

[CONTRIBUTION FROM THE MELLON INSTITUTE FOR INDUSTRIAL RESEARCH.]  
**THE ELIMINATION OF HYDROGEN CHLORIDE FROM CHLORO-  
HYDROCARBONS.<sup>1</sup>**

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The preparation of unsaturated compounds from aliphatic chloro compounds by the action of high temperatures was investigated by Nef.<sup>4</sup> His work, which was limited to ethyl, propyl, and *isobutyl* halides showed that ethyl chloride was completely dissociated into ethylene and hydrogen chloride at a temperature of 550°, propyl and *isobutyl* chlorides being completely converted in an analogous manner at 500°. The contact materials used by Nef were pumice stone and soda-lime.

Sabatier and Mailhe<sup>5</sup> in 1904 succeeded in preparing alkylenes from the corresponding aliphatic monochlorides by using as catalysts the chlorides of the divalent metals (Ni, Co, Fe, Cd, Pb, Ba, etc.) at 260°. By this method ethyl, propyl, *isobutyl* and *iso*-amyl chlorides when passed over barium chloride gave the corresponding olefins. At the same time the barium chloride used became gray in color owing to the simultaneous polymerization of a small proportion of the olefins formed. These authors found that the chlorides of monovalent elements exerted no catalytic action even at 350°.

Alumina was found by Senderens<sup>6</sup> to remove hydrogen chloride from propyl and *isobutyl* chlorides at 250°, whereas with no catalyst present *isobutyl* chloride was quite stable at 430°.

At 350°, propyl and *isobutyl* chlorides gave, with alumina as catalyst, yields of 97% of propylene and 95% of *isobutylene* respectively.

The cleavage of hydrogen chloride from mono- and dichloro-cyclohexanes by the use of the catalysts recommended by the above authors has been patented by the Badische Anilin-u. Soda Fabrik in a series of patents: U. S. patent 1,221,382 (1917); Brit. patent 5,429 (1912); and Ger. patents 254,473, and 255,538 (1913). The preparation of *isoprene* and similar diolefins from chlorinated derivatives of pentane and hexane under reduced pressure using alumina and barium chloride as catalysts has also been patented by this firm (French patents 435,312 and 434,586 (1911), Brit. patents 10,826 and 18,356 (1911) and Ger. patent 255,519).

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<sup>4</sup> Nef, *Ann.*, 318, 1 (1901).

<sup>5</sup> Sabatier and Mailhe, *Compt. rend.*, 138, 407 (1904); 141, 238 (1905).

<sup>6</sup> Senderens, *ibid.*, 146, 1211 (1908), and *Bull. soc. chim.*, [4] 3, 827 (1908).

The present investigation was undertaken with chlorine compounds of hexane, heptane, and cyclohexane in order to determine the most suitable conditions for the preparation of unsaturated compounds therefrom. It was also desired to ascertain the relative stability of dichloro- and monochloro compounds with various catalysts at the high temperatures involved in these dechlorinations. As the cleavage of these chlorides into hydrogen chloride and olefins or diolefins is always accompanied by a complete decomposition of a portion of the hydrocarbons formed, it is obvious that the catalyst must lose some of its effect as the reaction is prolonged owing to the deposition of carbon. This question was investigated by finding the change in catalytic activity as the same catalyst was used continuously for dechlorination.

Hexane, *isohexanes* and heptane fractions were isolated from Pennsylvanian straight-run gasoline by repeated fractionations; aromatic hydrocarbons were removed by means of a sulfuric-nitric acid mixture and the fractions redistilled several times through a 120 cm. Hempel column filled with magnesium turnings, and covered with asbestos paper; thus the fractions finally obtained were nearly pure hexane and heptane. Fractions 61° to 64°, 67.5° to 70°, and 97° to 100°, (all at 760 mm.) were collected, representing a mixture of *isohexanes*, *n*-hexane, and *n*-heptane respectively.

Cyclohexane obtained from the Dayton-Wright Division of the General Motors Corporation was carefully freed from benzene and refractionated twice, the fraction of boiling point 79° to 79.5° (740 mm.) being collected; the cyclohexane used for the preparation of chloro compounds melted at 4.5°. The product, therefore, was practically pure cyclohexane.

The paraffin hydrocarbons contained small amounts of polymethylenes as a result of their source and method of preparation. Owing to the comparatively large amounts required for this investigation, however, it was considered that the only practicable method was to isolate from a suitable gasoline all of the paraffin hydrocarbons required.

