JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 149–157 (1991)

FORMATION OF ADSORPTION COMPLEXES IN PHASE-TRANSFER NUCLEOPHILIC SUBSTITUTION. KINETIC ANALYSIS OF SOLID-PHASE SYSTEM

I. A. ESIKOVA AND S. S. YUFIT

N. D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, 47 Leninsky Ave., Moscow, U.S.S.R.

The kinetics of the nucleophilic substitution between n-hexyl bromide and solid potassium chloride (KCl) in toluene were studied in the presence of catalytic amounts of tetra-n-butylammonium bromide at 84 °C. This reaction is characterized by an induction period that disappears on activation of the solid salt. The substitution with the activated salt constitutes a reversible pseudo-first-order reaction with variable orders in the substrate and the catalyst equal to $0 \leqslant n \leqslant 1$. A quantitative increase in the solid KCl at first accelerates the substitution reaction, but when the level reaches KCl/RBr $\geqslant 7$ the rate constant is no longer influenced by the amount of salt. Comparing data obtained with kinetic equations for several possible substitution schemes, the mechanism of the reaction can be derived, including the formation of a ternary adsorption complex (TC) from the substrate, catalyst and solid salt. The data obtained allow the evaluation of the equilibrium constant of TC formation ($K_\Sigma = 20 \cdot 48\ l^2 mol^{-2}$) and the rate constant of its disintegration into substitution products ($k_+ = 0 \cdot 75 \times 10^{-2}\ s^{-1}$). Through kinetic analysis the adsorption sequence on the surface of the solid salt was determined, including primary formation of the binary complex KCl.QX and subsequent TC formation. The concentration of active KCl molecules, estimated on the basis of the primary kinetic data is 10^{-2} M and is commensurate with the catalyst concentration. This concentration of active KCl molecules is achieved owing to the formation of subcolloidal-sized particles in the process of the solid salt activation.

INTRODUCTION

Nucleophilic substitution is one of the reactions which form the theoretical basis of interphase catalysis.[1–8] In one of the first publications in this field, Starks[1] suggested that the essence of this catalysis consists in the nucleophile transfer by the catalyst from the aqueous to the organic phase, which he called the phase transfer catalysis (PTC). However, further studies[9–11] showed that the nucleophile transport does not always take place and, when it does, the kinetics of this reaction might be determined by interface processes rather than by nucleophile reactions in the organic phase. The role of adsorption processes is especially evident in reactions within the solid phase–liquid system. The investigation of such systems showed that a preliminary activation of the solid phase is necessary. The activation paths may be different with either addition of traces of water[12–14] or mechanical crushing of the solid phase.[15] The kinetics and mechanism of substitution under solid–liquid PTC conditions in the presence of traces of water are well known.[16–20] However, the reaction kinetics in the presence of dry salts have not been thoroughly studied.

By examining the halide exchange between n-hexyl bromide and solid potassium chloride (KCl) in toluene (at 84 °C, QX = Bu_4NBr) we determined the following regularities:[21] correlation between the free substitution energy and the energy of the crystalline lattice of solid salts (MCl, where M = Li, Na, K, Rb, Cs); and the influence of the cation in MCl on the character of the Arrhenius relationship. These data indicate that the solid salt participates in the rate-determining step of the substitution.

Since the choice of the reaction mechanism can be correct only in the presence of a complete set of necessary data, we studied the substitution kinetics and used the results obtained to discriminate between probable schemes for this reaction.

EXPERIMENTAL

In the reaction we used n-hexyl bromide (RBr), b.p. 155·5 °C, purity > 90%, and Bu_4NBr, m.p. 119 °C (benzene). Solid KCl had the following composition: particles of > 0·2 mm, 89%; 0·125–0·2 mm, 10·65%; 0·1–0·125 mm, 0·32%; and < 0·1 mm, traces;

0894–3230/91/030149–09$05.00

Received 22 March 1990
Revised 16 July 1990

average size 0·195 mm. The solid salt was preliminary activated, for which purpose it was placed in the reactor and intensively crushed before the run. The reaction was conducted at 80–84 °C in a reactor protected against air moisture. Usually MCl/RBr = 7. The mixing intensity was provided by a PTFE stirrer with a rotation speed of 1900–2300 rpm. Dried toluene was used as the solvent.[22]

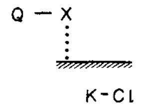
We determined the water content before and after the reaction; usually it was no more than 0·008% by mass. The initial reagents and reaction products were determined titrimetrically[23] and by gas chromatography with $C_{11}H_{24}$ as internal standard. In a wide range of reagent concentrations the reaction proceeded as a reversible pseudo-first-order reaction with no deviations due to accumulation of the reaction products. The equilibrium and rate constants were calculated by the Kezdy–Swinbourne method.[24]

