

80. Rubber, Polyisoprenes, and Allied Compounds. Part IV. The Relative Tendencies towards Substitutive and Additive Reaction during Chlorination.

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It has been previously observed that when chlorine reacts with rubber much hydrogen chloride is evolved, which suggests that the halogenation process may be one of substitution and not of addition at the double bonds. The character of this reaction as it applies to rubber and to other olefins containing the group $\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot$ has been examined. The main reaction appears undoubtedly to be substitutive, but the products show marked loss of unsaturation as determined by the iodine-value method. This loss is probably partly real, due to the occurrence of some degree of cyclisation, and partly apparent, due to inhibition by the incorporated chlorine atoms of ready iodine chloride addition during the determination.

ALTHOUGH the established mode of reaction of chlorine with unsaturated systems is primarily additive, it has recently been shown by Groll, Hearne, *et al.* (*Ind. Eng. Chem.*, 1939, **31**, 1239, 1413, 1530) that under suitable conditions substitutive reaction may not only occur, but may become the major reaction to the exclusion of addition. According to these authors, high temperatures in the range 300—600° seemed generally to be necessary if substitutive reaction is to predominate, but subsequently it was shown by Rust and Vaughan (*J. Org. Chem.*, 1940, **5**, 472) that a considerable degree of substitutive reaction can be realised at temperatures in the range 130—200° provided certain catalysts which can produce free radicals in contact with the halogen are present.

The polyisoprene system has been found to be particularly susceptible to substitutive attack by oxygen (Farmer and Sundralingam, *J.*, 1942, 116; Farmer and Sutton, *ibid.*, p. 139; Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348), and it has long been known that, as judged by the quantity of hydrogen chloride liberated, the chlorination of rubber proceeds largely by substitution in the earlier stages of reaction (McGavack, *Ind. Eng. Chem.*, 1923, **15**, 961). The character of the products thus produced, and the influence of the experimental conditions on the course of reaction, were not, however, studied in any detail by McGavack.

Since the production of hydrogen chloride in the treatment of an olefinic substance with chlorine is no certain indication that true substitution has occurred, new experiments have been made with the object of examining further the character of reaction in the case of rubber and of olefins of allied type. In these experiments attention has been given to the influence of light, oxygen, and temperature on the course of reaction. In order to avoid, as far as possible, complication due to the formation of olefin hydrochlorides through the addition of some of the liberated hydrogen chloride to the olefin, steps have been taken to remove all hydrogen chloride formed in the reaction rapidly from the reaction vessel by means of a stream of inert gas; also the reaction has been conducted at as high a temperature as possible, since the rate of absorption of hydrogen chloride by rubber solutions appears to decrease as the temperature is raised (Bloomfield and Ferry, unpublished observations). The upper limit of temperature has, unfortunately, been much restricted by the necessity of using those solvents which will both dissolve rubber and remain unattacked by chlorine at their boiling points, but even at the comparatively low upper limit thus enforced (77°) it is believed that there is little risk of the undesired hydrochloride-formation occurring.

Conditions of Reaction.—In order to ensure homogeneous chlorination of rubber it has been necessary to work with solutions of the hydrocarbon. The only readily available solvent suitable for use with rubber was carbon tetrachloride which had been freed from disulphide. Chloroform was used in some experiments but proved to undergo substitution too readily to be satisfactory, for, although in the reaction vessel the rubber became chlorinated preferentially to the solvent, yet in the condensing and absorbing systems some chlorination of the solvent vapour carried from the reaction vessel by the effluent gas occurred—especially when the operation was conducted in light—so giving fictitiously high values for the degrees of substitution attained. The chlorinations, except where the influence of oxygen was under examination, were carried out in strict absence of air in the apparatus described on p. 294.

Course of Reaction.—The results obtained under various conditions are summarised in the table, multi-stage chlorinations being regarded as single experiments and so appearing under one number. *If it be assumed that all the hydrogen chloride produced during chlorination arises by substitutive reaction* (and the validity of the assumption is considered later) it can be categorically stated as the result of the experiments that, for all reactions occurring in the dark or in the light, and at temperatures in the neighbourhood of 80°, the dissolved rubber is attacked wholly substitutively by chlorine, $-\text{C}_5\text{H}_8 - + \text{Cl}_2 = -\text{C}_5\text{H}_7\text{Cl} - + \text{HCl}$, and this applies just so long as the first molecule of chlorine per C_5H_8 unit is being consumed. After this stage additive reaction becomes recognisable (see expts. 10 and 11) and proceeds side by side with substitutive reaction until a second molecule of halogen per C_5H_8 unit has been consumed. When a third molecule of chlorine is brought into reaction (see expt. 10) the process becomes again exclusively substitutive and proceeds with increasing difficulty. Nevertheless, up to the stage represented by the interaction of 2.95 mols. of chlorine per C_5H_8 unit, 84% of the whole of the chlorine is found to have reacted substitutively. With regard to the uniformity or heterogeneity of reaction during the consumption of the second molecule of chlorine, expt. 11 indicates that there is some slight, but not very marked, tendency for the additive reaction to be greater during the consumption of the first half molecule than during that of the second. The reaction product at the stage when slightly more than

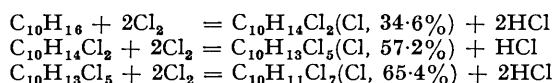
Summary of Chlorination Experiments with Rubber.

