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Abstract

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L. M. Kogan, N. S. Rabovskaya

INITIATION OF VINYL CHLORIDE POLYMERIZATION BY REACTIONS OF LOWER UNSATURATED CHLOROCARBONS WITH TRIETHYLALUMINUM

In investigating the properties of lower unsaturated chlorocarbons, it was of interest to determine the influence of these compounds on the polymerization of vinyl chloride in the presence of triethylaluminum and to compare the results with the recently discovered high activity of carbon tetrachloride in this reaction ([1]).

The following fully chlorinated compounds were tested: ethylene, propylene, butadiene-1,3, pentadiene-1,3, cyclopentadiene-1,3, and cyclopentene, for which, in specially staged earlier experiments, the fact of interaction with triethylaluminum in the absence of vinyl chloride had been established.

Experimental Part

Characterization of the starting substances. Vinyl chloride of high purity was obtained by additional purification of the rectified product in an apparatus consisting of sequentially connected columns with ammoniacal cuprous chloride solution (3 columns), two columns with distilled water, and a system of columns filled with glass wool, calcium chloride, silica gel, and activated aluminum oxide. Triethylaluminum with a content of the main substance of more than 95% (ethylaluminum ethoxide content up to 5%; halogen derivatives of aluminum alkyls were absent) was obtained by symmetrization of sesquibromide followed by thorough rectification. The chlorocarbons had the constants given in Table 1.

Table 1

Constants of chlorocarbons

Chlorocarbon	n_D^{20}	d_{20}^{20}	M.p., °C
CCl_4	—	—	—
C_2Cl_4	1.5050	1.6251	—

Chlorocarbon	n_D^{20}	d_{20}^{20}	M.p., °C
C_3Cl_6	1.5500	1.7680	—
C_4Cl_6	1.5560	1.6832	−18.6
C_5Cl_8	1.5720	1.7540	—
ψ-C_5Cl_6	1.5650	1.7122	6.5
ψ-C_5Cl_8	—	—	39.5–40.5

Experimental conditions. The experiments were carried out in ampoules made of molybdenum and Pyrex glass, of 100 ml volume, previously thoroughly deaerated in a special apparatus ([2]). In each experiment, 20 g of vinyl chloride and various amounts of $(C_2H_5)_3Al$ and chlorocarbons were used. The duration of polymerization was 10 hr, temperature 20°. The limiting viscosity number was determined at 20° from solutions in cyclohexanone.

Results of the experiments and their discussion. Neither the chlorocarbons nor triethylaluminum, taken separately, caused polymerization of vinyl chloride. Their joint presence, however, led to an effective polymer-formation reaction, which, apparently, is due to the interaction of the chlorocarbons with triethylaluminum, proceeding through the formation of radical-type products with abstraction of a chlorine atom. Indeed, the literature describes the reaction of carbon tetrachloride with triethylaluminum, leading to the forma-

···formation of alkylaluminum chlorides ([2], [3]). In specially designed experiments we showed that other chlorocarbons used in the present work also interacted with triethylaluminum. The nature of the interaction depended on the nature of the chlorocarbon taken. The least active was C_2Cl_4; C_2Cl_6 reacted somewhat more actively; the remaining chlorocarbons reacted very vigorously, and in most cases the reaction was explosive in character. In the reaction products a mixture was found

Table 2

Polymerization of vinyl chloride in the presence of chlorocarbons and $(C_2H_5)_3Al$

$C_{nCl}m$	PVC yield, %	$[\eta]$	$C_{nCl}m$	PVC yield, %	$[\eta]$
CCl_4	13.0–15.5	0.18–0.20	C_5Cl_8	11.5	0.14
C_2Cl_4	1.8–2.0	0.24	ψ-C_5Cl_6	4.5–5.2	0.15
C_3Cl_6	6.5	0.14	ψ-C_5Cl_8	7.5	0.15
C_4Cl_6	6.2–8.7	0.20			

of liquid and solid products containing C, H, and Cl. Hydrolysis of the reaction mass led to the formation of chloride ion, which indicates the presence

of alkylaluminum chlorides formed through abstraction of chlorine atoms from chlorocarbons, as in the case of CCl_4 ([2], [3]).

In the polymerization of vinyl chloride under the action of the initiating system studied ($3.3 \cdot 10^{-3}$ mole of $(C_2H_5)_3Al$ and $3.3 \cdot 10^{-2}$ mole of chlorocarbons), the yield of polyvinyl chloride depended on the nature of the chlorocarbon used (Table 2), which approximately corresponded to the activity of the individual chlorocarbons in the reaction described above.

All the tested unsaturated perchlorocarbons were less active than CCl_4, which apparently is explained by the passivating effect of the double bond. C_2Cl_4 proved to be the least effective. The other chlorocarbons occupied an intermediate position. It was noted that introduction into the C_2Cl_4 molecule of a reactive CCl_3 group increased the activity of the system. An analogous regularity was observed on going from C_4Cl_6 to C_5Cl_8. The lower activity of ψ-C_5Cl_8 compared with its linear isomer (C_5Cl_8) can be explained by the absence in the former of an active CCl_3 group.

At a constant content of $(C_2H_5)_3Al$, the polymer yield increased with an increase in the amount of chlorocarbon added; this was especially pronounced for carbon tetrachloride:

$$\text{With } CCl_4/(C_2H_5)_3Al = 10/1, \text{ PVC yield } 13 \div 15\%.$$

$$\text{With } CCl_4/(C_2H_5)_3Al = 45/1, \text{ PVC yield } 21 \div 26\%.$$

A decrease in the molar ratio of chlorocarbons to triethylaluminum led to an irregular reaction, often accompanied by an explosion. Thus, for example, an explosive character of the process was observed at a molar ratio of chlorocarbon to $(C_2H_5)_3Al$ of 2.5 and below, and also at a content of $(C_2H_5)_3Al$ greater than $3.3 \cdot 10^{-3}$ mole (the amount of chlorocarbons was not changed in this case).

The results presented show that unsaturated chlorocarbons in a mixture with triethylaluminum cause the polymerization of vinyl chloride under mild conditions, which is a consequence of interaction of the components of the initiating system. The activity of the system depends on the nature of the chlorocarbon used.

Moscow State University
named after M. V. Lomonosov

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REFERENCES

1. G. A. Razuvaev, K. S. Minsker, Yu. A. Sangalov, *DAN*, **158**, No. 1 (1964).

2. C. Edeh, H. Feilchenfeld, *J. Phys. Chem.*, **66**, 1354 (1962).

3. J. W. Collette, *J. Org. Chem.*, **28**, 2489 (1963).

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