RESULTS AND DISCUSSION

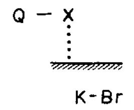
Kinetic peculiarities

The distinctive feature of this reaction in the solid phase–liquid system is the necessity for preliminary activation of the solid phase. Without such activation an induction period is observed.[15] Evidently, during the activation particles are formed that carry Cl^- ions, which are highly reactive in nucleophilic reactions. It is suggested that the KCl concentration be determined as the ratio of the number of active particles on the interface to the volume of the organic phase. The numerical estimation of this concentration seems to be difficult. We consider that a fair reproduction of the runs in a reactor of this type indicates establishment of a regime with a constant concentration of active particles at the interface, which varies according to the amount of salt used in the reaction. Comparison of the area of the solid salt surface with that of a KCl molecule shows that the concentration of KCl molecules open to contact is 10^{-2}–10^{-3} M (see Appendix 1) and that of active KCl particles is much less, i.e. it is commensurate with the catalyst concentration and is less than the substrate concentration in the organic phase.

Another question that requires special consideration is the influence of the salt product on the properties of the solid phase. Evidently, as a result of substitution part of the KCl is converted into KBr and hence there will be molecules of both types on the solid-state surface. As in our case KCl/RBr = 7, we expected that the change in the solid-phase composition would not substantially influence the kinetics, whereas if the salt product is introduced in the initial reaction system the process is inhibited (Figure 1). The observed influence of the salt product can be explained by the reversible unproductive bonding of a portion of catalyst as a result of its adsorption on the salt product surface:



(Productive bonding of QX)



(Unproductive bonding of QX)

In addition we found by the titrimetric method that KCl and KBr do not dissolve in toluene and that in toluene there is no ion exchange between solid KCl and Bu_4NBr.[9] As a result, we can state that the nucleophilic substitution proceeds on the solid-phase surface.

Possible intermediates and substitution mechanism

In such reactions an important role is played by adsorption processes on the KCl surface that form different adsorption complexes as intermediates:

$$MY_s + RX \rightleftharpoons MY.RX_{ads} \qquad (D1)$$

$$MY_s + QX \rightleftharpoons MY.QX_{ads} \qquad (D2)$$

$$RX + QX \rightleftharpoons RX.QX \qquad (D3)$$

$$\begin{array}{ll} MY.RX_{ads} + QX \searrow & \\ MY.QX_{ads} + RX \rightleftharpoons MY.QX.RX_{ads} & \\ RX.QX + MY_s \nearrow & (TC) \end{array}$$

A study of the influence of initial reagent concentrations on the substitution rate (Table 1) showed that the orders in all reagents were ($0 \leqslant n \leqslant 1$), i.e. after certain concentrations of KCl, RBr and QX have been reached further increases no longer influence the substitution rate constant. We considered that for the substitution it is necessary to coordinate all three components of the reaction system, i.e. KCl, RBr and QX. Therefore, we analysed possible models of this reaction (Table 2), representing complexes D1, D2, and D3 and TC as kinetically independent compounds. We obtained a number of kinetic equations for schemes differing in the sequence of reagent adsorption, the constants in various steps of the schemes and the lifetimes of different intermediates. It can be seen that if [RBr] > [QX] ≈ [KCl] then the equations obtained are often kinetically distinguishable. For instance, it is easy to make a choice between schemes with the

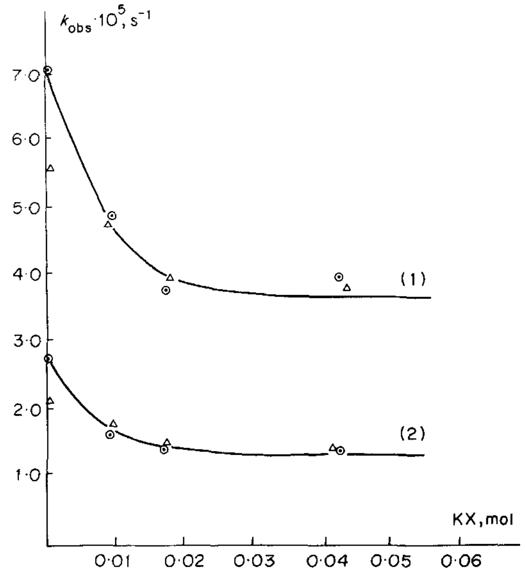


Figure 1. Influence of salt product (KX, where X = Cl or Br) on the observed rate constants of substitution: k_f (1) RBr → RCl ⊚ k_{op} (2) RCl → RBr Δ. Toluene; 84 °C; [RX] (where X = Br or Cl) = 0·97 M; [Bu_4NBr] = 0·04 M; solid salt, 0·85 mol; volume of organic phase, 12·5 ml

