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INVESTIGATIONS INTO THE SYNTHESIS AND PRODUCTION TECHNOLOGY OF CHLORINATED ALKENES AND CHLORINATED CARBON COMPOUNDS[1/]

by

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As is generally known, some of the most important of the many processes for the utilization of petroleum hydrocarbons in petrochemical synthesis are the halogenation reactions, especially chlorination. Products manufactured by means of such reactions are extensively used in various branches of the national economy. For a number of years we have been carrying out investigations into the chlorination of C_1–C_5 hydrocarbons - alkanes, alkenes and alkadienes of normal and iso structure - in a fluidized bed, and processes have been developed for the synthesis of carbon tetrachloride, tetrachloroethylene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachlorobenzene, vinyl chloride, etc., both from the individual hydrocarbons and from their separate fractions. It has been established that the use of fluidized material, through the intensive mixing thus secured, enables the exothermic heat of reaction to be removed in a uniform manner, thus ensuring that the chlorination process takes place normally to give the optimum yields of saturated, unsaturated and cyclic hydrocarbons according to the reaction:

$$\begin{array}{lcl} C_nH_{2n+2} & & C_nCl_{2n+2} \\ & & C_nCl_{2n} \\ C_nH_{2n} & \xrightarrow[-HCl]{Cl_2} & C_nCl_{2n-2} \\ C_nH_{2n-2} & & C_nCl_{2n-4} \end{array}$$

and obviating destruction of the hydrocarbon by the reaction

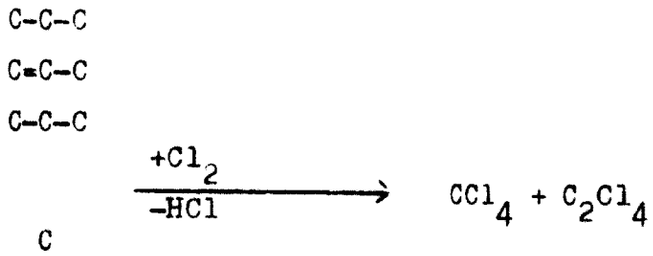
$$C_nH_{2n+2} + (n+1)Cl_2 \longrightarrow nC + 2(n+1)HCl$$

The investigations were carried out in two directions:

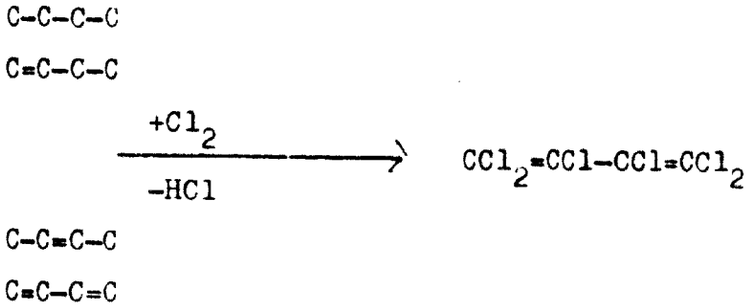
1. The synthesis of chlorinated carbon compounds and chloroalkenes by the direct chlorination of hydrocarbons;
2. The oxidative chlorination of alkenes and alkadienes.

It was discovered, through the strip chlorination of methane, ethane and ethylene, that the main product of the reaction is carbon tetrachloride and tetrachloroethylene, respectively. It was established, by the chlorination of C_3–C_4 hydrocarbons - alkanes, alkenes and alkadienes - both in the indivi-

dual state and in fractions with a stoichiometric proportion of components, that propane, propylene, isobutane and isobutylene are broken down and give full yields of carbon tetrachloride and tetrachloroethylene in accordance with the following reaction:



while n-butane, butylenes and butadiene are converted into hexachlorobutadiene:

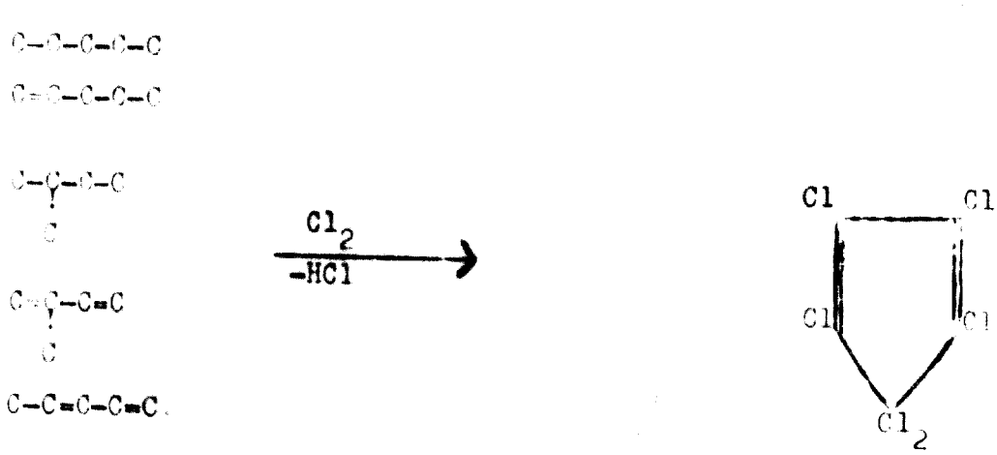


It was found that, in an excess of chlorine, C_5 hydrocarbons - n-pentane, isopentane, amylenes, isoprene, piperylene and their fractions - undergo cyclization, mainly with the formation of hexachlorocyclopentadiene, which is the basis component for synthesizing monomers of thermostable and heat-resisting polymeric materials.

