Pergamon

Tetrahedron 55 (1999) 6363–6374

TETRAHEDRON

Solid/Liquid Phase-Transfer Catalysis. Some Models and Solvent Influence

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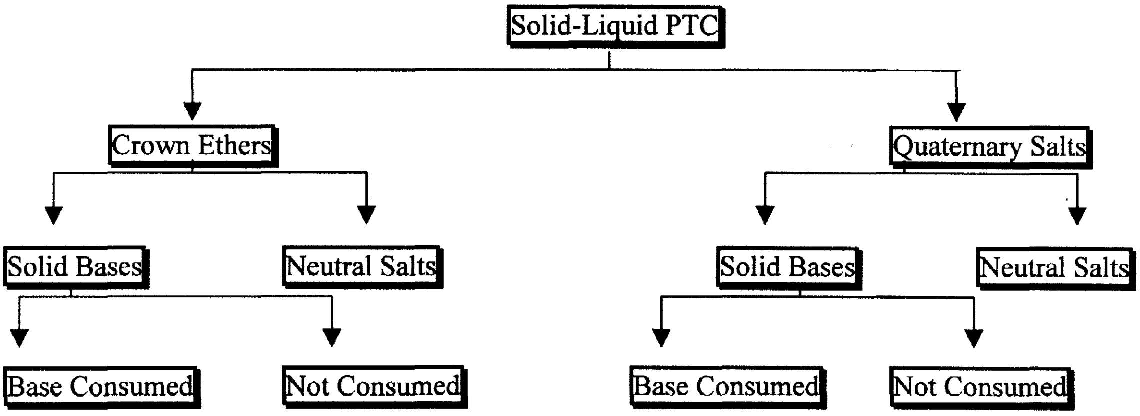
Received 24 December 1998; accepted 23 February 1999

Abstract: The applicability of the models developed earlier for the topochemical reactions in the solid/liquid phase-transfer catalysis is discussed. Depending on the solvent and the catalyst the reaction may be inhibited by the crust of the solid inorganic product. Solvents like MeCN and THF, and catalysts such as polyethylene glycols loosen this crust, thus preventing the inhibition. The solvent influence using the $E_T(30)$ parameter in different reactions in the solid/liquid system is investigated. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Some problems of solid/liquid PTC. Phase-transfer catalysis in a solid/liquid system has always attracted a lot of attention. The solid/liquid system is usually more reactive than a liquid/liquid one. Moreover, some reactions, such as the halogen replacement are better carried out in this system. Reactions carried out in a solid/liquid system have also good industrial perspectives in spite of some complexities caused by handling of a solid phase. The development of an industrial process ordinarily includes the kinetic studies.

There are a variety of arguments in the literature concerning the mechanism of a solid/liquid PTC. Some of them are caused by different reaction conditions. We think that, according to the catalyst and the solid reagent employed, the solid/liquid PTC reactions can be subdivided as follows:



It is evident that all these reactions can not proceed by the same mechanism. Palmer et al.[1] investigated various solid/liquid PTC substitution reactions using the rotating disk apparatus. They established that in the presence of the quaternary salts (quats) during the reaction the surface of the solid reactant is coated by the

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PII: S0040-4020(99)00212-4

solid product, thus poisoning it. To the contrary, in the presence of crown-ethers, the surface of the solid reactant is constantly renovated, possibly due to the presence of the omega-phase.[2]

The model of the solid reagent particle during the solid/liquid PTC reaction in the presence of quats is shown below.

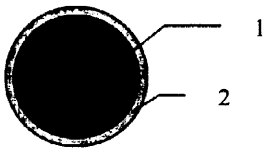


Fig. 1. A particle of a solid reagent during the solid/liquid PTC reaction: *1*–the nucleus; *2* – the crust of the solid reaction product.

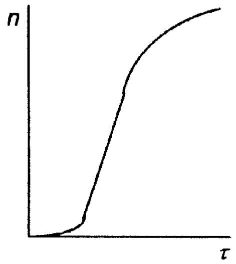


Fig. 2. The typical kinetic curve of the topochemical reaction:[3] *n* – amount of the product, τ–time

These processes closely resemble the so-called topochemical reactions the kinetics of which have been investigated in much detail.[3–5] The integral kinetic curves of these processes have an S-like form.

