93. The Course of Autoxidation Reactions in Polyisoprene and Allied Compounds. Part III.   The Oxidation of Rubber in the Presence of Acetic Acid or Acetic Anhydride.

By George F. Bloomfield.

Oxidation of rubber by oxygen in the presence of acetic anhydride leads to formation of highly oxygenated products containing a considerable proportion of acetoxyl groups.   The residual unsaturation of the products of highest acetoxyl content, taken in conjunction with other analytical characteristics, indicates that three, rather than two, acetoxyl groups normally combine with each isoprene unit attacked.   Although the bulk of the oxygen introduced is present in the form of acetoxyl groups, a portion occurs as carboxyl and carbonyl groups; also, whenever acetic acid is used (partly or wholly) in place of acetic anhydride, some free hydroxyl groups appear in the oxidised rubber.   The proportions of carboxyl and carbonyl groups observed can be satisfactorily correlated with the extent of chain-scission occurring during the oxidation, the groups in question forming the new ends of the severed molecules.   Hydrolysis of the acetylated products yields hydroxy-acids which readily undergo lactonic elimination of water.

Acetic anhydride and acetic acid can clearly act as auxiliary reagents in autoxidation reactions, and the detailed results obtained with rubber can be best accounted for on the basis of α-methylene peroxidation, followed by decay reactions involving incorporation of the auxiliary reagent as well as oxidative attack at the double bonds of the rubber.

Reference has been made in Part I (J., 1942, 121) to the facile oxidation which occurs when rubber is exposed to oxygen in presence of boiling acetic anhydride.   It might at first be suspected that oxidation is here greatly facilitated by destruction of the natural inhibitors present in the rubber by the acid medium employed (cf. Bruson, Sebrell, and Vogt, *Ind. Eng. Chem.*, 1927, **19**, 1187), but if this were the sole explanation of this rapid oxidation, then a sample of rubber from which the antioxidants had been removed by acetone extraction * would be expected to undergo oxidation in a neutral or alkaline medium at a rate comparable with that observed in the acidic medium, although the course of the secondary reactions, and hence the final products of oxidation, might well be considerably different in view of the diverse influence of acid and alkali on the mode of decay of the hydroperoxide of *cyclo*hexene (cf. Part I).

Bloomfield and Farmer (*J. Soc. Chem. Ind.*, 1935, **54**, 125T) first observed that the oxidation of olefins by oxygen can be much accelerated by the presence of acetic acid or anhydride, and similar observations by other authors have since been reported.   If in these reactions autoxidation proceeds by addition of oxygen at the unsaturated centres of rubber to give peroxide groups $\begin{smallmatrix} -C—C- \\ || \\ O—O \end{smallmatrix}$ according to the Engler–Bach hypothesis, it might be supposed that ultimately there would be formed partly or wholly acetylated diols by reason of the decay of the peroxides in the presence of acetic acid or acetic anhydride.   If, however, oxidative attack is directed in the first place to the α-methylene carbon atoms instead of to the unsaturated centres, tri-, di-, or mono-acetylated triol groups may be expected to arise at each $CH_2 \cdot C{:}C$ unit, as discussed in Part I.

The Oxidation Process.—At ordinary temperatures the oxidation of solid rubber took place quite slowly when the hydrocarbon was immersed in acetic anhydride or acetic acid, but at 120—140° oxidation proceeded rapidly and the products of oxidation were sufficiently degraded to dissolve in the hot acetic acid or anhydride, giving a resinous material which by submission to a suitable separative procedure (see Tables III and IV) could be resolved into various fractions of high oxygen content and of comparatively low molecular weight.   The undissolved rubber, on the other hand, although somewhat softer than it was originally, was only slightly oxygenated and but little degraded.   The reaction could be considerably accelerated by adding small proportions of organic or inorganic cobalt salts to the acid or anhydride medium, but no obvious change in the course of reaction attended these additions.

