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Development of ecologically balanced industrial technology for obtaining chlorine-containing monomers

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Plans for the development of the national economy foresee the promise of a radical upheaval of technological processes based on the more progressive achievements of the work of fundamental and applied scientific investigators. Chemical technologies occupy an important place when putting this programme into effect, and safeguard practically all regions of society. Halogen-containing compounds play an important role in industrial manufacture. This is particularly so for organochlorine compounds which are involved in a number of the largest multitonnage products. It is also known that their manufacture yields many ecological problems which are difficult to resolve. Thus the manufacture of polyvinyl chloride, which reaches a world volume of more than 20 million tons per year, yields up to 9% practically unusuable waste products. It is possible to regard as ecologically unbalanced the current manufacture of several other organochlorine substances, particularly chloroprene, the monomer for obtaining rubbers possessing several desirable properties (oil stability, ozone-stability, incombustibility, elasticity).

A set of studies has been carried out in the Institute of Chemistry of the Bashkir Scientific Centre, Urals Division of the Academy of Sciences of the USSR which were directed towards the creation of technological processes for obtaining chlorine-containing products allowing for modern ecological requirements.

As the basis of our concept we rejected gas phase or other high temperature reactions which are not as a rule capable of high selectivity. It is clear that under conditions of effecting multitonnage technology each percentage point of selectivity causes either the appearance of an enormous quantity of waste products or their abrupt curtailment. We included within our interests the technology of making unsaturated chlorohydrocarbons of composition C_2-C_4 which have high practical value.

Since the selectivity of these chemical processes is determined by the elimination of hydrogen halide from compounds obtained by the previous chlorination of the corresponding organic compounds, attention was paid mainly to the development of catalysts guaranteeing high yields of the desired products. At the same time serious attention was paid to the technological aspects having no less important value in the creation of ecologically safe manufacture. We therefore started from the premise assumed by us of the priority of liquid phase methods effected under mild conditions. The use of the closed cycle principle was an important concept. Thus sodium chloride was formed on alkaline dehydrochlorination and does not usually find regular use. In our scheme high purity sodium chloride is obtained, it may be used for electrolysis, for making sodium carbonate by the Solvay process and even in the food industry.

High efficiency catalysts guaranteeing practically complete selectivity for the alkaline dehydrohalogenation reaction have been developed by us based on new concepts in interphase catalysis. This unique phenomenon of organic synthesis discovered in the seventies immediately attracted the attention of numerous investigators who directed their work both to its use in the synthesis of various organic compounds and to establishing the mechanism for carrying out the catalytic process.[1–3] It is known that various quaternary compounds such as crown ethers, polyethyleneglycol, etc. display catalytic activity in interphase reactions and are widely used. Analysis of the known work on the theoretical aspects of catalysis of interphase reactions shows that there is no unequivocal understanding of the role of catalysts at present.

In our view the generally accepted concept, according to which anion exchange is the initial catalytic act in interphase processes catalysed by quaternary compounds, particularly quaternary ammonium salts, has not been argued sufficiently. Confirmation of the formation of the corresponding ion pairs in the organic phase by deprotonation of the substrate has not been confirmed by reliable proof. On the contrary there are ideas on the formation of alkoxides from the corresponding quaternary ammonium salts and alcohols in the presence of concentrated aqueous solutions of alkali metal hydroxides. All this indicates the absence up to the present of a theory explaining reliably the rules of interphase catalysis.

Since quaternary ammonium salts are widely used in practice as catalysts because of their availability and fairly high catalytic activity, our attention was concentrated on these compounds during the investigation.

The known high catalytic effect of tetraalkyl(trialkylbenzyl)-ammonium alkoxides in the dehydrohalogenation reaction of polyhaloalkanes under the action of concentrated aqueous solutions of NaOH served for a while as the reason for the direction of our investigations.[4]

Some data obtained on dehydrochlorinating 1,2-dichloroethane are shown for illustration (Table 1).

Table 1. The effect of anion structure on the rate (W) of formation of vinyl chloride (temperature 50–55 °C, molar ratio C_2H_4 : NaOH = 1 : 2, NaOH — 50%, reaction time 30 min, quantity of catalyst 0.3 mol%).

