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# Reports of the Academy of Sciences of the USSR

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1957

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**Abstract**

**Full Text**

## **Reports of the Academy of Sciences of the USSR**

1957. Volume 116, No. 5

**Chemistry**

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### **DEEP CHLORINATION OF PROPANE ON A MOVING CONTACT**

Recently, there has been an ever-increasing interest in products of deep chlorination of hydrocarbons, in particular alkanes. This is explained, in addition to purely theoretical interest, by the wide use of polychloro-substituted compounds as intermediates in the production of pesticides, synthetic fibers, and other products of organic synthesis.

As is known, the chlorination reaction of alkanes is accompanied by considerable heat evolution, which complicates the process and, in a number of cases, leads to the practical impossibility of synthesizing the desired chloride under industrial conditions.

From the standpoint of removing the heat of reaction and creating conditions that ensure deep chlorination of alkanes, attention is therefore deserved by the possibility of carrying out the chlorination reaction on a moving chemically inert heat carrier, by analogy with processes that have found broad application in petroleum refining.

#### **Fig. 1. Diagram of the model setup**

Owing to the direct contact of the reactants with the moving heat carrier, the necessary condition for removal of the heat of reaction is ensured comparatively easily while maintaining the temperature regime of the process.

In the periodical and patent literature, it has been proposed to carry out the chlorination reaction of methane in a boiling bed of catalyst and heat carrier<sup>(1-3)</sup>. However, no experimental work has been published.

Fig. 2. Dependence of the composition of propane chlorination products on a moving heat carrier on the reactant ratio: 1 –monochloropropanes, 2 –dichloropropanes, 3 –trichloropropanes, 4 –polychloropropanes

Figure 2: Fig. 2. Dependence of the composition of propane chlorination products on a moving heat carrier on the reactant ratio: 1 –monochloropropanes, 2 –dichloropropanes, 3 –trichloropropanes, 4 –polychloropropanes

## Experimental Part

Experiments on the chlorination of propane were carried out in a model unit with a moving heat carrier (mullite).\* The layout of the unit and the motion of the heat carrier are shown in Fig. 1.

Under the influence of gravity, the heat carrier moves from the separator through the regenerator and reactor at a rate determined by the output of the screw feeder; from the screw the heat carrier enters the pneumatic-transport hopper and then again the separator. Thus, a closed cycle of heat-carrier movement is achieved. Regeneration of the heat carrier by burning off the carbon deposited on it during the reaction was carried out by flue gases entering the regenerator. Hydrogen was used as the fuel.

**Fig. 2.** Dependence of the composition of propane chlorination products on a moving heat carrier on the reactant ratio: **1** –monochloropropanes, **2** –dichloropropanes, **3** –trichloropropanes, **4** –polychloropropanes

Pneumatic transport and the furnace were constructed according to the suction principle, which is more convenient than the pressure principle for carrying out chemical processes in general and, in particular, processes involving the use of reagents such as chlorine, since with such a pneumatic-transport system the possibility of gas leakage from the system is eliminated.

The heat carrier used was mullite (fused stone) with a granule diameter of 3–5 mm. The reactor was made of concrete based on high-alumina flour and chips, sodium silicofluoride, and water glass; the regenerator was made of refractory brick with a carbon-steel cone. All other parts were made of stainless steel.

The temperature of the heat carrier was measured by thermocouples installed in the regenerator, at the outlet of the heat carrier from the regenerator, at the inlet of the heat carrier to the reactor, and at its outlet from the reactor.

The reactants—propane and chlorine—were fed into the lower part of the reactor, and the products were withdrawn from the upper part of the reactor. Chlorine was fed in two or three stages. The reaction products were drawn off from the reactor through a ball condenser, in which the higher-boiling portion of the product was condensed, then passed through a column irrigated with water to wash out hydrogen chloride and through a column irrigated with a 20% solution of caustic potash to absorb free chlorine. The reaction products, washed free of hydrogen chloride and chlorine, passed through gas-washing bottles with

potassium iodide solution and sulfuric acid and were sent for condensation into traps cooled with a mixture of dry ice and acetone.

The noncondensed gases (unreacted propane, inert gases, etc.) were drawn off by a vacuum pump, and a portion of the gas was taken into a gasometer for analysis. Regulation of the hydraulic regime of the reactor was carried out by blowing flue gases into the lower part of the reactor. Withdrawal of the reaction product from the reactor was regulated according to the readings of differential manometers.

The initial propane had the same composition as in its thermal and catalytic chlorination under laboratory conditions:  $C_3H_8$  95.3 wt. %,

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\* The unit was kindly made available to us by Ya. P. Choporov, who was the first to carry out successfully on it the deep chlorination of methane. We take this opportunity to express our deep gratitude to him.