**Chlorination.**—Cyclohexane was chlorinated in the manner briefly described by Sabatier and Mailhe.<sup>7</sup> By the chlorination of 300 g. of cyclohexane at a temperature of 20° to 25° until an increase in weight of 50 to 75% of that theoretically required for the production of monochloro-cyclohexane was realized, the following products were obtained after several fractionations.

	G.
Cyclohexane recovered unchanged.....	40
Fraction 139–144°, monochloro-cyclohexane ( $d_4^{20}$ 1.002).....	150
Fraction 75–85° (15 mm.), dichloro-cyclohexane ( $d_4^{20}$ 1.179).....	105
Fraction 95–105° (15 mm.), trichloro-cyclohexane ( $d_4^{20}$ 1.266).....	24
Intermediate fractions and residue.....	50

<sup>7</sup> Sabatier and Mailhe, *Compt. rend.*, **137**, 240 (1903).

The dichloro- and trichloro-cyclohexanes were purified by two distillations at a pressure of 15 mm.

Hexane and *isohexane* were chlorinated in the vapor phase as first suggested by Schorlemmer<sup>8</sup> and also employed by Michael and Turner.<sup>9</sup> In our procedure, chlorine was introduced at about the middle point of a tube through which the hydrocarbon was being refluxed. A thermometer was inserted at the position where the chlorine was introduced and by this arrangement the course of the chlorination was followed closely.

By this method monochloro derivatives were the principal products and very small amounts of dichloro and more highly chlorinated compounds were formed. It was, however, essential that this chlorination be carried out in diffused light, as in full daylight a flame appears and carbon is formed. In order to obtain quantitative yields it is necessary to resort to absorption or very efficient cooling of the issuing hydrogen chloride, as otherwise some of the chlorinated products will be carried away with it and thus be lost.

The chlorinated products were washed with dil. alkali and water to free them from hydrochloric acid. With some of the chlorinated compounds it was necessary to use brine instead of water owing to the fact that the specific gravities of the compounds were very close to that of water.

A fraction distilling from 120° to 124° which was obtained from the chlorinated *n*-hexane after 4 fractionations, corresponds to 2-chloro-*n*-hexane.

Similarly, from the *isohexane* a fraction distilling from 119° to 123° was isolated. This fraction was a mixture of monochloro-hexanes.

Heptane was chlorinated in a way similar to that used with cyclohexane as already described.

Dichloro-heptanes constituting the fractions boiling from 90 to 100° (15 mm.) and monochloro-heptane forming the fraction 150 to 160° (760 mm.) were obtained after three fractionations.

The specific gravities and iodine numbers of these chloro compounds were determined. The iodine numbers of the chloro compounds were in all cases very small and in all probability were due to the presence of small amounts of olefins.

**Dechlorination.**—In the dechlorination process the chloro compounds were passed at the desired temperature through a glass tube which contained the catalyst. The products of the reaction were then led through a tube containing soda-lime maintained at a temperature of 100° or of 150° and were passed finally into a receiver cooled by an ice-bath. The purpose of the heated soda-lime tube was to remove hydrogen chloride and

<sup>8</sup> Schorlemmer, *Phil. Trans.*, 163, 111 (1872).

<sup>9</sup> Michael and Turner, *Ber.*, 39, 2154 (1906).

thus to prevent its recombination with the olefin. (This reaction was shown by Nef<sup>4</sup> to occur with butylene.) By this means the product obtained by condensation really indicates the true effect of the catalyst. The chloro compound was contained in a buret connected to the tube containing the catalyst through a 2-way glass stopcock; a stream of dry nitrogen could thus be passed through the catalyst when desired. The tube containing the catalyst was heated at 150 to 500° as desired by means of an electric resistance-furnace, the temperature being controlled by a rheostat. The length of the catalyst tube was 70 cm. The soda-lime tube, also, was heated in a similar manner. The temperatures of both the catalyst tube and the soda-lime tube were measured by means of iron-constantan thermocouples. Condensation of the vapors was effected by a tube, surrounded by an ice-bath, which extended into a test-tube with side arm. The side arm was connected to a train of bromine absorption tubes cooled in ice and the latter to a gasometer when desired. The temperature of the soda-lime tube was kept sufficiently high to prevent any of the chloro compound from condensing in this tube, but not high enough for its catalytic effect in the reaction to be measurable. The rate at which the chloro compound was introduced into the tube containing the catalyst could be regulated, with practice to any desired value. The compound was, in general, immediately vaporised owing to the high temperature of the catalyst. After the desired amount of chloro compound had been passed through the tube, the vapors remaining in the tube were driven out by means of a stream of dry nitrogen introduced through the 2-way stopcock and were condensed in the ice-water condenser.