This form of the curve is caused by the localisation of the process at the interface of phases 1 and 2 shown in Fig. 1, *i.e.* the solid reactant and the reaction product that was shown yet by Langmuir.[6] At the first moment of the reaction, there is no solid product on the surface and the reaction rate is low. Then, the nuclei (embryos) of the solid product phase are formed. In this way the interface of the two solid phases appears. The observed reaction rate increases with time due to the nucleation. The interface surface increases till the nuclei begin to overlap. This process ends with formation of a continuous crust of the solid product. The interface surface is reduced and the apparent reaction rate falls. The kinetics of nucleation were developed by several authors, Avrami[7] and Izmailov[8] being the most prominent. The simplest kinetic equation, widely used for the description of topochemical processes, is the Erofeev equation:[3, 9]

$$x = 1 - \exp(-k\tau^n), \tag{1}$$

where k is the rate constant, x is the conversion degree, and n is a parameter depending on the geometry of the nuclei.

In our opinion, this equation is more appropriate for the description of the solid/liquid PTC than more complicated ones recommended in the literature.[10] We intend to publish a detailed paper on the solid/liquid PTC mechanism shortly.

Significance of the Erofeev Equation: a brief overview. This equation was derived starting from molecular statistics.[9] The law of mass action was not used. Below is presented an extract of the author's reasoning.[9]

Let us denote by q_i^k the probability of the elementary event that the ith molecule of a reactant will not react in a kth interval of time:

$$0=t_0 < t_1 < \ldots\ t_{k-1} < t_k \ \ldots < t_n = t \tag{2}$$

Then the probability of the composite event, Q_i, that the ith molecule will not react till time t, can be expressed as the product of the elementary event probabilities:

$$Q_i = \prod_{k=1}^{k=n} q_i^k \tag{3}$$

The probability that ith molecule will react till time t is $P_i = 1 - Q_i$, and $p_i^k = 1 - q_i^k$ is the probability that the ith molecule will react in the kth interval of time. In these terms the equation (3) after taking a logarithm and going to the limit at $n \to \infty$ assumes the following form:

$$\ln(1 - P_i) = \lim_{n\to\infty} \sum_{k=1}^{k=n} \ln(1 - p_i^k) = -\int_0^t p_i dt \tag{4}$$

After summing equation (4) on all possible values of i, and introducing the normalising factor $1/N$, where N is overall number of the reactant molecules at time t=0, we obtain:

$$\frac{1}{N}\sum_{i=1}^{N} \ln(1 - P_i) = -\frac{1}{N}\sum_{i=1}^{i-N}\int_0^t p_i dt \tag{5}$$

For the finite time intervals P_i are practically the same for all the molecules of the reactant. Thus

$$\ln\left(1 - \frac{1}{N}\sum_{i=1}^{i-N} P_i\right) = -\int_0^t \left(\frac{1}{N}\sum_{i=1}^{i-N} p_i\right) dt \tag{6}$$

It is evident that

$$\left(\frac{1}{N}\sum_{i=1}^{i-N} P_i\right) = P, \qquad \left(\frac{1}{N}\sum_{i=1}^{i-N} p_i\right) dt = pdt \tag{7}$$

are the average probabilities that a molecule will react till time $t(P)$ or in the interval t, $t + dt$ (pdt) respectively. Thus it is obtained

$$P = 1 - \exp\left(- \int_0^t p dt \right) \tag{8}$$

At large enough N one can assume that P is the reactant conversion degree, x. So,

$$x = 1 - \exp\left(- \int_0^t p dt \right) \tag{9}$$

This is a generalised kinetic equation. No assumptions about the reaction mechanism were used in obtaining it. The author[9] derived the equation (1) from (9) using Mott's model[11] of reaction nuclei formation in a solid. Other equations also were proposed for the topochemical (gas-solid) reactions for the «shrinking core» and «non-reacting core» models.[4, 12] We have used the simplest one.