Expt. No.	Solvent.	Conditions.			Chlorine reacted, mols. per C ₅ H ₈ .	HCl formed, mols. per C ₅ H ₈ .	Substitutive reaction, %.	Product.		
		Light.	Atmos.	Temp.				Cl, %.	I.V.	[η]. ††
1	CCl ₄	near-dark	N ₂	77°	0.81	0.787	97	30.0	175	—
2	CHCl ₃	"	"	62	0.90	0.884	98	30.4	163	—
								28.2	(insol. portion)	44% of whole
3	CHCl ₃	"	"	62	1.84	<1.65	<88	49.1	42.5	—
								40.0	(insol. portion)	44.5% of whole
4	CCl ₄	"	"	77	1.61	1.16	72	52.8	41.5	—
5	CHCl ₃	dark	"	62	1.02	0.988	97	33.9	154	—
								27.1	(insol. portion)	24% of whole
6	CCl ₄	"	"	77	1.00	0.973	97	33.6	140	0.416
7	CCl ₄	"	"	77	1.85	1.29	70	—	—	—
8	CCl ₄	light	"	77	0.83	0.806	96	29.3	173	—
9	CCl ₄	dark	"	77	1.07	0.998	94	—	—	—
		"	"	"	0.54	0.184	34	—	—	—
		"	"	"	0.65	0.340	52	—	—	—
10	CCl ₄	dark	"	77	1.07	1.038	96	—	—	—
		light	"	"	1.01	0.499	49	—	—	—
		"	"	"	0.58	0.614	100	—	—	—
		"	"	"	0.29	0.318	100	—	—	—
					2.95	2.469	84	64.6	0	—
11	CCl ₄	"	"	77	1.12	0.973	86	—	—	—
		"	"	—	0.46	0.201	44	—	—	—
		"	"	—	0.50	0.338	67	—	—	—
					2.08	1.512	72	58.2	0	0.755 ††
12	CCl ₄	near-dark	N ₂ with trace of O ₂	77	1.04	1.012	98	—	—	—
13	CCl ₄	"	much O ₂	77	1.0	0.960	96	35.2	117	—
14 *	CCl ₄	"	N ₂	77	0.86	0.830	96.5	—	—	insol.
15 †	CCl ₄	"	"	77	1.04	1.030	99	—	—	insol.
16	CCl ₄	"	"	—30	1.0	0.822	>82	34.2	129	1.93
17 †	none	"	vac.	—80	0.58	0.230	ca. 40	35.9	118	—
18	CS ₂	"	N ₂	—80	1.0	0.671	67	34.4	—	—
19	CCl ₄ + HOAc	"	"	80	0.98	0.921	94	—	—	—
20 §	CCl ₄	"	"	77	1.18	0.986	84	42.9	—	1.04
21 §	CCl ₄	"	"	77	1.0	1.00	100	33.8	—	—
22	CCl ₄	"	"	77	0.67	0.626	93	27.2	—	—
23 **	CCl ₄	"	"	77	0.96	0.876	91	37.5	—	1.23
24	CCl ₄	"	"	77	0.15	0.147	98	6.75	317	—
25	CCl ₄	"	"	77	0.27	0.259	96	12.3	250	—

* Quinol present. † Phenyl- β -naphthylamine present. ‡ Dry crepe rubber employed. § Crepe rubber employed. || Milled crepe rubber employed. ** Gel rubber employed. †† Intrinsic viscosity in benzene + 15% MeOH, except that No. 12 was in benzene alone.

2 mols. of chlorine per C₅H₈ group have reacted at 77° is a tough solid containing 58.2% of chlorine, saturated to iodine chloride, and stable in air. The wholly substituted products obtained by reaction of 1 mol., or less than 1 mol., of chlorine per C₅H₈ group are still somewhat rubber-like, and are stable when kept in evacuated tubes; when, however, they are exposed to air, they evolve hydrogen chloride and become transformed into hard resinous masses with no rubber-like properties. When carbon tetrachloride is replaced by chloroform as solvent much the same course of reaction seems to be pursued, but its details cannot be observed very accurately owing to complications arising from chlorination of the solvent vapours (see above) and from the unavoidable separation of some solid chlorinated material which has a lower chlorine content than the product remaining in solution.

The course of reaction as determined by the quantity of hydrogen chloride evolved, may, therefore, be approximately represented up to the stage at which 3 mols. of chlorine have combined with each C₅H₈ group by the following equations, in which the double isoprene unit is used to avoid introducing half atoms :



Elementary analyses of the products obtained in expts. 10 and 11 agree closely with the requirements of these equations. Also various published carbon and hydrogen analyses for highly chlorinated rubbers (*e.g.*, cf. Schidrowitz and Redfarn, *J. Soc. Chem. Ind.*, 1935, 54, 263r) agree as regards the C : H ratio with the formula C₁₀H₁₁Cl₇, now advanced, rather than an earlier formula C₁₀H₁₃Cl₇ due to McGavack.

Influence of Light and Temperature.—The exclusively substitutive reaction occurring during the interaction

of the first molecule of chlorine proceeds to all appearance with equal facility in dark or in light (cf. expts. 6 and 8). It is concluded, therefore, that the substitutive type of reaction is in the main uninfluenced by light. The mixed reactions characterising the interaction of the second mol. of chlorine appear to proceed in darkness or in light, but reaction is accelerated by light. In the third stage reaction is slow in the absence of light.

Variations due to change in the temperature of reaction have only been followed over moderate- and low-temperature ranges, since the paucity of suitable solvents has restricted observations (see p. 289). At 80° the course of reaction described above is maintained, and no appreciable change in the dominant substitutive reaction is to be observed as the temperature falls to room temperature. At room temperature and below, however, some difficulty is experienced from secondary reaction, due to the tendency of the liberated hydrogen chloride to combine additively with the rubber; nevertheless, it has been possible to show that at temperatures as low as -30° reaction is still at least 82% substitutive (cf. expt. 16), and at yet lower temperatures, in spite of the fact that the additive reaction of chlorine becomes more pronounced, substitution is still important, amounting to at least 50% at -80°. Chlorination proceeds very readily at these low temperatures and it was even possible to bring to successful reaction a finely divided solid rubber (expt. 18), although here the product was not homogeneous.

The low-temperature chlorination products showed no sign of evolving hydrogen chloride when allowed to warm to room temperature, and indeed certain of the products (cf. expts. 17 and 18) were raised to and maintained at 80° in the absence of air for one hour without any significant amount of hydrogen chloride being evolved. It seems unlikely, therefore, that at the higher temperatures chlorination proceeds by the addition of chlorine at the ethylenic linkages followed by elimination of hydrogen chloride, thus simulating substitutive reaction although in fact it is truly additive.

