tra are given in Table 2). A mixture of isomers of (XIIc) with M⁺ 282 was obtained in the DHC of (VIc) (experiment 7, Table 1). Gas-liquid chromatographic analysis of (XIIc) gave two peaks with 2:1 ratio; the NMR spectrum did not contain signals for isomeric (XIIIc).

The alkaline DHC of (VIa), (VIc), and (VId) was carried out according to a procedure analogous to that described in our previous work [3]. The NMR spectra of products (XIIIa), (XIIIc), and (XIIId) are given in Table 2.

CONCLUSIONS

Chloroolefins or α -chlorostilbenes were synthesized by the dehydrochlorination of polychloroalkanes or 1,1-diary1-2,2-dichloroethanes catalyzed by Mo(CO)₆.

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COMPLEXES IN THE CATALYSIS OF THE LIQUID-PHASE DEHYDROCHLORINATION OF POLYCHLOROALKANES

s.	s.	Shavanov, G. A. Tolstikov,	and UDC	541.49:541.128:542.944.6:
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The dehydrochlorination of 1,1,2-trichloroethane by aqueous NaOH catalyzed by triethylbenzylammonium alkoxides (TEBAA) [1] proceeds with ≥99.9% yield

$$Cl_2CH-CH_2Cl \xrightarrow{TEBAA}{NaOH} Cl_2C=CH_2$$
 (1)

An oily orange product is formed in the organic layer upon conversion greater than 75%, when the vinylidene chloride formed is removed from the reactor.

The same effect is observed in the dehydrochlorination of 1,2-dichloroethane catalyzed TEBAA [2]

$$ClCH_2 - CH_2Cl \xrightarrow{\text{TEBAA}} ClCH = CH_2$$
(2)

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TABLE 1. Results of the Chromatographic Analysis of CAOP (%), $C_2H_4Cl_2:NaOH = 1:1.1$, 75-80°C, [NaOH] = 50%, TEBAC: $C_6H_5CH_2OH = 1:1$

CAOP layer	Di- chloro- ethane	Tri- ethyl- amine	Ben- zalde- hyde	Benzyl alcohol	Diethyl- benzyla- mine	Chloro- ethyl benzyl ether	Benzyl chloride	Dibenzyl ether
Upper (inactive) Lower (active) Lower after removal	8,4 X * 88.5 X 21,2	41.3 47.0 - 5.7	$0,2 \\ 0.22 \\ 0.1 \\ 1.0 \\ 0,5$	- 5.2 45,2 26,1	6,7 7,3 0,4 3,9 4,5	$0.1 \\ 1,09 \\ 4,7 \\ 40.8 \\ 33,2$	41,5 45.3 1,0 9,1 8,3	- 0,05 0,4 0,6
$C_2H_4Cl_2$	x	7,3	0,7	33,1	5,7	42,2	10,5	1,2

*X) without taking account of C₂H₄Cl₂.

Since it is easier to remove vinyl chloride from the reaction zone, we studied the composition and properties of the oily product of reaction (2).

The organic product was removed from the organic phase. Upon the addition of this product as a catalyst, the reaction rate is virtually the same as in catalysis by TEBAA. The catalytically active organic phase (CAOP) has a neutral medium; the chloride ion content calculated relative to triethylbenzylammonium chloride (TEBAC) is 1-3%. We propose that TEBAC is formed by the reaction of TEBAA with $C_2H_4Cl_2$ and this reaction is the major step under phase transfer catalysis conditions. This was supported by Dehmlow and Dehmlow [3], who proposed that tetraalkylammonium alkoxides may be formed from quaternary salts and alkali metal alcoholates in the inorganic phase or on the phase separation surface with subsequent transfer to the organic substrate, which may be represented by the following scheme:

 $[(C_{2}H_{5})_{3}CH_{2}C_{6}H_{5}N]^{+}Cl^{-} \xrightarrow[NoH]{} [(C_{2}H_{5})_{3}CH_{2}C_{6}H_{5}N]^{+}OR^{-}$ phase separation surface $[(C_{2}H_{5})_{3}CH_{2}C_{6}H_{5}N]^{+}OR^{-} \xrightarrow[OICH_{2}-CH_{4}Cl]{} [(C_{2}H_{5})_{3}CH_{2}C_{6}H_{5}N]^{+}Cl^{-}$ $+ ClCH==CH_{2} + ROH$

where R = Me, Et, and benzyl.

The presence of TEBAC in the organic residue was also confirmed by gas-liquid chromatography. The use of this method permits evaluation of the initially taken compound relative to the products of the decomposition which occurs on the column. For example, TEBAC dissolved in $C_2H_4Cl_2$ introduced into the chromatograph at 250°C column temperature decomposes largely to give triethylamine and benzyl chloride.

