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A Comparative Kinetic Study of Nucleophilic Substitution under PTC Conditions in Liquid-Liquid and Solid-Liquid Systems

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Abstract: The phenomenon of initial exponential burst (IB) on kinetic curves in the reaction with solid salts was observed in the study on the S_N2 substitution reaction of 2-octylmesylate with potassium halides under phase-transfer catalysis (PTC) conditions in liquid-liquid (l/l) and solid-liquid (s/l) systems. The mechanistic scheme describing the IB phenomenon in application to s/l PTC has been developed from the analysis of IB kinetic model known in enzyme kinetics. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Some problems on kinetics application in PTC. The phase-transfer catalysis (PTC) closely resembles biochemical processes. In fact, a heterogeneous system, which consists of two insoluble liquids (liquid-liquid system), can simulate the properties of a cell membrane. The reagent transfer through the interface from a polar medium (for example, aqueous phase) to a nonpolar one (organic phase) should possess the same properties as the transfer through a membrane. This assumption[1,2] has received further support through the kinetic analysis of some alkylation reactions which proceed under PTC conditions in the presence of 50% alkali solution.[3,4] It was found that some methods of kinetic data processing, which are mostly involved in investigations of enzyme kinetics,[5,6] can be suitable for interpretation of PTC kinetics. It suggests that the basic step, formation of enzyme-substrate complex, could take place in PTC reactions as well.

Actually, it is rare when the analysis of kinetic data performed in Lineweaver-Burk or Michaelis-Menten coordinates allows to detect the formation of intermediate substrate-catalyst complexes and tell about the mechanism of their formation and decomposition. Usually, all the kinetic curves obtained in PTC are well approximated by the exponential dependence and can be linearized in semilogarithmic coordinates that is typical for the first-order reactions. It restrictes though not excludes the possibility of kinetic analysis of PTC mechanism. Thus, it is significant if the complicated kinetic curves (S-likeness, nonlinearity in secondary logarithmic coordinates) are obtained. The analysis of such data allows one to draw the more detailed conclusions about the reaction mechanism. First of all, it is important to obtain the data on the complex formation and topology of the process.[7]

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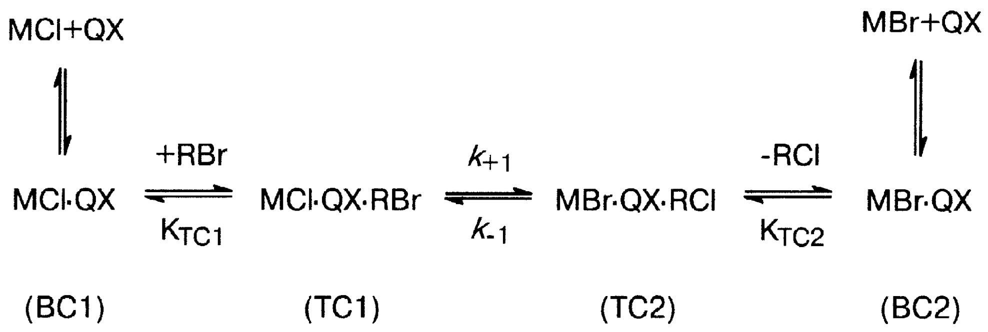
The mechanism of exchange processes in solid-liquid (s/l) PTC. Studying the reaction of n-hexylbromide with solid MCl[8] (M=Na, K, Rb) (Reaction 1) it was found that S-like form of the kinetic curve indicate a preliminary kinetic phase that is connected with the modification of the solid salt surface.

$$\text{n-}C_6H_{13}Br + KCl \xrightarrow{QX} \text{n-}C_6H_{13}Cl + KBr \qquad (1)$$

It allowed to assume that there are the active sites (AS) present on the solid surface. The reaction occurs on the AS through the formation of complexes of salt, catalyst, and substrate.[9,10] The detailed analysis of the kinetic data[11] and thermodynamic parameters[12] for reaction (1) indicated the consecutive formation of binary (BC) and ternary (TC) adsorption complexes[13] at the interface. The following mechanistic scheme has been proposed to explain the substitution mechanism in a system with solid ionophoric salt:

Scheme 1



EXPERIMENTAL

Liquid-liquid (l/l) system. Racemic 2-octylmesylate, prepared by a standard procedure[14] (2.04 g, 0.01 mole), solution of KF, KCl, KBr or KI (0.01 mole) in H_2O (1 ml), Aliquat® 336 (tricaprylylmethylammonium chloride) (0.3 ml, 0.0005 mole), undecane (0.3 ml) and toluene (7 ml) were placed into a water-jacketed reactor heated to 95°C. The reactor was equipped with a reflux condenser protected from water by calcium chloride tube, and mechanic stirrer (2000-2500 rpm). The reaction mixture was stirred for a few seconds until the reagents dissolved, then stirring was stopped, and the first reference was taken. This was considered as a zero time point and the stirring was continued. The stirring was stopped periodically, and, after required separation of the layers achieved, the references were taken from the organic layer through the reactor neck with a pipet.

