

## Reviews\*

### Some problems in PTC theory: solvation, crystalline lattice strength, and topology

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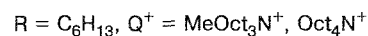
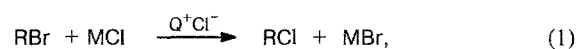
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It was shown that  $S_N2$ -type reactions both in solid—liquid and liquid—liquid systems can proceed at the interface through the formation of cyclic adsorption complexes. The conditions for the formation of the latter were formulated, and the kinetic and thermodynamic parameters of reaction with solid ionophoric salts were estimated. A linear relation between the energy of the crystalline lattice of the salt and its melting point was estimated, the latter being shown to be useful as a simplified estimation of the reactivity of solid salts in reactions where the crystalline lattice is destroyed. In solid—liquid systems the "benzene" effect of solvents was discussed. In highly basic nitrogen-containing solvents (pyridine, *etc.*), a substitution reaction proceeds in the absence of a PT catalyst. The role of hydration in liquid—liquid systems was discussed.

**Key words:** phase transfer catalysis (PTC), reaction mechanism, liquid—liquid and solid—liquid systems, role of solvents in PTC, "benzene" solvent effect, cyclic complexes at interface.

**Role of the interface.** A plentitude of investigations is devoted to studies of two-phase (heterogeneous) systems. These are mainly works in the field of heterogeneous catalysis where the catalyst represents one of the phases. In the phase transfer catalysis (PTC) method encompassing those reactions where reagents are placed in different phases, with liquid—solid systems one of the reagents is in the solid phase, while the other reagent and the catalyst are dissolved in the organic phase. With a system of two immiscible liquids both reagents are dissolved, but exist in different phases. Usually those are the organic and aqueous phases.

It is well known that the interface in a liquid—liquid system is an intricate voluminous formation.<sup>1</sup> The calculations showed<sup>2</sup> that the effective thickness of the phase boundary in the water—CCl<sub>4</sub> system is up to 9–10 Å due to the formation of capillary waves. The comparison of activities of two phase transfer catalysts (tetrabutylammonium (Oct<sub>4</sub>N<sup>+</sup>) and methyltriethylammonium (MeOct<sub>3</sub>N<sup>+</sup>) chlorides) in  $S_N2$ -substitution reaction (1) showed that:



the first-order rate constant in the case of MeOct<sub>3</sub>N<sup>+</sup> being  $1 \cdot 10^{-5}$ , and for Oct<sub>4</sub>N<sup>+</sup>  $3.2 \cdot 10^{-5}$ . The calcula-

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tions of solvation and energy parameters for the reaction by the Monte-Carlo procedure demonstrated<sup>3</sup> that the decrease in the number of carbon atoms in one of the radicals of  $Q^+$  ( $Q^+$  is the quaternary ammonium cation) results in an increase in the hydration degree of the tight ion pair  $MeOct_3N^+Cl^-$  (the hydration number is  $n = 3+2$ , as compared with  $Oct_4N^+Cl^-$  ( $n = 3+1$ )).

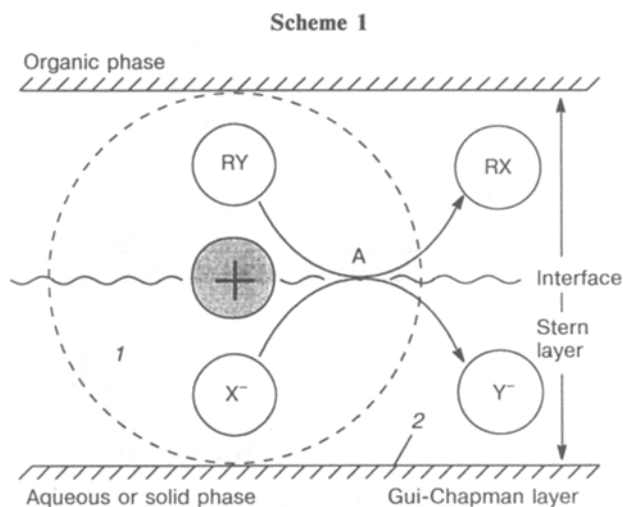
The fact that lowering the hydration degree results in increase in reaction rate is well known in the PTC. This increase could be attained both by binding of water molecules with adding alkali to the aqueous phase<sup>4,5</sup> as well as by the complete elimination of the aqueous phase.<sup>6</sup> So the interaction of the catalyst adsorbed at the interface with the aqueous phase exerts a strong influence over reaction rate thus demonstrating the significant role of this process in the PTC.

**Adsorption at the interface.** Adsorption of the biphyle molecule at the interface (nearly all phase transfer catalysts are biphyle) results in the formation of a double electrical layer typical of electrochemical systems. The process of interface filling proceeds according to the Langmuir or Freundlich equations.<sup>4,7</sup> The fixation of the catalyst at the interface inevitably results in the formation of two layers,<sup>8,9</sup> known in electrochemistry as the Stern layer and Gui—Chapman layer. The concentration of  $Q^+X^-$  molecules inside the Stern layer is increased, and the freedom of their motion is limited and is determined by diffusion factors. The concentration of  $Q^+X^-$  molecules inside the Gui—Chapman layer, compared to the bulk volume, is also increased, but the motion of molecules is less diffusion-restricted.

