

Kinetics of 'initial burst' in the solid–liquid phase-transfer catalysis. Nucleophilic substitution of 2-octyl mesylate with potassium bromide

S. S. Yufit* and S. S. Zinovyev

¹N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119992, Russia

Received 8 August 2000; revised 14 February 2001; accepted 17 February 2001

epoc

ABSTRACT: The S_N2 substitution of 2-octyl mesylate with solid KBr under the conditions of phase-transfer catalysis was studied kinetically using the model approach of 'initial burst.' It is suggested that such kinetics reflect the contribution of mass transfer and surface poisoning. The proposed model is used to explain the influences of catalyst, solvent, stirring speed, activation and agitation effects. The mechanistic scheme suggests that the reaction is described by two separate kinetic stages, one of which reflects the intrinsic rate-limited step and the other the mass transfer-controlled step. Copyright © 2001 John Wiley & Sons, Ltd.

Additional material for this paper is available from the epoc website at <http://www.wiley.com/epoc>

KEYWORDS: solid–liquid phase transfer; kinetics; catalysis; nucleophilic substitution; 2-octyl mesylate; potassium bromide

INTRODUCTION

The method of phase-transfer catalysis (PTC) in the presence of a solid phase as an inorganic reagent, the so-called solid–liquid (s/l) PTC, is a convenient technique in organic synthesis that has been widely studied over the last 20 years.¹ Occasionally, it has advantages over the common liquid–liquid (l/l) PTC and is sometimes successfully employed on an industrial scale.² There are a number of papers³ which have reported on the kinetics and varied mechanistic questions, although there is still no unanimity regarding either the mechanism or the topology of s/l PTC.

The complexity of s/l systems arises from the contributions of various side effects, such as adsorption and diffusion on the surface,⁴ modification of the surface by the reagent/substrate adsorption that sometimes causes surface poisoning,^{4,5} etc. These effects make s/l PTC resemble heterogeneous catalysis. In fact, the contribution of surface factors is sometimes very pronounced, so the reaction may not be limited by a chemical step but rather by the mass transfer through the solid–liquid interface barrier.

Also, one of the most challenging issues in s/l PTC is the topology of the chemical reaction step: whether it

occurs in the organic phase, at the solid–liquid interface or in the immediate vicinity to the surface. It has been shown⁶ that small additions (or residual traces) of water may have a substantial effect on the kinetics by either accelerating or slowing the reaction. Generally, water results in softening of the salt lattice and, as a result, in homogenization of the reaction step. We focus on the 'dry' systems where the lattice 'strength' does not allow separation of the anion, so the reaction proceeds preferably on the surface.

Kinetics of initial burst in s/l PTC

We have previously reported on the kinetics of nucleophilic substitution of hexyl bromide with solid MCl under PTC conditions.⁷ The reaction was shown to proceed on the solid surface via the consecutive formation of binary and ternary adsorption complexes formed by the substrate, onium salt and MCl.

We recently reported on the kinetics of the analogous substitution of 2-octyl mesylate with solid potassium halides under s/l PTC conditions.⁸ The kinetics of this reaction in an l/l system were previously studied by Landini and co-workers.⁹ However, in the s/l system it appears more complicated and informative and allows one to draw more detailed conclusions about the reaction mechanism. To describe the reaction kinetics we proposed the approach of 'initial burst' (IB),^{8,10} which gives a very accurate approximation of the data obtained.

*Correspondence to: S. S. Yufit, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119992, Russia.
E-mail: yufit@ioc.ac.ru