Under the same conditions, the CAOP decomposes into $C_2H_4Cl_2$, triethylamine, benzyl chloride, alkyl β -chloroethyl ether, benzyl β -chloroethyl ether, and ethanol. The structure of these products is determined by the nature of the alkoxide group in the triethylbenzylammonium alkoxide. Having established the composition of the CAOP, we carried out reaction (2) in the presence of TEBAC with the addition of equimolar amounts of methanol, ethanol, and benzyl alcohol, respectively. The reaction results virtually do not differ from those obtained using TEBAA and the greatest activity is found for the TEBAC-benzyl alcohol system. The CAOP obtained in this case does not differ in composition and catalytic activity from the product isolated upon catalysis by TEBA benzylate. We should note that the residual alkaline solution after the separation of the CAOP brought to 50% concentration does not catalyze reaction (2). Assuming that the catalyst upon the complete conversion of $C_2H_4Cl_2$ is transferred to the inorganic phase, retaining catalytic activity, we used the residual inorganic phase for repeated dehydrochlorination, initially bringing the concentration to 50%.

However, the reaction was also hardly observed in this case, which unequivocally indicates decomposition of the catalyst. This hypothesis is also indicated by the finding that an ethereal extract of the inorganic phase after reaction (2) in the presence of the TEBACbenzyl alcohol system contains β -chloroethyl ether, benzyl alcohol, and diethylbenzylamine, i.e., the products of catalyst decomposition.



The isolated CAOP was divided into three parts, which were extracted with equal volumes of water, 0.1 N aqueous hydrochloric acid, and 20% aqueous NaOH. In the former two cases, the catalytic activity of the CAOP is not retained. On the other hand, upon alkaline treatment, the CAOP catalyzes reaction (2). These results indicate that the catalyst is in the organic phase under phase transfer catalysis conditions by the action of concentrated alkali.

The CAOP upon separation and maintenance for 3-4 h forms two layers. The amount of $C_2H_4Cl_2$ in the upper layer is $\leq 10\%$ of its total amount in the CAOP. Chromatographic analysis indicates mainly triethylamine and benzyl chloride, which are the products of the thermolysis of TEBAC, and small amounts of benzaldehyde, diethylbenzylamine, and chloroethyl benzyl ether. The CAOP in the upper layer is analogous in its catalytic activity to pure TEBAC.

The lower layer containing most of the $C_2H_4Cl_2$, benzyl alcohol, and chloroethyl benzyl ether catalyzes the dehydrochlorination similarly to TEBA benzylate. Benzaldehyde, benzyl chloride, diethylbenzylamine, and dibenzyl ether are found in small amounts. Triethylamine was detected under these conditions. The amount of chloroethyl benzyl ether increases if a significant amount of $C_2H_4Cl_2$ is removed from the CAOP prior to the chromatographic analysis and triethylamine is detected in significant amounts in this case. The results of the chromatographic analysis of the CAOP layers are given in Table 1.

The data in Table 1 indicate that the upper, catalytically inactive layer consists mainly of TEBAC, which is not bound in a complex with benzyl alcohol. On the other hand, the presence of all the benzyl alcohol in the lower layer indicates its binding to the quaternary salt. Complexation is also indirectly indicated by the failure to detect triethylamine, which is the product of the thermolysis of TEBAC, in the case of a large excess of $C_2H_4Cl_2$ in the lower layer by chromatographic analysis. In this case, the stability of the complex is apparently dependent on the amount of $C_2H_4Cl_2$ since triethylamine is detected in rather large amounts after the removal of 60-80% of the $C_2H_4Cl_2$ from the CAOP. TEBAC apparently is present in the free state. An increase in the amount of free TEBAC is also indicated by the increase in the chloride ion content. On the other hand, diethylbenzylamine was determined by potentiometric titration upon removal of $C_2H_4Cl_2$ from the CAOP. The presence of diethylbenzylamine may be attributed only to decomposition of the complex, since the concentration was carried out at 40-50°C, at which the decomposition of free TEBAC does not occur.

Further evidence for the formation of a catalytically active complex is the presence of β -chloroethyl benzyl ether in the lower layer of the CAOP. The hypothesis that this product is formed from $C_2H_4Cl_2$ and benzyl alcohol by the action of concentrated NaOH was not confirmed. Stirring 1,2-dichloroethane, benzyl alcohol, and 50% aq. NaOH taken in equimolar ratio at 75-80°C in the absence of TEBAC does not lead to the formation of β chloroethyl benzyl ether. We may assume that this compound is the product of the decomposition of the complex. The content of β -chloroethyl benzyl ether increases with decreasing $C_2H_4Cl_2$ content in the CAOP. This finding that $C_2H_4Cl_2$ is also a component of the complex and, as seen in Fig. 1, the maximum amount of β -chloroethyl benzyl ether is formed when the $C_2H_4Cl_2$ content in the CAOP is 18-22%. Inflections are observed on the curves in this region for triethylamine and benzyl chloride. Hence, the decomposition of the complex proceeds partially with rearrangement resulting in the formation of β -chloroethyl benzyl ether. The remainder decomposes into the initial components. The catalytic system is most efficient when the TEBAC:benzyl alcohol ratio is 1:3-4. This ratio likely provides for the complete use of TEBAC for formation of the complex. The CAOP isolated in this case does not separate into layers.