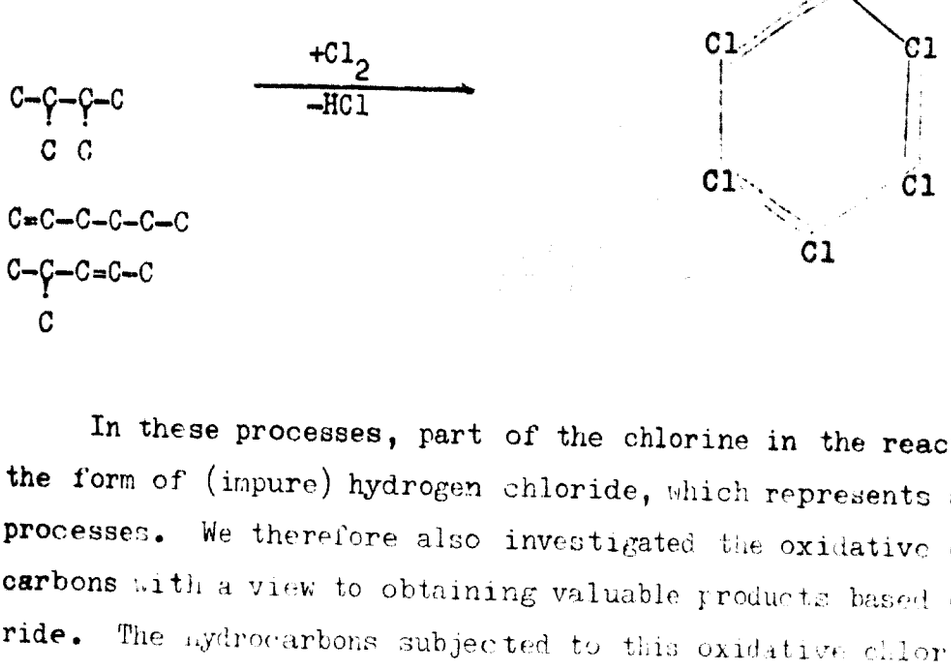
Table 1

Names of hydrocarbons	yields of chlorhydrocarbons, per cent					
	CCl_4	C_2Cl_4	C_4Cl_6	C_5Cl_6	C_6Cl_6	other chlorinated carbon compounds
methane	99.5	0.3	-	-	-	0.2
ethane	-	75	-	-	5	20
ethylene	-	80	-	-	5	15
propane	45	45	-	-	8	2
propylene	45	45	-	-	8	2
isobutene	60	32	-	-	7	1
isobutylene	61	31	-	-	6	2
n-butene	8	10	70	-	7	5
n-butylenes	7	9	75	-	6	3
n-pentane	6	7	8	65	6	8
isopentane	4	6	10	70	5	5
isoprene	3	4	6	80	6	1
hexanes	3	3	4	10	80	-

NOTE: process temperature: 350 - 500°C
molar ratio of chlorine to hydrocarbon: stoichiometric



Saturated, unsaturated, iso and normal C_6 hydrocarbons also undergo cyclization with formation of the full yield of hexachlorobenzene;



In these processes, part of the chlorine in the reaction is given off in the form of (impure) hydrogen chloride, which represents a waste product of the processes. We therefore also investigated the oxidative chlorination of hydrocarbons with a view to obtaining valuable products based on this hydrogen chloride. The hydrocarbons subjected to this oxidative chlorination were ethylene, propylene, propane, butanes of various structures, and butadiene.

It was established from the investigations that under the conditions of oxidative chlorination ethylene is converted into vinyl chloride, propylene into allyl chloride, and butadiene into chloroprene. Some conversions of synthesized chlorinated carbon compounds were also investigated.

As a result of this work, it was established that at high temperatures (600–800°C) all chlorinated carbon compounds, unlike hydrocarbons, are converted mainly into hexachlorobenzene.

First of all, hexachlorobutadiene was condensed with maleic anhydride and the best conditions for securing the maximum yield (100 per cent) of the new addition product 1,1,4,4,5,6-hexachloro-5-cyclohexene-2,3-dicarboxylic anhydride were determined. This reaction opens up new possibilities for the synthesis of a whole range of compounds which are excellent monomers for the production of thermostable polymeric materials.

On the basis of the research work carried out, the use on an industrial scale of the process for the production of carbon tetrachloride by the chlori-

nation of methane in a fluidized bed has been recommended, and this process is now being introduced in the Soviet Union. The processes for the production of allyl chloride by the oxidative chlorination of propylene and for the production of vinyl chloride from ethylene are now being further tested.

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