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EXCHANGE IN TWO-PHASE CATALYTIC SYSTEMS.

COMMUNICATION 1. NUCLEOPHILIC REPLACEMENT OF BROMINE IN HEXYL BROMIDE BY CHLORINE AND THE ROLE OF THE SOLID SALT M^+Cl^-

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The nucleophilic replacement reaction has been well studied in homogeneous solutions [1] and in the two-phase catalyst system of aqueous salt solution—organic phase (OP) [2-4]. In this work we investigate the replacement of Br by Cl in hexyl bromide in the presence of a solid phase (SP), the chlorides of the alkaline metals M^+Cl^- and the onium salts Q^+X^- in benzene and toluene

$$\underset{\text{OP}}{n\text{-}C_6H_{13}Br} + \underset{\text{SP}}{M^+Cl^-} \underset{}{\overset{Q^+X^-}{\rightleftarrows}} \underset{\text{SP}}{M^+Br^-} + \underset{\text{OP}}{n\text{-}C_6H_{13}Cl}$$

EXPERIMENTAL

In the reaction were used hexyl bromide RBr, bp 155.5°C, concentration of the major product > 90%; the solvents were thoroughly dried benzene or toluene; the solid salts M^+Cl^- were chemically pure or analytical grade; the catalysts were: $(C_4H_9)_4HBr$ (mp 119°C), $(C_8H_{17})NBr$ (mp 95°C), or $(CH_3)_3H_{33}NBr$ (mp 231-236°C). The chemically pure grade KCl consisted of particles 0.2 mm in diameter (89%); 0.125-0.2 mm (11%); 0.1-0.125 (32%); and 0.071-0.1 mm (traces). The mean diameter of the particles $\bar{\ell}$ = 0.195 mm.

The reaction was run at 80-84°C in a thermostatted flat-bottomed reactor (30 mm i.d.), fitted with a reflux condenser with a potassium chloride tube and an effective Teflon stirrer (rate of revolution 1900-2300 rpm). Ordinarily 13 g of the solid salt MCl were taken for the reaction, the molar ratio MCl/RBr = 8.9; 7.0; 4.3 for NaCl, KCl, and RbCl, respectively; concentrations of RBr were between 0.97 and 1, of QX between 0.02–0.06 mole/liter. As the reaction progressed, samples were taken from the organic layer and the concentration of RBr and hexyl chloride, RCl, were determined by GLC.

The sole product of the reaction was RCl, the consumption of RBr corresponding to the formation of RCl. The degree of conversion after 13 h in the presence of 0.02 mole/liter $(C_8H_{17})_4NBr$ did not exceed 7% for NaCl, 23% for KCl, and 43% for RbCl. Figure 1 shows the kinetic curves obtained in the presence of the different salts and catalysts.

The study of the granulated state of the solid phase (KCl) was performed for the run for which there was no preliminary activation of the salt (cf. below). For the microscopic analysis, a sample of KCl from the reactor was placed on a microscope slide and photographed. The photograph of the particles (enlarged 125 diameters) was analyzed statistically. The data obtained are summarized in Tables 1 and 2. At the same time the concentrations of RBr and RCl were determined (Table 3).

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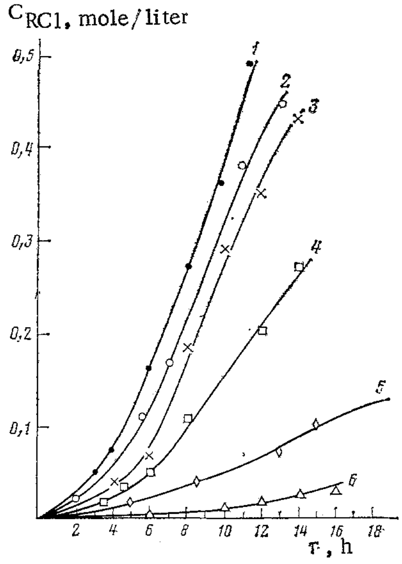

Fig. 1. Kinetic curves for the formation of hexyl bromide (benzene, 80°C, [RBr] = 1 mole/liter, 13 g solid salt): 1) KCl, $[Bu_4NBr]$ = 0.02 mole/liter, 2) RbCl, $[Oct_4NBr]$ = 0.02; 3) KCl $[Oct_4NBr]$ = 0.06; 4) KCl, $[Oct_4KBr]$ = 0.04; 5) NaCl, $[Oct_5NBr]$ = 0.02; 6) KCl, $[Me_3CtNBr]$ = 0.02 mole/liter.