It was hoped to bring about more regulated oxidation, and so to obtain more graded oxidation products, by bringing the rubber to reaction in solution, but in fact no significant oxidation occurred unless rubber recovered from one of the above oxidations conducted in the presence of acetic anhydride or acetic acid, and so already slightly oxidised, was used in place of fresh rubber, or unless the oxidation was started, but not indefinitely continued, in a medium relatively poor in hydrocarbon solvent (p. 359).   Even under these modified conditions oxidation did not proceed beyond the incorporation of a few units % of oxygen unless the solution was irradiated or an organic salt of cobalt was added as a catalyst.   In the latter case reaction proceeded to an advanced stage, yielding highly oxygenated products which, for all oxidations conducted in the presence of acetic anhydride, were very similar to those obtained in the absence of a solvent for the rubber.   When, however, oxidation was accelerated by irradiation the reaction appeared to pursue a somewhat different course, since then rather less than half of the combined oxygen was found in acetoxyl groups (see p. 360).

It was necessary before proceeding further with the examination of the oxidation products formed in presence of acetic acid or its anhydride to ensure that no serious part of the oxygenation of rubber arose by the direct addition of acetic acid at the ethylenic centres of the hydrocarbon (cf. addition of acetic or di- or trichloroacetic acid to amylene; Konovalov, *Z. physikal. Chem.*, 1888, **2**, 380; Nernst and Hohmann, *ibid.*, 1893, **11**, 352).   Accordingly, samples of rubber were treated for many hours with boiling acetic anhydride and others with boiling acetic acid in an atmosphere of carefully purified nitrogen.   Under these conditions no combination of the rubber with either reagent could be detected.   Furthermore, when rubber was sealed in an

* In the following account, unless otherwise specifically indicated, the term *rubber* means acetone-extracted crepe rubber.

evacuated tube together with acetic anhydride and sufficient benzene to promote considerable dissolution of the rubber, it was recovered substantially unchanged even after many hours' heating at 140°.

The main features therefore of the reaction under consideration are : (1) Rubber takes up substantial amounts of oxygen in presence of acetic acid or anhydride, but reaction is very slow and restricted in character unless a temperature well above 100° is used; (2) the rubber becomes increasingly degraded as the oxygen content of the product rises; and (3) only a portion of the oxygen incorporated is in the form of acetoxyl groups, especially where the presence of a hydrocarbon diluent causes the acetic acid or anhydride to be in low concentration.

The Constitution of the Highly-degraded Products.—Further study of the major reaction products obtained severally by use of undiluted acetic anhydride and acetic acid at 120—140° (products A and P, p. 359) showed that acetoxyl contents as high as 50% could be obtained without entire removal of the unsaturation of the rubber; the magnitude of the acetoxyl contents in the acetic anhydride products arising at similar stages of oxygenation appeared to be mainly a function of the freedom of the anhydride from acetic acid and use of acetic acid alone gave products of lowest acetoxyl content.

The products were non-peroxidic, acid substances (containing titratable carboxyl groups) and for the most part showed a significant content of unesterified hydroxyl groups. The chief analytical characteristics are given in Table I (blank spaces represent undetermined values).

TABLE I.

Highly Oxidised Products.

Product.	Medium.	Catalyst.	OAc, % (corr.).*	CO$_2$H, % (corr.).*	OH, %.	I.V.	M.	Analysis, %. C.	H.	O (diff.).	O content (OAc + CO$_2$H + OH).
A(i)	Ac$_2$O	None	50·5	6·0	—	49	—	59·85	6·9	33·25	31·7
A(ii)	,,	,,	44·0	4·0	—	—	—	63·1	7·4	29·5	26·7
A(i)2	,,	,,	55·0 †	7·1 †	—	—	—	—	—	—	—
A(i)3	,,	,,	42·2	5·7	2·5(ca.)	80	—	64·0	6·9	29·1	29·3
A(i)5	,,	,,	44·1	8·0	nil	71	716	61·1	6·9	32·0	29·6
A(i)6	,,	Co(NO$_3$)$_2$	39·6	6·0	nil	77	1143	63·9	6·9	29·2	25·8
A(i)7	,,	,,	47·3	5·4	0·3	71	1215	62·7	6·9	30·4	29·8
A(i)8	C$_6$H$_6$ + Ac$_2$O	CoL$_2$ ‡	36·8	6·0	0·3	91	1361	61·8	7·2	31·0	24·6
A(i)9	C$_6$H$_5$Cl + Ac$_2$O	None	36·1	6·3	4·0	90	1161	63·9	7·0	29·1	27·9
P(i)	AcOH	,,	33·2	8·2	3·0	98	—	62·2	7·25	30·55	26·6
P(i)2	,,	,,	31·8	5·6	5·2	—	—	63·6	7·4	29·0	26·2
P(i)3	,,	,,	27·8	7·8	4·1	90·5	—	63·6	7·3	29·1	24·5

* For the significance of the correction applied to these figures, see p. 358.
† Uncorrected value. ‡ *I.e.*, cobalt linoleate.