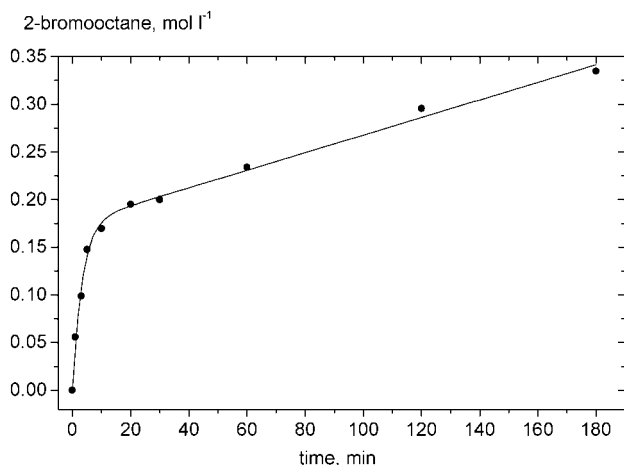
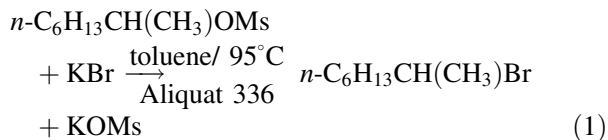


Figure 1. Kinetics of IB in the substitution of 2-octyl mesylate (1 M in 10 ml toluene solution) with solid KBr (12 g, <0.1 mm fraction) catalyzed by Aliquat 336 (for other conditions, see Experimental section). The curve is the non-linear least-squares fit (NLSF) of the experimental data (dots) using Eqn. (2)

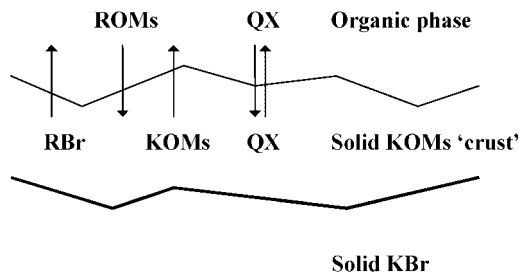
The IB kinetics have not been studied with respect to PTC before, although there are papers reporting on similar kinetic features in analogous systems.^{11,12} This investigation was directed towards a more detailed study of such kinetics in the reaction of 2-octyl mesylate with solid KBr [Eqn. (1)]. This simple model reaction was chosen to gain an insight into the basic mechanistic picture, although the results obtained cannot be generalized for other systems.



A typical reaction profile representing the IB kinetics is shown in Fig. 1. The reaction initially proceeds at a high rate of first order. After reaching a certain degree of conversion, it turns into a regime which is described by a lower rate and zero-order kinetics, and proceeds to complete conversion in such a fashion.

As we suggested earlier,⁸ the solid product KOMs forms a so-called 'crust' over the KBr particle and gradually poisons the reacting surface. The amount of 'crust' grows to a certain extent until the rate of 'crust' accumulation becomes equal to the rate of its removal. Once this equilibrium amount of 'crust' has been reached, the reaction is no longer limited by the chemical step, but proceeds in the mass transfer regime. A pictorial representation of the exchange processes in our system is shown in Scheme 1.

Similar kinetics are observed in some heterogeneous topochemical reactions which are described by the



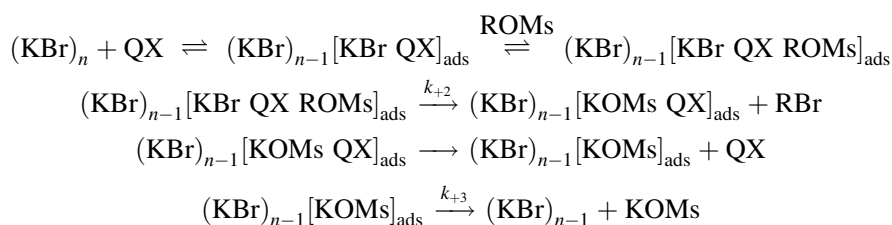
Scheme 1

Avrami–Erofeev equation.¹³ This approach is based on the continuous deceleration of the reaction due to the growing contribution of diffusion through the solid product 'crust,' which constantly accumulates over the reacting particles. Recently, this approach has also been applied to describe s/l PTC kinetics,¹¹ although the reported case is not identical with ours. In the topochemical model, the amount of 'crust' grows constantly, so the reaction does not become zero-order.