Influence of Oxygen, Anti-oxidants, and Polarity of Solvent.—Rust and Vaughan (*loc. cit.*) have found that small proportions of oxygen catalyse the substitutive vapour-phase chlorinations of simple olefins at high temperatures, whereas larger proportions inhibit both substitutive and additive reactions—although, strangely enough, the liquid-phase chlorination of *isobutylene* was found to be exclusively substitutive and entirely unaffected by oxygen. In the case of rubber the exclusively substitutive mode of reaction characterising the interaction of the first molecule of chlorine remains unaffected whether a trace or a substantial proportion of oxygen is mixed with the chlorine (cf. expts. 12 and 13), but the products obtained when oxygen was present were of poor stability.

Similarly, the substitutive character of chlorination during the interaction of the first molecule of reagent was unaffected by the addition of the anti-oxidants quinol and phenyl- β -naphthylamine, but the products were again markedly unstable, and appeared to undergo a species of vulcanisation, since, in contrast to the behaviour of the chlorinated rubbers obtained when no anti-oxidants were used, they could not be re-dissolved when once they had been isolated from solution. The vulcanising action of quinol might well be due to the formation of a little tetrachlorobenzoquinone, which has a marked vulcanising action on rubber (cf. Fisher, U.S.P. 1,918,328; Farmer, *Trans. Faraday Soc.*, 1942, **38**, 340), but its cause in the case of the amine is unknown.

Since Kemp (*Ind. Eng. Chem., Anal.*, 1934, **6**, 52) has indicated that the presence of glacial acetic acid is of assistance in suppressing substitutive reaction between iodine chloride and rubber, the influence of this polar solvent has been tested in the chlorination reaction of rubber. No more than a slight inhibitory action on substitution appears to accrue from the introduction of substantial amounts of acetic acid into the solvent used for the chlorination (carbon tetrachloride) since at 80° in near-darkness substitutive reaction to the extent of 94% was observed. The product was again not very stable.

Influence of Chlorination on Molecular Size.—When chlorine is passed into rubber solutions, a marked decrease of viscosity is commonly observed, probably owing to a reduction in the molecular weight of the rubber. Some quantitative observations have been made in collaboration with Dr. Gee, to whom the author's thanks are due. For this purpose the reaction product was isolated from solution, redissolved in benzene plus 15% methyl alcohol, and its intrinsic viscosity $[\eta]$ determined in dilute solution, as described by Gee (*Trans. Faraday Soc.*, 1940, **36**, 1162). It was found that samples of sol rubber having $[\eta] = 2.75$ passed when chlorinated at 80° to the point at which each C_5H_8 group had reacted with 1 mol. of chlorine into "mono"-chloro-substitution products $(C_5H_7Cl)_n$, having $[\eta]$ of the order of 0.4. A sample of acetone-extracted crepe rubber of $[\eta] = 2.3$ gave a "mono"-chloro-substitution product of $[\eta] = 1.04$,* and a sample of gel rubber ($[\eta]$ not measured but probably in excess of 2.5) gave a chlorination product † of $[\eta] = 1.23$. In the last two cases degradation was much less severe. The character of the degradation is not yet known with certainty, the phenomenon of molecular-weight reduction appearing not only as the normal and invariable result of autoxidation reaction (cf. preceding papers), but also as a quite usual concomitant of reaction when a variety of reagents are employed with rubber. The apparent degradation effected by chlorine does not appear to extend beyond the stage of "mono"-chloro-substitution, and because in general the phenomenon appears most marked when the sol fraction of rubber is being employed, it seems likely that the phenomenon is an autoxidation effect arising from

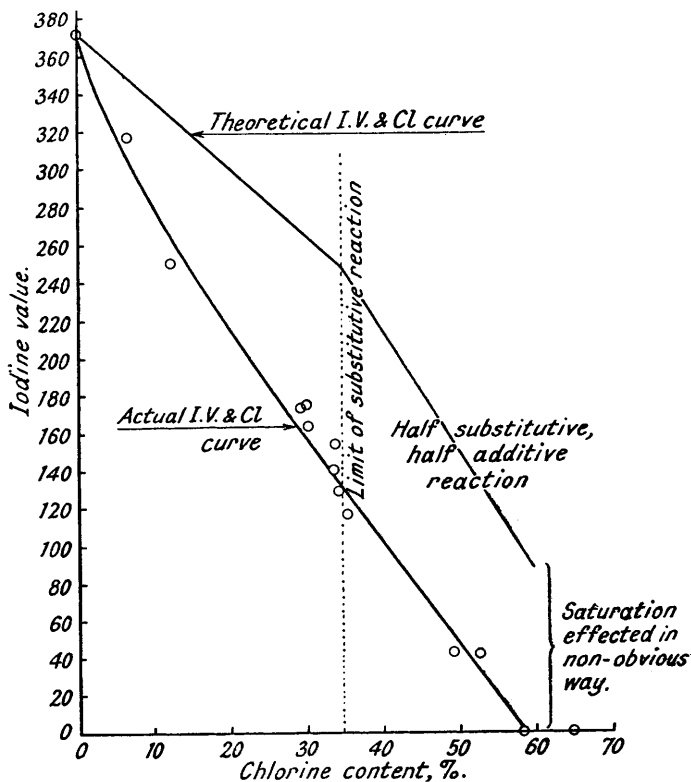
* The corresponding value for the molecular weight obtained by osmotic-pressure determination was 240,000, which is to be compared with the value of ca. 300,000 to be expected if no degradation had occurred.

† Probably wholly "mono"-chloro-substituted, so far as the rubber is concerned, but that cannot be fully demonstrated owing to the considerable proportion of non-hydrocarbon impurity present.

small concentrations of oxygen which are either already dissolved or incorporated (as peroxide groups) in the rubber, or gain access in spite of precautions during the preparation and subsequent manipulation of the reaction products. If this explanation is correct, it would be expected that the degradative effect would largely disappear if the chlorination of sol rubber were carried out at low temperatures (*i.e.*, under conditions which decelerate autoxidation) and this is observed in practice, since the "mono"-chlorinated product has then $[\eta] = 1.93$. It is of interest that the "mono"-chlorination of gel rubber, like that of sol rubber, seems to be substitutive, although the course of reaction is here obscured owing to the rather high concentration of non-hydrocarbon substances in gel rubber.