There is a discrepancy (average 2·7%) between the total oxygen content of the products as determined by elementary analysis and by summation of the acetoxyl, carboxyl, and hydroxyl oxygen. This is to be expected, since the scission of polyisoprene chains at the double bonds by autoxidation reactions normally gives rise to carbonyl groupings (see Part I). Direct determination of the carbonyl content in two examples [A(i)5 and P(i)3] gave values (3·9 and 6·4%) which were actually in excess of this difference. In the determination of hydroxyl contents by the precision method of Bolland (*Trans. Inst. Rubber Ind.*, 1941, **16**, 267) the usual vigorous evolution of methane was accompanied by a progressive slow evolution of gas, possibly due to enolisation of carbonyl groups, and the hydroxyl contents in Table I have been derived by neglecting the slow reaction [A(i)3 excepted]. Most of the molecular weights shown are to be regarded as maximum values, since the solubility of the products in benzene decreased after a time, and only in the case of A(i)5 was it possible to determine the molecular weight immediately after preparation. Saponification of the acetylated materials under conditions excluding any possibility of further oxidation resulted in decomposition of the acetoxyl groups and formation of additional hydroxyl groups. In Table II are given analytical details for the saponification products of six of the materials listed in Table I.

TABLE II.

Composition of Saponification Products.

Products from which derived.	I.V.	OH, %.	CO$_2$H, %.	C, %.	H, %.	O, %.
A(i)3 (42·2% OAc)	112	18	8·1	68·3	7·5	24·2
A(i)5 (44·0% OAc)	124	12·4	11·6	66·4	7·6	26·0
A(i)7 (47·3% OAc)	114	20	8·2	67·5	7·6	24·9
A(i)9 (36·1% OAc)	167	13·5	8·5	68·8	7·8	23·4
P(i)2 (31·8% OAc)	—	11·0	7·3	67·1	7·4	25·5
P(i)3 (27·8% OAc)	143	11·7	9·9	69·4	7·8	22·8

The presence of many free hydroxyl groups in the saponified materials appears to lead to considerable dehydration, possibly by lactone formation (largely intramolecular) with the carboxyl groups already present : not only were the hydroxyl contents much lower than were to be expected, but titration of the acid groups gave satisfactorily sharp end-points only when the materials were treated with excess of alkali and back-titrated. The carboxyl contents of the hydroxy-acids were somewhat greater than those calculated from the apparent

B B

carboxyl content of the parent acetylated substances, and this was to be expected, since it was not possible to determine the carboxyl contents of the latter with very high precision owing to the presence of readily hydrolysable acetoxyl groups. The discrepancy was not generally large and an appropriate correction has been applied to the carboxyl contents of the acetylated substances in Table I. The application of this correction also involved a small correction to the acetoxyl contents. The compositions of the saponified materials derived from products of high acetoxyl content are in fairly good agreement with those calculated from the composition of the parent acetylated materials on the assumption that lactonic elimination of water between the carboxyl groups and a corresponding proportion of the hydroxyl groups has occurred, but there is less agreement in the materials originally of lower acetoxyl content, owing possibly to some lactonisation already present between carboxyl groups and free hydroxyl groups in the acetylated material.