Catalyst	10^4 W, mol litre^{-1} sec^{-1}	Dichloroethane conversion, %
$(C_2H_5)_3NCH_2C_6H_5^+Cl^-$	8.6	28.5
$(C_2H_5)_3NCH_2C_6H_5^+CH_3O^-$	13.9	45.7
$(C_2H_5)_3NCH_2C_6H_5^+C_2H_5O^-$	16.8	56.3
$(C_2H_5)_3NCH_2C_6H_5^+C_4H_9O^-$	20.7	68.1
$(C_2H_5)_3NCH_2C_6H_5^+C_7H_{15}O^-$	21.7	71.6
$(C_2H_5)_3NCH_2C_6H_5^+C_6H_5CH_2O^-$	31.6	99.5
$(C_2H_5)_3NCH_2C_6H_5^+ClC_6H_4CH_2O^-$	37.9	99.7 *
$(C_4H_9)_4N^+OH^-$	9.3	30.8
$(C_4H_9)_4N^+Cl^-$	9.2	30.6
$(C_4H_9)_4N^+Br^-$	9.6	31.8

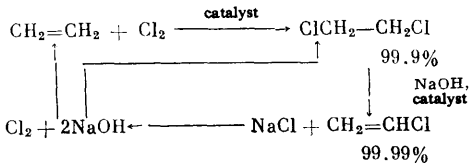
* Reaction time 24 min.

As is seen from the data of Table 1 tetraalkyl(trialkylbenzyl)-ammonium alkoxides display significantly higher catalytic activity compared with other quaternary ammonium salts. It was natural to study this phenomenon deeply in competing β-elimination and

nucleophilic substitution reactions having in mind the constantly increasing ecological requirements for the manufacture of unsaturated C_2-C_4 chlorohydrocarbons. Absolute priority was given to a fundamental investigation of the mechanism of the catalysts found since according to our concept it must have a general character independent of the type of interphase reaction. In addition a true understanding of the catalytic process creates a basis for its control. The conclusion drawn from our investigations was that the catalysis of β-elimination is effected not by the individual quaternary ammonium salts but by the formation of complexes by them.[5-8]

The reaction occurs synchronously in the organic phase and on the surface separating the phases. The principal complex is an associate of the quaternary ammonium salt and proton-donating compounds. Associates are solvated in the organic phase with the organohalogen substrate and interact with organic base on the phase separation surface. The mechanism proposed excludes anion exchange of the catalyst as the initial catalytic act. It is also important that the catalytic activity of the complex is determined both by the basicity of the proton-donating component and by the charge on the nitrogen atom in the tetraalkyl(trialkylbenzyl)-ammonium cation. The presence of an allyl substituent increases catalytic activity appreciably (allyl effect). On this basis a series of highly effective and readily available catalysts for β-elimination in polyhaloalkanes has been developed. The application of these catalysts to the process of obtaining vinyl chloride by the alkaline liquid phase dehydrochlorination of 1,2-dichloroethane affords virtually the first ecologically clean technology.

We are proposing a new strategy for industrial establishments making polyvinyl chloride based on closed cycles with complete chlorine consumption at the place of manufacture. One such cycle comprises the preparation of chlorine and sodium hydroxide by electrolysis, the selective chlorination of ethylene and the dehydrochlorination of 1,2-dichloroethane, and preparation of polymer by ecologically pure technology and, finally, the return of sodium chloride to electrolysis. The efficiency of the process may be judged from the stage of synthesising vinyl chloride. A reactor with a working volume of 1 m^3 has a throughput of 20 000 to 40 000 tons per year. Since the monomer is obtained with a purity never previously achieved in industry the waste products are reduced to a fraction of a percent. The manufacture of polyvinyl chloride resin suitable for making articles of the highest quality and a long use period may be developed from the high purity monomer. The preparation of articles for medicinal techniques, including single-use syringes, is a particularly important use for high purity polyvinyl chloride. The ecologically balance cycle developed for obtaining vinyl chloride may be depicted schematically in the following manner.