The Unsaturation of the Chlorination Products.—In the foregoing account the chief criteria of substitutive reaction have been the production of 1 mol. of hydrogen chloride per mol. of chlorine reacted, the analytical data, and the considerable thermal stability of additive chlorination products where these have been formed. Although there is no evidence to show that under the conditions of reaction (especially the temperature range) adopted there is any considerable production of hydrogen chloride by the *secondary* decomposition of previously

FIG. 1.
The relative tendencies towards substitution and additive reaction during chlorination.



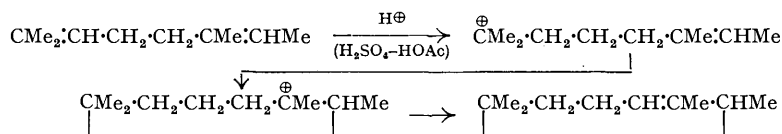
formed, double-bond-addition products, a hypothesis of double-bond re-formation by elimination of hydrogen chloride, either instantaneously as a concomitant of additive reaction of chlorine at a double bond, or from an activated dichloride, cannot be entirely rejected without information as to the precise position of the double bond in the chlorinated molecule. Rust and Vaughan (*J. Org. Chem.*, 1940, 5, 449) have shown that, although ethyl chloride is stable at temperatures exceeding 415° , yet at 280° in the presence of chlorine it undergoes considerable decomposition to give ethylene and hydrogen chloride. Hence some further check on the reality of the substitutive reaction is desirable. When, however, resort is made to observation of the changes which occur in the unsaturation of the rubber as chlorination proceeds, there is the perplexing discovery that simultaneously with the liberation of hydrogen chloride the unsaturation as measured by the iodine value (I.V.) progressively decreases, and the decrease is sufficiently marked to indicate that (apparently) a very substantial degree of additive reaction has occurred. For instance, for substitutive reaction in which each mono-olefinic C_5H_8 unit passes into C_5H_7Cl , the I.V. should decrease from 373 to 248, but in practice it falls to a value between 130 and 150. It is thus necessary to seek an explanation of the apparent partial saturation of the chlorination products in terms of the invalidity of the iodine method of determining unsaturation as applied to chlorinated rubbers, or else in terms either of the occurrence of cyclisation of the rubber chains due to chlorination, or of the inhibiting influence of the substituent chlorine atom in each C_5H_7Cl group on the reactivity of the double bond. An effect of the last type would fall in line with a vicinal effect of substituent chlorine

reported by Rust and Vaughan (*J. Org. Chem.*, 1941, 6, 479) whereby the substitution of further chlorine atoms into the system $\text{>CCl}\cdot\text{C}<$ is inhibited by the halogen already present, and with the known low order of additive reactivity of iodine chloride to double bonds containing negative substituents, *e.g.*, dichloroethylene.

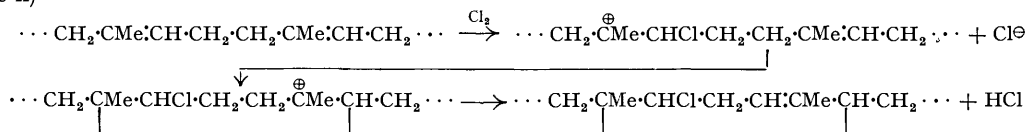
It should be stated that the iodine-value method (Kemp's procedure) has given over a long period results of the most admirable consistency in the determination of the unsaturation of polyisoprenes and other unconjugated polyolefinic systems. Variations in the time of reaction and in the proportion of iodine chloride employed have produced only minor changes in the iodine values observed, so that the above-mentioned anomaly is not to be traced to unsuitable experimental conditions. Peracetic acid, when used as a reagent for determining unsaturation, gave values for chlorinated rubbers substantially lower than those given by iodine chloride. It is, however, significant that when "mono"-chloro-substituted rubbers $(\text{C}_5\text{H}_7\text{Cl})_n$ reacted additively with further amounts of chlorine, they became saturated (to iodine chloride) at the expected points having regard to their initial unsaturation as determined by the iodine-value method. For instance, "mono"-chloro-rubbers having the theoretical I.V. appropriate to their constitution (248) would be expected to add a whole molecule of chlorine per C_5H_8 group before becoming saturated, whereas "mono"-chloro-products having the commonly-observed I.V. 124 should require to add only half a molecule. The latter requirement is found to be fulfilled in practice, since complete saturation (as measured by the I.V.) of the rubber halide was attained at a total chlorine content of 58.2% (cf. expts. 3, 4, 10, and 11) as the result of a combination of substitutive reaction with $1\frac{1}{2}$ mols. and additive reaction with $\frac{1}{2}$ mol. of chlorine per C_5H_8 unit. During the interaction of the first molecule of chlorine per C_5H_8 group (*i.e.*, during the main substitutive stage) the observed I.V.'s soon began to fall below the theoretical values for homogeneous substitutive reaction; beyond this stage an undoubted additive reaction set in, the decrease in I.V. becoming more rapid. The relationship between chlorine content and I.V. is shown in Fig. 1.

Cyclisation as a Cause of Decreased Unsaturation.—The ease with which the open-chain di-isoprene, dihydromyrcene, cyclises in presence of sulphuric-acetic acid is well known. One double bond in the diolefinic C_{10} unit is lost in this manner, and it is conceivable that reaction between chlorine and rubber could proceed in a comparable manner, *i.e.*, without definite $\text{C}_5\text{H}_8\text{Cl}_2$ units ever being formed. Possible mechanisms for these reactions are set out below :

(Scheme i)



(Scheme ii)



In order to examine this possibility, the behaviour of 1-methylcyclohexene, dihydromyrcene ($\overline{\text{C}}_2$), and squalene ($\overline{\text{C}}_8$) towards chlorine has been investigated.