Solid-liquid system. Solid salt ($KF·2H_2O$, KCl, KBr or KI) was thoroughly dried under vacuum. The portion of dried salt (0.1 mole) was placed into a water-jacketed reactor at 95°C. The reactor was equipped with a reflux condenser protected from water by calcium chloride tube, and mechanic stirrer (2000-2500 rpm). The salt was activated[8,11] by stirring in the reactor for 30 min just before the reaction began. The stirring was stopped and racemic 2-octylmesylate prepared by a standard procedure[14] (2.04 g, 0.01 mole), undecane (0.3 ml) and toluene (7 ml) were placed into the reactor. The reaction mixture was stirred for a few seconds, then the stirring was stopped and the first reference was taken. Thereafter, Aliquat® 336 (0.3 ml, 0.0005 mole) was placed into the reactor, the stirring was continued and this moment was considered as a zero time point. Further procedures were as above.

The solid salt was silted through the 0.1, 0.125, 0.2 mm sieves. The specific surface area was calculated (implying the cubic structure of crystals) from the density and molecular weight of solid KBr. The specific amount of salt present on the surface was calculated from the ionic radii of K^+ and Br^- ions and specific surface area of certain KBr fraction. The estimated value varied in the range $1.6\text{-}3.4\times10^{-5}$ mole of KBr on surface per mole for the 0.1-0.125 mm salt fraction.

Kinetic measurements. A glass column 2.4×0.005 m packed with Chromaton N-AW DMCS (0.16-0.2 mm) with 5% of SE-30 was used for GLC analysis. The concentrations of 2-octylmesylate, 2-chloro-, 2-bromo- and 2-iodooctane were calculated according to the reference (undecane) concentration. The chromatographic yields in the l/l system were 50-80% (Cl^-, Br^-, and I^- ions). For the s/l system, the chromatographic yields reached up to 80% but most the experiments were terminated at about the 50% conversion.

For the reaction in the l/l system, all the kinetic data were processed by the first-order kinetic equation at about 50% conversion. The kinetic data on the reaction in the s/l system with chloride, bromide and iodide ions were processed by the kinetic equation (4).[5] The calculations were conducted by means of the "MicroCal Origin" PC program.

RESULTS AND DISCUSSION

The difference between l/l and s/l systems. To investigate the PTC mechanism of S_N2 substitution in the s/l system we studied the substitution of mesylate group for halogen in 2-octylmesylate (Reaction 2, X=Cl, Br, I, F) as a model reaction.

$$\text{n-}C_6H_{13}CH(CH_3)OMs+KX \xrightarrow[\text{Aliquat 336}]{\text{Toluene/95°C}} \text{n-}C_6H_{13}CH(CH_3)X+KOMs \qquad (2)$$

It was shown earlier[15] that reaction (2) in the l/l system proceeds with quantitative yields and is consistent with S_N2 mechanism.

Reaction (2) has been started with potassium chloride, bromide, iodide and fluoride in both l/l and s/l systems in the conditions similar to those for reaction (1).[8] Replacing a "bad" leaving group (Cl, Br, I, F) with a "good" one (mesylate group) the kinetics in the s/l system changed significantly. We observed a rare phenomenon for PTC, the "initial burst"[5] (IB) on kinetic curves (Fig. 1), while the kinetics in the l/l system was well described by the first-order rate law. The first-order constants for l/l system are presented in Table 1.