Solvent influence in PTC: a short discussion. An attentive study of Starks' monograph[13] shows that there are only a few examples of a systematic study of the solvent influence on PTC. However, such a study can provide a deep insight into the reaction mechanism. Thus, Landini[14] showed that the nucleophilic substitution of methanesulfonate by bromide in a liquid/liquid system is favoured by decreasing the polarity of the solvent. On the opposite, the ethylation of desoxybenzoin by bromoethane is promoted by polar solvents.[15] The same trend was observed in the reaction of trifluoroethoxide with chlorophosphazene.[16] The rate constant was extraordinarily well correlated with the E_T (30) parameter. In the displacement of bromine in bromoheptane by chloride no definite dependence of the reaction rate on the solvent parameters was obtained.[17]

The straight correlation lines drawn by the authors[17] are, in our opinion, fairly arbitrary. The same authors[17] divided the solvents into two groups, aromatic and non-aromatic ones. Still, tetrachloromethane and ethanol are not aromatic and pyridine is clearly aromatic.

In another study,[18] the reaction of sodium 4-nitrophenolate with iodomethane in the liquid/liquid system was investigated. The results are presented in Fig. 4. It is seen that no correlation exists.

The empirical solvent polarity parameter $E_T(30)$, proposed by Dimroth and Reichardt,[19] and based on the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium-*N*-phenoxide betaine dye (**1**), has been successfully applied in correlating many reaction rates and solvent properties.

Betaine dye **2** is more lipophilic and, therefore, more soluble in nonpolar solvents, whereas betaine dye **3** is water-soluble and hydrophilic. In this work, we studied the solvent influence in the number of solid/liquid PTC reactions, using the betaine dyes **2** and **3** as intrinsic polarity probes.

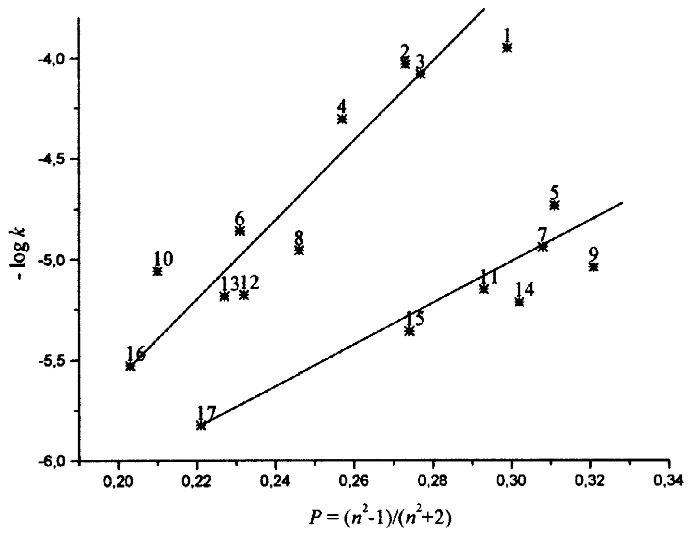


Fig. 3. Solvent influence on the nucleophilic displacement reaction of 1-bromoheptane by chloride (P is the polarizability parameter, n is the refractive index):[17] 1 – pyridine; *2* –hexamethylphosphoric acid triamide; *3* – 1-methylpyrrolidin-2-one; *4* – *N,N*-dimethylformamide; *5* – acetophenone; *6* – pentan-2-one; *7* – benzonitrile; *8* – terahydrofuran; *9* – nitrobenzene; *10* – acetonitrile; *11* – toluene; *12* – nitromethane; *13* – ethyl acetate; *14* – anisole; *15* – tetrachloromethane; *16* – methanol; *17* – ethanol.