Another attempt to describe similar kinetics in gaseous–solid phase substitution was made by Mitchenko and Dadali,¹² who suggested that the reaction is described by two kinetic regimes because of two different types of catalytic sites on the surface. However, neither this model nor the Avrami–Erofeev model^{11,13} can be used in the present case, because they do not describe the stationary kinetic regime, which corresponds to the linear part of the kinetic curve.

We propose a model which is based on the principles of the three-stage Michaelis–Menten kinetics^{10a} and is applicable in some enzyme-catalyzed reactions. As a starting point, we assume that the active site (AS) on the KBr surface plays a role similar to that of an enzyme.⁸ As in enzyme kinetics, these AS are consumed in the initial stage and regenerated thereafter. The proposed mechanism is given in Scheme 2.

The first kinetic regime is conditioned by the adsorption of PT agent (QX) and substrate (ROMs) on the KBr surface resulting in the adsorption (subscript 'ads' in Scheme 2) complex $(\text{KBr})_{n-1}[\text{KBr QX ROMs}]_{\text{ads}}$, which then decomposes and gives RBr. These steps overall are reflected in the pseudo-first-order rate constant k_{+2} , which defines the reaction rate in the pre-steady state. The second regime includes regeneration of the PT agent and renewal of the KBr surface. Decomposition of the imaginary complex $(\text{KBr})_{n-1}[\text{KOMs}]_{\text{ads}}$ and regeneration of a new KBr AS lead to the removal of solid 'crust' and are defined by the k_{+3} constant. If $k_{+2} \gg k_{+3}$ the reaction would turn into the steady-state as soon as all AS are consumed, i.e. when the surface becomes poisoned by the 'crust'. In this regime, the reaction rate is mostly defined by k_{+3} . We assign $[E]_0$ to the number of KBr sites, which react in the pre-steady-state regime and most of which then become bound in $(\text{KBr})_{n-1}[\text{KOMs}]_{\text{ads}}$ in the steady state. A zero-order



Scheme 2

dependence is observed because the rates of the AS consumption and regeneration become equal in the steady state, i.e. the concentration of $(\text{KBr})_{n-1}[\text{KOMs}]_{\text{ads}}$ is stationary (and is close to the $[\text{E}]_0$ value). The following integral rate expression can be derived for this model:^{8,10}

$$\begin{aligned}
 [\text{P}] &= \frac{k_{+2}k_{+3}[\text{E}]_0 t}{k_{+2} + k_{+3}} \\
 &+ \frac{k_{+2}^2[\text{E}]_0 \{1 - \exp[-(k_{+2} + k_{+3})t]\}}{(k_{+2} + k_{+3})^2} \quad (2)
 \end{aligned}$$

where $[\text{P}]$ is the monitored RBr concentration in organic phase, t is time and k_{+2} , k_{+3} and $[\text{E}]_0$ are kinetic parameters. The use of this expression allows one to calculate three independent kinetic parameters (k_{+2} , k_{+3} and $[\text{E}]_0$) from a single run.

This work was aimed at further investigation of the IB kinetics in application to s/l PTC. A number of experiments were performed to study the effects of different reaction conditions on the calculated k_{+2} , k_{+3} and $[\text{E}]_0$ values.

EXPERIMENTAL

General procedure and sampling. Solid KBr was ground and sieved to obtain fractions of salt with particle sizes <0.1, 0.1–0.125, 0.125–0.2 and >0.2 mm. Each fraction was then thoroughly dried under vacuum prior to the reaction. A portion of dried KBr (a certain fraction of sieved or non-sieved salt) was loaded into a water-jacketed three-necked reactor thermostated at 95 °C supplied with a reflux condenser and a mechanical stirrer. After the salt had been pre-activated by stirring in the reactor for 30 min, a solution of racemic 2-octyl mesylate prepared by a standard procedure¹⁴ (2.04 g, 0.01 mol) and undecane (0.3 ml) in toluene (7 ml) was placed in the reactor. The reaction mixture was stirred for a few seconds, whereupon the stirring was stopped and the first reference sample (zero-time point) was taken. Immediately after the first sample had been taken, tricaprylmethylammonium chloride (Aliquat 336) (0.15 ml, 0.25 mmol) was placed in the reactor and the stirring was continued. If not indicated otherwise,

the stirring rate was kept near 2000 rpm. After the reaction had been started, the stirring was stopped periodically and, after the required separation of organic and solid phases had been achieved, samples of the organic phase (~0.1 ml) were taken with a pipette through the reactor neck. The reaction was terminated after acceptable kinetic profiles had been obtained (40–70% conversion for most experiments) or was allowed to proceed to completion. All the reagents and solvents were of 'chemical by pure' grade and were used without further purification.