$C_2H_6$  4.2 wt. %,  $C_4H_{10}$  0.5 wt. %. In experiments Nos. 101–104 (see Table 1) liquid chlorine was used, and in the remaining experiments electrolytic gaseous chlorine. The experiments were carried out at a temperature of 360–395° and a space velocity of 60–180 hr<sup>-1</sup>. The effect of the propane-to-chlorine ratio and of the space velocity on the yield and composition of the reaction products was studied. The results of the experiments performed are given in Table 1 and in Figs. 2–3.

**Fig. 3.** Effect of space velocity on the composition of the products of propane chlorination on a moving heat carrier. Designations as in Fig. 2

As can be seen from Table 1, changing the chlorine-to-propane ratio from 1.58 to 2.1 leads to a slight decrease in the yield of di- and trichloropropanes and to an increase in the yields of polychloropropanes. A further increase in the chlorine-to-propane ratio to 2.38 (experiments Nos. 109, 110) at relatively high space velocities leads to an increase in the yield of di- and trichloro derivatives to 80–81%, as compared with 68–73% for a chlorine-to-propane ratio equal to 2.1. The amount of monochloropropanes formed is insignificant

#### Table 1

**Results of experiments on thorough chlorination of propane in a model unit with moving contact**

Experiment No.	Temperature, °C	Duration of experiment, min	Fed to reactor: chlorine, n.l.	Fed to reactor: propane, n.l.	Molar ratio $Cl_2/C_3H_8$	Space velocity, $hr^{-1}$	Product	Product	Product	Product
							composition, wt. % (according to distillation data): monochlorides	composition, wt. % (according to distillation data): dichlorides	composition, wt. % (according to distillation data): trichlorides	composition, wt. % (according to distillation data): higher chlorinated
101	395	43	31.8	14.8	2.15 : 1	42	7.3	39.5		53.2
102	360	60	44.8	21.4	2.1 : 1	60	2.0	25.3	43.1	29.6
103	365	90	67.1	34.5	1.95 : 1	92	3.4	32.1	42.8	21.7
104	371	90	134.4	63.4	2.12 : 1	180	4.1	27.6	45.1	23.2
105*	371	26	38.7	21.4	1.8 : 1	55	1.1	25.7	47.8	25.4
106	381	60	89.6	42.5	2.11 : 1	120	1.0	27.6	41.1	30.3
107	368	90	100.8	64.0	1.58 : 1	150	2.5	28.5	46.8	22.2
109	370	39	87.2	36.7	2.38 : 1	113	3.4	31.6	48.0	17.0
110	373	60	134.4	56.8	2.37 : 1	174	2.4	31.1	50.1	16.4

\* In experiments Nos. 105–110, chlorine is fed directly after electrolysis of an aqueous sodium chloride solution.

(1–4%) and remains almost constant when the chlorine-to-propane ratio is varied from 1.58 to 2.38.

Changing the space velocity from 60 to 180  $hr^{-1}$  at a chlorine-to-propane ratio equal to  $\sim 2.1 : 1$  has little effect on the composition of the product. An increase

in space velocity leads to a slight increase in the yield of di- and trichloro derivatives of propane at the expense of a decrease in the yield of polychloropropanes (see Fig. 3).

Replacing nitrogen purging by flue gases containing 14–16% oxygen and replacing liquid chlorine by electrolytic chlorine had no appreciable effect on the composition of the chloro derivatives, i.e., under these conditions oxygen did not hinder the chlorination reaction.

Feeding chlorine in three stages instead of two leads to a decrease in pyrolysis and the yield of polychloropropanes. Within the investigated limits of the chlorine-to-propane ratio, no breakthrough of free chlorine was observed.

Experiments on a model unit with a moving heat-carrier contact showed that the yield of dichloride does not exceed 25–30%. With an increase in the ratio of chlorine to propane, an increase was observed in the ratio of chlorine contained in hydrogen chloride to chlorine in the product, which indicates an increase in the degree of pyrolysis. The products obtained were separated in a rectification column with glass packing, equivalent in plate-separating capacity to 20 theoretical plates, into individual fractions. The characteristics of the fractions are given in Table 2.

**Table 2**

Fraction	$d_4^{20}$	$n_D^{20}$	Cl, %	Mol. wt.
Monochloropropanes	1.0601	1.4200	—	81.3
Dichloropropanes	1.2807	1.4560	65.4	116.2
Trichloropropanes	1.4095	1.4846	73.2	150.5
Higher chlorides	1.5480	—	—	211.6

As a result of the separation of the individual fractions, 1,1-, 1,2-, 1,3- and 2,2-dichloropropanes, 1,1,2- and 1,2,3-trichloropropanes, and 1,1,1,2- and 1,1,2,2-tetrachloropropanes were isolated and their physicochemical properties were determined. The higher chlorides were not investigated.

The results of the experiments carried out on deep chlorination of propane on a moving layer of heat carrier showed that this process may be important for more thorough chlorination of propane and for the use of the reaction products for destructive chlorination in order to obtain carbon tetrachloride and tetrachloroethylene. The moving heat carrier and stepwise introduction of chlorine are evidently the decisive factors ensuring the normal course of the reaction in such deep chlorination of propane.

Received  
20 VII 1956

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