Two equivalents of sodium hydroxide are formed at the electrolysis stage for each equivalent of vinyl chloride. This is one of the positive factors in the organisation of the manufacture of unsaturated organochlorine monomers with complete consumption of chlorine. In this case half of the quantity of sodium hydroxide obtained becomes a commercial product. Comparative data are given in Table 2 which characterise the features of vinyl chloride manufacture by the gas method and by the liquid dehydrochlorination of dichloroethane.

$$CH_2Cl—CH_2Cl \begin{cases} \longrightarrow CH_2=CHCl + HCl, \\ \longrightarrow CH_2=CHCl + NaCl. \end{cases}$$

Table 2. Technological process for obtaining vinyl chloride.

Main features of manufacture	Gas phase method	Liquid phase dehydrochlorination of dichloroethane
Reaction selectivity, %	95–98	99.99
Dichloroethane conversion, %	50–60	99.5–99.6
Conditions:		
Temperature, °C	500–550	55–60
Pressure, atm	20–30	without pressure
Unutilisable waste products, thousands of tons per 10 million tons	500–110	1–2

Such features of existing processes as the incomplete conversion of the initial dichloroethane and the high temperature and pressure, are some of the factors raising the price of the final product and complicating the overall maintenance of the technological process. The large quantity of waste products also compels critical treatment of this technology. The structure and composition of the waste products are such that the problem of their utilisation has not been solved and it is doubtful whether it may be solved in a forseeable time. There are harmful organochlorine products, spent sulphuric acid and 'sooty-resinous pulp' (according to the terminology of the production workers) among the waste products. Special areas are separated off for the burial of similar 'gifts'. Consequently the start-up of pilot-plant equipment to operate at the Kaustik Sterlitamaksk Industrial Company is an urgent requirement. The putting into operation of new technology is impossible without its careful analysis under factory conditions. Here it is necessary to add that the unit cost of vinyl chloride obtained by the technology proposed allowing for capital outlay and profit rate will be several percent lower than by the gas phase method. From the ecological point of view the technology proposed by us is preferable.

The closed cycle concept proposed by us has also been suggested for the manufacture of chloroprene rubber. We are convinced that the adoption of our proposal will loosen the stiff ecological knots tying the technology used at present.

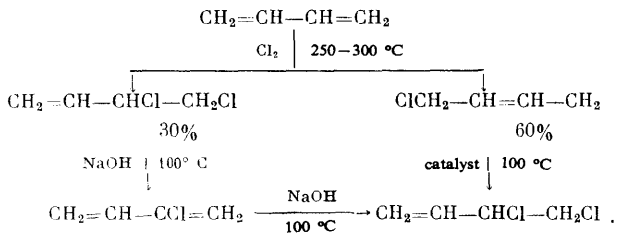
Data from operating a pilot-plant indicate that technology giving almost 10 times less chlorine-containing waste products and leading to practically zero quantities of waste water may be possible. It is extremely important to simplify the technological process, to miniaturise the devices and to replace alloy by more available materials. In addition provision is made in the proposed process for the preparation of dichlorobutane, which is not manufactured in the USSR.

Our principle of operation has replaced the high temperature vapour phase by liquid phase processes taking place under mild conditions which we have applied to the chlorination of butadiene. This step in the existing industrial synthesis of chloroprene, which yields an extremely large quantity of waste products and direct losses (the recurrent result of being out of order due to corrosion of expensive imported compressors and other equipment), is converted

by our proposed catalytic liquid phase method into a step clearly moving the ecological characteristics of the whole technology in a better direction. It therefore turned out to be important that the products of more extended chlorination resulting without fail in the gas phase chlorination of butadiene, were completely absent. As a result of this the need to create special places for burial was reduced.

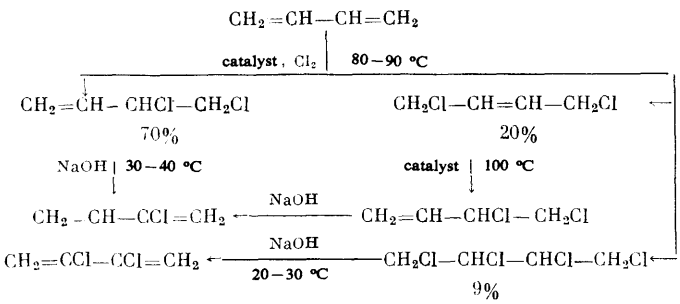
The features of the process for obtaining chlorine-containing monomers by the existing manufacture and by the method developed by us are shown below.

Existing technology



Unutilisable waste products are 7–9% on chlorination, the total quantity of waste products is 250 kg per ton of chloroprene.