Gas chromatographic (GC) analyses and kinetic measurements. GC analyses were conducted at a column temperature of 80–150 °C depending on the type of a compound under study. A glass column (2.4 × 0.005 m i.d.) packed with Chromaton N-AW DMCS (0.16–0.2 mm) saturated with a 5% solution of SE-30 was used. The concentrations of 2-octyl mesylate and 2-bromooctane were calculated from the ratios of the GC peak areas for the analyzed compound and the internal standard (undecane) using the known concentration of undecane in the organic phase and the calibration coefficients 1.67 and 1.8 for 2-octyl mesylate and 2-bromooctane, respectively. If the reaction proceeded to completion the GC yields were near 90%.

The kinetic data, i.e. the product concentrations (mol l⁻¹) plotted against time (min), were then processed using MicroCal Origin v. 3.5 software. The non-linear least-squares fitting (NLSF) method was performed to compute the kinetic parameters. Equation (2) was used for the fitting of most of the experimental data, except the experiments which were described by the first-order kinetics or where an initial rate analysis was performed. The values of k_{+2} , k_{+3} and $[\text{E}]_0$ were calculated with an accuracy corresponding to 20% and lower standard errors of NLSF.

RESULTS AND DISCUSSION

Stirring and preliminary activation

It has been shown by different authors^{7,15} that mechanical agitation during or prior to the reaction may have a pronounced influence on the kinetics of PTC. The typical S-like dependences of the rate constants on stirring speed

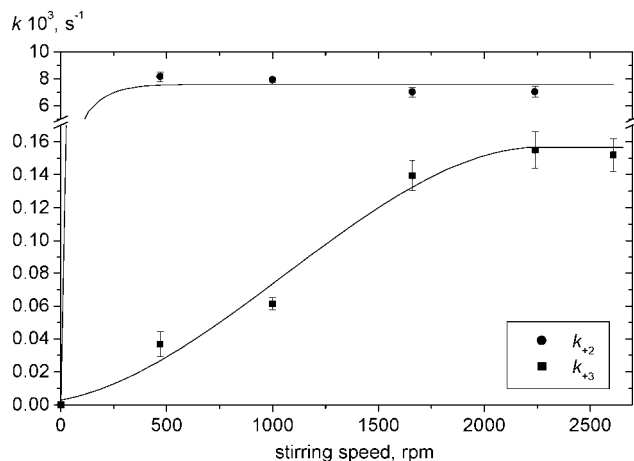


Figure 2. Effect of stirring speed on rate constants k_{+2} and k_{+3} in the substitution of 2-octyl mesylate (0.76 M in 10 ml toluene solution) with solid KBr (12 g, salt fraction 0.1–0.125 mm) catalyzed by Aliquat 336 (0.025 M). Error bars indicate the standard errors of k_{+2} and k_{+3} calculation by NLSF

are observed in most cases. Basically, the rate vs stirring curves reach saturation at comparatively low agitation speeds (100–300 rpm) if the reaction is not much affected by mass transfer. In contrast, if the observed constant reflects the mass transfer-limited step, as is typical for s/l PTC, saturation is reached at about 1000 rpm or higher. Once the saturation of the rate constant has been reached, the reaction is considered to be in a kinetic regime,^{1c} which means the absence of any diffusion contribution for the true chemically controlled reaction. As for the mass transfer-controlled reaction, the rate constant at which the saturation is reached can be conditioned by the *in posse* degree of dispersion/emulsification, as has been demonstrated by Starks,^{15a} or by the form of the stirrer and/or reactor.