The strong electrostatic field of the ion at the interface pulls molecules together, thus promoting the elementary act of reaction (pull-together catalysis) and determines the mechanism of the PTC reaction.

Reaction (1) proceeding by  $S_N2$  mechanism is shown on Scheme 1 as a graph.<sup>10</sup> The movement of the reagent molecule brings it at the interface inside the electrostatic field of  $Q^+$  (phase transfer catalysts are usually onium cations). Closing in on the substrate  $RY$ , the counterion  $X^-$  forms with the latter at point A a reaction complex, whose decay results in the formation of the reaction product  $RX$ , which leads into the bulk of the liquid phase.

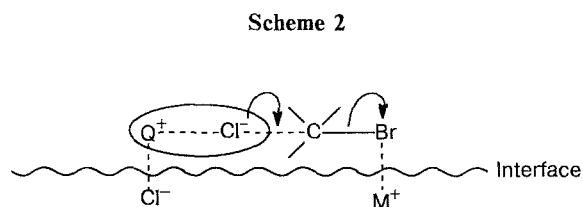
Taking into account the quantum chemical restrictions and the extremely low values of the dissociation constants of ion pairs in the low polar weakly solvating solvents as well as phase electroneutrality and steric demands, one can formulate the five requirements that should be satisfied for all proposed mechanisms of PTC  $S_N2$  reaction<sup>11</sup>: 1) the retention of the stereochemistry of the intermediate complex according to the quantum chemistry rules, *i.e.*, the linear arrangement of reacting molecules; 2) providing for the leaving group solvation; 3) conforming to the phase electroneutrality demand during ion transfer through the interface (*i.e.*, the synchronous transfer of similarly charged ions); 4) no dissociation of ion pairs in the organic phase thanks to energy



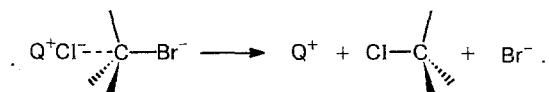
1, the electrostatic field of the quaternary ammonium cation  $Q^+$  at the interface; 2, the provisory boundary of the Stern layer in the aqueous phase (*aq*) or the surface of the solid phase. A is the site of ternary complex (TC) formation.

restrictions; 5) mutual compensation of dehydration (desolvation) and hydration (solvation) heat effects in the course of the sole elementary act of reaction.

These demands are met completely only in the case of the ternary intermediate complex adsorbed at the interface (Scheme 2).

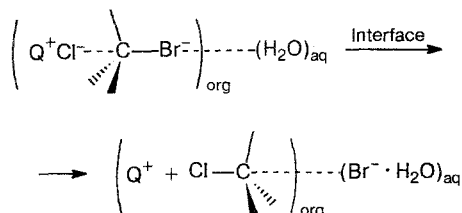


Really if one would take a look at the stereochemistry of conventional scheme of the  $S_N2$  substitution in a homogeneous solution that conforms to quantum chemical restrictions (complying with the requirement 1) it is seen that the demand 4 would be violated because the reaction results in the dissociation of the ion pair that is highly improbable in case of such organic solvents as hexane, toluene, *etc.*:



If we will take into account the possibility of the solvation of the leaving group by the most powerful solvating agent, *i.e.*, water (complying with requirement 2), then the act of reaction would violate require-

ment 3, because there would be no compensating transfer of the anion from the aqueous phase (*aq*) to the organic one (*org*):



All these "violations" of the above mechanistic restrictions are abolished if the binary complex resides at the interface thus giving rise to the formation of the ternary complex that conforms to all the five requirements to the PTC substitution mechanism. Just these considerations are deciding in evaluation of the reality of the proposed mechanism.

The adsorption reaction mechanism can be realized in liquid-liquid systems if the lifetime of the substrate adsorbed at the interface is large enough for the reaction act to proceed (see also the discussion of these problems in Ref. 12).

The complete set of structural, energetic, quantum-chemical, and thermodynamic factors together with the clearly expressed biphylity and complexing properties of all phase transfer catalysts make it possible for the proposed mechanism to be realized in all PTC reactions.

**Reactions inside ion pairs.** The different consequences of proton oscillations in hydrate shells of  $\text{OH}^-$  and  $\text{F}^-$  ions have been discussed elsewhere (*cf.* Ref. 4).



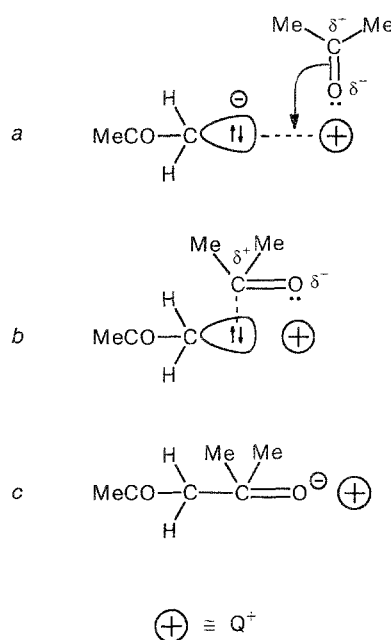
In the first case the number and composition of the participating species are not changed, while in the second case two new species are formed, *i.e.*, there takes place a chemical reaction. However, in both of the cases the superposition of the states due to proton oscillations inside the ion pair should result in strengthening of the separated ion pair. This was confirmed in Ref. 13, where it was shown that at certain arrangement of  $\text{H}_2\text{O}$  molecule inside the separated ion pair  $(\text{CH}_3)_3\text{C}^-//\text{H}_2\text{O}//\text{Cl}^-$  there appears a fairly deep (up to 5 kcal mol<sup>-1</sup>) minimum on the potential energy surface marking the stabilization of this separated ion pair. It is evident that under certain conditions the stabilization of the separated ion pair could result in the acceleration of reactions with its participation. This can explain the acceleration of PTC reactions already observed on adding the minute amounts of water to anhydrous systems,<sup>14,15</sup> as water would hydrate the anion including itself inside the separated ion pair.