Method developed by us



Unutilisable waste products are 0.5–1% on chlorination. Total quantity of waste products are 20–30 kg per ton of chloroprene.

New catalysts have enabled the development of ecologically clean technology for the synthesis of Triallate, an effective herbicide against wild oats. The process is characterised by little waste and a high quality product. The key problem in this technological process is the synthesis of 1,1,2,3-tetrachloropropene from 1,2,3-trichloropropane. This is a four-step process [reactions (1)–(4)], the step selectivity is low, which gives a large quantity of unutilisable chlorine-containing waste products. To this it is necessary to add a large volume of waste water containing harmful and as yet unidentified contaminants.

$$CH_2Cl-CHCl-CH_2Cl \xrightarrow[90\ ^\circ C]{NaOH} \underset{70\%}{CH_2=CCl-CH_2Cl}, \quad (1)$$

$$CH_2=CCl-CH_2Cl \xrightarrow{Cl_2} \underset{25\%}{CH_2Cl-CCl_2-CH_2Cl}, \quad (2)$$

$$CH_2Cl-CCl_2-CH_2Cl \xrightarrow{Cl_2} \underset{35\%}{CH_2Cl-CCl_2-CHCl_2} + HCl(?), \quad (3)$$

$$CH_2Cl-CCl_2-CHCl_2 \xrightarrow[90\ ^\circ C]{NaOH} \underset{71\%}{CH_2Cl-CCl=CCl_2}, \quad (4)$$

$$(iso\text{-}C_3H_7)_2NH + COS + NaOH \rightarrow (iso\text{-}C_3H_7)_2N-\overset{\overset{O}{\|}}{C}-SNa \xrightarrow{CH_2Cl-CCl=CCl_2} \rightarrow \underset{85\%}{(iso\text{-}C_3H_7)_2N-\overset{\overset{O}{\|}}{C}-S-CH_2-CCl=CCl_2}. \quad (5)$$

In addition the final step is characterised as unstable due to the lability of the intermediate product, which also reduces the manufacturing efficiency.

The new technology developed by us and tested in laboratory and pilot-plant equipment possesses high selectivity at all steps and is illustrated in the scheme shown below. It must be stressed that the catalysts found proved to be extremely effective particularly at the step of obtaining Triallate.

$$CH_2Cl-CHCl-CH_2Cl \xrightarrow[catalyst]{NaOH} \underset{98-99\%}{CH_2=CCl-CH_2Cl}, \quad (6)$$

$$CH_2=CCl-CH_2Cl \xrightarrow{Cl_2} \underset{92\%}{CH_2Cl-CCl_2-CH_2Cl}, \quad (7)$$

$$CH_2Cl-CCl_2-CH_2Cl \xrightarrow[catalyst]{NaOH} \underset{96\%}{CH_2Cl-CCl=CHCl}, \quad (8)$$

$$CH_2Cl-CCl=CHCl \xrightarrow{Cl_2} \underset{98-99\%}{CH_2Cl-CCl_2-CHCl_2}, \quad (9)$$

$$CH_2Cl-CCl_2-CHCl_2 \xrightarrow[catalyst]{NaOH} \underset{100\%}{CH_2Cl-CCl=CCl_2}, \quad (10)$$

$$(iso\text{-}C_3H_7)_2NH + COS + CH_2Cl-CCl=CCl_2 \xrightarrow[0-10\ ^\circ C]{catalyst} \rightarrow \underset{98-99\%}{(iso\text{-}C_3H_7)_2N-\overset{\overset{O}{\|}}{C}-S-CH_2-CCl=CCl_2}. \quad (11)$$

The advantage of the developed technology is a sharp drop in waste products and also an appreciable reduction (6–7 times) in the quantity of waste water. The process achieves an ecological balance previously inaccessable.

The examples given graphically demonstrate the unlimited possibilities for chemistry to solve ecological problems in practice. It is necessary to carry out an analysis of the existing technology, to develop processes absolutely acceptable from the point of view of preserving the environment and to develop, together with ministries, a long-term plan of fundamental and applied investigations directed towards the creation of chemical processes new in principle. A fairly radical reconstruction of the chemical industry must be expected in line with trends in the development of modern science and chemical technology and the urgently dictated requirements of ecology.

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