The calculated constants for the reaction under study vs agitation speed are presented in Fig. 2. The k_{+2} value reaches a plateau starting with a very slow stirring speed, whereas it takes nearly 2000 rpm for k_{+3} to reach saturation. The observed dependences indicate the different natures of the observed constants. According to the proposed mechanism, k_{+2} represents the consumption of AS, which is a purely intrinsic chemical process and therefore would not depend much on stirring. In contrast, k_{+3} describes the step of AS regeneration, which is virtually the mass transfer-controlled process of surface renewal. It is more affected by stirring because its nature is more physical. The $[E]_0$ value does not depend on stirring, which means that the amount of working AS does not increase in the studied range of stirring.

We have previously reported that in the bromine–chlorine substitution of hexyl bromide with solid metal chlorides under s/l PTC conditions, the preliminary

mechanistic activation of salt had an accelerating effect and led to the elimination of the induction period on kinetic profiles.^{7a} However, in the present case the preliminary activation has little or no effect on kinetics (for results, see Supplementary Material). Consequently, the KBr surface is developed enough without any preliminary agitation. On the other hand, if the reaction is started with a coarse salt (>0.2 mm sieved particles) and proceeds for a long time some acceleration is observed during the steady state (see Supplementary Material). Seemingly, the larger salt particles are easily ground, so the rate increases because of the increase in the surface area and in the amount of AS. A larger amount of AS means a higher $[E]_0$ value, which defines the steady-state rate.

Effect of initial substrate concentration

The influence of the initial substrate concentration ($[S]_0$) on the reaction kinetics was also studied (see Supplementary Material). The observed rate constants k_{+2} and k_{+3} depend linearly on $[S]_0$. The $[E]_0$ value is not affected by the changes in substrate concentration, which is consistent with the proposed model (Scheme 2). Indeed, the degree of surface poisoning by the ‘crust’ would be defined by the surface properties only and not by the component concentrations, except that of QX, which can modify the reacting surface.⁸ Obviously, an increase in $[S]_0$ would lead to acceleration of the steps responsible for the consumption of AS and accumulation of the ‘crust,’ which explains the observed increase in k_{+2} . Therefore, k_{+2} , as an intrinsic constant, is first order in substrate.

On the other hand, an increase in substrate concentration causes the same substantial increase in k_{+3} , which is at variance with the model, because k_{+3} represents for the surface renewal and is not connected with any chemical step involving substrate. The observed increase in k_{+3} vs $[S]_0$ is the result of deviation from the IB model in the experiments with low concentrations of substrate ($[S]_0 = 0.25, 0.4$, and 0.6 M; see Supplementary Material). In these cases, approximation of the steady state becomes misleading, because $[S]_0$ must not be comparable to the ‘burst’ magnitude ($[E]_0$), which is approximately 0.2 M, so the model cannot be used for the accurate estimation of k_{+3} .

Influence of PT agent on reaction kinetics

The PT agent usually plays an essential role in the kinetics of PTC. We studied a number of onium salts (see Supplementary Material) having different quaternary cation structures and coupled with Cl^- , Br^- , I^- and HSO_4^- anions. The use of crown ethers was also studied. The kinetic profiles of reaction (1) catalyzed by these