From the percentage of liquid condensed, the yield of dechlorinated product was calculated; see, for example, Table III. The specific gravity and iodine numbers of this condensate indicate the proportion of unsaturated compounds formed, since the iodine number of the unsaturated compound is known. The iodine number serves as an index to the amount of unsaturation only in the case of olefins; in the case of diolefins the iodine value obtained is far below that corresponding to the true extent of the unsaturation. This point will be covered fully in a later paper. The iodine numbers were determined by Hanus method, giving half-hour contact with the iodine solution in the dark (0.10 g. of olefin to 25 cc. of Hanus solution).<sup>10</sup>

The bromine collected any unsaturated compounds which were not condensed by the ice-bath and from the amount of gas *evolved during the*

<sup>10</sup> It was thought unnecessary to make chlorine determinations on the condensates since a consideration of the specific gravity, iodine number, and distillation characteristics furnishes a sufficiently accurate index to their composition. Owing to the great differences between the boiling points of the chloro compounds and the olefins obtained from them, an analysis by fractionation shows the extent to which the elimination of hydrogen chloride has been effected.

time the liquid was being introduced into the catalyst tube, the extent of decomposition occurring could be ascertained.

The following contact materials were used as catalysts in the dechlorination process: unglazed porcelain, unglazed porcelain which had been soaked in a strong solution of barium chloride and then dried, and alumina (commercial aluminum hydroxide worked to a plastic mass with water, and then dried at the temperature at which it was used); Pyrex glass was used in some experiments since any effect glass may have in the course of the reaction is due presumably to surface action only.

The experiments carried out with the Pyrex glass should, therefore, indicate only the effect of variation of the temperature on the reaction.

**Dependence of Dechlorination on Rate of Introduction of Chloro Compound.**—Experiments were made with monochloro-*isohexane* to determine the effect of varying the rate at which the chloro compound was passed over the catalyst on the amounts of hydrogen chloride removed. These experiments were carried out at 200°, 300°, and 400°, using unglazed porcelain as the catalyst. The soda-lime tube was maintained at 150° during these experiments.

TABLE I.  
IODINE NUMBERS OF CONDENSATES FROM MONOCHLORO-*ISOHEXANE*.  
Iodine number of *isohexene* = 302 (calc.).

Temperature of catalyst, ° C.	Time, Min.	10 cc. passed over catalyst in		
		15.	30.	60.
200	228	209	243	252
300	246	216	275	290
400	253	271	263	292

In general, the iodine numbers and specific gravities of the condensates were in agreement (see, for example, Table III), *i. e.*, the higher the iodine number the lower is the specific gravity.

From these experiments it will be observed that as the rate of introducing the chloro-*isohexane* is lowered, the dechlorination proceeds more completely, but the effect produced by the difference between the two rates, 10 cc. in 15 minutes and 10 cc. in 2 hours, is not very great, inasmuch as fairly complete dechlorination is effected even at 200° by passing 10 cc. over the catalyst in 15 minutes.

It will also be noticed that the effect of temperature from 200° to 400° is not very marked in the preparation of *isohexylene* from chloro-*isohexane*.

As a result of the experiments described in Table I, it was decided to adopt the uniform rate of 20 cc. in one hour for passing the chloro compound over the catalyst in all the experiments described later.

**Loss of Catalytic Power on Prolonged Use.**—These experiments were carried out to determine the effect on the catalytic activity of unglazed

porcelain produced by a continuous use of the same material for the preparation of *isohexane*. As has already been stated, the dechlorination of chloro compounds at temperatures above 200° is apparently always accompanied by a simultaneous decomposition of a part of the olefins, which produces a deposition of carbon on the catalyst.

TABLE II.

## IODINE NUMBERS OF CONDENSATES.

50 cc. of Chloro- <i>isohexane</i> was Used at Each Temperature.					
Temperature of catalyst, ° C.	Time (Hours).				
	1/4.	1/2.	1.	2.	2 1/2.
200	247	231	183	106	77
300	248	246	240	188	143
400	284	257	235	181	183

A decline in the activity of the catalyst occurs at all temperatures but is most marked at 200°; at the same time, the pieces of unglazed porcelain become darker in color owing to the decomposition of hydrocarbons. It was found that, as would be expected, the blackening was the more noticeable the higher the temperature. At 500° to 550° the rate of decomposition of olefins was found to be very rapid, as at these temperatures large amounts of uncondensable gases which were unattacked by bromine were formed.