The proton transfer inside the separated ion pair is a common chemical reaction. One can imagine ion pairs where transfer of electron pair (or of one electron, or of a "hole") occurs, *i.e.*, the new chemical bond is formed.

It is well known that yet Ingold<sup>16</sup> had suggested the formation of so-called "quadruplets" in substitution reactions. These are in fact the binary reactant complexes. Ingold believed that in the act of reaction the quadruplet unfolds itself, and the reaction proceeds according to quantum-chemical restrictions. However the reaction can proceed in another way that we call the reaction inside an ion pair.

Actually, if the solvent-separated ion pair is separated by the reacting molecule, then the reaction may proceed inside the ion pair (Scheme 3).

Scheme 3



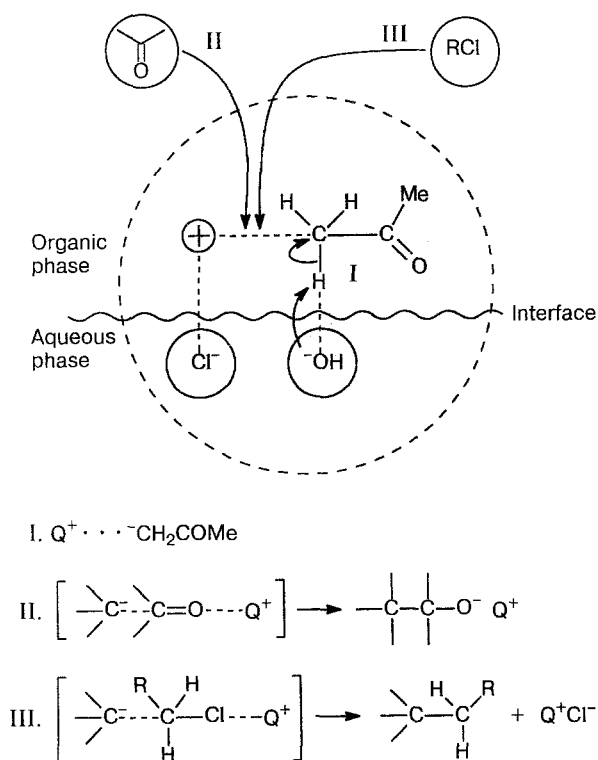
*a.* Coordination of the ion pair  $\text{MeCOCH}_2^- \cdots \text{Q}^+$  with acetone molecule; *b.* quasi-separated ion pair  $\text{MeCOCH}_2^-//(\text{Me})_2\text{CO}//\text{Q}^+$ ; *c.* alkoxide  $\text{Q}^+$  (tight ion pair)  $\text{MeCOCH}_2(\text{Me})_2\text{CO}^- \cdots \text{Q}^+$ .

Scheme 3 illustrates the aldol condensation of acetone inside the ion pair consisting of onium cation and acetone anion. The first step is the formation of a typical Ingold quadruplet. Then the second solvating acetone molecule "stumbles" into the ion pair making it "solvent-separated". And finally, the electron transfer results in the formation of the reaction product, *i.e.*, the alkoxide of the diacetone alcohol.

Just the same explanation can be applied for many other reactions that include intermediate ion pairs.

Scheme 4 presents more complicated two-step alkylation of acetone. The first deprotonation step may result in three reaction products: one tight and two separated ion pairs. The tight ion pair would be unreactive because of the shielding of the reaction center in acetone anion  $A^-$  by counter-ion  $Q^+$ . For the activation of the former this ion pair must dissociate (reaction I). In case of formation of the acetone-separated ion pair (reaction II) the aldol condensation would proceed inside the ion pair (see Scheme 3), and if haloalkyl  $RCI$  gets inside the ion pair then the alkylation of acetone occurs (reaction III). Many other reactions can be described in just the same way, according to the existing experimental data. An enormous amount of six-centered mechanisms discussed<sup>17</sup> includes also reactions inside ion pairs thus opening possibilities of quantitative description of these mechanisms.

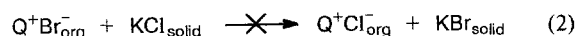
Scheme 4



Note. Notations are listed in Scheme 1.

#### Reactions on solid surfaces (solid—liquid systems).

Earlier<sup>18–20</sup> it was shown that PTC substitution reactions of type (1) in solid—liquid systems occur on the surface of ionophoric salt. The absence of the exchange shown below served as direct evidence of this fact:

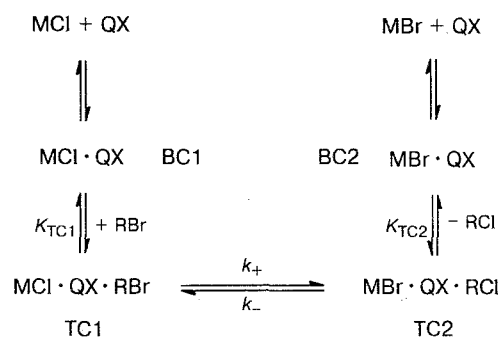


The above reaction is the basis of the commonly recognized PTC mechanism for liquid—liquid systems. Be-

cause reaction (1) proceeds in the absence of (2) it is evident that the process occurs at the interface.