1-Methylcyclohexene may be regarded as a dialkyl derivative of monomeric rubber, $\text{R}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{R}$, and it is significant that the product obtained by interaction of the hydrocarbon at 80° with 1 mol. of chlorine retains most of the original olefinic unsaturation and 0.79 mol. of hydrogen chloride is liberated in its formation. The precise degree of unsaturation retained at the end of this stage amounts on an average to $\overline{0.76}$ per mol. of the product as determined by the iodine value; hence the overall reaction appears to be *ca.* 79% substitutive as shown by hydrogen chloride evolution and 76% by iodine-value determination. The product is found, in fact, to consist mainly of chloro-1-methylcyclohexene admixed with a smaller quantity of 1-methylcyclohexene dichloride—the latter being a substance of considerable thermal stability. Hence, substitutive chlorination appears to be a major reactivity in the case of this olefin, but it is significant that the unsaturation of the monochloro-substitution product appears to be somewhat lower (I.V., 172) than that calculated (I.V., 180), even when allowance is made for the presence of the dichloride found.

Dihydromyrcene (dimeric rubber) gives in reaction with 1 mol. of chlorine a mixed product, the formation of which is accompanied by the liberation of 0.82 mol. of hydrogen chloride. This was found to consist mainly of unsaturated monochloro-compounds (doubtless several isomeric compounds) from which a fairly pure *monochlorodihydromyrcene* could be isolated. Here, however, the difference between the observed and the calculated values for the unsaturation was more marked (*e.g.*, I.V. : found, 252; calc., 284) than it was with 1-methylcyclohexene, and a still greater difference was found when 2 mols. of chlorine reacted with dihydromyrcene (*i.e.*, 1 mol. per C_5H_8 unit). In this case the total reaction product, formed with simultaneous liberation of 0.80 mol. of hydrogen chloride, showed an average loss of unsaturation as measured by the I.V. of $\overline{0.28}$, and the pure *dichlorodihydromyrcene* isolated as the major reaction product showed an apparent loss of unsaturation of $\overline{0.22}$ (*e.g.*, I.V. : found, 190; calc., 245). That this effect is due largely, though not entirely,

to a cyclisation mechanism is shown by reduction of the halide, whereby somewhat cyclised dihydromyrcene of I.V. 347 is obtained, whereas if the lowered unsaturation of the dichlorodihydromyrcene had been entirely due to cyclisation, then an I.V. of 285 would have been expected for the regenerated hydrocarbon.

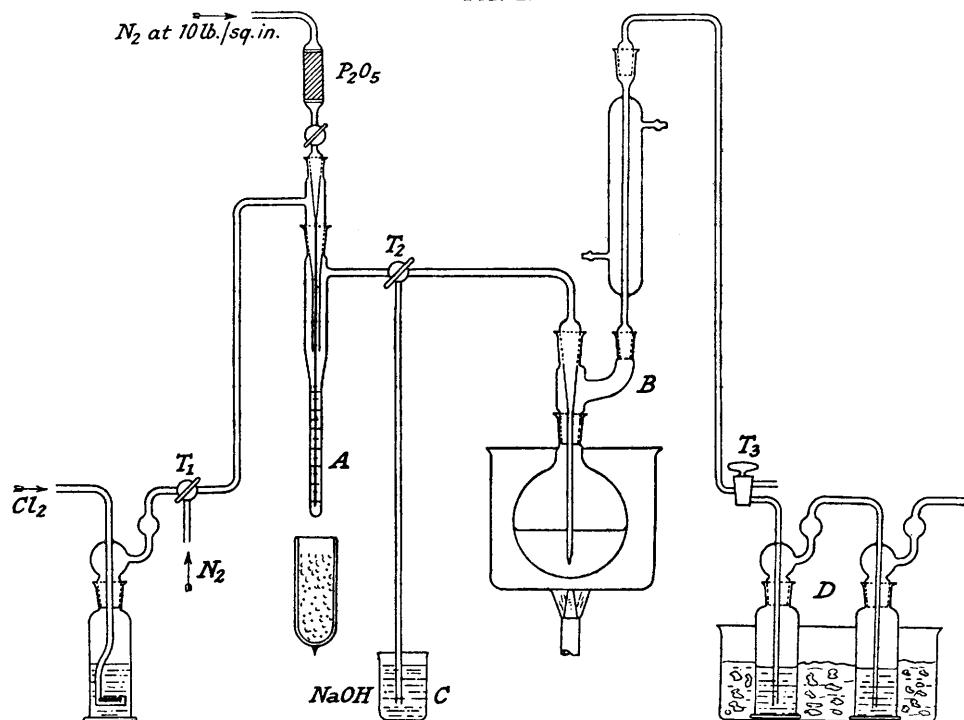
Interaction of squalene with 0.85 mol. of chlorine per C_8H_8 unit liberated hydrogen chloride in quantity corresponding to 90% substitutive reaction, and the unsaturation of the total product as measured by the I.V. fell considerably short of the calculated value (found, 184; calc., 230). Reduction of the halide gave a somewhat cyclised hydrocarbon of I.V. 312 (theoretical value, 372).

The conclusions to be drawn are as follows: (1) Substitutive chlorination of 1-methylcyclohexene appears to proceed by a direct mechanism, since no question of cyclisation here arises. (2) There is experimental indication that some degree of cyclisation accompanies the chlorination of dihydromyrcene, and if this forms in fact an essential part of the chlorination-cyclisation process represented in scheme ii (and is not merely a subsidiary and independent post-chlorination process due to the catalytic action of hydrogen chloride on the olefinic substance) it appears to be quite insufficient to account for more than a portion of the diminution in unsaturation observed to accompany chlorination. Hence there seems good ground for believing that the chlorination of dihydromyrcene is largely substitutive in character, and that the loss of unsaturation measured by the fall in iodine value is partly a real one to be attributed to cyclisation, but partly an apparent one due to marked steric inhibition of iodine chloride addition at those double bonds which adjoin $\cdot CHCl\cdot$ or $\cdot CCl_2\cdot$ groups or which themselves form part of $CCl=C$ groups. (3) In the case of rubber, chlorination is probably in the main truly substitutive, but the cyclisation and the steric factor doubtless both play a part in causing the apparent reduction in unsaturation as measured by iodine value.