These results may provide a basis for understanding the mechanism of the phase transfer reactions without considering ion exchange as the major factor for action of the catalyst. The catalyst in reaction (2) is a complex containing a quaternary ammonium salt, hydroxylcontaining compound (alcohol or water), and organochlorine substrate in 1:3-4:2-4 mole ratio. The basis of the complex is an aggregate formed in the organic phase from the quaternary salt and alcohol or water. This aggregate reacts on the phase separation surface with NaOH to increase the positive charge in the tetraalkylammonium cation and negative charge in the alkoxy anion. The latter leads to an increase in the basicity of the aggregate and solvation with the organochlorine substrate becomes possible.

Redistribution of electron density occurs in the complex formed, stabilized by interaction with NaOH from the side of the phase separation surface with solvation with $C_2H_4Cl_2$ from the side of the organic phase. This redistribution leads to the synchronous loss of HCl from the aggregate and organochlorine substrate.

In light of the tendency of ion pairs to form dimers and trimers [3], the complex may be represented as follows:



This scheme shows that the reaction proceeds in the organic phase and on the phase separation surface.

EXPERIMENTAL

The products of the decomposition of TEBAA, TEBAC, and the CAOP were analyzed on a Tsvet-102 chromatograph with a flame ionization detector using a 6-m column packed with 10% trifluoropropylsilicone SKTFT-50Kh on Inerton AW (0.16-0.2 mm). The temperature programming was from 41 to 250°C at 11 K/min. The injector temperature was 260°C, V = 144 ml/min.

TEBAC was obtained from triethylamine and benzyl chloride [4], mp 188-190°C (from benzene-ethanol). The concentration of the triethylbenzylammonium alkoxides was determined by titration with 0.1 N HCl in the presence of methyl red.

<u>Triethylbenzylammonium Ethoxide</u>. A sample of 2.3 g Na was dissolved in 80 ml ethanol and, upon cooling, 23 g triethylbenzylammonium chloride was added. The mixture was stirred for 60 min and maintained for 12 h until NaCl was completely precipitated. After filtration, the content of triethylbenzylammonium ethoxide was 28%. Concentration to 40-50% was carried out in vacuum at room temperature. <u>TEBA Benzylate</u>. A sample of 9.2 g Na was dissolved in 108 g benzyl alcohol. The mixture was stirred for 2 h until the sodium was dissolved and then 22.7 g TEBAC was added at room temperature. The mixture was stirred for 2 h. The NaCl precipitate was filtered off. Titration indicated 29.2 g (84%) TEBA benzylate.

<u>Dehydrochlorination of C₂H₄Cl₂</u>. A sample of 98 g $C_2H_4Cl_2$ and 1 g TEBA benzylate (70% ethanolic solution) were placed into a reactor equipped with a stirrer and temperature control device. A sample of 44 g NaOH was added as a 50% aqueous solution with stirring at 75-80°C. The vinyl chloride formed released through the reflux condenser was trapped at -70°C. The reaction with total conversion of $C_2H_4Cl_2$ was complete after 1 h.

<u>Isolation of the CAOP</u>. A sample of 294 g $C_2H_4Cl_2$, 2.27 g TEBAC, and 1.08 g benzyl alcohol were added to a reactor equipped with a stirrer and temperature control device. A sample of 131 g NaOH as a 50% aqueous solution was added with stirring at 75-80°C. The vinyl chloride released was trapped at -70°C. After the release of 140 g vinyl chloride, the reactor was cooled and the organic layer was separated to give 52 g product, which was divided into three equal portions. A sample of 17 g CAOP was placed into a separatory funnel and shaken with 20 ml distilled water. The organic layer was separated and poured into a reactor containing 98 g $C_2H_4Cl_2$. Then, 44 g NaOH as a 50% aqueous solution was added with stirring at 75-80°C. After 1 h, 5 g (8%) vinyl chloride was obtained.

A sample of 17 g CAOP was treated with 20 g of 0.1 N HCl. The organic layer was separated and used as the catalyst for the dehydrochlorination of 98 g $C_2H_4Cl_2$. The yield of vinyl chloride was 5 g (8%).

A sample of 17 g CAOP was shaken in a separatory funnel with 20 ml of 20% aq. NaOH. The organic layer was separated and used as a catalyst for the dehydrochlorination of 98 g $C_2H_4Cl_2$ at 75-80°C by the action of 44 g NaOH as a 50% aqueous solution. After 1 h, 59 g (95%) vinyl chloride was obtained.

CONCLUSIONS

1. The liquid-phase dehydrochlorination of polychloroalkanes catalyzed by quaternary ammonium salts proceeds with the formation of a catalytically active complex in the organic phase.

2. The catalytically active complex contains a quaternary ammonium salt, hydroxylcontaining compound, and organochlorine substrate. The dehydrochlorination proceeds in the organic phase and on the phase separation surface.

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