The analysis of the kinetic data<sup>21</sup> together with thermodynamic and activation parameters<sup>22</sup> allowed us to suppose the step-by-step formation of the cyclic ternary complex.<sup>23</sup> The resulting data are consistent with a substitution mechanism that includes the formation of two pairs of binary and ternary complexes obtained from  $RY$ ,  $MX$  and  $QX$  adsorbed on solid salt surface (Scheme 5; where  $K$  is the equilibrium constant,  $k$  is the rate constant,  $BC1$ ,  $BC2$  are binary complexes, and  $TC1$  and  $TC2$  are the ternary ones).

Scheme 5



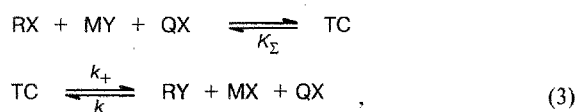
Analysis of the substitution energetics when solid ionophores with different strengths of the  $M-Cl$  bond react, showed that the rearrangement of the ternary complexes is the rate-limiting step. The possible structures of these ternary complexes are expected to provide for adherence to the detailed balancing principle in this reversible reaction. In construction of the ternary complex models the following three factors should be taken into account: (1) according to steric and quantum-chemical requirements the reaction proceeds *via* the  $S_N2$  mechanism, and it is assumed that the rear part of the carbon atom associated with the leaving group  $Y^-$  is attacked by the  $X^-$  ion; (2) the quantum-chemical study of these systems<sup>24</sup> indicates that during such an attack the  $X^-$  ion is capable of being diverted from the  $X^- \cdots C-Y$  axis by up to  $20^\circ$  without a noticeable rise in the system's energy (10 % maximum); (3) the  $Cl^- \cdots Q^+ \cdots Cl^- \cdots M^+$  and  $Br^- \cdots M^+ \cdots Cl^- \cdots Q^+$  electrostatic interactions do not exhibit any predominant direction so that the arrangement of the component ions is controlled only by the strength of these interactions.

Note also that in the formation of ternary complexes the ion—ion and ion—dipole interactions impose some requirements on the geometry of the entering species. In this context, the effect of the geometric factors will be significant, and the reaction rates depend on the size of the catalyst  $Q^+$  cation. The use of bulkier  $Q^+$  cations results in a sharp deceleration of the substitution reaction. The rate constant in the presence of  $Bu_4NBr$  is four-fold that in the case of  $Oct_4NBr$ , although the

latter is completely dissolved in toluene. The reaction rates in the presence of different QX have no connection with the solubility of the catalyst in toluene, since the addition of RBr to the system brings about complete dissolution of all the QX salts at 70°C.

The volume of the catalyst anion also effects the reaction rate, and a satisfactory linear relationship between  $\log k_{\pm}$  and reciprocal anion radius  $1/R$  ( $\text{\AA}^{-1}$ ) both for the forward and the reverse reaction were established.

The kinetic analysis of different reaction mechanisms performed by I. A. Esikova<sup>22</sup> allowed the one to be isolated conforming with all kinetic peculiarities of the reaction (3):



$$\begin{aligned} k_{\text{obs}} &= \frac{k_+ K_{\Sigma} [\text{MY}]_0 [\text{QX}]_0}{1 + K_{\Sigma} [\text{RX}]_0 ([\text{QX}]_0 + [\text{MY}]_0)}; \\ 1/k_{\text{obs}} &= \frac{1}{k_+} K_{\Sigma} [\text{MY}]_0 [\text{QX}]_0 + \\ &\quad + [\text{RX}]_0 \frac{[\text{QX}]_0 + [\text{MY}]_0}{k_+} [\text{MY}]_0 [\text{QX}]_0; \\ 1/k_{\text{obs}} &= \frac{[\text{RX}]_0}{k_+} [\text{MY}]_0 + \frac{K_{\Sigma} [\text{MY}]_0 + [\text{RX}]_0}{[\text{QX}]_0 k_+}; \\ 1/k_{\text{obs}} &= \frac{1}{k_+} K_{\Sigma} [\text{MY}]_0 [\text{QX}]_0 + \\ &\quad + \frac{[\text{RX}]_0}{k_+} \left( \frac{1}{[\text{MY}]_0} + \frac{1}{[\text{QX}]_0} \right); \\ 1/k_{\text{obs}} &= \frac{[\text{RX}]_0}{k_+} \left( \frac{[\text{RX}]_0}{k_+} + \frac{K_{\Sigma} [\text{QX}]_0}{k_+} \right) \frac{1}{[\text{MY}]_0}. \end{aligned} \quad (4)$$

According to Eq. (4), a limit of the observed rate constant ( $k_{\text{obs}}$ ) will be observed under certain initial

