

LII.—*The Optical and Chemical Properties of Caoutchouc.*

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IN a paper on Essential Oils, published in the *Trans.*, 1886, 609, one of us gave some observations on the refraction and dispersion of caoutchouc, as well as on isoprene and cautchene derived from it by distillation. As these seemed to show that the caoutchouc is a hydrocarbon in which at least two pairs of carbon-atoms are doubly linked, it was deemed interesting to pursue the inquiry further.

We have met with great difficulties, partly from the doubtful purity of the substance, partly from the readiness with which it undergoes transmutations. We think, however, that some of the results arrived at may not be without value.

The earlier workers on the subject were able to get the natural juice of the tree, but the analyses, including those of Faraday and Greville Williams, indicate the presence of some impurities. At the present day, the juice is no longer imported. The substance we used was the best Para rubber, kindly placed at our disposal by Mr. Willoughby Smith, as well as another specimen of it, and of Penang rubber obtained from Mr. Hancock.

Para Rubber.

This rubber was pale in colour, in pretty uniform laminæ, and had a sp. gr. of about 0.92. On analysis, it contained, as might have been expected from its origin, some inorganic constituents. In Willoughby Smith's specimen, this was found to be 0.46 per cent., and in Hancock's 0.38 per cent. Another constituent was water, and to an extent that was not expected by us. Willoughby Smith's specimen gave 10.6 and 11 per cent., Hancock's 7.1. As this water came off at 100°, it probably indicates nothing but insufficient drying.

It is well known that part of the caoutchouc is soluble in benzene and other solvents, and that a part is insoluble. Faraday also speaks of albumin as one of the constituents of the juice. We found the best solvent to be chloroform. This very slowly dissolves the whole of the hydrocarbon, leaving a sort of network of the nitrogenous body. In one experiment, this residue was found to be about 4 per cent. of the whole weight. We are inclined to believe that the less soluble modification of the hydrocarbon which has been frequently observed, is produced during the drying of the juice, for we find that if the more soluble part be heated, it is more or less changed, and less susceptible of subsequent solution. The change increases as the

temperature is raised, and also with the length of time during which the heat continues. This will account for the very varied results obtained by different experimenters as to the proportions of soluble and insoluble caoutchouc.

We made many attempts to separate these two modifications, and to remove the oxidised product which commonly occurs with them. The most promising method seemed to be to dissolve the rubber in cold chloroform, and precipitate partially with a little alcohol. The precipitate obtained was generally dried in a vacuum, in order to avoid oxidation. We failed, however, to produce any good separation, and the results of analyses gave usually about 3 per cent. of oxygen, nor was this oxygen removed by the action of sodium on the solution. One small specimen, however, gave the following numbers, which closely approach those deduced from $C_{10}H_{16}$:—

0.1164 gram gave 0.3733 CO_2 and 0.1258 H_2O .

	Found.	Calculated.
Carbon.....	87.46	88.24
Hydrogen	12.00	11.76
	<hr/> 99.46	<hr/> 100.00

Optical Analysis.

Accepting it as a fact, that the carbon and hydrogen in the principal constituent of caoutchouc are in the same proportions as in the essential oils, there remains the question as to the arrangement of the elements. It is quite easy to conceive that the $C_{10}H_{16}$ is so built up that only one pair of carbon-atoms is double linked as in the terpenes, or two pairs as in the citrenes, or there may be three pairs. Nor does it follow that $C_{10}H_{16}$ is its molecular formula: C_5H_8 exists as one of its distillation products, and $C_{15}H_{24}$ is not uncommon among essential oils. Now a knowledge of the refraction and dispersion of the substance would probably determine the first question, and might throw light on the second.

The theoretical refraction and dispersion equivalents of $C_{10}H_{16}$ in the three conditions above mentioned, would be as follows, assuming that each pair of doubly-linked carbon-atoms would produce the same increment as in the aromatic series.

$C_{10}H_{16}$.	$\frac{P^{\mu_A} - 1.}{d}$.	$\frac{P^{\mu_H} - \mu_A}{d}$.
1 pair of doubly-linked carbons ..	73.0	4.0
2 " " " ..	75.2	4.8
3 " " " ..	77.4	5.6

In order to determine this point, a number of specimens prepared in various ways were dissolved in benzene, and the optical determinations made as usual. The following are the whole of the results obtained, with the exception of three which were known to be untrustworthy.