TABLE 1. Fraction of KCl Particles of Different Sizes (%) Determined by Microscopic Analysis of KCl Samples during the Course of the Experiment (average particle diameter ℓ = 195.4·10^3 nm, sample size 120-570 particles)

Particle diameter, μm	Time, min						
	120	180	240	300	420	540	670
0–8	2.5	27.16	31.18	33.7	41.9	61.3	64.0
8–16	10.0	32.1	47.6	46.7	42.2	30.9	32.3
16–24	22.3	17.3	9.9	11.5	11.0	6.6	3.7
24–32	17.4	8.64	6.6	4.44	3.67	1.2	–
32–40	16.5	6.5	4.25	0.74	0.61	–	–
40–48	6.57	3.3	0.47	2.2	0.62	–	–
48–56	10.7	4.6	–	0.72	–	–	–
56–64	10.0	0.4	—	–	–	–	–
64–72	0.8	–	—	–	–	–	–
72–80	3.3						

The instantaneous rate (w_i) was calculated for different times during the experiment (Fig. 2, curve 2) using the equation

$$w_i = w_+ - w_- = k_+ C_{RBr} - k_- C_{RCl} = k_+ [C_{RBr} - (C_{RCl}/K_r)]$$

where k_+ is the rate of the forward reaction; C_{RBr} and C_{RCl} are the instantaneous concentrations; and the value for K_r = 3.33 is taken from an experiment run under the same conditions, but after preliminary activation of the KCl. The calculated values for k_+ as a function of time are given in Table 3.

To obtain uncomplicated kinetic curves (Fig. 2, curve 2), the dry salt was preliminarily activated, placed for 40 min in the reactor at the temperature of the experiment, after which Bu_4NBr was added and heated to the same temperature as the RBr.

The kinetic curves obtained for the presence of activated salt were calculated as the reverse of the pseudo-first-order forward reactions using the Kezdi–Swinbourne method [6]. The influence of the mole ratio KCl/RBr on the rate constant and equilibrium was studied at 84°C for a concentration of $(C_4H_9)_4NBr$ of 0.04 mole/liter in toluene (Table 4). The calculation of the total surface area of the solid salt KCl was made assuming that the particles of the salt are cubes (Table 5).

RESULTS AND DISCUSSION

A characteristic feature of replacement with a solid salt is the sigmoidal shape of the kinetic curves for the consumption of the substrate and the accumulation of the reaction

TABLE 2. Change in Mean Particle Diameter ($\bar{\ell}_i$) of KCl and Total Surface Area of All Particles throughout the Experiment

Time, min	$\bar{l}_i$[a], μm	s^*[b], μm	Surface area of all particles, 10^{-18} nm^2/mole	Time, min	$\bar{l}_i$[a], μm	s^*[b], μm	Surface area of all particles, 10^{-18} nm^2/mole
0	195.4	–	1.1	300	12.1	8.9	20.0
120	30.3	19.57	7.6	420	10.5	7.1	22.5
180	17.5	13.0	16.0	540	7.8	5.4	23.0
240	11.2	8.0	21.0	670	7.2	4.5	23.5

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a) Weighed arithmetic mean value of the length of a cube $\ell_i = \Sigma\rho_i\ell_i/\Sigma\rho_i$, where ρ_i is the fraction of particles with edge length ℓ_i [5].
b) Weighted arithmetic mean deviation

TABLE 3. Change in Instantaneous Rate (w_i) and Rate Constants for the Forward Reaction (k_+) as a Function of Time (KCl 13 g; 84°C; toluene, [Bu_4NBr] = 0.02 mole/liter)