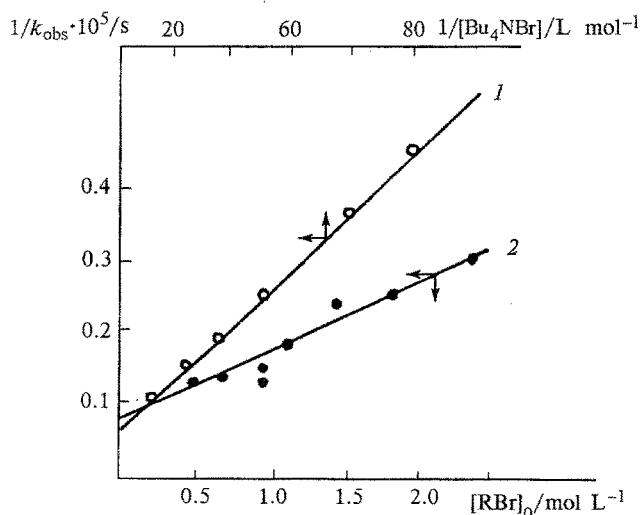


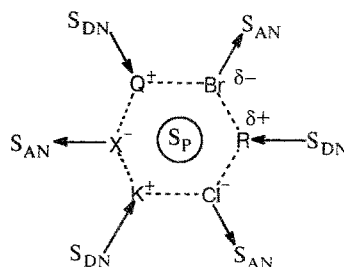
Fig. 1. Linear anamorphosis of the summary kinetic equation (4) for the reaction (3).

concentrations of reagents that is characteristic for Langmuir-like curves. Actually inverting of both sides of Eq. (4) results in subsequent linear relationships ( $1/k_{\text{obs}}$  vs.  $1/[\text{Q}^+]$ ) represented in Fig 1 for reaction (3).

The comparison of enthalpy changes during formation of ternary complexes including different solid salts MCl and MBr ( $M = \text{Li, Na, K, Rb, Cs}$ ), allows one to suppose that the energy of their formation is linked with the crystalline lattice energy of the respecting salt, the less being the latter the less strong are the former. In the case of CsCl the formation of a ternary complex is even endothermic corresponding thus to its high reactivity.<sup>20</sup> This hypothesis is confirmed by the analysis of  $\Delta H_{\text{TC2}}$  values for the reverse reaction: the lower values of crystal lattice energies of bromides result in a zero values of  $\Delta H_{\text{TC2}}$ . It allows one to believe that in case of salts with the "weak" crystalline lattice (little values of crystalline lattice energy  $\Delta H$ ) the reaction scheme may be transformed in such a way that TC1 and TC2 would not constitute kinetically independent species any more, but would become "diffusion" pre-equilibrium complexes.

Starting with the earlier published data<sup>19</sup> on the dependence of  $k_{\text{obs}}$  on  $[\text{QBr}]_0$  and  $[\text{RBr}]_0$  in the reaction with KCl, we determined the formation constant of TC1,  $K_{\text{TC1}} = 20.48 \text{ M}^{-2}$ , and the rate constant of its rearrangement to TC2,  $k_+ = 0.75 \text{ s}^{-1} \cdot \text{M}^{-2}$  at 84 °C. Using the equation  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta H_{\text{TC}} = -11.7 \text{ kcal mol}^{-1}$  (see Ref. 21), we estimated the entropy of formation for TC1 and that of activation involved in the step-by-step rearrangement of all TCs. It was found that  $\Delta S_{\text{TC1}} = -26.8 \text{ e.u.}$ , and  $\Delta S^* = +47 \text{ e.u.}$  A correlation of these values suggest that the structure of the TCs is more rigid than that of the transition state during the complex rearrangement. This agrees well with the idea that the solid-phase molecule forms a part of the TCs. It is believed that the transition between the TC1 and TC2 occurs *via* a cyclic state with a delocalized bond system (Scheme 6; arrows show the direction of acceptor (A) or donor (D) forces of solvent molecules (S) and their polarization component ( $S_p$ )).

Scheme 6

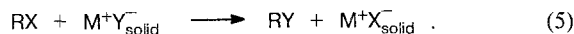


The large positive value of  $\Delta S^*$  may be explained by the destruction of the solid salt crystalline lattice, resulting in the appearance of lattice-free  $M^+$  and  $\text{Cl}^-$

(or  $\text{Br}^-$ ) ions and, hence, a sharp rise in the entropy of the system.

Hence the above substitution mechanism with participation of TC1 and TC2 involves the destruction of crystalline lattice of the solid ionophore by means of a catalyst that was demonstrated earlier also for other reactions.<sup>25,26</sup> It seems that the desorption of QBr from the surface of MCl is not necessary for the reaction to proceed, the movement of QBr on the crystal surface is more probable. This phenomenon is well known in the heterogeneous catalysis. In this case we have a modification of PTC that should be called the "true inter-phase catalysis," and not the "phase transfer catalysis," because a catalyst does not transfer any solid phase.