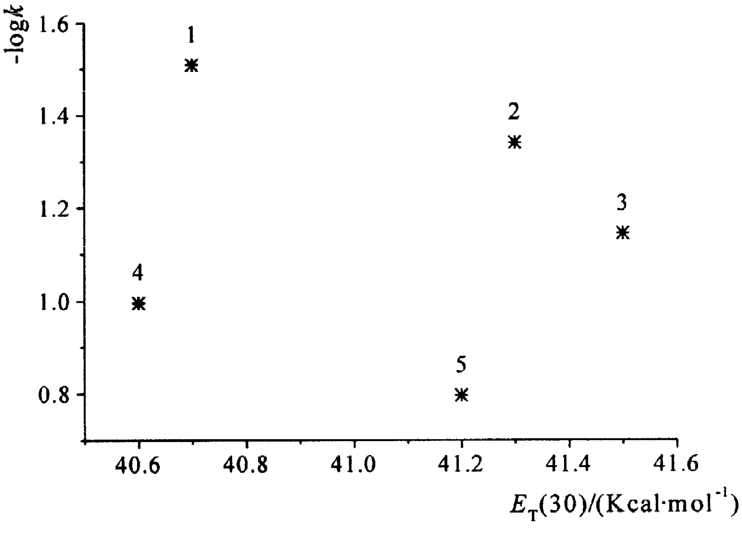
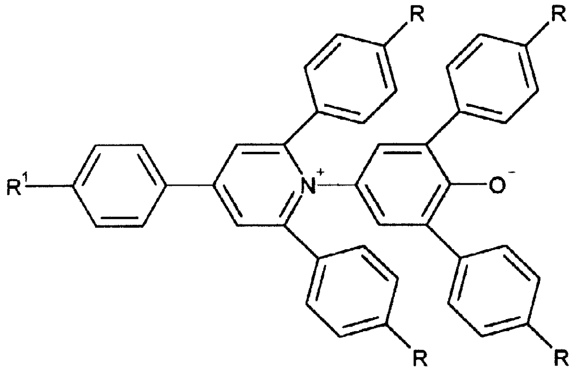


Fig. 4. Solvent influence on a liquid/liquid PTC reaction.[18]
1 – dichloromethane; *2* – 1,2-dichloroethane; *3* – benzonitrile;
4 – acetophenone; *5* – nitrobenzene.



1: R = R^1 = H; **2**: R = R^1 = $C(CH_3)_3$; **3**: R = H, R^1 = COONa

EXPERIMENTAL

(Cloromethyl)benzene / acetate substitution. Pure (chloromethyl)benzene (99% by HPLC) (Fluka®) (1 ml, $8.8 \cdot 10^{-3}$ mol), 1.98 g CH3COONa ($1.76 \cdot 10^{-2}$ mol), tricapryl-methylammonium chloride (Aliquat 336®) (0.026 ml, $4.4 \cdot 10^{-4}$ mol), and 9 ml of an *n*-hexane-nitrobenzene mixture were placed into a water-jacketed reactor, equipped with baffles, a reflux condenser, and a mechanic stirrer (2000-2500 rpm) and kept at 303 K for 0.5 h. The reaction was monitored by taking samples of the reaction mixture and analysing them by HPLC. HPLC analysis was performed on the chromatograph «Milikhrom». Analysis conditions: 40×2 mm column packed with Silasorb® C18 (5 μm), λ = 240 nm, eluent CH_3CN-water (80 : 20 v/v), eluent rate 200 μl/min, sample volume 1 μl.

Michael addition of methyl acrylate to dimethyl malonic ester. In a typical run, pure dimethyl malonic ester (99% by HPLC) (Fluka®) (1 ml, $4.6 \cdot 10^{-3}$ mol), methyl acrylate (1.5 ml, $9.2 \cdot 10^{-3}$ mol), PEG-300 (0.07 g, $2.3 \cdot 10^{-4}$ mol), KOH (0.28 g, $5.0 \cdot 10^{-3}$ mol), and 22.5 ml of an *n*-heptane/nitrobenzene mixture were placed into the above-described reactor at 328 K. The reaction was monitored as before by HPLC analysis of the reaction mixture. Analysis conditions: as before (eluent CH_3CN-water (70 : 30 v/v).

Elimination of HCl from (2-chloroethyl)benzene. In a typical run, (2-chloroethyl)benzene (1 ml, $7.9 \cdot 10^{-3}$ mol), KOH (2.2 g, 0,039 mol), tricapryl-methylammonium chloride (Aliquat 336®) (0.013 ml, $2.2 \cdot 10^{-4}$ mol) and 20 ml of an *n*-heptane/acetonitrile mixture were placed into the above-described reactor at 298 K. The reaction was monitored as before by HPLC analysis of the reaction mixture. Analysis conditions: 40×2 mm column packed with Silasorb® C600 (5 μm), λ = 270 nm, eluent *n*-heptane, eluent rate 200 μl/min, sample volume 1 μl.