When an attempt was made to divert secondary reaction along a different route by the use of an alkaline auxiliary reagent (alcoholic potassium hydroxide) in place of the acid ones used before, no significant oxidation occurred at temperatures in the neighbourhood of 80—100°, and even at 140° only 3% of combined oxygen was introduced after 64 hours, but an oxidation conducted in the presence of pyridine proceeded to a more advanced stage represented by the combination of 8·6% of oxygen, of which, however, only one-third appeared in the form of hydroxyl, carbonyl, and carboxyl groups. As in the case of acid auxiliary reagents, considerable molecular degradation occurred.
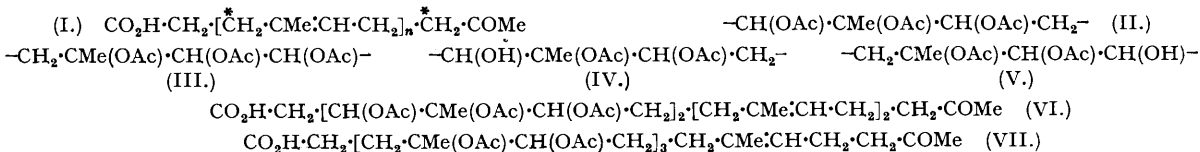
Mechanism of the Reaction.—Before considering the acetoxyl content in relation to the residual unsaturation of the highly oxygenated products, it is necessary to take into account chain scission, since the extent of degradation occurring during oxidation is such that end-groups must constitute an appreciable part of the molecule. Indeed, the observed orders of magnitude of the carbonyl and carboxyl contents are just such as would be expected to characterise chain scission products of molecular weight 700—1000 in which the groupings in question are confined to the ends of chains.

The autoxidation reaction now under consideration differs from that described in Part I in being thermal rather than mainly photochemical in character. Hence the course followed (and this applies especially to secondary reaction) may be very different from that previously discussed. If it be *assumed*, however, that oxidation necessarily consists at the first stage of the absorption of molecular oxygen in giving not merely peroxide groups but hydroperoxide groups, and that the decomposition of these, instead of following the ordinary thermal or photochemical course, is directly influenced by the presence of an auxiliary reagent (acetic anhydride, etc.), it becomes possible to make important comparisons between the observed and the expected character of the reaction products. It is obvious that in any particular oxidation the participation of the auxiliary reagent may be belated or for one cause or another fall short of completeness, and in this case the secondary reactions will comprise both normal thermal peroxidic degradations and " influenced " degradations. Also it may reasonably be assumed, since there is as yet no evidence to the contrary in any recorded autoxidation, that the oxidising power of the peroxide groups expends itself primarily in attacking the unsaturated centres in the molecule where such are present, so giving rise to chain-scission. The normal molecular form of the reaction products may accordingly be expected to be some oxygenated and acetoxylated modification of (I), in which $n < 6$, in which the most probable points of hydroperoxidation are at the asterisked carbon atoms.

Some of the inner isoprene units in the small fragments of the original rubber chains will have escaped reaction altogether, others in the main will (as indicated in Part I) have passed in the presence of acetic anhydride into acetoxylated units containing in all probability the systems (II) or (III), or to some extent (especially where the oxidation is conducted in the presence of acetic acid) the systems (IV) or (V). There does indeed appear to be one free hydroxyl group for every two acetoxyl groups in the oxidation products of higher hydroxyl content as the figures below indicate :

Product	A(i)9	P(i)	P(i)2	P(i)3
OH equivalent of OAc content, %	10·4	9·6	9·2	8·0
Free OH content, %	4·0	3·0	5·2	4·1

In the most highly acetylated products the acetoxyl content can be related to the iodine value without any complication arising from the presence of free hydroxyl groups, and these products conform closely with the structural type represented by (I). For instance, a substance (VI) requires C, 60·0; H, 7·45; OAc, 47·8; CO,
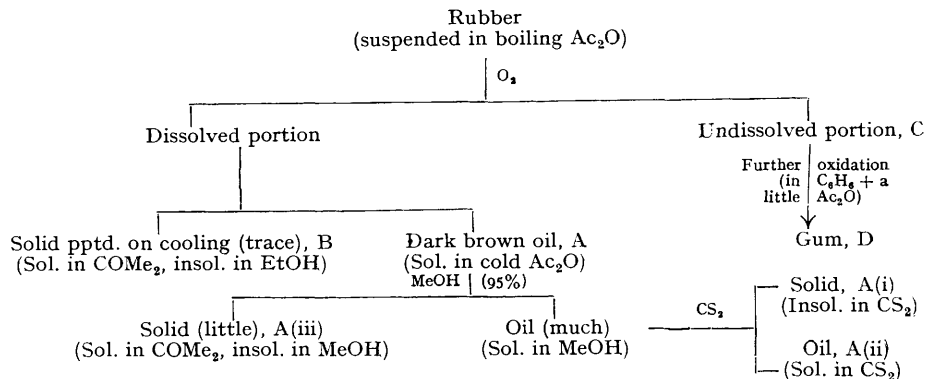
(I.) $CO_2H \cdot CH_2 \cdot [\overset{*}{C}H_2 \cdot CMe \colon CH \cdot CH_2]_n \cdot \overset{*}{C}H_2 \cdot COMe$ $-CH(OAc) \cdot CMe(OAc) \cdot CH(OAc) \cdot CH_2-$ (II.)