TABLE I.

No. of preparation.	Strength of solution.	Refraction equivalent.	Dispersion equivalent.
1	16·44	76·02	5·13
2	16·66	76·90	4·90
3	13·27	74·20	5·02
4	19·71	73·42	5·31
5	11·44	73·23	4·87
6	30·40	74·58	5·01
7	5·83	75·11	5·60
8	14·14	76·94	5·01
9	12·83	75·69	5·19
10	18·24	76·87	5·67
11	17·58	77·59	5·34
12	8·24	75·43	5·44
13	15·38	75·69	5·40
14	10·32	74·46	6·13
15	12·18	76·02	5·69
16	9·42	76·52	5·63
17	13·92	76·01	5·18

Nos. 1 and 2 were made from the original rubber as dissolved in chloroform and dried at 100°. The others, from 3 to 13, were made from the substance that was precipitated by alcohol from the chloroform solution. This precipitate was dried in different ways: No. 3 at 100° in hydrogen gas; No. 4 in a Sprengel vacuum at 40°; No. 5 over sulphuric acid for seven days; Nos. 6, 7, 8, were parts of the same preparation of which the carbon and hydrogen constituted 97·2 per cent. No. 8 was No. 7 concentrated by evaporation. No. 10 and 11 are alluded to below. No. 13 was dried in hydrogen at 100°. Nos. 14 and 15 were the first and second fractions of a precipitate obtained by adding alcohol to an ethereal solution of the original Para rubber. Nos. 16 and 17 were respectively the first and second precipitates similarly obtained from an ethereal solution of Penang rubber. It will be observed that there is no well-marked difference between these first and second precipitates.

Now, although the refraction and dispersion equivalents in the above table vary more than is easily accounted for, they all agree in showing that the $C_{10}H_{16}$ must have more than one pair of carbon-atoms doubly linked. All the dispersion equivalents and 11 of the

refraction equivalents, also exceed what theory requires for two pairs of carbon-atoms so combined. They fall short of what would be required by three pairs, at any rate in the case of refraction, but it must be remembered that the presence of a little oxygen in the substances examined will pull down the refraction and dispersion considerably. 3 per cent. of oxygen for instance would make a reduction of at least 1.4 in the refraction column and 0.13 in the dispersion column, and if the addition of oxygen caused some of the carbon to be saturated, the reduction would be still greater. It is worthy of remark that the lowest figures are in No. 5, where there was a long exposure to air during drying.

The best observations are Nos. 10 and 11. For these, the chloroform solution was very carefully mixed with alcohol, which caused the caoutchouc as it separated to rise to the surface like cream. After separating, this cream was heated in hydrogen at 140° , and afterwards dried in a Sprengel vacuum at 125° . In this way, we succeeded in preparing a substance of which the hydrocarbon formed 99.46 per cent. The analysis has already been given. The solution was made in the case of No. 10 by dissolving a known weight of this caoutchouc in a known weight of benzene. In the case of No. 11, the strength of the solution was determined by subsequent evaporation. The observations show a heightening of both optical properties, in fact, the mean refraction equivalent 77.23 and dispersion equivalent 5.50 almost coincide with the calculated figures 77.4 and 5.6 given above.

We have little doubt, therefore, that the main constituent of caoutchouc is a compound which for $C_{10}H_{16}$ has three pair of carbon-atoms doubly linked.

If this be the case, the molecular formula cannot be C_5H_8 , like isoprene, or $C_{15}H_{24}$, like cedrene, as these would give respectively one and a half and four and a half pairs of carbon-atoms united by double linking. It cannot contain the hexagonal ring, but must be expressed graphically by a chain formula. This may account for the wide difference of properties between caoutchouc and the various essential oils.

Halogen Compounds.

An endeavour was made to test the previous conclusions by chemical methods. The chloroform solution appeared to offer a good opportunity of studying the action of halogens on caoutchouc, and the results were, considering the small amount of oxygen always present, sufficiently definite.