Dichlorocarbene addition to styrene. In a typical run, styrene (1 ml, $8.7 \cdot 10^{-3}$ mol), $CHCl_3$ (1.1 ml, 0.014 mol), toluene (internal standard, 2 ml), benzyl-triethyl ammonium chloride (TEBA) ($6.6 \cdot 10^{-3}$ g, $2.9 \cdot 10^{-5}$ mol) and 50 ml of a solvent were placed into the above-described reactor at 298 K. The reaction was monitored as before by GLC analysis of the reaction mixture. GLC analysis was performed on the chromatograph «Tsvet-100» with thermal conductivity detector. Analysis conditions: injector temperature 250° C, stainless-steel column 2.0×0.004 m packed with Chromaton N-AW DMCS (0.125-0.16 mm) with 5% SE-30. Starting temperature 110° C, final temperature 300° C, temperature programming 20° C/min, carrier gas He, 2 l/h.

Recording of UV-VIS spectra. UV-VIS-spectra were recorded on a Specord M-400 UV-VIS spectrophotometer, using cells with1 cm pathlength.

Betaine dyes. Betaine dyes **2** and **3** were synthesised according to the procedures described earlier.[20, 21]

RESULTS AND DISCUSSION

(Chloromethyl)benzene / acetate substitution. The interaction of (chloromethyl)benzene with sodium acetate is the classical example of a PTC S_N2 reaction.

$$PhCH_2Cl + AcONa \xrightarrow{\text{Aliquat-336}} PhCH_2OAc \qquad (10)$$

This reaction was already studied by Yadav and Sharma.[22] However, with our conditions, the reaction did not follow simple kinetic laws.

The possible reaction scheme is shown below:

$$Q^+Cl^- + AcONa_s \rightleftharpoons Q^+Cl^- \cdot AcONa_s$$

$$Q^+Cl^- \cdot AcONa_s + PhCH_2Cl \rightleftharpoons Q^+Cl^- \cdot AcONa_s \cdot PhCH_2Cl$$

$$Q^+Cl^- \cdot AcONa_s \cdot PhCH_2Cl \longrightarrow Q^+Cl^- \cdot NaCl_s \cdot PhCH_2OAc$$

$$Q^+Cl^- \cdot NaCl_s \cdot PhCH_2OAc \rightleftharpoons Q^+Cl^- \cdot NaCl_s + PhCH_2OAc$$

$$Q^+Cl^- \cdot NaCl_s \rightleftharpoons Q^+Cl^- + NaCl_s$$

The formation of the ternary complexes and the absence of exchange of anions between the catalyst and the solid salt was proved earlier.[23]

It is found that the Erofeev equation describes much better the observed kinetics, than other simple kinetic equations. In this particular case, σ^2 is 0.00036 for the Erofeev equation and 0.02373 for the first-order equation. This is strong evidence in favour of the scheme proposed above. Nevertheless, this evidence is surely not definite. It must be underlined that it is nearly impossible to elucidate the detailed reaction mechanism using only the kinetic data. Moreover, this model may not be the only one for fitting the data. Modelling is a mix of science and art and a discussion in any depth about modelling would take too long to be done here. Basically, the model should be the simplest possible representation that is still able to reproduce the behaviour of the system under investigation. It is a wide-spread mistake to forget that there is no unambiguous relationship between a model and a mechanism. A sample of this mistake is the recent work of Mitchenko and Dadali, who studied the reaction of solid KCl with iodoalkanes.[24] Just because the kinetic curve was described by the sum of exponents (a lot of curves can be thus described) they assumed the presence of two kinds of reaction centres on the salt surface without any further evidence.

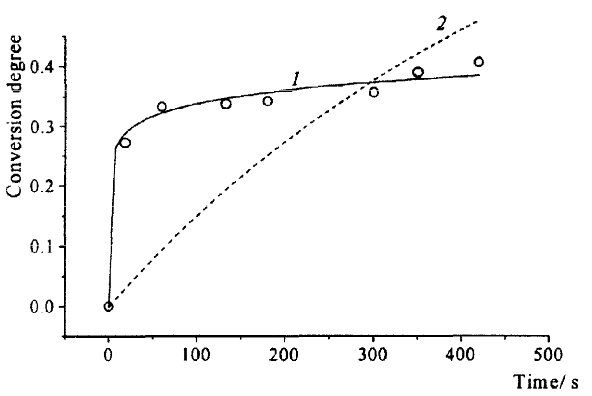


Fig. 5. A typical kinetic curve of reaction (10). Points – experimental, lines – least squares fit.
1: Erofeev equation (1); *2*: first-order kinetics.