Time, min	Concen. mole/liter		$w_i \cdot 10^4$, mole/liter	$k_+ \cdot 10^3$, sec^{-1}	Time, min	Concen. mole/liter		$w_i \cdot 10^4$, mole/liter	$k_+ \cdot 10^3$, sec^{-1}
	RBr	RCl				RBr	RCl		
0	0.97	0.0	1.34	1.38	300	0.57	0.35	2.0	4.3
60	0.86	0.052	1.46	1.76	360	0.51	0.41	1.68	4.31
120	0.79	0.139	1.85	2.47	420	0.46	0.50	1.085	3.5
180	0.71	0.204	2.5	3.85	480	0.41	0.52	1.01	4.07
240	0.64	0.277	2.4	4.38					

TABLE 4. Influence of Amount of KCl on Reaction Parameters

$$\mathbf{RBr + KCl \underset{k_-}{\overset{k_+}{\rightleftarrows}} RCl + KBr}$$

(toluene, 84°C, [Bu_4NBr] = 0.04 mole/liter)

KCl, g	RBr, mole	KCl/RBr molar	k_+	k_-	$K_r = k_+/k_-$
			$10^5 \cdot$ sec^{-1}		
3.5	0.025	2.08	4.01	1.23	3.26
6.5	0.025	3.6	5.26	1.57	3.34
13	0.025	6.9	6.9	2.66	2.58
13	0.0175	9.92	7.39	2.2	3.37
19	0.025	10	6.42	2.47	2.6
13	0.01	15.7	7.92	2.83	2.8

product (cf. Fig. 1). The shape of the curves does not change with changing concentration of QX or type of salt, although the rate of the process does not increase. This led us to hypothesize that the sigmoidal shape of the kinetic curves is not due to the fact that the process consists of sequential reactions, and is not caused by autocatalysis.

From the data of the microscopic analysis it was established that during the course of the reaction the total surface area of the solid phase changes from $1.12 \cdot 10^{18}$ to $22.5 \cdot 19^{18}$ nm^2/mole. However, the use of different size fractions of sieved crystals in the reaction, the surface area of which ranged from $1.12 \cdot 10^{18}$ to $4.5 \cdot 10^{18}$ nm^2/mole, did not result in the disappearance of the sigmoidal shape of the kinetic curves (cf. Fig. 2, curve 1).

At the same time, if preliminary breakup of the solid salt is performed directly in the reactor before the experiment, the induction period disappears, and the reaction is described by the usual equation for a pseudo-first-order reversible reaction (cf. Fig. 2, curve 2). From the sigmoidal kinetic curve obtained for a special experiment (cf. experimental section) it can be seen that to 150-180 min, the specific rate of replacement increases, and then remains practically constant and equal to the specific rate in an analogous run carried out after preliminary activation of the KCl, i.e., the system enters the steady-state regime. Comparing the specific rates of replacement with the values for the total surface area of

TABLE 5. Calculation for Total Surface Area of 1 Mole of Solid Salt KCl and Number of Moles of KCl Contained by It As a Function of KCl Particle Size (area of projection of KCl S_{projec} = 1.972 nm^2, using crystallographic ionic radii of Cl^- and K^+ [7])

Length of particle edge, l, mm	Number of particles of given size $\cdot 10^{-7}$	Surface area $S \cdot 10^{-18}$, * nm^2/mole	Number of moles† KCl on the surface of the solid phase, $n \cdot 10^4$
0.01	7170	22.5	1.9
0.03	265	7.5	0.635
0.05	55	4.5	0.36
0.10	7.2	2.25	0.19
0.125	3.67	1.8	0.15
0.20	0.895	1.125	0.094

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*$S = 6M/d\ell$, where d = 1.99 g/cm^3, the density of KCl [7]; ℓ is the length of the edge of a cubic particle; M is the molecular weight.

†Number of moles of KCl $n = S/S_{project} \cdot N_A$, where N_A is Avogadro's number.