EXPERIMENTAL.

Solvents.—Commercial carbon tetrachloride was purified by subjection to exhaustive chlorination in light in presence of a trace of iodine, followed successively by washing with alcoholic sodium hydroxide, then with water, drying over

FIG. 2.



calcium chloride, again chlorinating at the b. p. in light to destroy any trace of alcohol, refluxing over bleaching powder, washing, drying, and distilling over paraffin wax to remove hexachloroethane. The distillate was redistilled over mercury and finally rectified through a good Widmer column. Thus purified, it gave on submission to chlorination at its b. p. in a nitrogen atmosphere only traces of hydrogen chloride. The chloroform and carbon disulphide employed were of "AnalaR" grade.

Rubber.—Except where otherwise stated, the rubber employed was sol rubber,* [7] 2.75, from which the most soluble (and most oxygenated) fractions had been rejected.

Nitrogen.—All nitrogen employed except in two experiments was commercial "purified" nitrogen which had been thoroughly freed from oxygen by passage through Fieser's sodium hyposulphite solution (*J. Amer. Chem. Soc.*, 1924, 46, 2639).

Apparatus.—This is shown in Fig. 2. The solution of rubber was placed in the flask B; then the whole apparatus

* Obtained by diffusion of rubber into light petroleum.

was evacuated *via* stopcock *T*₃ and afterwards filled with purified nitrogen *via* stopcock *T*₁. A stream of nitrogen (entering through *T*₁) was kept circulating through the apparatus throughout the chlorination. The amount of chlorine required for use in any one experiment was condensed in the graduated tube *A*, and this was effected by connecting a chlorine cylinder and sulphuric acid wash-bottle to stopcock *T*₁, and applying solid carbon dioxide to *A*; meanwhile the stopcock *T*₂ was closed to *B* and opened to the alkali trap *C*. As soon as sufficient chlorine was condensed, the cylinder was disconnected, and all uncondensed chlorine was swept out of the apparatus by a stream of nitrogen. Then *T*₂ was re-opened to *B*, and the measured volume of chlorine in *A* caused to volatilise slowly into the rubber solution by allowing the temperature of *A* to rise gradually. The ebullition of the liquid chlorine and the removal from the latter of traces of dissolved oxygen were aided by passing purified nitrogen from a reservoir in which it was confined at 10 lb./sq. in. through a fine capillary jet inserted into *A*. Hydrogen chloride and unreacted chlorine in the effluent gases were absorbed in the system *D* (ice-cooled) containing 2*N*-sodium hydroxide.

Comparative experiments for determining the influence of light on the course of reaction were conducted in diffused sunlight reinforced by the radiation from a 300-watt incandescent lamp, and in darkness; other experiments were made to test (separately) the influence of oxygen, anti-oxidants, polar liquids, and different temperatures of reaction.

Chlorination of Rubber.—General method. The reaction procedure described above was used. For each determination of the hydrogen chloride and unreacted chlorine present in the absorption system *D*, the solution in the latter (containing chloride, hypochlorite, and excess of sodium hydroxide) was suitably diluted (to 500 c.c.) and an aliquot part (25 c.c.) titrated first with 0.1*N*-sodium arsenite to determine the hypochlorite present and to convert it into chloride. The total chloride was then determined by acidifying the resulting solution with acetic acid and diluting it to 100 c.c., from which 10 c.c. were taken for titration with 0.025*N*-silver nitrate, dichlorofluorescein being used as internal indicator (cf. Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495). The trustworthiness of the procedure was tested by a blank run in which no rubber solution was used: 2.66 g. (1.6 c.c.) of liquid chlorine (*d*^{79°} 1.663) were vaporised into the chlorination vessel, so giving in the absorption system hypochlorite equivalent to 2.63 g. of introduced chlorine and total chloride equivalent to 2.62 g. of chlorine. No harmful effect due to the traces of carbon tetrachloride which escaped into the absorption system was observed, but in a few experiments in which chloroform was used as solvent or in which somewhat volatile and hydrolysable chlorination products were expected, the absorption system was slightly modified. In these cases two wash-bottles of water were used to absorb the hydrogen chloride, and a third, containing 2*N*-sodium hydroxide, to absorb the excess of chlorine. The small amount of free chlorine in the first two wash-bottles was determined by the arsenite method, and total chloride by the volumetric method as described above. The hypochlorite in the third wash-bottle was determined separately.

The chlorinated rubber was isolated from solution by precipitation into alcohol, and the adhering solvent removed at room temperature under reduced pressure (finally in a high vacuum). All chlorine contents were determined by the Carius method.

The essential details of the various experiments, not already covered by the table, are set out below. Generally, 5 g. of rubber in 300 c.c. of solvent were used in the reaction flask.

Expt. 1. This gave a soft, pale yellow, rubbery material; yield, 7.1 g. (Found: C, 62.4; H, 7.6; Cl, 30.0; I.V., 175. Calc. for the substitutive reaction of 0.81 mol. of chlorine: C, 62.5; H, 7.55; Cl, 30.0%; I.V., 265). The product rapidly darkened on exposure to air and eventually became hard and dark brown, hydrogen chloride being liberated in the process; when stored in sealed evacuated tubes, however, it remained unchanged.

Expt. 2. The reaction solution (red) contained a considerable amount of insoluble matter, which when separated formed a red solid (3.3 g.) having Cl, 28.2%. The solution yielded a soft, red, rubbery mass (4.2 g.) (Found: Cl, 30.4%; I.V., 163), unstable in air, turning yellow and liberating hydrogen chloride.

Expt. 6. The product of reaction of 1 mol. of chlorine per C₅H₈ group (7.2 g.) had Cl, 33.6; I.V., 140 (Calc. for C₅H₇Cl: Cl, 34.6%; I.V., 248).