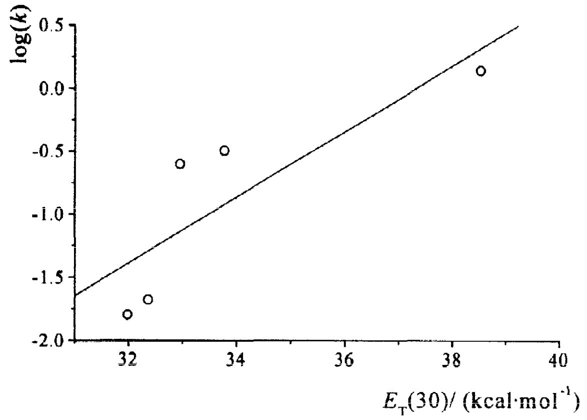


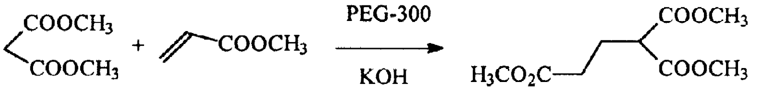
Fig. 6. Influence of the solvent on the rate of reaction (10)

The values of the $E_T(30)$ parameter for the binary *n*-hexane / nitrobenzene mixtures were determined using betaine dye **2**. It was shown that the E_T values for betaine dyes **1** and **2** are in excellent linear correlation.[25] The values of $E_T(30)$ were calculated according to the equation

$$E_T(30)/(\text{kcal/mol}) = \{[28591/\lambda'_{\max}\,(\text{nm})] - 1.808\}/0.9424$$

In the above equation, $\lambda'_{\max}$ corresponds to the wavelength of the absorption maximum of betaine dye **2**. In order to determine the solvent influence the reaction was run in different binary mixtures of *n*-hexane / nitrobenzene. The results are presented in Fig. 6. Although the correlation is not very good, the trend is clearly seen. Increase in the solvent polarity stabilises the ion pair formed by the reactant anion and the quaternary cation. It seems that the reaction is not controlled solely by mass transfer, but the organic-phase reaction takes place as well.

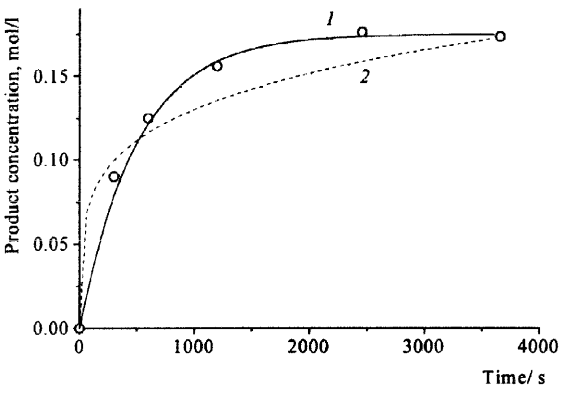
Michael addition of methyl acrylate to dimethyl malonic ester. This is an example of a reaction with solid base participation when base is not consumed. We have used the most common donor and acceptor.



(11)

The scheme of solid/liquid PTC reactions in the presence of polyethylene glycols and crown ethers is widely described in the literature.[2, 13]

The choice of PEG-300 as the catalyst was not accidental. It was said[26] that polyethylene glycol is «the poor chemist's crown ether». It should form the omega-phase[2] on the surface of the base, thus providing for its constant renovation. Indeed, the kinetic curves obtained differ dramatically from the one in Fig. 5.



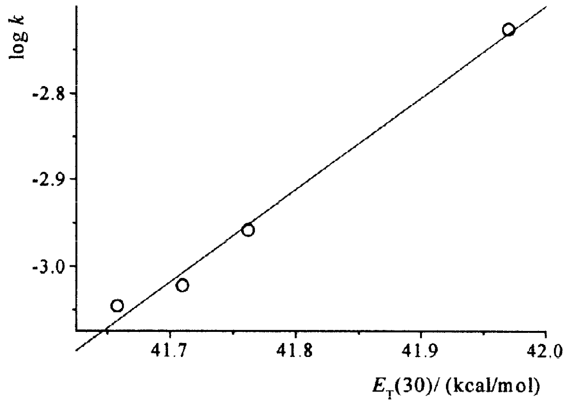


Fig. 7. A typical kinetic curve of reaction (11). Points – experiment, lines – least squares fit.
1: first-order kinetics; *2*: Erofeev equation (1).