**"Strength" of the crystalline lattice.** All the existing data suggest that the crystalline lattice energy should be taken into account in consideration of any processes in solid—liquid systems. However the determination of its value is fairly difficult, and sometimes there are no published data. Because the crystalline lattice energy ( $\Delta H_{\text{cr.l.}}$  or  $U_{\text{cr.l.}}$ ) is connected with most different properties of the crystal one may suppose that such a relation exist also for the crystal melting point. As it was indicated above, reaction in a solid—liquid system with ionophoric salt results in the destruction of the crystalline lattice because anion of the  $\text{M}^+\text{Y}^-$  salt (KCl for example) is included in the reaction products:



Separation of ions from the crystalline lattice is equivalent to the melting and should be connected with the crystalline lattice energy. Actually, such a link does exist. Fig. 2 shows the relationship between the crystalline lattice energy and the salt melting point. It is clearly seen that salt melting points linearly depend on the crystalline lattice energies and form several series, concerned with cation and anion types. One should note the difference between simple symmetrical halide anions

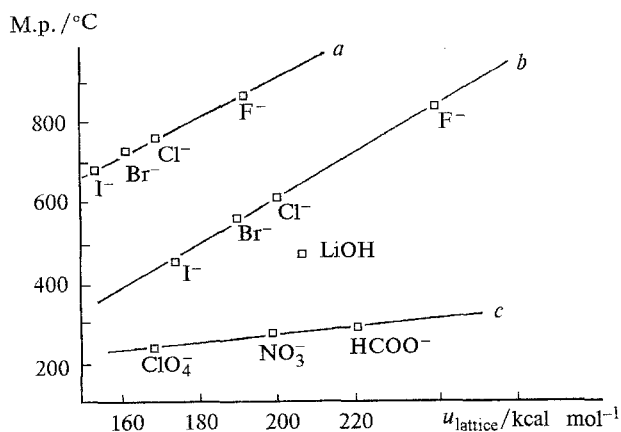


Fig. 2. Crystalline lattice "strength": melting point—crystalline lattice energy relationship for some salts: potassium halides (a), lithium halides (b), other lithium salts (c).

Table 1. The comparison of some anion parameters in formates and chlorides

| Parameter   | Chlorides                    | Formates            |
|---|------------------------------|---------------------|
| Anion radii <sup>a</sup> /Å                                     | 1.81                         | 2.4–3               |
| Crystalline lattice energy <sup>a</sup> /kcal mol <sup>-1</sup> | 168.0 (KCl),<br>201.4 (LiCl) | 220.7 (HCOOLi)<br>— |
| Lattice "strength" <sup>a</sup> (m.p.)/°C                       | 776 (KCl)                    | 273 (HCOOLi)        |
| Nucleophilicity <sup>b</sup> /EN                                | 1.21                         | (0.95)              |
| Basicity  | –3.0                         | (+6.46)             |
| Symmetry <sup>c</sup>   | Spherical                    | Planar              |

<sup>a</sup> See Ref. 27; <sup>b</sup> see Ref. 28; <sup>c</sup> see Ref. 24.

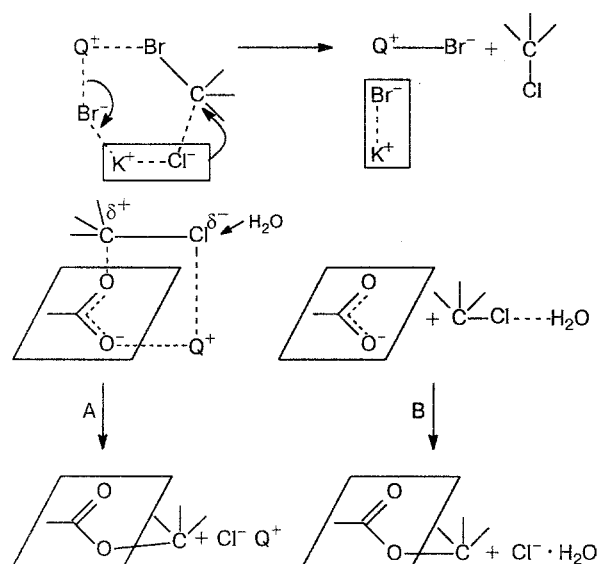
and more complex anions of the formate type. It allows one to introduce the term "the crystalline lattice strength" numerically equal to the melting point as one more tool for the comparing the properties of different solids in PTC.

It is evident that the small "crystalline lattice strength" would facilitate the reaction accelerating as it was observed actually. Thus rates of substitution of different potassium halides (reaction (5)) exactly correspond to their "crystalline lattice strength". The comparison of the "crystalline lattice strength" of salts lying on one line in Fig. 2, with that for salts on the other one can sometimes provide more information than the comparison of their  $\Delta H_{\text{cr.l.}}$ .

Table 1 lists some parameters of lithium formate and chloride (lithium salts are chosen because for lithium formate the value of the crystalline lattice energy is known). The analysis of these data allows to reveal three main distinctions, *i.e.*, the type of symmetry, basicity and the "crystalline lattice strength." These distinctions can explain the observed differences in kinetics and mechanisms in  $\text{S}_{\text{N}}2$ -substitution (reaction (5)). First of all this relates to the different influence of water. For planar ions of the formate type with the low "crystalline lattice strength" there was observed a sharp acceleration of the reaction rate (and yield) on addition of small amounts of water,<sup>14</sup> and for spherical halide ions with the high "crystalline lattice strength" small amounts of added water exert no influence on the reaction rate.<sup>23</sup>

The discussed parameters differ quite strongly for the symmetrical halide ion and planar formate ion. They differ in their "strength" (*i.e.*, melting point of lithium salts) on 337 °C, and in their basicity nearly on 9 units of pK and moreover they have different signs of the latter. While for the cubic crystalline lattice of chlorides free unshielded ions as centers of formation adsorption complexes are typical; the formate lattice is flaky,<sup>27</sup> and the ion itself is planar that results in counterions shielding the approach to oxygen atom from any side. These differences result in different reaction mechanisms for formates and halides.