$-CH_2 \cdot CMe(OAc) \cdot CH(OAc) \cdot CH(OAc)-$ $-CH(OH) \cdot CMe(OAc) \cdot CH(OAc) \cdot CH_2-$ $-CH_2 \cdot CMe(OAc) \cdot CH(OAc) \cdot CH(OH)-$
(III.)   (IV.)   (V.)

$CO_2H \cdot CH_2 \cdot [CH(OAc) \cdot CMe(OAc) \cdot CH(OAc) \cdot CH_2]_2 \cdot [CH_2 \cdot CMe \colon CH \cdot CH_2]_2 \cdot CH_2 \cdot COMe$ (VI.)

$CO_2H \cdot CH_2 \cdot [CH_2 \cdot CMe(OAc) \cdot CH(OAc) \cdot CH_2]_3 \cdot CH_2 \cdot CMe \colon CH \cdot CH_2 \cdot CH_2 \cdot COMe$ (VII.)

3·8; CO_2H, 6·1%; I. V., 69; M, 740 [cf. A(i)5 and A(i)7], whereas the alternative mode of distribution of the acetoxyl groups in a substance such as (VII), in which no α-methylene hydroperoxidation has taken place, so limiting the attachment of acetoxyl groups to two in each C_5H_8 unit attacked, would require a considerably lower iodine value (34) if the acetoxyl content is to remain the same.

<center>EXPERIMENTAL.</center>

Oxidation of Rubber in Boiling Acetic Acid or Acetic Anhydride.—The rubber (20 g.) was immersed in acetic acid or acetic anhydride (200 c.c.) which was boiled under reflux while a brisk stream of oxygen was bubbled through. The
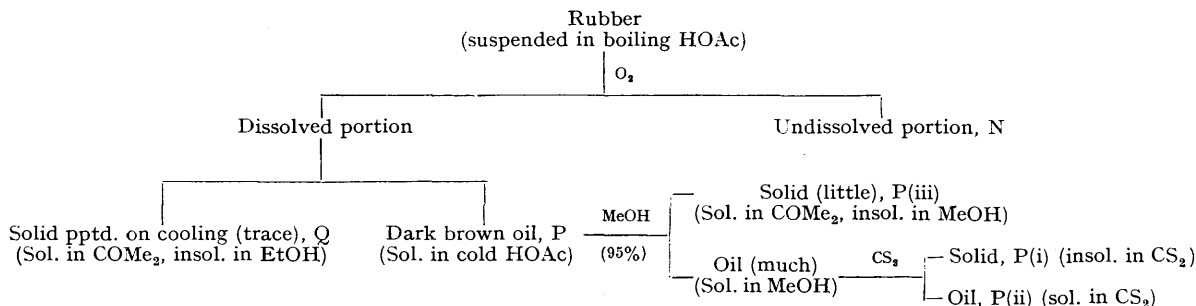
pieces of rubber disintegrated, and a portion dissolved giving a dark brown solution. After at least 20 hours' treatment the hot solution was decanted from a small amount of undissolved rubber. The solution, on cooling, desposited a little resinous matter. The material remaining in solution was isolated by evaporation of the acetic acid or anhydride under reduced pressure, the residue being submitted to the separative procedure indicated in Table III.

TABLE III.