Nevertheless at 300 and 400° the decrease in the activity of the catalyst is not so marked as at 200° owing to the fact that at these temperatures the reaction takes place readily even in the absence of catalytic material and consequently the greater decline in catalytic effect is masked by the spontaneous decomposition of the chloro compound.

In all of the experiments to be described later, care was taken to renew the catalyst often to prevent this decrease in the activity of the catalyst from giving results which would be attributed to some variation in the conditions of the experiments. However, it must be borne in mind, particularly in the dechlorination of dichloro compounds, that variations in the catalyst during the course of an experiment may influence the results. Thus there seems reason to suppose that the effect of rise of temperature is always to increase the amount of hydrogen chloride formed. In some experiments, this effect was not observed, a result due, in all probability to the greater decrease in power of the catalyst during the experiment owing to the greater decomposition at the higher temperature.

In Table III the full record of a series of experiments on the rate of dechlorination at different temperatures is given. The rate increases up to 350°, while the amount of decomposition, as evidenced by the gas evolved, increases very rapidly above 350°. The iodine number of 225 (at 300 and 350°) indicates that about 75% of hexylene is present in these

TABLE III.

## DECHLORINATION OF CHLORO-HEXANE.

Chloro-hexane;  $d_0^{20}$ , 0.895.

Iodine Number of Hexylene = 302 (Calculated).

Catalyst: Unglazed Porcelain Impregnated with Barium Chloride.

Temperature of catalyst. ° C.	Percentage <sup>a</sup> recovered.	Condensate.		Gas evolved per 10 cc. chlorohexane.
		$d_0^{20}$	Iodine number.	
150	95	0.854	38	...
200	87	0.815	125	Nil
250	86	0.756	180	80
300	80	0.741	224	200
350	87	0.740	225	100
400	87	0.766	190	260
450	88	0.756	196	325
500	70	0.794	169	900

<sup>a</sup> These yields throughout this paper are percentages by volume of the condensate based on the volume of the chloro compound used and are not necessarily theoretical yields. In this instance the two values are almost identical.

condensates. Even at 150° quite a marked dechlorination of the chlorohexane was effected and this temperature is much below those recorded by earlier investigators for lower aliphatic chlorides.

TABLE IV.

## EFFECT OF VARIOUS CATALYSTS ON DECHLORINATION OF CHLORO-HEXANE.

Temperature of contact material.	Iodine number of condensate.	
	Unglazed porcelain.	Pyrex glass.
200	211	157
250	250	161
300	240	163

On comparing Tables III and IV, it is seen that unglazed porcelain alone acted as a more efficient catalyst than unglazed porcelain impregnated with barium chloride; and also that Pyrex glass gave poorer results than either of the two catalysts.

TABLE V.

Dichloro-hexane;  $d_0^{20}$ , 1.067

Iodine Number of Hexadiene = 620 (Calculated).

Catalyst.	Temperature. ° C.	Yield. %.	Condensate.	
			$d_0^{20}$	Iodine number.
Unglazed porcelain + BaCl <sub>2</sub> . . . . .	200	88	0.996	64
	300	88	0.942	123
	400	84	0.920	142
Unglazed porcelain alone . . . . .	350	75	0.874	188
	400	95	0.896	160
	450	90	0.875	176
	500	..	0.876	170

Thus again unglazed porcelain alone acted as a more efficient catalyst than unglazed porcelain impregnated with barium chloride. It will be noted that the dechlorination did not proceed as readily in this case and that apparently a higher temperature is necessary with the dichloro compound than with the monochloro compound. Decomposition of the hydrocarbons also occurred to a greater extent than was the case with the monosubstituted chloro compounds.

TABLE VI.  
CHLORO-HEPTANE;  $d_{40}^{20}$  0.914.  
Iodine Number of Heptylene = 260. (Calc.).

Iodine Number of Condensates Using Various Catalysts.				
Temperature of catalyst, ° C.	Unglazed Porcelain.	Alumina.	Unglazed porcelain barium chloride.	Pyrex glass.
150	100	...	...	...
200	127	198	178	52.5
250	192	238	187	64
300	260	254	170	83
400	265	250	180	181

Alumina is the most active catalyst up to 250° but of all the catalysts used it apparently lost its catalytic effect most rapidly as the result of carbonization. Pyrex glass is inferior to all of the other contact materials in promoting dechlorination at these temperatures and probably brings out only the influence of temperature on the reaction.

From the condensates obtained in these experiments, the olefins were readily separated by fractionation.

Thus, from 70 cc. of chloroheptane condensate the fractions described in Table VII were obtained. It will be noted that Fraction 90 to 110° has an iodine number close to that of heptylene.