Scheme 7



The spherical symmetry of  $\text{Cl}^-$  ion, i.e., the freedom of approach from any side allows the formation of the very favorable cyclic complex where a catalyst not only coordinates the reagents, but also solvates the leaving group. In that case there is no need in its hydration (Scheme 7). That results in small sensitivity of such reaction to water addition.

In the case of formate the formation of such complex is impossible and the reaction can proceed by two pathways. One of those is the reaction inside an ion pair (path A), and the second one is the reaction of the formate ion itself (path B). In the second case the participation of the solvating agent is necessary. This role can be played by water, than the reaction would become strongly water-sensitive.

**Influence of solvents on  $\text{S}_{\text{N}}2$  reaction in solid-liquid system.** The problem of solvent influence on chemical reactions is as old as the chemistry itself. There was proposed a multitude of methods for estimation of solvent properties. In the book<sup>28</sup> it was shown that six main "scales":  $E_T$ ,  $Y$ ,  $\log k_{\text{ion}}$ ,  $\beta$ ,  $\Omega$ ,  $S$ , are linearly related with the seventh one ( $Z$ ) and, consequently related with each other. In Ref. 29 it is proved that all other "scales" can be reduced to the donor (DN) and acceptor (AN) numbers. Actually in this way some common for all the solvents property, i.e. their ability to donor-acceptor interactions is isolated. However, this is a purely chemical quality, and some physical properties of solvents such as dielectric constants and Hildebrand solubility parameters and others are not reflected by these scales.

Presently there is only one systematic study of solvent influence in PTC performed by the French investigators for the liquid-liquid system. They have studied 15 different solvents but did not come to any certain conclusion.<sup>5</sup> For the solid-liquid system we have studied 17 solvents<sup>32</sup>, some of them being investigated also by the French authors (Table 2). In all these solvents

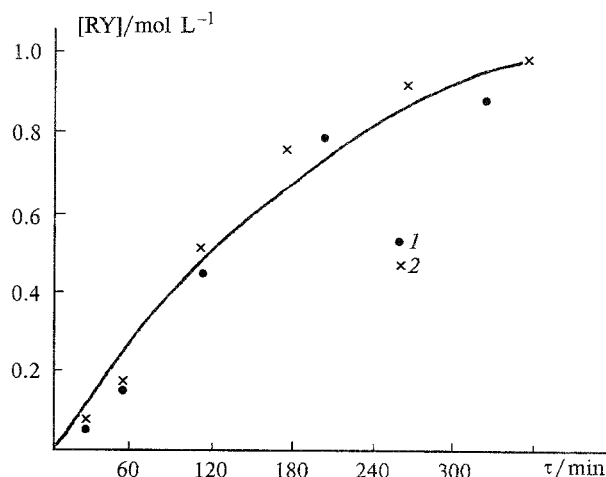
**Table 2.** Pseudo first-order rate constant for reaction (1) in various solvents and associated parameters<sup>32</sup>

| No. | Solvent                        | $k \cdot 10^{-5}$<br>$\text{s}^{-1}$ | AN   | DN   | log $\epsilon$ | $P^*$ |
|-----|--------------------------------|--------------------------------------|------|------|----------------|-------|
| 1   | Pyridine                       | 11.22                                | 11.5 | 43.0 | 1.09           | 0.299 |
| 2   | Hexamethyl phosphorus triamide | 9.33                                 | 12.3 | 38.1 | 1.471          | 0.273 |
| 3   | 1-Methylpyrrolidin-2-one       | 8.3                                  | 14.0 | 27.3 | 1.518          | 0.277 |
| 4   | DMFA                           | 4.95                                 | 16.1 | 25.1 | 1.565          | 0.257 |
| 5   | Acetophenone                   | 1.85                                 | 12.9 | 14.1 | 1.24           | 0.311 |
| 6   | Pentan-2-one                   | 1.39                                 | 10.3 | 12.6 | 1.23           | 0.231 |
| 7   | Benzonitrile                   | 1.15                                 | 13.8 | 12.0 | 1.401          | 0.308 |
| 8   | THF                            | 1.11                                 | 7.8  | 20.6 | 0.869          | 0.246 |
| 9   | Nitrobenzene                   | 0.91                                 | 13.8 | 3.7  | 1.541          | 0.321 |
| 10  | Acetonitrile                   | 0.876                                | 18.9 | 13.2 | 1.574          | 0.21  |
| 11  | Toluene                        | 0.709                                | 3.3  | 3.9  | 0.376          | 0.293 |
| 12  | Nitromethane                   | 0.667                                | 19.3 | 4.8  | 1.555          | 0.232 |
| 13  | Ethyl acetate                  | 0.657                                | 8.7  | 10.9 | 0.779          | 0.227 |
| 14  | Anisole                        | 0.61                                 | 7.6  | 7.9  | 0.636          | 0.302 |
| 15  | $\text{CCl}_4$                 | 0.44                                 | 8.6  | 0    | 0.35           | 0.274 |
| 16  | Methanol                       | 0.297                                | 41.3 | 12.0 | 1.513          | 0.203 |
| 17  | Ethanol                        | 0.15                                 | 37.1 | 6.5  | 1.386          | 0.221 |

\*  $P = (n^2 - 1)/(n^2 + 2)$ , see Ref. 28; for data for AN and DN, see Ref. 26.

the reaction proceeds by the same pseudo first-order kinetics.