The phenomenon of IB is characterized by the first-order dependence on the initial stage of conversion and by zero-order dependence up to the high conversions (up to 80%). The change in the order during the reaction course points out at the change of a rate limiting step for complex process. Zero-order kinetics at high conversion degrees for a complex catalytic reaction indicate the presence of a steady-state phase which is described by Michaelis-Menten kinetics.[16]

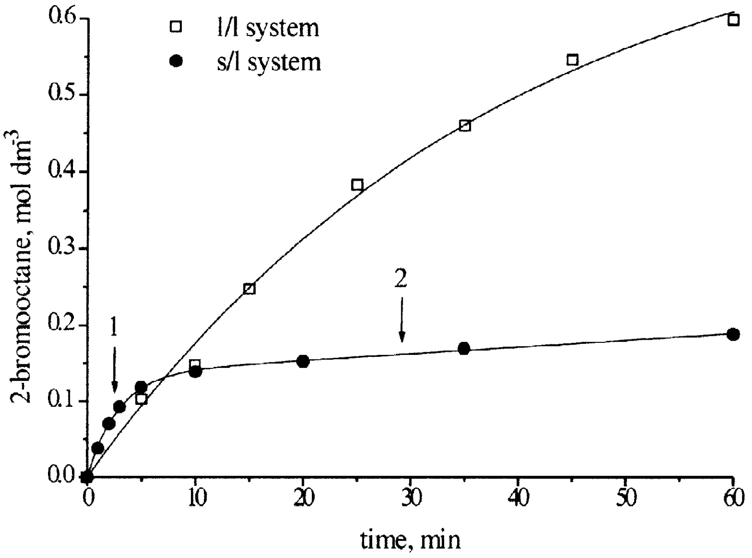


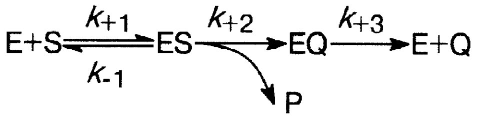
Figure 1. Formation of 2-bromooctane in l/l and s/l systems. The IB kinetics in the reaction with solid salt; segments 1 and 2 indicate the presteady and steady state kinetic phases. Dots: experiment; curves: the least square fit to the first-order rate equation (l/l) and equation (4) (s/l).

The analysis of IB kinetic model. Enzyme kinetics. The analytic form of integral kinetic equation for reaction (2) can be expressed as a sum of linear and exponential terms (Eqn 3) where A and B are the apparent rate constants on segments (2) and (1) of the kinetic curve (Fig. 1), [X] is the concentration of product formed by the first order law, and t is the time.

$$[P]=At+[X](1-\exp(-Bt)) \tag{3}$$

Such a behavior is known for some enzyme-promoted reactions,[5,17] or similar catalytic processes[18] and for heterogeneous catalysis[19,20] The simplest possible scheme, that could yield the dependence by equation (3), is realized by a three-stage catalytic cycle (Scheme 2).

Scheme 2



The substrate, S, is complexed on the AS of a catalyst E. The presteady state kinetic phase yielding the phenomenon of IB suggests that the key product P is formed before the step of product Q formation and regeneration of E. The final step should be process-limiting, *i. e.* $k_{+3} < k_{+1}[S]$, k_{-1}, k_{+2}. The substrate concentration is assumed to be constant since in such reactions $[E]_0 << [S]$ ($[E]_0$ is the initial concentration of AS). Assuming that there is a fast equilibrium at the first step, the kinetic equation for scheme (2) reduces to equation (4).

$$[P] = \frac{k_{+2}k_{+3}[E]_0 t}{k_{+2}+k_{+3}} + \frac{k_{+2}^2[E]_0\{1-\exp[-(k_{+2}+k_{+3})t]\}}{(k_{+2}+k_{+3})^2} \qquad (4)$$

In cases when $k_{+3} << k_{+2}$, equation (4) reduces to the form of equation (3) where A, B, and [X] are equal to $k_{+3}[E]_0$, $k_{+2,}$ and $[E]_0$ respectively. The detailed analysis of the mathematical model for scheme (2) is given elsewhere.[21]

The data obtained for the series of experiments in the s/l system is well approximated by equation (4). We suppose that such a scheme can be applied to PTC reactions according to our conceptions on the mechanism in the s/l system (Scheme 1).