Rubber
(suspended in boiling Ac$_2$O)

| O$_2$ |

Dissolved portion   Undissolved portion, C

Further oxidation
(in C$_6$H$_6$ + a
little Ac$_2$O)
↓
Gum, D

Solid pptd. on cooling (trace), B   Dark brown oil, A
(Sol. in COMe$_2$, insol. in EtOH)   (Sol. in cold Ac$_2$O)
                  MeOH | (95%)

Solid (little), A(iii)   Oil (much)   —   CS$_2$
(Sol. in COMe$_2$, insol. in MeOH)   (Sol. in MeOH)

— Solid, A(i)
(Insol. in CS$_2$)

Oil, A(ii)
— (Sol. in CS$_2$)

In oxidations conducted in acetic anhydride, the yield of the brown solid product A(i) was about the same as that of the oil A(ii), the resinous products B and A(iii) being formed in relatively small amount. The solid A(i) softened at about 50° and melted to a gum at somewhat higher temperatures; a portion of the oil A(ii) was sufficiently degraded to be volatile at *ca.* 0·1 mm. pressure. When the oxidations were conducted in acetic acid, the amount of the corresponding products [solid P(i) and oil P(ii) : see Table IV] were reduced, and the oil P(ii) was formed in greater amount than the solid P(i).

TABLE IV.

Rubber
(suspended in boiling HOAc)

| O$_2$ |

Dissolved portion   Undissolved portion, N

Solid pptd. on cooling (trace), Q   Dark brown oil, P   MeOH   — Solid (little), P(iii)
(Sol. in COMe$_2$, insol. in EtOH)   (Sol. in cold HOAc)   (95%)   (Sol. in COMe$_2$, insol. in MeOH)

Oil (much)   CS$_2$ — Solid, P(i) (insol. in CS$_2$)
(Sol. in MeOH)   └─ Oil, P(ii) (sol. in CS$_2$)

When cobalt nitrate (0·4 g.) was added to the acetic acid or anhydride the amount of rubber dissolving in a comparable time was greater than in the absence of catalyst, but the products were very similar. The yield of the solid reaction product was, however, much greater than that of the oil, and in a typical experiment 29·6 g. of a solid reaction product [A(i)6] were obtained from 30 g. of rubber Complete removal of the cobalt salts from the reaction products presented much difficulty.

Oxidation of Rubber in Acetic Acid or Anhydride, using a Supplementary Solvent.—Oxygen was first led for 40 hours into a solution of rubber (10 g.) in benzene (500 c.c.) containing acetic anhydride (50 c.c.), a temperature of 80° being maintained. No significant degree of oxidation occurred. A similar result was obtained when an *iso*propyl acetate-acetic anhydride medium (at 90°) was used. When, however, a sample of the slightly degraded product C (Found : C, 88·0; H, 11·7%) was dissolved in benzene containing a little acetic anhydride, some evidence of oxidative attack became apparent after oxygen had been passed for 10 hours at 80°. The solution was then much less viscous, and removal of the solvent at this stage yielded a brown gum D, which was soluble in warm ethyl acetate, ether, hydrocarbon solvents, methyl ethyl ketone, and dioxan, but insoluble in alcohol or acetone (Found : C, 85·8; H, 11·6; OAc, *ca.* 2%).

Product D was soluble in a mixture of benzene (2 vols.) and acetic anhydride (1 vol.), but an oxidation of *rubber* attempted in this mixture proceeded only very slowly. When, however, the rubber (10 g.) was placed in a mixture of benzene (50 c.c.) and acetic anhydride (50 c.c.) and heated at 80° in contact with a stream of oxygen for 12 hours, and afterwards further benzene (50 c.c.) was added, then all of the rubber dissolved in the course of a further 8 hours' treatment with oxygen at 80°, so giving a solution of low viscosity. Removal of solvents gave a pale yellow, turbid gum behaving similarly to the material D towards solvents. When a solution of this new product in light petroleum (1000 c.c.) was allowed to stand, a pale yellow powder (0·2 g.) separated : this was removed by centrifuging and washed with light petroleum (Found : N, 9·4%). The resulting clear solution yielded on evaporation of the solvent a clear transparent pale yellow gum J {Found : C, 87·0; H, 11·8; N, nil; OAc, 0·86%; I. V., 353; intrinsic viscosity [η] (in benzene + 15% methanol), 0·244, from which M = 25,000}. In another oxidation conducted under similar conditions but using a mixture of equal volumes of acetic acid and anhydride a product K, very similar to J, was obtained {Found : C, 87·5; H, 11·95; OAc, 0·54%; I. V., 362; [η] (in benzene +15% methanol), 0·354, from which M = 36,000}, but when only acetic acid in admixture with the same proportion of benzene was used, a tacky, rubber-like substance L resulted {Found : C, 87·85; H, 11·9; OAc, nil; [η] (in benzene), 1·59, from which M = 95,000}.*

* The original rubber had M (by viscosity), *ca.* 300,000. These molecular weights have been determined by Dr. G. Gee, to whom the author's thanks are due.