The reaction acceleration without a catalyst in highly basic nitrogen-containing solvents was quite surprising. In these solvents the less was the accelerating solvent effect (zero rate) the more pronounced was the catalyst influence. Thus the reaction rate in pyridine (DN = 33.1) did not depend on catalyst, but there was observed little unexplained lag-time not related with the possible solvent quaternizing (Fig. 3). In all other solvents reaction proceeds only in the presence of a catalyst.



**Fig. 3.** Kinetic curve of the reaction (5). Catalyst  $\text{Bu}_4\text{NCl}$ ,  $\text{RX} = \text{C}_6\text{H}_{13}\text{Br}$ ,  $\text{RY} = \text{C}_6\text{H}_{13}\text{Cl}$ ,  $\text{M}^+\text{Y}^- = \text{KCl}$ ,  $\text{M}^+\text{X}^- = \text{KBr}$ . Solvent pyridine. The curve corresponds to first-order kinetics. 1, reaction without a catalyst; 2, catalytic reaction.

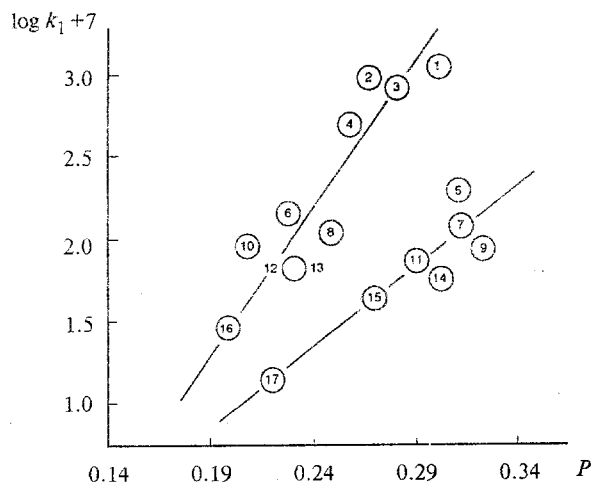


Fig. 4. The effect of the polarizability ( $P$ ) of the solvents (Table 2) on  $\log k_{\text{obs}}$  in reaction (1).<sup>32</sup>  $Q^+ = \text{Bu}_4\text{N}^+$ .

The dissolution of the solid salt did not result in the reaction acceleration. Moreover, the reaction is very slow in alcohols that provide rather high salt solubility, possibly due to anion solvation.

In opposite to discussed earlier liquid—liquid system,<sup>5</sup> in the solid—liquid system there was not obtained any link with solvent acceptor numbers that could prove ion interactions by the authors' opinion.<sup>5</sup> On the opposite this fact confirms our hypothesis that ions do not effect the course of a reaction in the solid—liquid system. There is satisfactorily positive correlation between rate constants and donor numbers. The comparison with a sum of donor and acceptor numbers<sup>29</sup> did not improve the correlation.

There was observed no certain relationship between the reaction rate and majority of solvent "physical" parameters. All things being equal the reaction is faster in solvents with lower dielectric constant thus confirming the hypothesis that PTC reactions are hindered by the dissociation of ion pairs. However there is no significant correlation with this parameter just as in liquid—liquid system. At the same time there is satisfactory positive correlation between  $\log k_{\text{obs}}$  and such purely "physical" parameter as the solvent polarizability (and subsequently various functions incorporating refraction index). This analysis allows to divide all the studied solvents into two groups, one of which include all aromatic ones and  $\text{CCl}_4$ , and the other one — all the remaining (Fig. 4).

So, in reaction (1) in the solid—liquid system the so-called "benzene effect" is displayed.<sup>33</sup> Its essence is that benzene in spite of its low dielectric constant effects many chemical reactions just as strongly as polar solvents.\* The high polarizability of the aromatic ring is believed<sup>35,36</sup> to be the cause of the "benzene effect," and

if concerns  $\text{CCl}_4$ , it is possibly the result of the formation of charge-transfer complexes.<sup>37,38</sup>

So there is observed some dualism in the effect of aromatic solvents. On one hand a solvent molecule acts as a donor-acceptor agent polarizing respective reagents' bonds. From the other hand, the interaction of the solvent  $\pi$ -electron system with reagents and intermediates due to the presence of aromatic ring is stronger in case of greater charge "spreading" in the intermediate complex (Scheme 6).

Aromatic solvents are characterized by high polarizability and poor solvation. That makes it clear why pyridine that has high donor number DN, along with its "aromaticity" is the "best" solvent. It is evident that in choice of solvents one should take into account depending on the reaction mechanism both donor-acceptor properties of the solvent as well as its polarizability (see Scheme 6).

It is well known that the scales of solvent donor and acceptor numbers were obtained with the help of model reactions. Consequently using of these models it is possible to discuss the solvent influence on the ternary complex adsorbed on the solid salt surface. The interaction, shown in Scheme 6, quite satisfactorily explains the observed solvent influence and also makes it possible to choose solvent appropriate for the reaction.

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\* For a discussion of this problem see Ref. 34.



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