We did not succeed in obtaining a simple additive compound with chlorine. On passing the gas into a chloroform solution of caoutchouc containing about 1 per cent. of the hydrocarbon—the experiment being

made in weak diffused light—fumes of hydrochloric acid were at once evolved, and this continued for a very long time. The general results of many experiments indicate that substitution and addition were taking place simultaneously. On evaporating the solution, a residue was always obtained in slightly yellow scales. Different specimens did not give the same results on analysis. The best preparation which we succeeded in making gave the following figures :—

0.0575 gram gave by Carius' method 0.1515 AgCl.

0.1067 ,, 0.1108 CO₂ and 0.0305 H₂O.

Carbon	28.32
Hydrogen	3.17
Chlorine	65.18
	<hr/>
	96.67

The presence of oxygen renders the true interpretation of these figures somewhat uncertain, but they agree fairly with the ratio C₁₀H₁₄Cl₈, which will require for 28.32 per cent. of carbon, 3.3 per cent. hydrogen and 66.95 per cent. chlorine. Such a result is in accordance with the view that the hydrocarbon contains six unsaturated atoms of carbon, and is not easily explained on any other supposition.

Action of Bromine.—Bromine acts energetically on caoutchouc dissolved in chloroform, fumes of hydrobromic acid being evolved. But a weak solution of bromine in chloroform, while acting at once, does not give rise in the first instance to a very rapid separation of hydrobromic acid, though upon standing, the gas slowly appears. This suggested the making of a synthetic and volumetric determination of the proportions in which caoutchouc and bromine combine. Standard solutions of each were therefore prepared, and the latter was added from a burette to a measured quantity of the former. As the close of the experiment was approached, the bromine disappeared a little less quickly. The flask containing the liquid was then shaken, and a drop taken out by means of a glass rod was brought into contact with a drop of potassium iodide starch solution. When the blue iodide of starch appeared, the presence of free bromine was shown, and this was taken to indicate the completion of direct combination between the bromine and caoutchouc.

The following are the figures obtained :—

The solution of bromine contained 0.03609 gram per c.c.

The solution of caoutchouc contained 0.02458 gram per c.c.

TABLE II.

Caoutchouc taken.	Bromine used.	Bromine used, calculated for 136 parts of caoutchouc.
0.1229 gram	0.2670 gram	295.5
0.1229 "	0.2634 "	291.5
0.4917 "	1.0570 "	292.4
		Mean.. 293.1

This number (293) was judged to be somewhat too low, since the very faintest indication of free bromine had been accepted as an indication of completed action. A better and quicker method of determining the value was founded on the subsequent observation that iodine did not act on the solution of caoutchouc in chloroform. It occurred to us that by first adding an excess of bromine, and then a strong solution of potassium iodide, we should get a quantity of iodine set free equivalent to the excess of bromine, and the free iodine could be estimated at leisure by thiosulphate.

On trial of this method, very fairly accordant results were obtained:—

The solution of bromine contained 0.03684 gram per c.c.

The solution of caoutchouc contained 0.0281 gram per c.c.

TABLE III.

Caoutchouc taken.	Bromine added.	Excess of bromine.	Bromine required.	Bromine required for 136 parts caoutchouc.
gram.	gram.			
0.141	0.3684	0.05157	0.3168	305.5
0.141	0.3684	0.05268	0.3157	304.5
0.141	0.3684	0.05157	0.3168	305.6
0.1692	0.4420	0.0663	0.3757	302.6
0.1692	0.4052	0.0405	0.3647	293.1
0.141	0.3352	0.0221	0.3131	301.9
0.141	0.3205	0.0051	0.3151	303.9
0.141	0.3168	0.00368	0.3131	301.9
0.282	0.6447	0.0173	0.6274	302.5
0.141	0.3278	0.0081	0.3197	308.3

The average result is that 136 grams of caoutchouc combine with 303 grams of bromine.* Supposing that 1 mol. of $C_{10}H_{16}$ combined

* Greville Williams has employed bromine to test the saturating power of caoutchene, one of the hydrocarbons obtained by the destructive distillation of caoutchouc. The properties of caoutchene allowed a simpler procedure to be followed. His experiments show that 136 grams of caoutchene combine with 315 grams of bromine.

directly with 4 atoms of bromine to form the tetrabromide $C_{10}H_{16}Br_4$, it would require 320 grams of bromine. When we consider that the caoutchouc experimented on contained about 3 per cent. of oxygen, the figures obtained appear as satisfactory as could be expected. The result does not agree of course with the constitution assigned above to caoutchouc, and can be reconciled only on the supposition either that the action of the halogen has produced an isomeric change, or that the tetrabromide formed is not yet a saturated compound.