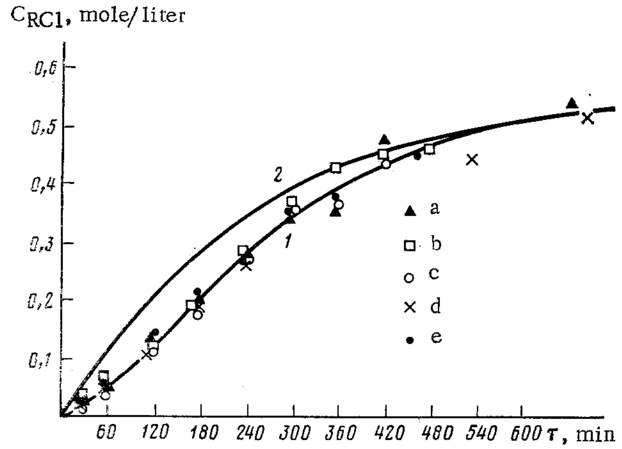

Fig. 2. Kinetic curves for the formation of hexyl bromide (toluene, 84°, [RBr] = 0.97 mole/liter, KCl 13 g, $[Bu_4NBr]$ = 0.02 mole/liter) before activation (1) and after activation (2): a) unsieved salt; b) 0.1-0.25 mm; c) 0.071-0.1; d) 0.05-0.071; e) 0.05 mm.

the solid salt (cf. Table 2) corresponding to a given time it can be seen that there is a satisfactory correlation between them (Fig. 3). Consequently, the sigmoidal behavior of the curve is related, within certain limits, to the increase of the surface area of the solid phase.

A more detailed analysis shows that not all of the surface participates in the reaction, but only part of it. Actually, at the moment when the system enters the steady-state regime the solid consists essentially of particles of subcolloidal size (cf. Table 1). The increase in the specific rate of replacement in the non-steady-state segment depends linearly on the fraction of particle < 24 μm (Fig. 4). Thus, the formation during the breakup of the solid phase of subcolloidal particles is responsible for its activation, which is apparently related to the formation of active sites on the fresh cleavages of the crystals. In the case of nucleophilic replacement such a site may be a nonequilibrium Cl-ion on a surface fracture, which may have an enhanced reactivity to nucleophilic reaction. If activated salt is used in the reaction, then a "steady-state" regime is established from the very beginning. Increasing the absolute amount of KCl (cf. Table 4) leads to an increase in the maximum concentration of Cl^- ions available for reaction, and as a result, to an increase in the rate constant of the replacement reaction. At the same time, after a certain value, further increases in the amount of KCl have practically no effect on this rate constant.

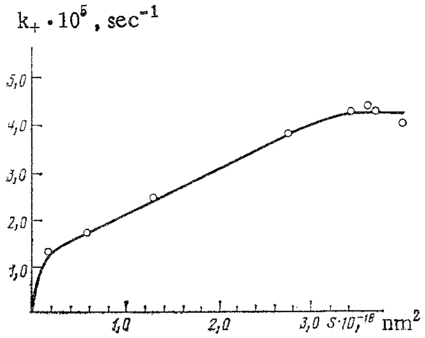

Fig. 3

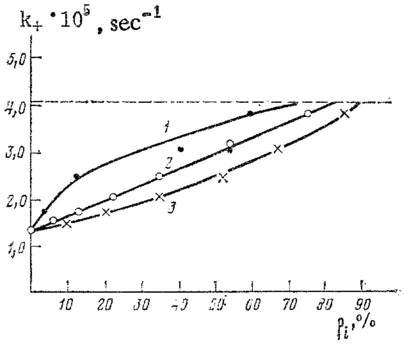

Fig. 4

Fig. 3. Instantaneous specific rate of replacement as a function of surface area of the KCl particles (toluene, 84°C, [RBr] = 0.97 mole/liter, KCl 13 g, $[Bu_4NBr]$ = 0.02 mole/liter).

Fig. 4. Instantaneous specific rate of replacement on fraction of KCl particles of diameter, μm: 1) ≥16; 2) ≥24; 3) ≥32.