Use of a Catalyst.—Oxidations were conducted under similar conditions to those described in the preceding paragraph with the addition of cobalt linoleate (0·2 g. per 10 g. of rubber). When a mixture of acetic acid, acetic anhydride, and benzene was treated with oxygen in the presence of this catalyst (at 80°) the product was very similar to that obtained from rubber, acetic anhydride, and oxygen at 140°. Like the latter product, it was divided into solid A(i)8 (10 g.) and liquid (3 g.) fractions which were respectively insoluble and soluble in carbon disulphide. Replacement of the acid–anhydride mixture by acetic acid alone led under the same conditions of oxidation to the formation of a less highly oxidised product, which by selective dissolution yielded the following fractions : alcohol–soluble portion, 3 g. (Found : C, 71·8; H, 9·2; OAc, 14·0; CO$_2$H, 4·0%) ; acetone-soluble portion, 3·0 g. (Found : C, 79·7; H, 10·4; OAc, 10·6; CO$_2$H, 1·5%) ; petroleum-soluble, acetone-insoluble portion, 3·6 g. (Found : C, 81·7; H, 10·9; OAc, 4·6%).

Oxidation in Presence of a Mutual (High-boiling) Solvent for the Reactants.—Rubber (10 g.) was swollen in chlorobenzene (100 c.c.), acetic anhydride (150 c.c.) added, and the mixture heated during 40 hours at 140° while a brisk current of oxygen was passed through. The separative procedure indicated in Table III was applied to the highly oxygenated product, and fractions severally soluble (5·4 g.) and insoluble [solid A(i) 9, 3·4 g.] in carbon disulphide were isolated. When the anhydride was replaced by acetic acid, the oxidation followed a different course and yielded a gum wholly soluble in light petroleum and in carbon disulphide, but insoluble in alcohol and in acetone.

Oxidation in Presence of Acetic Anhydride, with Irradiation.—A solution of acetic anhydride (25 c.c.) in benzene (50 c.c.) did not absorb oxygen when exposed at 30—40° in a Pyrex flask for 4 hours to ultra-violet light (" Hanovia " U.V.S. 500) ; moreover, the solution contained thereafter only a trace of peroxidic material. Accordingly, rubber (10 g.) in benzene (50 c.c.) and acetic anhydride (50 c.c.) was submitted to the action of oxygen at 80° until dissolved (cf. preceding experiments). Further benzene was then added, and the solution was oxidised at 30—40° under radiation as above for 16 hours. The solution, which had absorbed altogether 1,800 c.c. of oxygen, was concentrated under reduced pressure, and the gummy product isolated by pouring the concentrate into alcohol and removing the residual solvent in a high vacuum (Found : C, 68·2; H, 9·15; OAc, 20·0; peroxidic oxygen, *ca.* 1%; equiv., 2060; I. V., 210).

Saponification of Highly Acetylated Products.—To a solution of the acetylated material in the minimum quantity of 95% ethyl alcohol was added 2% aqueous sodium hydroxide (100 c.c. per g. of substance). The solution was boiled under reflux for 6 hours in an atmosphere of nitrogen, a little benzene being added to suppress frothing. The bulk of the solution was reduced considerably by evaporation under reduced pressure, and the remainder was acidified, whereupon the hydrolysis product was precipitated as a sludge, which was separated and washed on the centrifuge. In the later stages of washing the product readily passed into colloidal solution in water unless a few drops of a dilute acid were added. The product was rapidly dried at room temperature and reduced pressure, redissolved in alcohol, and separated from silica. The alcohol was finally removed at room temperature, yielding a friable solid, insoluble in hydrocarbons, readily soluble in alcohol, acetone, acetic acid, and pyridine. The yield was almost quantitative provided that care were exercised to prevent losses while washing the precipitate.

