the final value becomes (0.028 − 0.008) = 0.02%. This value should be looked upon as possibly somewhat low, as the evidence thus developed points to the rubber molecule being an alcohol.

The value of 0.04% of oxygen as measured by combustion seems somewhat in discrepancy with the value of 0.02% as measured by active hydrogen determination, but a critical study of the possible errors involved in both methods by no means precludes the probability that the true value for the oxygen lies between these two and that hydroxylic oxygen was the only kind of oxygen present in the samples. By computing the molecular weight corresponding to the assumed presence of only one atom of oxygen in each rubber molecule, it is found that 0.04% of oxygen corresponds to a molecular weight of 40,000, while 0.02% corresponds to 80,000 (or 585 and 1170 isoprene units, respectively). This is in substantial harmony with the mol. wt. of 53,000, as determined by sulfur addition,[4] and suggests that the rubber molecule is a high molecular weight member of a pseudo homologous series occurring in nature, starting with geraniol and increasing by isoprene units to rubber.

One definite discrepancy with respect to present-day conceptions of the rubber molecule exists in the data. This is the abnormally high H/C ratio. Experience with the analysis indicates that this ratio is accurate to within ±0.0001. The theoretical H/C ratio for C_5H_8 with C as 12.0048 and H as 1.0081 is 0.13436. The indicated ratio for the original natural rubber is 0.1346. This is in perfect agreement with the value reported by the Bureau of Standards[2] and is 0.00024 too great, or 0.18% in excess, or one extra hydrogen atom for each 70 isoprene units. This is too small a number of isoprene units for it to be an end-group hydrogen. Likewise, if impurities are assumed to be responsible, a deficiency of 0.18% is required to account for it as water, 0.14% as alcohol or 0.75% of a non-volatile paraffinic hydrocarbon must be present, none of which fits the other data and/or the present accepted theories about the rubber molecule.

Oxidation Data

The data presented relative to the oxidation of rubber are to be taken as merely a preliminary study of the application of the analytical methods used to the problem of the chemistry of the oxidation of rubber. The results are, however, significant. As rubber undergoes oxidation, either by milling or exposure to oxygen and sunlight, the following events occur. The H/C ratio decreases, the combined oxygen increases, the active hydrogen increases and the molecular weight (measured by cryoscopy in benzene) decreases. The thionyl Grignard results still lack significance.

In addition to the data reported, the following experiment was performed. A fresh sample of heavily oxidized rubber was placed in a sealed tube and heated for several hours. Oxygen gas was evolved, the combined oxygen decreased to about half of its original value, the active hydrogen decreased slightly, the H/C ratio decreased and, judging by appearance, the molecular weight had greatly decreased.

These observations and data are sufficient to suggest several deductions as to the probable course of events.

1. Oxygen attaches to the rubber molecule in some peroxide linkage.
2. This linkage rearranges to an OH group with the liberation of O.
3. Some of the OH groups join with H and are eliminated as H_2O; hence the lowering of the H/C ratio.
4. The molecule is ruptured during or as the result of one of the above events.

Experimental

Combustion.—The apparatus developed by the Bureau of Standards[2] was used with the following alterations. A Jena Supremax tube was welded to a large Pyrex slip-joint at one end, and this joint was used without lubricant to connect to the purifying train. All combustions were done in air. Generally a platinum boat was used, but undegraded natural rubber was burned without a boat.

Preparation of the Samples.—Sol rubber samples were obtained by fractional precipitation, handled and stored as previously described.[3] The synthetic rubber samples were prepared from purified isoprene by polymerization over Na-K, *in vacuo*. Polymerization was so rapid that cooling was needed to prevent explosions.

Degradation.—Rubber cement (5% in benzene) was placed in an oxygen-filled round-bottom flask, and exposed to sunlight at room temperature. Dry oxygen was fed periodically to make up for the amount used.

Active Hydrogen Determination.—The apparatus was made of sealed Pyrex glass (see Fig. 1), the reaction chamber (a) being an ordinary 300-cc. Kjeldahl flask; the buret (b) was about 7 cc. in capacity and was kept at a known temperature by means of a water circulation jacket.

The reagents used were:

(1) Rubber cement in C. P. benzene. This benzene, which is also used as a wash liquid, must be run as a blank to determine its methane liberation value.

(2) Methylmagnesium iodide in butyl ether, of approximately 1.5 molecular concentration. This reagent is rid of all incidental gases by evacuation and is kept in sealed ampoules containing 7-cc. portions until it is ready to be used. One ampoule is used for each determination.

(3) C. P. triphenylcarbinol, for standardization.

Procedure.—Fill the buret completely with mercury; close the stopcock (c); evacuate the flask completely through (a); place a quantity of rubber cement in (a), such that it will generate from 1.5 to 3.5 cc. of methane; suck it into the flask, and wash (a) with C. P. benzene several times, until the total volume in the flask is about 200 cc. Heat cautiously with a small flame, while evacuating steadily through (a), and shaking vigorously, until the volume is reduced to about 50 cc.; close (b) in such a manner that a small amount of benzene distillate remains above it as a seal. Place the batch of methylmagnesium iodide in (a); reduce it to about one-half of its volume by cautious evacuation, in order to remove any possible gases; allow this reagent to be sucked into the flask, closing (b) just in time to retain a small portion above it as a seal. Heat the mixture cautiously, while shaking frequently; this causes the methane to collect in the side-arm, from where it can be drawn into the buret, together with a small amount of benzene. Close (c), and allow the flask to cool slightly; then reheat with shaking. By watching the ring of benzene condensation rising in the side arm, it is possible to ascertain whether or not more methane is being liberated. Usually two or three successive heatings are sufficient, after which pure benzene reaches the buret. The amount of gas in the buret is then measured, corrected for standard conditions, for benzene vapor and for the previously determined blank.

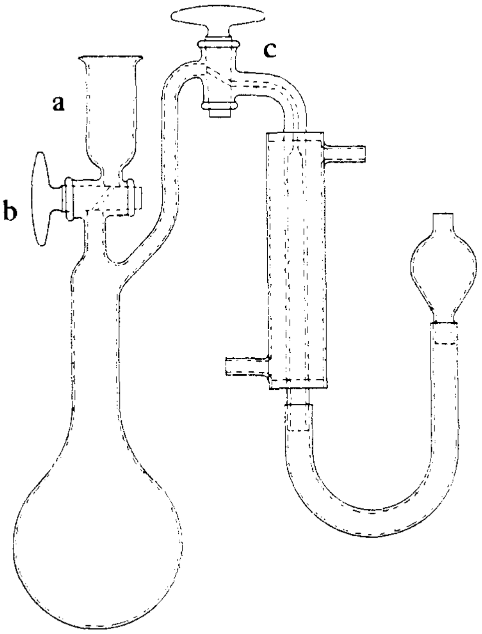

Fig. 1.

ANALYSIS OF TRIPHENYLCARBINOL

Sample, g.		0.0322	0.0370
Methane, cc.	Calcd.	2.77	3.19
	Found	2.53	3.14

Summary

It has been shown that natural rubber contains oxygen, while synthetic rubber is oxygen free. This oxygen appears to be of an hydroxylic type, and its quantity corresponds to about one hydroxyl group for each one thousand isoprene units of the rubber molecule.

Rubber has been allowed to oxidize and a mechanism is proposed to interpret the quantitative data recorded.

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