Fig. 8. Effect of solvent in the reaction (11) $E_T(30)$ determined in the presence of the catalyst

One can reasonably suppose that Fig. 7 supports our assumption about the different models of solid/liquid interaction in PTC reactions catalysed by quaternary salts and polyglycols or crowns. The reaction was also run in different binary *n*-heptane / nitrobenzene mixtures. The better correlation in Fig. 8 is possibly the result of a narrowed interval of $E_T(30)$ variation. Nevertheless, the trend remains.

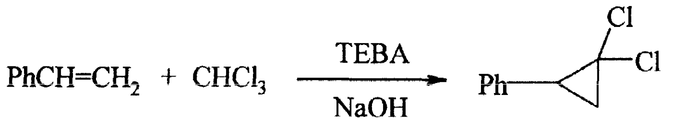
Elimination of HCl from (2-chloroethyl)benzene. This is an example of a reaction with solid base participation in which the base is consumed.

(12)

The reaction was run in a binary acetonitrile / *n*-hexane mixtures with prevailing acetonitrile content. They were homogenised by the presence of the starting compound. As in the previous case, the kinetic curves were also described by a first-order equation. The absence of reaction inhibition can be possibly explained by the partial solubility of KCl in acetonitrile. This provides for the renovation of the solid surface, thus preventing the formation of the product crust on it. Therefore, the renovation of the surface may be effected not only by the catalyst, but also by the solvent. Due to the narrow possible range of variation of the solvent mixture composition, we were not able to obtain the solvent-polarity dependence. However, it was noted, that on increasing the polarity of the liquid media, the reaction rate also increases.

Dichlorocarbene addition to styrene. The addition of dichlorocarbene to a C=C bond is a very important synthetic reaction. Its mechanism in the liquid/liquid system was established by Mąkosza and coworkers.[27, 28]

However, much less attention was devoted to the reaction in the solid/liquid system. Starks' monograph (Ref. 13, pp. 424) cites only two papers dealing with the dichlorocarbene addition in this system, catalysts being various PEGs and TEBA. It is very curious that the reaction yield in the presence of PEG proceeds to completion, whereas with TEBA as the catalyst it stops at 77% conversion. This fact somewhat supports our hypothesis of the deciding role of the crust of the solid inorganic product in reaction inhibition. We decided to employ dichlorocarbene addition to styrene as the model reaction.



(13)

When run at ambient temperature (24 °C), the reaction proceeds quite cleanly, without any appreciable amounts of side-products. The results obtained in different solvents are shown in Fig. 9.

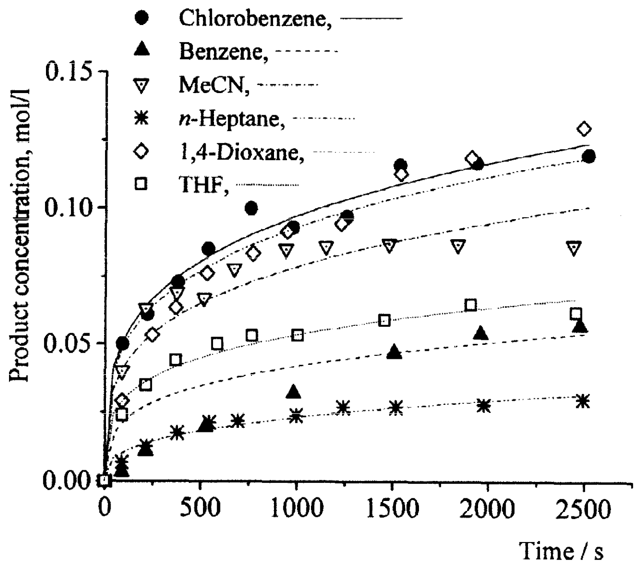


Fig. 9. Kinetic curves of reaction (13), carried out in different solvents. $[\text{styrene}]_0 = 0.143$ mol/l; $[\text{TEBA}]=4.7\cdot10^{-4}$ mol/l. Points – experimental, curves – least squares fit.