formation of only binary complexes. Thus, for Scheme 2 there is a first-order dependence only for RBr and for Scheme 3 there is a first-order dependence for both QX and MY. For QX and MY in Scheme 2 the reagent order may change depending on the concentration ratios. These schemes do not conform to the kinetic data that we obtained and should not be considered. Hence we may postulate the obligatory formation of a ternary adsorption complex (TC) in the system (Scheme 4). Indeed, the kinetic analysis shows that in this case the orders in each component would be variable ($0 \leqslant n \leqslant 1$). The saturation effect observed corresponds to virtually complete conversion of QX (if [QX] < [MY]) or MY (if [QX] > [MY]) into TC.

Kinetic data processing

Processing of the data in Table 1 according to equation (4) (Appendix 2) results in satisfactory linear dependences (Figures 2 and 3) of k_{obs} on each reagent concentration by inverting both sides. The mathematical analysis performed allows us to determine the values of the constants k_+ and K_Σ and also [KCl] when we use 13 g of KCl and 25 ml of the organic phase in the reaction. It is evident that the TC formation is a thermodynamically advantageous process ($K_\Sigma = 20{\cdot}48\,l^2\,mol^{-2}$). At the same time, the rearrangement inside TC and its disintegration proceed with a rate constant $k_+ = 0{\cdot}75 \times 10^{-2}\,s^{-1}$. The values of k_+, K_Σ and k_{obs} were used in equation (4) to determine the concentration of the active molecules of

Table 1. Kinetic parameters of the reaction

$$\underset{(RBr)}{n\text{-}C_6H_{13}Br} + KCl_s \overset{QX}{\rightleftharpoons} \underset{(RCl)}{n\text{-}C_6H_{13}Cl} + KBr_s$$

Initial reagents					
[RBr] (M)	[QX] (M)	KCl (g)	$K_{eq} = \frac{k_f}{k_{op}}$	$k_f \times 10^5 (s^{-1})$	$k_{op} \times 10^5\ (s^{-1})$
0·475	0·04	13	3·5	7·4	2·2
0·7	0·04	13	3·4	7·4	2·2
0·97	0·04	13	2·87	6·67	2·35
1·25	0·04	13	2·68	5·39	2·01
1·71	0·04	13	2·66	4·07	1·53
2·0	0·04	13	2·64	3·92	1·48
2·4	0·04	13	2·7	3·28	1·22
0·97	0·01	13	3·5	2·2	0·62
0·97	0·02	13	2·7	4·0	1·47
0·97	0·029	13	3·4	5·4	1·6
0·97	0·08	13	3·3	9·3	2·8
0·97	0·04	3·5	2·73	2·54	0·93
0·97	0·04	3	2·88	3·4	1·2
0·97	0·04	6·5	2·75	5·05	1·74
0·97	0·04	19	2·6	6·42	2·47

[a] Toluene; 84 °C; QX = Bu_4NBr; volume of the organic phase, 25 ml. RBr → RCl(k_f); RCl → RBr(k_{op})

Table 2. Kinetic equations, orders in components and characteristic dependences for different schemes of substitution

Scheme No.	Reactions	Kinetic equation[a]	Orders RX	Orders MY	Orders QX	Characteristic dependences $1/(k_{obs} \cdot [RX]_0) = A - B/X$ $X = [RX]_0$	$X = [MY]_0$	$X = [QX]_0$
1	$MY + RX \overset{K}{\rightleftharpoons} DI$ $DI + QX \underset{k_-}{\overset{k_+}{\rightleftharpoons}} DI' + QY$ $DI' \rightleftharpoons MX + RY$	$[MY]_0 \ll [RX]_0$ $k_{obs} = \dfrac{k_+ K[MY]_0[QX]_0}{1 + K[RX]_0}$	$0 \leqslant n \leqslant 1$	$n = 1$	$n = 1$	+	–	–
2	$MY + QX \overset{K}{\rightleftharpoons} D2$ $D2 + RX \underset{k_-}{\overset{k_+}{\rightleftharpoons}} D2' + RY$ $D2' \rightleftharpoons QX + MX$	(a) $[QX]_0 \approx [MY]_0$ $k_{obs} = \dfrac{k_+ K[MY]_0[QX]_0}{1 + K([MY]_0 + [QX]_0)}$	$n = 1$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	–	+	+
		(b) $[QX]_0 > [MY]_0$ $k_{obs} = \dfrac{k_+ K[MY]_0[QX]_0}{1 + K[QX]_0}$	$n = 1$	$n = 1$	$0 \leqslant n \leqslant 1$	–	–	+
		(c) $[QX]_0 < [MY]_0$ $k_{obs} = \dfrac{k_+ K[MY]_0[QX]_0}{1 + K[MY]_0}$	$n = 1$	$0 \leqslant n \leqslant 1$	$n = 1$	–	+	–
3	$QX + RX \overset{K}{\rightleftharpoons} D3$ $D3 + MY \underset{k_-}{\overset{k_+}{\rightleftharpoons}} D3' + MX$ $D3' \rightleftharpoons QX + RY$	$[QX]_0 \ll [RX]_0$ $k_{obs} = \dfrac{k_+ K[MY]_0[QX]_0}{1 + K[RX]_0}$	$0 \leqslant n \leqslant 1$	$n = 1$	$n = 1$	+	–	–