Oxidation in the Presence of Chloroacetic Acid.—The rubber (20 g.) was placed in molten chloroacetic acid (200 c.c.) maintained at 140° whilst a stream of oxygen was passed through for 50 hours. The bulk of the rubber remained undissolved, but appeared to have undergone some change since, after being extracted with acetone to remove residual chloroacetic acid, it was recovered as a tough, non-elastic, insoluble mass. The chloroacetic acid itself, decanted from the afore-mentioned insoluble matter, was very dark and yielded a brown precipitate on being poured into water. The dried precipitate (1·8 g.) (Found : Cl, 2·9%) was sparingly soluble in alcohol and in acetone, insoluble in benzene, carbon disulphide, and ethyl acetate, but readily soluble in benzene–acetone.

Attempted Oxidation in Alkaline Media.—Rubber (20 g.) was placed in 0·5N-alcoholic potassium hydroxide (300 c.c.) and heated at 80° whilst oxygen was passed through the solution for 40 hours. No rubber dissolved during this time, and the recovered rubber contained very little oxygen (Found : C,.87·6; H, 11·7%) ; this was next placed in benzene (300 c.c.) containing 100 c.c. of 0·5N-alcoholic potassium hydroxide, and the oxidation resumed at 80°. After 30 hours no extensive degree of oxidation had occurred (Found : C, 87·3; H, 11·7%). Rubber (10 g.) in pyridine (100 c.c.) was submitted to the action of oxygen at 100°. The rubber passed into solution, and after continuation of the treatment for 40 hours the pyridine was removed under reduced pressure. The residue was treated with warm aqueous hydrochloric acid (2N), taken up in ether, and this solution was well washed and dried. Removal of the ether yielded a dark brown gum {Found : C, 80·7; H, 10·7; N, trace; OH (including OH in CO$_2$H groups), 2·0%; CO + CHO, equivalent to 1% oxygen ; equiv., 3,600; [η] (in benzene +15% methanol), 0·095, from which $M = 7,900$}.

Analytical Methods.—*Acidity* was determined by titration of a dilute solution of the sample (0·1 g.) in aqueous alcohol (100 c.c.) with 0·1N-sodium hydroxide, phenolphthalein being the indicator. The high dilution was necessary in order that the colour of the solution should not mask the end-point. The *acetoxyl content* of materials of small total oxygen content was determined by dissolving the sample (0·5—1·0 g.) in benzene, adding alcoholic potassium hydroxide, and refluxing the mixture for 4—6 hours in an atmosphere of nitrogen. For highly oxygenated materials, 0·1 g. was dissolved in 95% ethanol (10 c.c.), 25 c.c. of 0·2N-potassium hydroxide (aqueous) were added, and the solution was boiled for at least 4 hours in an atmosphere of nitrogen under a reflux condenser guarded by a soda-lime tube. From the alkali consumed was deducted the amount required to neutralise the acidity of the sample. The *iodine values* were determined by the Kemp–Wijs method (*Ind. Eng. Chem. Anal.*, 1934, **6**, 52) : the oxidation products did not give a reaction for peroxidic oxygen and hence did not liberate iodine from potassium iodide. *Molecular weights* of the highly oxygenated materials were determined cryoscopically in benzene, and *hydroxyl contents* of materials soluble in benzene, toluene, or anisole by Bolland's method (*loc. cit.*). The highly hydroxylated products were not soluble in the foregoing solvents, and accordingly pyridine was used with a slight modification to Bolland's procedure since the Grignard pyridine complex appeared to be slightly volatile in a high vacuum. This modification involved placing a stopcock in the tube connecting the two limbs of the reaction vessel, and thereafter distilling the pyridine contained (together with a little methylmagnesium iodide) in the right-hand limb on to the sample in the other limb. Later, the stopcock was closed, and further reagent (in toluene) introduced into the right-hand limb. After the usual preliminary degassing, the stopcock was reopened, and the reagent allowed to flow on to the sample. After this point the normal procedure was followed. If there was any premature reaction with traces of the reagent which had volatilised with the pyridine, the methane so produced was confined in the closed limb of the reaction vessel and was not lost in the preliminary degassing operations.