What is the initial burst in s/l PTC? The phenomenon of IB on kinetic curves in a system with solid salt points out the essential difference between l/l and s/l systems, which probably lies in the conditions of the interface. The interface in the l/l system is being constantly renewed so that the reaction rate is not limited by the processes of product desorption and/or formation of nonproductive complexes at the interface. Sometimes, these effects are also critical in the l/l system and are caused by the low agitation rate and/or by the high density of aqueous phase (for example, in the reactions with 50% alkali solutions).[22]

At the same time the rate of reaction with solid salt is often limited by the rate of surface renewal or mass-transfer. In this case the reaction would proceed with a high rate by the first-order law in the beginning (intrinsic-rate-limited process) and by the zero-order law at steady state as soon as all the AS on the surface are consumed and/or the surface is coated with inactive products (mass-transfer-limited process). We suppose that this very phenomenon is observed in reaction (2) (Fig. 1).

Nevertheless, there is a substantial inconsistance with the enzyme kinetics. The IB magnitude which is characterized by AS concentration $[E]_0$ is not identical to catalyst QX concentration and can be much higher than [QX]. The conversion on segment 1 of kinetic curve (Fig. 1) can reach up to 40% while QX is present in only 2.5-5% of the initial substrate concentration. Thus, [QX] does not match the concentration of AS $[E]_0$, and the nature of the phenomenon observed is not that of the enzyme kinetics, but is only a schematically similar process. The approximation of our data by equation (4) allowed us to calculate the parameters $[E]_0$, k_{-2}, and k_{+3} with adequate accuracy. Their role in our system will be discussed below.

Table 1. Kinetic Parameters for Reaction (2) in L/L and S/L Systems.

Salt	$k \times 10^4$, s^{-1} **(l/l)**	$k_{+2} \times 10^3$, s^{-1}	$k_{+3} \times 10^4$, s^{-1}	$[E]_0 \times 10$, mol dm^{-3}
KCl	2.9	1.6	1.7	2.0
KBr	3.7	> 5	3.9	0.6
KI	6.7	0.7	1.5	1.2
KF	—*		4.2×10^{-6} mol dm^{-3} s^{-1}**	

* No reaction observed

** Initial rate

The IB was observed in the reactions with all potassium halides except fluoride (only minute conversion was observed for the time studied). The rate constants for l/l and s/l systems are presented in Table 1. There is no correlation between the kinetic parameters of IB model and the nucleophilicity of halides or their crystall lattice energy because these parameters are not only dependent on the nature of salt. It will be shown below that such a condition as solid surface area may also affect the rection kinetics.

The series of experiments on varying the amounts of solid KBr and [QX] in the system showed that $[E]_0$, $1/k_{+2}$ and $1/k_{+3}$ are dependent on the molar ratio of KBr to QX (Figs. 2, 3). The $[E]_0$ value linearly increases with increase in KBr-QX molar ratio (Fig. 2). It means that the increase in QX concentration leads to the decrease in the amount of AS. Therefore, QX does not act as a catalyst in framework of scheme (2). Nevertheless, the dependences of k_{-2} and k_{+3} reverse magnitudes on the KBr-QX molar ratio points out to the catalytic effect of [QX] on the observed constants of consumption and regeneration of AS (k_{+2} and k_{+3} respectively). Moreover, the reaction does not proceed in the absence of QX.

The analogous dependences for all three parameters (Figs. 4, 5) were obtained vs. the specific surface area of solid KBr that was calculated for various fractions of silted salt (see experimental part).

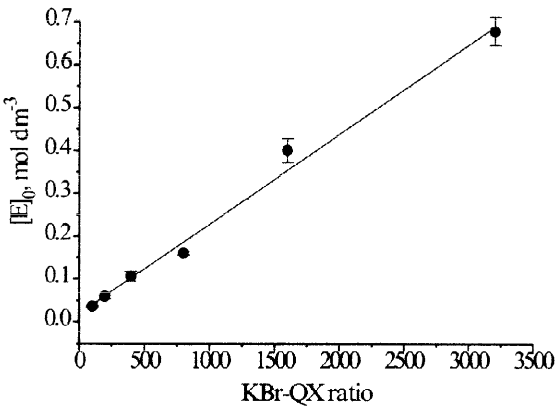


Figure 2. $[E]_0$ vs. KBr-QX molar ratio.

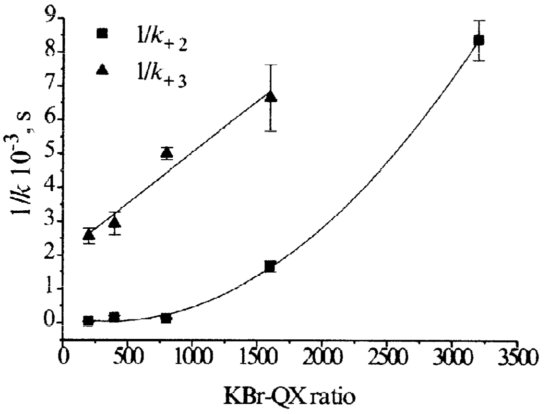


Figure 3. $1/k_{+2}$, $1/k_{-3}$ vs. KBr-QX molar ratio.