4	$RX + MY + QX \overset{K_\Sigma}{\rightleftharpoons} TC$ $TC \underset{k_-}{\overset{k_+}{\rightleftharpoons}}$ $RY + MX + QX$	$[RX]_0 \gg [QX]_0 \approx [MY]_0$ $k_{obs} = \dfrac{k_+K_\Sigma[MY]_0[QX]_0}{1 + K_\Sigma[RX]_0(QX_0 + MY_0)}$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	+	+	+
5	$MY + QX \overset{K}{\rightleftharpoons} D2$ $D2 + RX \overset{K'}{\rightleftharpoons} TC$ $TC \underset{k_-}{\overset{k_+}{\rightleftharpoons}} RY + D2'$ $D2' \rightleftharpoons MX + QX$	$[QX]_0 \approx [MY]_0 \ll [RX]_0$ $k_{obs} = \dfrac{k_+K_\Sigma[MY]_0[QX]_0}{1 + (K + K_\Sigma[RX]_0)([QX]_0 + [MY]_0)}$ $K_\Sigma = KK'$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	+	+	+
6	$MY + RX \overset{K}{\rightleftharpoons} D1$ $D1 + QX \overset{K'}{\rightleftharpoons} TC$ $TC \underset{k_-}{\overset{k_+}{\rightleftharpoons}} D1' + QX$ $D1' \rightleftharpoons RY + MX$	$[QX]_0 \approx [MY]_0 \ll [RX]_0$ $k_{obs} = \dfrac{k_+K_\Sigma[MY]_0[QX]_0}{1 + K[RX]_0 + K_\Sigma[RX]_0[QX]_0}$ $K_\Sigma = KK'$	$0 \leqslant n \leqslant 1$	$n = 1$	$0 \leqslant n \leqslant 1$	+	–	+
7	$RX + QX \overset{K}{\rightleftharpoons} D3$ $D3 + MY \overset{K'}{\rightleftharpoons} TC$ $TC \underset{k_-}{\overset{k_+}{\rightleftharpoons}} D3' + MX$ $D3' \rightleftharpoons RY + QX$	(a) $[MY]_0 \approx [QX]_0 < [RX]_0$ (b) $[MY]_0 \approx [RX]_0 > [QX]_0$ $k_{obs} = \dfrac{k_+K_\Sigma[MY]_0[QX]_0}{1 + K[RX]_0 + K_\Sigma[RX]_0[MY]_0}$ $K_\Sigma = KK'$	$0 \leqslant n \leqslant 1$	$0 \leqslant n \leqslant 1$	$n = 1$	+	+	–

[a] The equations are deduced for the condition when the equilibrium is achieved for the steps of the adsorption complex formation which precede the limiting step. Assuming that the contribution of the last term may be neglected, the equation expression under the square root sign ($1/k_{obs} = f([QX]_0, [MY]_0, [R\ Br]_0)$ is simplified. The calculation of k_{obs} by strict and approximate equations results in a systematic deviation of k_{obs} of +10%. The character of the dependences $k_{obs} = f([QX]_0)$, $k_{obs} = f([MY]_0)$ and $k_{obs} = f([R\ Br]_0)$ does not change.

KCl open for contact with the organic phase. These KCl values, depending on the initial amount of the solid salt, are shown in Figure 4. Since the accuracy of determination of k_{obs} is ± 20%, we may conclude that a quantitative increase in the salt content in the system results in a proportional increase in the permanent concentration of active KCl molecules.