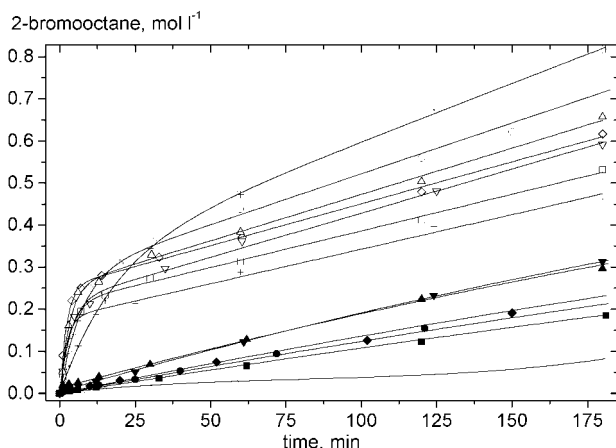


Figure 3. Kinetic profiles of Eqn. (1) in the presence of different PT agents: $\diamond$, TBAB, $(C_4H_9)_4NBr$; ∇ , TBAH, $(C_4H_9)_4NHSO_4$; $\square$, TBAI, $(C_4H_9)_4NI$; $\circ$, TCMAC, $CH_3(C_8H_{17})_3NCl$; $\bullet$, TEAC, $(C_2H_5)_4NCl$; $\blacklozenge$, TEAB, $(C_2H_5)_4NBr$; $\blacksquare$, TEAI, $(C_2H_5)_4NI$; $\triangle$, TEAAB, $C_{15}H_{31}(C_2H_5)_3NBr$; $\blacktriangle$, TEBAC, $PhCH_2(C_2H_5)_3NCl$; $\blacktriangledown$, TPMPB, $CH_3(Ph)_3PBr$; $+$, TOAB, $(C_8H_{17})_4NBr$; $\times$, DB18C6, dibenzo-18-crown-6; $*$, CTMAB, $C_{16}H_{33}(CH_3)_3NBr$. Conditions: 1 M ROMs and 0.03 M PT agent in 10 ml toluene solution, 12 g KBr (<0.125 mm salt fraction), stirring speed 1500 rpm

catalysts are presented in Fig. 3 (for calculated kinetic parameters, see Supplementary Material).

Visually, all the studied catalysts can be subdivided into two major groups: catalysts that cause the IB kinetics and catalysts that result in a slow first-order reaction. The first group is constituted by the onium salts, which are lipophilic enough and have no aromatic substituents. The second group is the onium salts, which either are not lipophilic enough and poorly soluble in the reaction medium (toluene) or have aromatic substituents. First-order kinetics are observed in this case, because the intrinsic reaction (consumption of AS, k_{+2}) is slower than surface renewal (regeneration of AS, k_{+3}) from the beginning and, therefore, the steady state is not reached.

The use of dibenzo-18-crown-6 results in an even slower reaction. Apparently, crown ethers represent a single class of catalysts, in the presence of which the reaction preferably proceeds via the extraction mechanism,¹⁶ as has also been suggested elsewhere.^{3a,9b} Indeed, crown ethers belong to a different structural and functional group of catalysts since they bind the cation of an inorganic salt.

Surprisingly, onium salts containing one or more aromatic substituents, such as TPMPB and TEBAC, also seemingly form a single group of PT agents (see caption of Fig. 3 for compound abbreviations). These salts, unlike their aliphatic analogues, also result in a comparatively slow first-order reaction. Low reaction rates in the presence of these catalysts might be connected with a stronger adsorption of the aromatic quats on the KBr

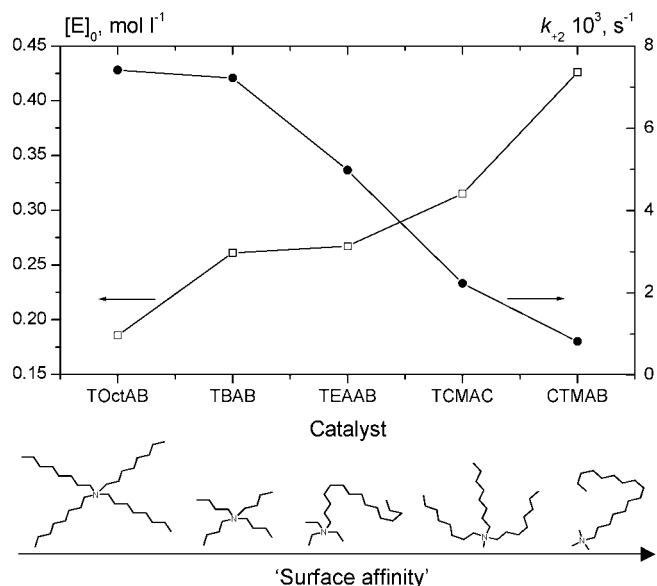


Figure 4. 'Surface affinity' as a function of the quaternary cation structure and its influence on the IB kinetics. $\bullet$, k_{+2} ; $\square$, $[E]_0$

surface. This would lead to a higher activation barrier of the transition state and to stronger surface poisoning by the onium salt.