TABLE VII.			
Boiling Point, ° C.	Volume, Cc.	$d_{20}^{20}$	Iodine Number.
90-110	37	0.744	237
110-145	14	0.823	157
145-155	13	0.903	53

TABLE VIII.  
DICHLORO HEPTANE;  $d_{40}^{20}$  1.068.  
Iodine Number of Heptadiene = 518. (calc.).

Temperature of catalyst, ° C.	Catalyst.	
	Unglazed porcelain.	Alumina.
200	163	181
300	170	173
350	194	126
400	216	114

Here again it will be noted that alumina is more effective at low temperatures than unglazed porcelain but that its catalytic activity *decreases*



with rise in temperature. A number of experiments carried out with chloro derivatives of cyclohexane, proved that these compounds split off hydrogen chloride more readily than the corresponding aliphatic compounds.

TABLE IX.  
Monochloro-cyclohexane;  $d_4^{20}$ , 1.003.  
Iodine Number of Cyclohexene = 310 (calc.).

Temperature of catalyst. °C.	Unglazed porcelain.	Catalyst alumina.	Pyrex glass.
200	245	260	192
250	275	256	172
300	272	234	214
400	297	152	274

Alumina is the most active catalyst with monochloro-cyclohexane at the lower temperatures; Pyrex glass probably demonstrates again only the influence of temperature in increasing the unsaturation of the product as 400° is approached.

TABLE X.  
Dichloro-cyclohexane;  $d_4^{20}$ , 1.179.  
Iodine Number of Dihydro-benzene = 317. (calc.).

Temperature of catalyst. °C.	Unglazed porcelain.	Alumina.
200	113	132
250	146	167
300	175	170
400	188	117

TABLE XI.  
Trichloro-cyclohexane;  $d_4^{20}$ , 1.266.  
Catalyst: Unglazed Porcelain.

Temperature of catalyst. °C.	Specific Gravity.	Benzene. %.
250	1.009	10
350	1.061	..
450	0.984	20

The percentage of benzene was determined by conversion into *m*-dinitrobenzene.

Experiments were also carried out with chlorobenzene, but apparently no dechlorination was produced even at 500°. According to Kramers<sup>11</sup> chlorobenzene is changed slowly into diphenyl and decomposition products at a red heat.

Thus it will be seen that, of the compounds tested, chlorobenzene is the most difficult to decompose and chloro-cyclohexane the most unstable at high temperatures. The condensates obtained from the experiments described above readily gave fairly pure olefins and diolefins on fractiona-

<sup>11</sup> Kramers, *Ann.*, **189**, 135 (1877).

tion and this method of removing hydrogen chloride from a chloro compound of a hydrocarbon can be recommended as a general method for the preparation of olefins in the case of monochloro-compounds. In the case of dichloro compounds, the yields of diolefins are small at low temperatures because of poor conversion, while at higher temperatures decomposition of the diolefin produced presumably occurs and there is a poor yield in these cases also.

In the following table are given the properties of some olefins prepared by this method.

TABLE XII.  
Properties of Hydrocarbons.

	Boiling point. °C.	$d_0^{20}$ .	Iodine number.
<i>Is</i> ohexene.....	64-65	0.684	294
<i>n</i> -Hexene.....	65-66	0.691	285
<i>n</i> -Heptene.....	97-98	0.727	237
Cyclohexene.....	80-81	0.809	303.5

It is quite unnecessary and useless to prepare a special catalyst for this operation (unless carbonization is prevented by some special method) since the catalyst loses its specific activity after a very short period of service.

#### Summary.

1. The chloro compounds of hydrocarbons containing 6 or 7 carbon atoms can be classified in the following order according to the ease with which hydrogen chloride is split off: hydro-aromatic, aliphatic and aromatic.
2. The stability of monochloro compounds of aliphatic hydrocarbons at a given temperature decreases with increasing molecular weight (at least until there are 7 carbon atoms in the chain).
3. There is much more extensive decomposition and greater difficulty in separating all the chlorine from dichloro compounds than from monochloro compounds.
4. Of the three catalysts alumina, unglazed porcelain and unglazed porcelain impregnated with barium chloride, alumina is the most efficient; but all three lose their activity rapidly owing to the "poisoning" produced by the decomposition of the hydrocarbons. (The "poisoning" in these cases is probably a mechanical effect due to the deposition of "carbon" on the catalyst).
5. A method for the preparation of olefins and diolefins from chloro compounds of hydrocarbons has been investigated and the method shown to be quite satisfactory for olefins. With diolefins, secondary decompositions occur and poor yields are obtained.