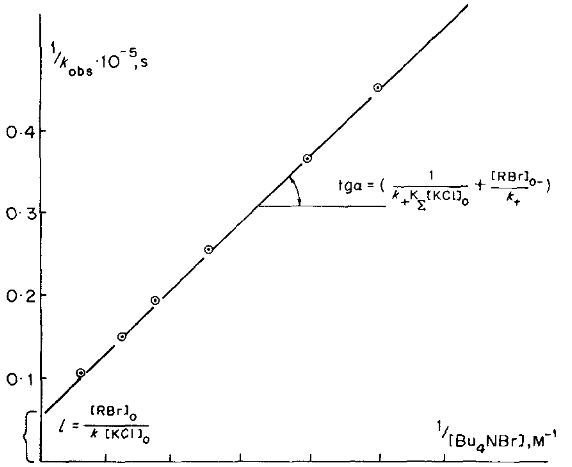


Figure 2. Dependence of $1/k_{obs}$ on $1/[QX]_0$ in accordance with equation (4)

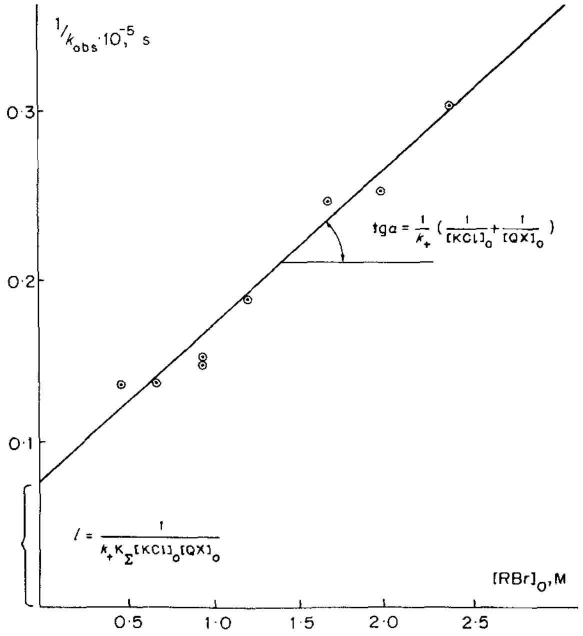


Figure 3. Dependence of $1/k_{obs}$ on $[RBr]_0$ in accordance with equation (4).

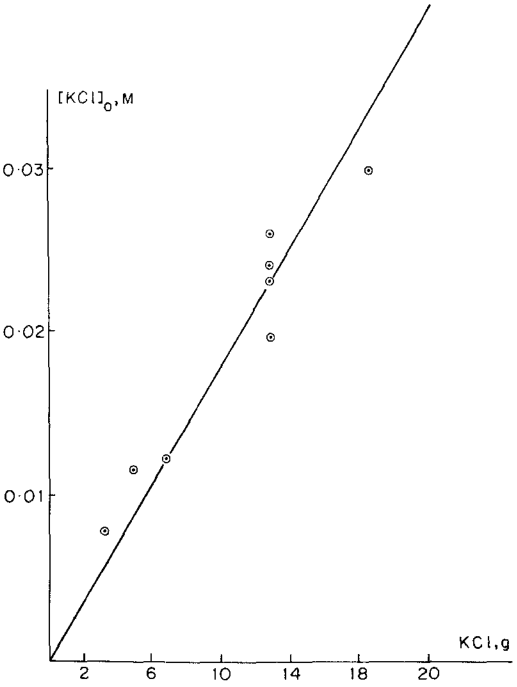
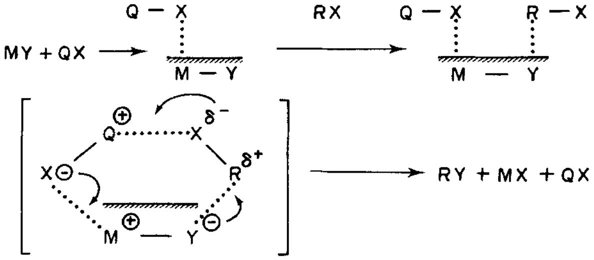


Figure 4. Correlation between the amount of KCl taken in the reaction and the permanent concentration of active KCl molecules in the reaction mixture.

These kinetic results are valid for processes with activated salt participation. We consider that the essence of activation consists in the formation of active particles of a subcolloidal size. Analysis of the data obtained (see Appendix 1) shows that a KCl concentration of 0·023 M may be achieved when the size of the solid-state particles is only 5×10^{-4} mm. If there is no preliminary activation of the salt, then the process is either substantially slowed or virtually absent. The latter case has often been mentioned in the literature.[2,12-14] There is an opinion[16-19] that traces of water forming a special layer (thin-layer PTC) substantially influence the rate of the solid-phase reaction. The action of water may be different (to increase, to decrease or to have no influence on the reaction rate), which indicates the complication of the phenomenon. For example, water may enter into the crystalline lattice of the solid salt and destroy it (effect of acceleration[14]). This supports previously obtained data on the correlation between the energy of the $K_2CO_3.nH_2O$ crystalline lattice and the free energy of alkylation.[25] On the other hand, the addition of an extra amount of water may lead to the formation of a mini-layer of saturated aqueous solution at the surface of the crystals. In the latter case the nucleophilic reaction rate should decrease on account of the anion hydration. The decrease in reaction rate takes place at different solid salt/water ratios, which depend on the type and the condition of the reaction.[20] This is why we think that mechanical activation of the solid phase may be more preferable than the addition of drops of water, especially for salts with a high energy of the crystalline lattice.