The role of anion is not so pronounced. Judging from the first-order constants for TEAC, TEAB, TEAI and from k_{+2} for TBAB, TBAI and TBAH (see Supplementary Material), only a slight increase in the reaction rate is observed in the order $Br^- > Cl^- > I^- > HSO_4^-$.

Considering the results obtained for the onium salts, which result in the IB kinetics, we have arrived at some interesting correlations. In Fig. 4, the calculated rate constant k_{+2} and $[E]_0$ value are plotted against the quat structures placed in the order TOctA, TBA, TEAA, TCMA, CTMA. On moving from TOctA to CTMA, there is an increase in $[E]_0$, which takes place simultaneously with a decrease in the reaction rate. We assume that these correlations arise from a so-called 'surface affinity' of these quats, which increases in this order (Fig. 4). We use this abstract term to describe the comparative strength of the quat adsorption on the surface. On the one hand, this property would be affected by the hydrophilicity of the cations; on the other hand, it would also depend on structural geometric factors or how close nitrogen can approach the surface,^{15b} as visually demonstrated in Fig. 4.

A possible explanation for the observed correlations is that the bulky lipophilic and symmetric quats cannot closely approach the surface, and therefore the resulting transition complex is weaker and the rate (k_{+2}) is higher. On the other hand, bulky quats cover more surface area per each reacting AS, so the amount of working AS is lower, which results in a lower $[E]_0$ value.

Remarkably, the catalysts, which are less efficient from the standpoint of reaction rate (k_{+2}) but have a

higher IB magnitude ($[E]_0$) basically result in a higher overall rate (in terms of total conversion per time). It is clearly seen in Fig. 3 that the higher 'burst' magnitude means a faster reaction, because the k_{+3} constant, which mainly affects the steady-state rate, is virtually equal in most cases (see Supplementary Material).

Solvent Influence

We also investigated the influences of a number of solvents on the kinetics of Eqn. (1). Since the intrinsic rate constant (k_{+2}) exerts more influence in the initial part ('burst') of the kinetic profiles, only the initial rate analysis was performed (see Supplementary Material).

Organic solvents of various types were studied, namely non-polar (carbon tetrachloride, toluene, anisole and hexane), polar protonic (methanol) and aprotic (DMSO, DMF, acetonitrile, pyridine). The majority of the solvents studied do not influence the reaction rate much. We found no acceptable correlations of the reaction rate with various properties of the solvents (see Supplementary Material). However, some increase in the rate is observed for DMSO, while the reaction is slower in methanol and acetonitrile. These data overall suggest that the reaction proceeds on the surface, in contrast to the homogeneous processes where the solvent influence is more pronounced. In general, the absence of a pronounced solvent effect seems to be typical for PTC, as has also been demonstrated by a few other papers on this topic.^{11,17}

CONCLUSION

We applied the kinetic model of 'initial burst' to study model substitution reactions under s/l PTC conditions. This novel approach gives a more selective and accurate analysis of kinetic data and allows one to estimate not only the intrinsic rate constant, but also the potential reactivity of the surface and the rate of surface renewal. The results obtained suggest that the reaction takes place on the solid salt surface and is described by two different kinetic regimes reflecting (1) the intrinsic reaction step on the surface, which is first order in substrate, and (2) the physical process of surface renewal, which is more influenced by mechanical agitation. It has also been shown that the catalysts of the choice are lipophilic onium salts with no aromatic substituents, while the reaction is very slow in the presence of crown ethers.

The proposed model may find a use in other PTC processes which are described by similar kinetic profiles, by giving a more detailed mechanistic picture and, occasionally, clues on how to improve the reaction rate.

Supplementary material

Three tables describing the influences of preliminary salt

activation, PT catalyst and solvent, two figures depicting the deviation from the IB model due to salt agitation and the effect of initial substrate concentration, and the accompanying text are available as supplementary data at the EPOC website at <http://www.wiley.com.epoc>.