Attempts were made to isolate this compound by evaporating down the solution, or by precipitating with a large excess of ether. The precipitate was a white, solid body, but it always proved to be unstable on drying, with loss of hydrobromic acid.

Prolonged Action of Bromine.—A fair excess of a solution of bromine in chloroform was added to a solution of caoutchouc in chloroform, and allowed to act at ordinary temperatures for three days. Fumes of hydrobromic acid were evolved all the time. The solution was then poured into a considerable quantity of ether, which caused a white precipitate. This was separated by filtration and washed with ether. When dried at 60° , it was quite white, and easily powdered.

0.1312 gram gave 0.1091 CO_2 and 0.0348 H_2O .

0.1226	„	0.2095 AgBr	} Estimated by Carius' method.
0.1054	„	0.1819 „	
0.1270	„	0.2182 „	

	Found.				Calculated for $C_{10}H_{16}Br_5$.
	I.	II.	III.	IV.	
Carbon	22.67	—	—	—	22.43
Hydrogen	2.94	—	—	—	2.80
Bromine	—	72.71	73.43	73.10	74.76

Remembering that some oxygen was present, the experimental results agree sufficiently well with those calculated from the formula $C_{10}H_{16}Br_5$. It seems not improbable that this body is formed from a compound, $C_{10}H_{16}Br_6$, by the elimination of HBr .

Iodine.—We have already stated that iodine has little or no action on caoutchouc dissolved in chloroform. It is, perhaps, worthy of note that Adriani (*Chem. News*, 2, 278) says that the action of iodine on the globules in the natural juice is more marked than that of bromine.

Action of Heat.

The ordinary statement is that caoutchouc, when heated, softens and melts at about 200° ; that if cooled again it never becomes hard as before.

We found that the fusing point depended partly upon the exposure of the substance to air, oxidation affecting the result. 0.5 gram of caoutchouc was heated at 200° for two hours in a sealed tube filled with hydrogen. There was only a slight superficial fusion, and scarcely any decomposition.

A solution of caoutchouc in toluene was also heated in a sealed tube at 200° for two hours, and the solvent then distilled off at 112° in a Sprengel vacuum. It left a hard residue, and there was no odour of decomposition. Even when heated at 210° in a Sprengel vacuum, caoutchouc was found to be only superficially melted, though after that treatment it dissolved very slowly in benzene.

In order to ascertain whether the optical properties of caoutchouc were changed by heating, we dissolved some of Hancock's Para rubber in toluene, determined its refraction and dispersion, then exposed the solution in a sealed tube to a temperature of 200° for three hours, and after cooling, examined it afresh. The solution was found far more limpid than it had previously been. The other properties were as follow. The solution contained 12.85 per cent. of caoutchouc:—

	Temperature.	Sp. gr.	μ_A .	μ_H .
Before heating ..	19.4°	0.8706	1.4896	1.5295
After ,, ..	18.5	0.8708	1.4895	1.5294

These figures are practically identical, and it may be concluded that if the heating has produced any change, it has not affected the proportion of carbon-atoms doubly linked. It is evident also that its molecular volume in solution has not been affected.

The optical properties of the caoutchouc as deduced from the above figures are: refraction equivalent, 76.46; dispersion equivalent 5.40, which confirm the observations made from the solutions in benzene.

When caoutchouc is heated considerably above 200°, it is converted into a mixture of liquid oils which are believed to be isomeric or polymeric with the original substance. From the distillate have been separated and more or less fully described, isoprene, caoutchene, and heveene.

Isoprene, C_5H_8 , has been already shown to contain two pairs of doubly-linked carbon-atoms (Trans., 1886, 619).