Mechanism of TC formation

The substitution scheme becomes more complicated when the lifetime of the binary complex is commensurate with that of other kinetically independent species. Since the sequence of the interaction of the reagents may be different, we considered three possible variants of TC formation (Schemes 5, 6 and 7, in Table 2). It can be seen that only Scheme 5 envisages variable orders for all three components. In Schemes 6 and 7 there is a first-order dependence for one of the components. Hence the kinetic analysis allows one to consider a number of possible schemes and to choose that which conforms completely to the experiment. In our case this is Scheme 5, where the process takes place on the solid-phase surface as a result of consecutive adsorption of the catalyst (MY.QX complex) and the substrate (MY.QX.RBr complex) on the salt surface:



We may assume that rearrangement inside the TC proceeds simultaneously through the six-centre cyclic transition state. We intend to discuss the mechanism of this process in more detail in subsequent publications.

CONCLUSION

We have established that in a reaction with one reagent in the solid state the substitution mechanism includes the formation of the adsorption complexes. This conclusion is based on the following facts. Nucleophilic substitution does not take place in the absence of the catalyst, and there is no ion exchange between the catalyst and the solid salt. This indicates that even if our system is not perfectly dry, the water present cannot promote the process. The kinetic curves have an induction period which disappears after the salt activation, i.e. formation of a sufficient number of active sites on KCl crystals. The kinetics of reaction with the activated salt correspond to the laws of the reversible pseudo-first-order reaction. The reaction orders for RBr and Bu_4NBr are variable ($0 \geqslant n \geqslant 1$). There is a complex relationship between the reaction rate constant observed and the amount of KCl. At first the substitution rate increases, but above a certain concentration additional amounts of KCl no longer influence it. There is a correlation between the substitution free energy and the energy of the MCl crystalline lattice.

To interpret the kinetic data obtained, different substitution schemes were studied. The analysis indicates the formation of the intermediate TC including the solid salt (KCl), substrate and catalyst. This complex is formed as a result of consecutive adsorption of the catalyst and substrate on the solid salt surface. The adsorption sequence is predetermined.

Therefore, one of the catalyst functions in PTC includes the coordination of reagents on the solid-phase surface to form the adsorption complex. Disintegration of this complex leads to reaction products. This makes PTC closer to other types of catalysis. The suggested mechanism may be of a general character and may be realized in any PTC processes that include adsorption. Evidently the common scheme of the substitution will also be correct in the presence of traces of water. However, the latter may complicate the real mechanism of the substitution in this system because of the parallel process following different routes.

ACKNOWLEDGEMENTS

We thank Dr E. P. Serebryakov for his support of the study and O. I. Danilova for help with the experimental work.

APPENDIX 1

Calculation [15] of the surface area of 1 mol KCl and determination of the number of molecules situated on the surface and accessible for contact with the organic phase were performed for solid-phase particles of different size. It was assumed that the particles have the shape of blocks. The surface area of the solid phase was calculated as

$$S = \frac{6M}{dl}$$

where M is the molecular weight of KCl, d its density and l the length of the rib. The number of moles of KCl on the surface of the solid phase is calculated by the equation

$$N = \frac{S}{S_{\mathrm{pr}} \times 6 \cdot 02 \times 10^{23}}$$

where S_{pr} is the projection area of 1 mol KCl and $6 \cdot 02 \times 10^{23}$ is Avogadro's number.

This value changed depending on the l value:

l (mm)	0·0005	0·001	0·005	0·010	0·050	0·100	0·200
$N \times 10^4$	36·2	19	3·6	1·9	0·36	0·19	0·095
$[\mathrm{KCl}] \times 10^2$	2·3	1·3	0·23	0·13	0·026	0·013	0·0065

It can be seen that the N value and the permanent KCl concentration vary considerably. The bottom row of data shows KCl values for cases when the reaction mixture contained 13 g of KCl and 25 ml of organic phase.

APPENDIX 2

Kinetic analysis of Scheme 4

$$\mathrm{RX} + \mathrm{MY} + \mathrm{QX} \underset{K_\Sigma}{\rightleftharpoons} \mathrm{TC}$$

$$\mathrm{TC} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{RY} + \mathrm{MX} + \mathrm{QX}$$

Here K_Σ is the equilibrium constant of TC formation and k_+ is the rate constant of TC disintegration on the reaction products.