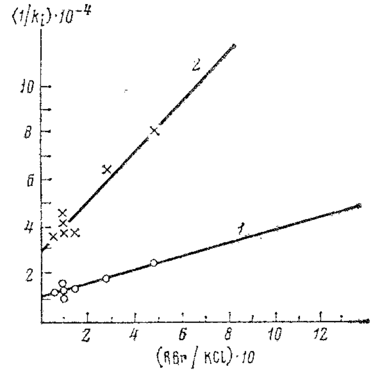

Fig. 5. Observed rate constants for the forward (1) and reverse (2) reactions as functions of molar ratio KCl/KBr in reciprocal coordinates (toluene, 84°C, $[Bu_4NBr]$ = 0.04 mole/liter).

Plotting these data in inverse coordinates produces a satisfactorily linear relationship (Fig. 5). Taken together with the data of Fig. 4 this suggests that the limiting of the rate of the process is caused by its proceeding according to a mechanism including an equilibrium stage involving surface "active" molecules of the KCl and the reagent in the organic phase, the concentration of the reagent necessarily being less than the concentration of the accessible KCl molecules (or of the active Cl^- ions). It can be assumed that such a reagent may be the catalyst in monomer form of a complex of it with the substrate.

CONCLUSIONS

1. The acceleration of the nucleophilic replacement reaction of the bromine in hexyl bromide by chlorine in the two-phase catalytic system solid salt M^+Cl^-—organic phase is related to the increase in the surface area of the solid phase and the formation of subcolloidal particles bearing the active sites.

2. The process follows the ordinary laws for a pseudo-first-order reversible reaction after preliminary activation of the solid salt.

3. Increasing the molar ratio of KCl/RBr leads to an acceleration of the replacement process only up to a certain limiting value, which may be related to the presence of an equilibrium interaction between the active sites on the surface of the solid salt and the catalyst or a complex of the catalyst with the substrate.

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STRUCTURE OF SOME OLIGOPHOSPHAZENES

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Phosphazo compounds are of interest as modifiers for polymer materials [1, 2]. In the present paper, the structure of oligomeric phosphazo compounds with chloroethoxy, dianilido, and aminoethoxy groups directly bonded to the P atom was studied to elucidate the mechanism of the modifying action.

EXPERIMENTAL

The phosphazo compounds were obtained in a pilot-plant unit according to [3] by reactions of partial or total replacement of chlorine atoms in dichlorophosphazene in the presence of sodium ethoxide, aniline, or ammonia in neutral solvents. Dichlorophosphazene was obtained according to [3].

The characteristics of the investigated phosphazo compouns are given in Table 1. To establish the structure of the products, we used $^{31}P-\{^1H\}$ NMR spectra, pyrolytic mass spectrometry, and IR spectroscopy.

The ^{31}P NMR spectra were recorded on a Bruker WP-200SY spectrometer (81.01 MHz), and the external standard was a 1% H_3PO_4 solution. The mass spectra were recorded on an AEI MS-30 mass spectrometry with direct sample feed into the ion source at a pyrolysis-cell temperature of 150°C; the ionizing voltage was 70 eV, and the temperature of the ionization chamber was 250°C. The IR spectra of the powders were recorded on a UR-20 instrument in tablets with KBr, and the IR spectra of the liquid products were recorded in a thin layer.

DISCUSSION OF RESULTS

The $^{31}P-\{^1H\}$ NMR spectrum of dichlorophosphazene contained three narrow signals at 20.1, −6.2, and −15.2 ppm. The most intense signal, at −6.2 ppm, corresponded to the cyclic tetramer, and the signals at 20.1 and −15.2 ppm corresponded to the phosphazene trimer and the cyclic compound $(PCl_2)_n$ with n = 6, respectively [4]. From the correlation of the integrated intensities of the signals, it follows that the product was mainly a cyclic tetramer (~86 wt.%) with impurities of a cyclic trimer (~11 wt. %) and a cyclic oligomer of higher molecular weight (~3 wt. %).

The IR spectrum of dichlorophosphazene contained an intense band at 1310 cm^{-1} characteristic of P—N in the cyclic tetramer [5]. The broadening of this band was related to the presence of other phosphazenes. The tetramer form of the product was also confirmed by the presence of intense bands of symmetric vibrations of P—N—P bonds in the eight-membered ring at 895, 800, and 780 cm^{-1}. Strong bands at 520 and 600 cm^{-1} and also a weak band at 460 cm^{-1}

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