In all solvents except THF, the Erofeev equation (1) produced better fit results than the usual first-order equation. Usually, the difference in the values of σ^2 was about an order of magnitude.

The scheme of this reaction and that of the reaction (12), in all possibility, are somewhat similar to the one that we proposed to (chloromethyl)benzene / acetate substitution. It should be underlined that the Erofeev equation is not the only one adequately describing the reaction inhibition. One may suppose that the inhibition is caused by the decomposition of the quaternary salt. Indeed, the experimental points are quite beautifully fitted with the equation[29] describing this effect:

$$-\ln(1-x) = -(k/k_d)(\exp(-k_d t) - 1),$$

where k_d is the rate constant of the catalyst decomposition.

Nevertheless, it was shown[30, 31] that the rate of the catalyst decomposition at an ambient temperature is quite low. Thus, the inhibition can hardly be caused by this effect. Also, no aggregation of the solid reactant particles leading to decrease in the surface area was observed. On the opposite, the intensive stirring (~2500 – 3000 rpm) sometimes caused the breakdown of particles, especially in the case of solid alkalis.

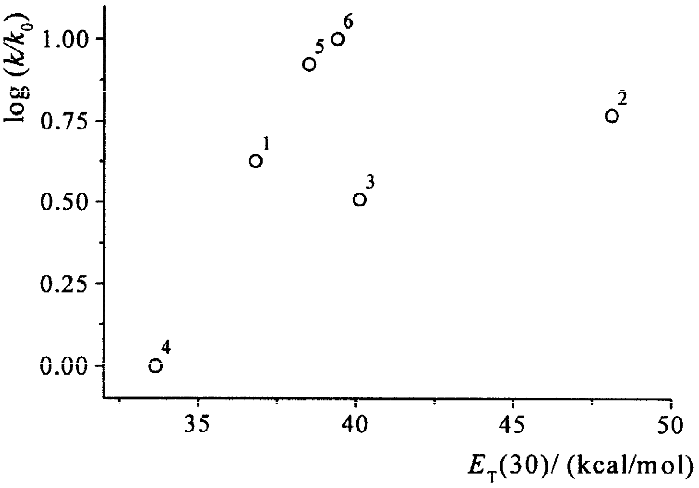


Fig. 10. Solvent influence on the reaction (13) (rate constants relative to *n*-heptane as «slowest» solvent). 1 – benzene; 2 – acetonitrile; 3 – THF; 4 – *n*-heptane; 5 – 1,4-dioxane; 6 – chlorobenzene.

The values of $E_T(30)$ in benzene, chlorobenzene, and *n*-heptane were determined using betaine dye **2**, in the other solvents – using betaine dye **3**. The determination of $E_T(30)$ was performed using not only the pure solvents, but real reaction mixture. The values of $E_T(30)$ obtained by means of betaine dye **3** were reduced to standard values using equation (14)

$$E'_T\ [\text{kcal/mol}] = (0.932 \pm 0.014) \cdot E_T(30)\ [\text{kcal/mol}] + (3.335 \pm 0.685) \qquad (14)$$

where E'_T is the value for betaine dye **3**.[21]

From the Fig. 10 it is evident that an increase in the solvent polarity favours the reaction. However, there is no direct correlation. The reaction rate is unexpectedly high in chlorobenzene or, from another view, unexpectedly low in acetonitrile. It seems that specific solvent/solute interaction could not be excluded in this case.

Nevertheless, in spite of the absence of the direct correlation between the solvent polarity parameter and the rate constant in solid/liquid PTC, the $E_T(30)$ values are a helpful tool for the determination of the general trend. They are tabulated for a large number of the solvents[25] and with some prudence, they can be used for predicting the solvent influence on chemical reactions.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Mrs. T. Koldaeva for the valuable help in recording the betaine dye spectra. F. Sirovski acknowledges the financial help of the Russian Foundation of Basic Research (grant No. 98/0342771).[32]

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32. Part of this work was presented as an oral communication at the 14th International Conference on Physical Organic Chemistry (ICPOC-14), August 16-21, 1998. Florianapolis, Santa Catarina, Brazil.