According to the experimental data observed, the rate constant for the forward reaction is

$$k_{\mathrm{obs}} = w_0/[\mathrm{RX}]_0 = k_+[\mathrm{TC}]_{\mathrm{eq}}/[\mathrm{RX}]_0$$

and the equilibrium constant of overall process is

$$K_{\mathrm{eq}} = K_\Sigma k_+/k_-$$

The equilibrium concentrations of TC, RX, QX and KCl may be written as

$$[\mathrm{TC}]_{\mathrm{eq}} = K_\Sigma[\mathrm{RX}]_{\mathrm{eq}}[\mathrm{MY}]_{\mathrm{eq}}[\mathrm{QX}]_{\mathrm{eq}} \quad (1)$$

$$[\mathrm{RX}]_{\mathrm{eq}} = [\mathrm{RX}]_0 - [\mathrm{TC}]_{\mathrm{eq}} \approx [\mathrm{RX}]_0 \quad (2)$$

$$[\mathrm{QX}]_{\mathrm{eq}} = [\mathrm{QX}]_0 - [\mathrm{TC}]_{\mathrm{eq}} \quad (3)$$

$$[\mathrm{MY}]_{\mathrm{eq}} = [\mathrm{MY}]_0 - [\mathrm{TC}]_{\mathrm{eq}} \quad (4)$$

Then,

$$[\mathrm{TC}]_{\mathrm{eq}} = K_\Sigma[\mathrm{RX}]_0([\mathrm{MY}]_0 - [\mathrm{TC}]_{\mathrm{eq}})([\mathrm{QX}]_0 - [\mathrm{TC}]_{\mathrm{eq}}) \quad (5)$$

Equation (5) has the following solution:

$$1/[\mathrm{TC}]_{\mathrm{eq}} = \tfrac{1}{2}(A + \sqrt{A^2 - 4/[\mathrm{MY}]_0[\mathrm{QX}]_0}) \quad (6)$$

where

$$A = 1/[\mathrm{MY}]_0 + 1/[\mathrm{QX}]_0 + 1/K_\Sigma[\mathrm{RX}]_0[\mathrm{MY}]_0[\mathrm{QX}]_0$$

The second square root in equation (5) has no physical meaning. Thus,

$$1/k_{\mathrm{obs}} = [\mathrm{RX}]_0/k_+[\mathrm{TC}]_{\mathrm{eq}}$$

$$1/k_{\mathrm{obs}} = [\mathrm{RX}]_0/2k_+(A + \sqrt{A^2 - 4/[\mathrm{MY}]_0[\mathrm{QX}]_0}) \quad (7)$$

After multiplying both parts of equation (7) by $[\mathrm{QX}]_0[\mathrm{MY}]_0$, we obtain

$$[\mathrm{MY}]_0[\mathrm{QX}]_0/k_{\mathrm{obs}} = ([\mathrm{RX}]_0/2k_+) \times \{[\mathrm{QX}]_0 + [\mathrm{MY}]_0 + 1/K_\Sigma[\mathrm{RX}]_0 + \sqrt{([\mathrm{QX}]_0 + [\mathrm{MY}]_0 + 1/K_\Sigma[\mathrm{RX}]_0)^2 - 4[\mathrm{MY}]_0[\mathrm{QX}]_0}\} \quad (8)$$

Unfortunately, equation (8) is very complex for analysis. However, when $[\mathrm{QX}]_0 \approx [\mathrm{MY}]_0 \ll [\mathrm{RX}]_0$ it is possible to suggest that

$$([\mathrm{QX}]_0 + [\mathrm{MY}]_0 + 1/K_\Sigma[\mathrm{RX}]_0)^2 > 4[\mathrm{MY}]_0[\mathrm{QX}]_0 \quad (9)$$

and the last term in the square root in equation (8) can be neglected. Then

$$[\mathrm{MY}]_0[\mathrm{QX}]_0/k_{\mathrm{obs}} = [\mathrm{RX}]_0/k_+([\mathrm{QX}]_0 + [\mathrm{MY}]_0 + 1/K_\Sigma[\mathrm{RX}]_0) \quad (10)$$

Hence

$$k_{\mathrm{obs}} = \frac{k_+K_\Sigma[\mathrm{MY}]_0[\mathrm{QX}]_0}{1 + K_\Sigma[\mathrm{RX}]_0([\mathrm{QX}]_0 + [\mathrm{MY}]_0)} \quad (11)$$

According to equation (11), a limit of the reaction rate will be observed under certain initial concentrations of MY, RX and QX. By inverting both sides of equation (11) one may obtain the equation:

$$1/k_{\mathrm{obs}} = 1/k_+K_\Sigma[\mathrm{MY}]_0[\mathrm{QX}]_0 + [\mathrm{RX}]_0([\mathrm{QX}]_0 + [\mathrm{MY}]_0)/k_+[\mathrm{MY}]_0[\mathrm{QX}]_0 \quad (12)$$