Expt. 10. The final product of a chlorination conducted in four stages was a fine, white, stable powder (14.5 g.) having C, 32.1; H, 3.1; Cl, 64.6%; I.V., 0; empirical formula C₁₀H_{11.5}Cl_{6.8}.

Expt. 12. The nitrogen used in this experiment contained about 1% of oxygen. The product of reaction of 1 mol. of chlorine per C₅H₈ group resembled that obtained in *expt. 6*, except that the former was somewhat the less stable.

Expt. 13. Here the nitrogen stream was replaced by a mixture of 60% of oxygen and 40% of nitrogen. The reaction solution was of lower viscosity than usual and yielded a brown product containing no combined oxygen and of such poor stability that hydrogen chloride was liberated even in a vacuum (Found: C, 57.7; H, 7.0; Cl, 35.3%; I.V., 117).

Expt. 16. Sol rubber (5 g.) dissolved in carbon tetrachloride (500 c.c.) was placed in a flask fitted with a stirrer, dropping funnel, nitrogen inlet tube, and an outlet tube connected with the absorption system *D* shown in Fig. 2. The rubber solution was cooled to -30°, and into the cooled solution 181 c.c. of carbon tetrachloride containing 5.3 g. of dissolved chlorine were run as rapidly as possible whilst the hydrogen chloride formed was swept into the absorption system by a brisk current of nitrogen. The reaction mixture (685 c.c.) was poured into sufficient alcohol to give a total volume of 2 l. of which 25 c.c. were titrated with 0.025*N*-sodium hydroxide. The value of 82% substitutive reaction observed (cf. table) must be regarded as a minimum, since the occurrence of some additive reaction between the hydrogen chloride formed and the unsaturated centres of the rubber cannot be excluded at the reaction temperature employed. The product formed under these conditions by the action of 1 mol. of chlorine per C₅H₈ group was a soft, rubbery mass, similar to that obtained in *expt. 6*, but more stable (Found: Cl, 34.2%; I.V., 129; [η], 1.93).

Expt. 17. Finely shredded crepe rubber was placed in a tube connected by a stopcock to a 2-l. reservoir, the whole being evacuated to 10⁻⁴ mm., and the stopcock closed. A tube of chlorine (5 g.) frozen in liquid air, and a flask containing 2*N*-sodium hydroxide, both fitted with stopcocks, were then attached to the apparatus which was again evacuated and sealed off. The tube containing the rubber was then immersed in solid carbon dioxide, and the chlorine allowed to warm and vaporise therein. Under these conditions it was expected that any hydrogen chloride formed would, on account of its considerable vapour pressure at -80°, volatilise into the 2-l. reservoir from which it could be periodically absorbed in the sodium hydroxide by momentarily opening the communicating stopcock. By operating in this way a total of 2.02 g. of unreacted chlorine and 0.6 g. of chlorine as hydrogen chloride were absorbed, the remaining 3 g. of chlorine having reacted with the rubber, 42% substitutively. The figures thus obtained can only be regarded as approximate. There was no evidence of hydrogen chloride production when the chlorinated product was allowed to warm to room temperature; also, no free hydrogen chloride could be detected after the chlorinated product had been maintained at 80° for an hour. The product was a rather hard, stable substance, but not homogeneous, so the values given for chlorine content and I.V. in the table for this experiment are unlikely to be truly representative of the product as a whole.

Expt. 18. Sol rubber (2 g.), dissolved in carbon disulphide (250 c.c.), was placed in the apparatus used for *expt. 16*, and cooled to -80°. A solution of chlorine (2.5 g.) in carbon tetrachloride (30 c.c.) was then run in at -70° to -80°. Some insoluble matter at once separated, and some hydrogen chloride was formed. The reaction product was placed in alcohol which had been previously cooled to -80°, the precipitated material was transferred rapidly to more alcohol at -80°, and there manipulated to free it from residual hydrogen chloride, and finally the precipitate was placed in alcohol at room temperature before being freed from solvent at reduced pressure (finally in a high vacuum). The values obtained

(cf. table) pointed to the occurrence of at least 67% substitutive reaction. Only mere traces of hydrogen chloride were found in the alcohol in which the product had been placed at room temperature, and in the vacuum system either at room temperature or at 80°, thus indicating that no evolution of hydrogen chloride had occurred on warming the chlorinated rubber from -80° to 80°.

Properties of Monochlororubber, (C₅H₇Cl)_n.—The substituted rubbers obtained by the action of 1 mol. of chlorine per C₅H₈ group were generally soluble in benzene and chlorinated hydrocarbons, but the solubility decreased when the specimens were stored, owing to their gradual deterioration. In this deterioration small amounts of hydrogen chloride were liberated over long periods at room temperature, but no high proportion of chlorine was lost (> 0.6% of combined chlorine) when the specimens were heated for 5 hours at 70–80°. The products became more stable after they had been boiled with water, but in this process not more than 3% of combined chlorine was removed, and the products so treated were no longer soluble. Refluxing the products in benzene containing aqueous-alcoholic potassium hydroxide caused a similar diminution in the chlorine content.

On treatment with zinc in boiling benzene containing acetic acid, the products lost all their chlorine, so giving a finely divided, insoluble powder resembling the products commonly formed from rubber by reagents such as stannic, antimony, ferric, and zinc chlorides.

Chlorination of Dihydromyrcene.—*Expt. 26.* Chlorine (4.6 g.) was passed into dihydromyrcene (3.90 g.; I.V., 364) dissolved in carbon tetrachloride (90 c.c.) at the b. p. of the latter, the apparatus shown in Fig. 2 and the modified absorption system described on p. 295 being used. There were found (a) unreacted chlorine 0.73 g., whence reacted chlorine = 3.9 g. (0.98 mol.), and (b) chlorine as hydrogen chloride, 1.56 g., corresponding to 80% substitutive reaction. The reaction solution was made up to 100 c.c., and 2-c.c. portions were taken for direct determination of unsaturation of the crude reaction product (Found : I.V., 166. Calc. for 80% substitutive reaction : I.V., 182).