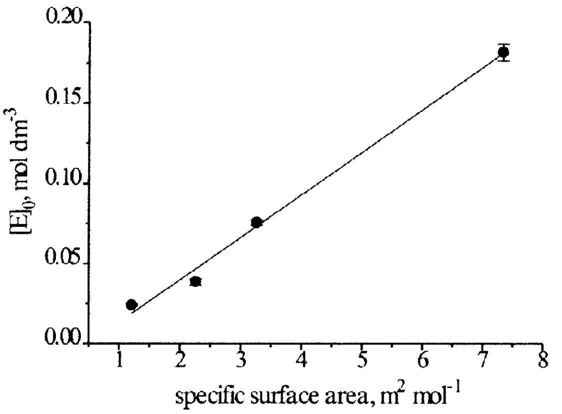


Figure 4. $[E]_0$ vs. specific surface area.

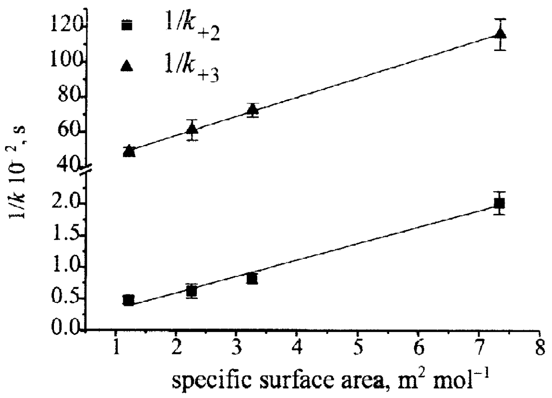
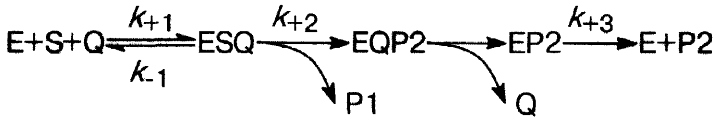


Figure 5. $1/k_{+2}$, $1/k_{+3}$ vs. specific surface area.

The results obtained indicate the role of the solid phase interface in the phenomenon of IB. Obviously, the more the surface area is, the more AS are involved. We suppose that in framework of IB kinetic model, the AS, where the reaction proceeds, are the active sites on the solid KBr surface. The process could be considered as a catalytic cycle resulted from consumption and regeneration of AS on the solid surface. On the contrary, it should be pointed out that $[E]_0$ calculated from experiment is not equivalent to the concentration of AS originally present at the interface as it is in enzyme kinetics. The number of AS that can be involved in the process is three orders in magnitude lower than the obtained $[E]_0$ value. The $[E]_0$ is also higher than [QX] though QX should be binded with AS in order for the process to proceed.

The mechanism proposed. The high conversion of substrate (product formation) during the presteady state (segment 1 on kinetic curve) could be explained by the following scheme where the catalytic cycle for QX (Q) is shorter than that for AS (E):

Scheme 3



where S is a substrate, P1 and P2 are the products. It is assumed that the $[E]_0$ value corresponds to the amount of salt-product (KOMs) adsorbed on the surface (complex EP2 on Scheme 3), which is likely to stop the transfer of reagent to AS. In other words, as the salt-product accumulates on the surface, its desorption and/or diffusion processes could become rate-limiting. Thus, the reaction kinetics would be described by the zero-order law at the steady state phase. And yet, it does not change the nature of observed k_{+2} and k_{+3} as the parameters responsible for the processes of consumption and regeneration of AS, respectively.

On the other hand, the KBr-QX molar ratio also affects the $[E]_0$, *i. e.* the increase in QX surface concentration results in the decrease in the amount of AS. It is known that the excess of QX adsorbed on the surface may lead to the poisoning of the KBr surface due to the formation of nonproductive complexes of catalyst on the surface.[23] In our case it reduces the amount of working AS even though it increases the observed rate constants.