Caoutchene, $C_{10}H_{16}$, was shown at the same time to have two pairs of doubly-linked carbon-atoms. The ratio of unsaturated carbon to molecular weight is here only half that of isoprene.

We prepared two specimens of caoutchene by repeated fractional distillation; the first from a quantity of oil made by ourselves from Para caoutchouc, the other from oil obtained from Messrs. Hopkin and Williams. The examination of these gave the figures shown in

Tables IV and V, Nos. 1 and 2. The second specimen, when distilled from sodium several times, gave the figures of No. 3, showing that it was practically unchanged, notwithstanding the appearance of a little red flocculent matter.

Heveene.—From the same two mixtures, we also separated a liquid boiling at about 315°. It was dark in colour and became darker on standing. The results of observation are given in Nos. 4 and 5, and are very accordant.

The product boiling above 320° was still darker in colour. The observations made upon it are given in No. 7. The sp. gr. is increased, but the specific optical properties remain practically the same as those of heveene.

As the refraction equivalent in these cases was a little lower than we should have expected on the supposition that these bodies of higher boiling point were similar in composition to caoutchouc, we thought they might contain some quantity of an oxygen product. On treating our heveene with sodium, we found that some hydrogen was liberated, and it was therefore redistilled from sodium several times. A nearly colourless oil was obtained having an intense blue fluorescence. This caused the spectrum to be nearly cut off between G and H. The results of observation are given in No. 6, showing that it has been only slightly increased in refraction and dispersion. Several attempts to obtain the vapour-density failed, apparently through some molecular change taking place in the vapour itself when highly heated.

TABLE IV.

No.	Substance.	Boiling point.	Temp.	Sp. gr.	Refractive index.		
					A.	F.	H.
1	Caoutchene	174—176°	18·0°	0·8377	1·4657	1·4807	1·4950
2	„	173—177	19·0	0·8361	1·4644	1·4791	1·4938
3	„	173—178	22·0	0·8350	1·4638	1·4793	1·4939
4	Heveene	300—320	17·8	0·9146	1·5009	1·5172	—
5	„	310—316	16·5	0·9291	1·5090	1·5265	—
6	„	312—318	22·6	0·9245	1·5074	1·5249	1·5421
7	Higher product ..	above 320	16·3	0·9487	1·5190	1·5371	—

After distilling off the highest product there remained a quantity of a substance not volatile at low redness, and which on cooling became quite hard. As the whole had been originally distilled, we may suppose that this product had been formed by the subsequent action of heat; indeed there were other indications that polymerisa-

TABLE V.

No.	Substance.	Refraction equivalent.	Dispersion equivalent.	
			F - A.	H - A.
1	Caoutchouc	75·60	2·44	4·76
2	„	75·54	2·39	4·78
3	„	75·54	2·53	4·90
4	Heveene	74·48	2·43	—
5	„	74·51	2·56	—
6	„	74·64	2·58	5·11
7	Higher product	74·40	2·60	—

tion took place during redistillation. It is probable also that there are bodies produced which are intermediate in boiling point between those examined.

The general results of the destructive action of heat upon caoutchouc may therefore be considered as involving no change in the proportion of carbon to hydrogen, but changes of structure in the hydrocarbon which are best represented by the following optical constitutional formulæ. In this table, C'' is used for carbon having the refraction equivalent 6·1 and dispersion equivalent 0·66.

Substance.	Optical constitutional formulæ.
Caoutchouc	$nC''_6C_4H_{16}$
Isoprene	C''_4CH_8
Caoutchouc	$C''_4C_6H_{18}$
Heveene	$nC''_2C_3H_8$

Since the paper was read at the Society's meeting, we have endeavoured to determine the molecular weights of caoutchouc and heveene by Raoult's method.

For heveene, we obtained depressions of 1·85° C. and 1·52° C. with solutions containing respectively 9·37 and 7·68 grams to 100 of benzene. These figures give 248 and 247·5 for the molecular weight of heveene, which strongly indicates the formula $C_{20}H_{32}$.

As to caoutchouc, the depression obtained with a solution containing 9 parts to 100 of benzene was so very small that its molecular weight must be at least 50 times that of heveene, if the method holds good.