Expt. 27. Chlorine (11.0 g.; 1.01 mols. per C₅H₈ unit) was passed into dihydromyrcene (10.62 g.) in the absence of a solvent at 90–100°. All the chlorine reacted, giving 4.36 g. of hydrogen chloride, corresponding to 80% substitutive reaction. Distillation of the product gave 11 g. of fragrant liquid, b. p. 42–65°/0.05 mm., and 6 g. of a less volatile residue which decomposed below its b. p. The volatile fraction on redistillation at 10⁻³ mm. yielded a small fraction, b. p. 35–46°, and a main fraction, b. p. 46–48°, which proved to be nearly pure dichlorodihydromyrcene (Found : Cl, 33.1; I.V., 202. Calc. for C₁₀H₁₆Cl₂ : Cl, 34.25%; I.V., 245).

Expt. 28. Chlorine (8.04 g.; 0.5 mol. per C₅H₈ group) was passed into 15.62 g. of dihydromyrcene: 3.3 g. of the chlorine appeared as hydrogen chloride, so corresponding to 82% substitutive reaction. The fragrant liquid product was distilled at 0.2 mm., giving the fractions: (i) b. p. 35–42°, (ii) b. p. 42–44°, (iii) b. p. 44–46°, (iv) b. p. 46–48°, (v) b. p. 46–48°, (vi) a small residue. The fractions (ii)–(iv) were combined and redistilled at 15 mm., so giving three fractions of b. p. < 88°, 88–90°, and 90–92° severally. The middle fraction proved to be fairly pure monochlorodihydromyrcene (Found : Cl, 21.4; I.V., 252. C₁₀H₁₇Cl requires Cl, 20.55%; I.V., 294).

Expt. 29.—The formation of dichlorodihydromyrcene (*expt. 27*) was repeated, freshly prepared dihydromyrcene (I.V., 373) being used. The fractionated product gave dichlorodihydromyrcene, b. p. 48–50°/0.01 mm. (Found : C, 58.1; H, 8.1; Cl, 33.85; I.V., 190. C₁₀H₁₆Cl₂ requires C, 57.95; H, 7.8; Cl, 34.25%; I.V., 245. The corresponding additive product C₁₀H₁₆Cl₂ would require C, 57.4; H, 8.7; Cl, 33.9%; I.V., 123). Reduction of the product with zinc dust and glacial acetic acid at 50–60° gave dihydromyrcene, b. p. 56°/15 mm. (Found : C, 87.0; H, 13.0; I.V., 347. Calc. for C₁₀H₁₈ : C, 86.9; H, 13.1%; I.V., 373).

Chlorination of Squalene.—*Expt. 30.* Chlorine (5.1 g.) was passed into a solution of squalene of $n_D^{20} 1.4954$ (4.68 g.) in carbon tetrachloride (90 c.c.) at the b. p. of the latter, the apparatus shown in Fig. 2 being used. There were found: (a) unreacted chlorine, 0.95 g., whence reacted chlorine = 4.15 g. (0.85 mol.), and (b) chlorine as hydrogen chloride, 1.86 g., corresponding to 90% substitutive reaction. The chlorinated product was a viscous oil which darkened on exposure to air with liberation of hydrogen chloride (Found : Cl, 33.6; I.V., 184. Calc. for 90% substitutive reaction of 0.85 mol. of chlorine : Cl, 32.8%; I.V., 230). Reduction of the product with zinc dust and glacial acetic acid gave some distillable liquid and an undistillable residue. The former, $n_D^{20} 1.4958$, was a somewhat modified squalene of lower unsaturation than the original specimen (Found : C, 87.5; H, 12.5; I.V., 313. Calc. for C₃₀H₅₀ : C, 87.7; H, 12.3%; I.V., 372).

Chlorination of 1-Methylcyclohexene.—*Expt. 31.* Chlorine (6.25 g.) was passed into a solution of 1-methylcyclohexene [8.14 g.; I.V., 278 (Calc. : 265)] in carbon tetrachloride (20 c.c.) at the b. p. of the latter, the apparatus shown in Fig. 2 and the modified absorption system again being used. There were found: (a) unreacted chlorine, nil, whence reacted chlorine = 1.04 mols.; and (b) chlorine as hydrogen chloride 2.74 g., corresponding to 79% substitutive reaction. The unsaturation of the total product was determined directly from an aliquot portion of the reaction solution (Found : I.V., 145. Calc. for 79% substitutive reaction of 1.04 mols. of chlorine : I.V., 150). Distillation of the product gave (i) a little low-boiling material, (ii) a fraction, b. p. 56°/15 mm. (5 g.), and (iii) a fraction, b. p. 50–70°/0.01 mm., but principally 55–60°/0.01 mm. The fraction, b. p. 50–70°/0.01 mm., was saturated to permanganate and to bromine (I.V., 12) and doubtless consisted of the addition product 1-methylcyclohexene dichloride. Fraction (ii), on the other hand, represented a constant-boiling mixture of this with chloro-1-methylcyclohexene (7.5% of the former) (Found : C, 63.5; H, 8.45; Cl, 28.3; I.V., 172. Calc. for C₇H₁₁Cl : C, 64.35; H, 8.45; Cl, 27.2%; I.V., 193. Calc. for 92.5% of C₇H₁₁Cl + 7.5% of C₇H₁₂Cl₂ : C, 63.3; H, 8.4; Cl, 28.3%; I.V., 180). Reduction of the constant-boiling mixture (5 g.) with zinc and glacial acetic acid at 60–70° gave 1-methylcyclohexene, b. p. 109–110°/758 mm. (2.3 g.), contaminated with a trace of chlorinated hydrocarbon (Found : C, 86.65; H, 12.55; I.V., 264. Calc. for C₇H₁₂ : C, 87.4; H, 12.6%; I.V., 265), together with a chlorinated compound of b. p. 36–38°/0.01 mm. (Found : C, 69.3; H, 9.5; Cl, 21.1%; I.V., 148).

A further sample of chloro-1-methylcyclohexene was obtained similarly, but without solvent being used during chlorination. This sample (b. p. 56°/15 mm.) had Cl, 28.3%; I.V., 174.

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