The activation energy for k_{+2} was found to be 76±5 kJ/mol that is typical for a substitution reaction. At the same time E_a for k_{+3} is below 25 kJ/mol, which is typical for physical processes. The change in temperature had no influence on $[E]_0$ value in the studied range of temperatures. Therefore, the use of equation (4) for describing the IB kinetics in s/l PTC (Scheme 3) is justified.

On the basis of the kinetic data for reaction (2) and the exchange concepts developed for s/l system (Scheme 1), we propose that the following processes define the mechanism for reaction (2):

$$\mathrm{KBr}_{\,s} + \mathrm{QCl}_{\,l} \longrightarrow \mathrm{KCl}_{\,s} + \mathrm{QBr}_{\,l} \tag{5}$$

$$\mathrm{QBr}_{\,l} + \mathrm{ROMs}_{\,l} \longrightarrow \mathrm{QOMs}_{\,l} + \mathrm{RBr}_{\,l} \tag{6}$$

$$\mathrm{QOMs}_{\,l} + \mathrm{KBr}_{\,s} \not\longrightarrow \mathrm{QBr}_{\,l} + \mathrm{KOMs}_{\,s} \tag{7}$$

$$\mathrm{QOMs}_{\,l} + \mathrm{KBr}_{\,s} \rightleftharpoons \mathrm{QOMs{\cdot}KBr}_{\,ads} \tag{8}$$

$$\mathrm{QOMs{\cdot}KBr}_{\,ads} + \mathrm{ROMs}_{\,l} \rightleftharpoons \underset{\mathrm{(TC)}}{\mathrm{QOMs{\cdot}KBr{\cdot}ROMs}_{\,ads}} \tag{9}$$

$$\mathrm{QOMs{\cdot}KBr{\cdot}ROMs}_{\,ads} \xrightarrow{k_{+2}} \mathrm{RBr}_{\,l} + \mathrm{QOMs{\cdot}KOMs}_{\,ads} \tag{10}$$

$$\mathrm{QOMs{\cdot}KOMs}_{ads} + \mathrm{KBr}_{s} \rightleftharpoons \mathrm{QOMs}_{l} + \mathrm{KOMs{\cdot}KBr}_{ads} \tag{11}$$

$$\mathrm{KOMs{\cdot}KBr}_{ads} \xrightarrow{k_{+3}} \mathrm{KOMs}_{s} + \mathrm{KBr}_{s} \tag{12}$$

The study on halogen exchange between catalyst QX and solid salts MX shows[9] that reaction (5) proceeds irreversibly with a high rate, while there is no exchange between QOMs and KBr (Reaction 7).[24,25] However, it does not prohibit the formation of the adsorption complex of QX and KBr (Process 8) even if the exchange between them is not possible.

It is known, that homogeneous equilibrium (6) is shifted to the right and is established very quickly[7], *i. e.* there is a fast exchange of Cl for Br^- (Reaction 5) and Br^- for OMs^- (Reaction 6). Therefore, during the reaction the catalyst exists as QOMs.

The linear dependencies of $1/k_{+2}$ on KBr-QX ratio (Fig. 3) and solid surface specific area (see Fig. 5) suppose the equilibrium (8). Indeed, the higher the QX concentration and/or lower the area of solid KBr surface, the higher the concentration of QX adsorbed on the surface. This leads to the increase in observed k_{+2} and, therefore, accelerates the reaction at the presteady state phase of RBr formation.

After the formation and decomposition of the ternary complex TC (Steps 9, 10) the QOMs is desorbed to join the cycle at step (8). It can also join the cycle at step (9). Actually, there is no need in catalyst desorption as it has been pointed out earlier.[24]

The rate-limiting step at the steady state kinetic phase that defines the observed k_{+3} is the desorption of salt-product KOMs (regeneration of AS). The increase in k_{+3} with increase in the catalyst concentration on the surface (Figs. 3, 5) is probably connected with the facilitation of KOMs desorption due to the adsorption of QOMs.

CONCLUSIONS

The new approach to the analysis of s/l PTC kinetics has been developed in the present work. We suppose that such kinetics (three-stage Michaelis-Menten kinetics) can have the application in other PTC processes as well. If the reaction is studied for a long enough period of time, *i.e.* the steady state can be reached, then one can make the conclusions about the role of surface in the process under study and even reduce the reaction time varying the conditions as it is required according to the model presented.

The realization of the presented model for reaction (2) could be connected with a nature of the leaving group, its adsorption properties, and the ease of bond rapture.

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