Solutions of equation (12) concerning RX, MY or QX are as follows:

$$1/k_{\mathrm{obs}} = [\mathrm{RX}]_0/k_+[\mathrm{MY}]_0 + (1/k_+K_\Sigma[\mathrm{MY}]_0 + [\mathrm{RX}]_0/k_+)1/[\mathrm{QX}]_0 \quad (13)$$

$$1/k_{\mathrm{obs}} = 1/k_+K_\Sigma[\mathrm{MY}]_0[\mathrm{QX}]_0 + [\mathrm{RX}]_0(1/[\mathrm{MY}]_0 + 1/[\mathrm{QX}]_0)/k_+ \quad (14)$$

$$1/k_{\mathrm{obs}} = [\mathrm{RX}]_0/k_+[\mathrm{QX}]_0 + ([\mathrm{RX}]_0/k_+ + 1/k_+K_\Sigma[\mathrm{QX}]_0)1/[\mathrm{MY}]_0 \quad (15)$$

Equations (13) and (14) are represented in Figures 2 and 3, respectively.

REFERENCES

1. Ch. M. Starks, *J. Am. Chem. Soc.* **93**, 195 (1971).
2. Ch. M. Starks and R. M. Owens, *J. Am. Chem. Soc.* **95**, 3613 (1973).
3. D. Landini, A. M. Maia, F. Montanari and F. M. Piris, *J. Chem. Soc., Chem. Commun.* 950 (1975).
4. A. Brändström and M. Kolind-Andersen, *Acta Chem. Scand.* **29**, 201 (1975).
5. D. Landini, A. Maia and F. Montanari, *J. Am. Chem. Soc.* **100**, 2796 (1978).
6. A. W. Herriott and O. Picker, *J. Chem. Soc. Chem. Commun.* 112 (1977).

7. J. P. Antoine, I. de Aguirre, E. Janssens and F. Thyrion, *Bull. Soc. Chim. Fr.*, 207 (1980).
8. D. Landini, F. Maia and F. Rolla, *J. Org. Chem.* **47**, 2264 (1982).
9. O. I. Danilova, I. A. Esikova and S. S. Yufit, *Izv. Akad. Nauk SSSR, Ser. Khim.* 314 (1988).
10. M. Makosza, *Usp. Khim.* **47**, 2174 (1977).
11. E. V. Dehmlow. M. Lissel and J. Heider, *Tetrahedron* **33**, 366 (1977); E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.* **16**, 493 (1977).
12. Y. Sasson. and H. A. Zahalka *J. Chem. Soc., Chem. Commun.* 1347 (1983).
13. M. Yonovich-Weiss and Y. Sasson *Isr. J. Chem.* **26**, 243 (1985).
14. W. P. Weber and G. Gokel, *Phase Transfer Catalysis in Organic Synthesis.* Springer Verlag, Berlin, Heidelberg, New York, 1977.
15. O. I. Danilova, I. A. Esikova and S. S Yufit, *Izv. Akad. Nauk SSR, Ser. khim* 2422 (1987).
16. H. A. Zahalka and Y. Sasson, *Can. J. Chem.* **67**, 245 (1989).
17. O. Arrad and Y. Sasson, *J. Am. Chem. Soc.* **110**, 185 (1988).
18. G. Bram A. Loupy and M. Pedoussaut, *Tetrahedron Lett.* 4171 (1986); G. Bram, A. Loupy and J. Sansoulet, *Isr. J. Chem.* **26**, 291 (1985).
19. O. Arrad and Y. Sasson, *J. Chem. Soc., Chem. Commun.* 148 (1988).
20. A. Dehmlow and H. Ch. Ratha, *J. Chem. Res. (S)* 384 (1988); *(M)* 2901 (1988).
21. S. S. Yufit, I. A. Esikova and O. I. Danilova, *Dokl. Akad. Nauk SSR* **295**, 621 (1987).
22. A. Wiessberger, E. S. Proskayer, J. A. Riddick and E. E. Toops, Jr, *Organic Solvents. Physical Properties and Methods of Purification.* Interscience, New York (1955).
23. V. A. Klimova, *Main Micromethods of Organic Compounds Analysis*, p.111. Khimia, Moscow (1975).
24. E. Kornish-Bouden, *Basis of Enzyme Kinetics*, p. 22. Moscow (1979). Principles of Enzyme Kinetics, A. Cornish-Bowden, Butterworths, London, Boston (1976).
25. S. S. Yufit and I. A. Esikova, *Dokl. Akad. Nauk SSR* **265**, 358 (1982).