REFERENCES

- (a) Starks CM, Liotta CL. *Phase-Transfer Catalysis: Principles and Techniques*. Academic Press: New York, 1978; (b) Dehmlow EV, Dehmlow SS. *Phase Transfer Catalysis* (3rd rev., Engl. edn.). VCH: Weinheim, 1993; (c) Yufit SS. *Mekhanizm Mezhfaznogo Kataliza [Phase Transfer Catalysis Mechanism]*. Nauka: Moscow, 1984 (in Russian).
- Sirovski F. *Org. Proced. Res. Dev.* 1999; **3**: 437–441.
- (a) Wong K, Wai APW. *J. Chem. Soc., Perkin Trans. 2* 1983; 317; (b) Zwan MC, Hartner FW. *J. Org. Chem.* 1978; **43**: 2655; (c) Zahalka HA, Sasson Y. *Chem. Soc., Chem. Commun.* 1984; 1652; (d) Perosa A, Selva M, Tundo P. *J. Org. Chem.* 1999; **64**: 3934.
- Melville JB, Goddard JD. *Chem. Eng. Sci.* 1985; **40**: 2207–2215.
- (a) Yee HA, Palmer HJ, Chen SH. *Chem. Eng. Prog.* 1987; **83**: 33–39; (b) Arrad O, Sasson Y. *J. Chem. Soc., Chem. Commun.* 1988; 148–149; (c) Esikova I. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1989; **38**: 2690, 2697; [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1989; **38**: 2463, 2469].
- (a) Arrad O, Sasson Y. *J. Am. Chem. Soc.* 1988; **110**: 185–189; (b) Sasson Y, Weiss M, Loupy A, Bram J, Pardo C. *J. Chem. Soc., Chem. Commun.* 1986; 1251; (c) Liotta CL, Berkner J, Wright J, Fair B. *ACS Symp. Ser.* 1997; **659**: 29–40; (d) Dehmlow EV, Rath HCh. *J. Chem. Res. (S)* 1988; 384–385; (*M*) 1988; 2901–2917.
- (a) Yufit SS, Kryshchal GV, Esikova IA. *ACS Symp. Ser.* 1997; **659**: 52–67; (b) Esikova IA, Yufit SS. *J. Phys. Org. Chem.* 1991; **4**: 149–157; (c) Esikova IA, Yufit SS. *J. Phys. Org. Chem.* 1991; **4**: 341–345; (d) Yufit SS, Esikova IA. *J. Phys. Org. Chem.* 1991; **4**: 336–340.
- (a) Yufit SS, Zinovyev SS. *Tetrahedron* 1999; **55**: 6319–6328; (b) Yufit SS, Zinovyev SS. *Rus. J. Org. Chem.* 1998; **34**: 1282–1285 (in Russian).
- (a) Landini D, Quici S, Rolla F. *Synthesis* 1975; 430; (b) Landini D, Montanari F. *J. Chem. Soc., Chem. Commun.* 1974; 880; (c) Anelli P, Quici S. *J. Chem. Soc., Perkin Trans.* 1988; **2**: 1469–1471.
- (a) Cornish-Bowden A. *Principles of Enzyme Kinetics*. Butterworths: London, 1976; (b) Oullet L, Stewart JA. *Can. J. Chem.* 1959; 737.
- Sirovski F, Reichardt C, Gorokhova M, Ruban S, Stoikova E. *Tetrahedron* 1999; **55**: 6363–6374.
- Mitchenko SA, Dadali YuV. *Russ. J. Org. Chem.* 1998; **34**: 190–194 (in Russian).
- (a) Rozovsky YaA. *Geterogennyye i Khimicheskie Reaktsii. Kinetika i Makrokinetika [Heterogeneous and Chemical Reactions. Kinetics and Macrokinetics]*. Nauka: Moscow, 1980; 180–300 (in Russian); (b) Kutepov AM, Bondareva TI, Berengarten MG. *Obschaya Khimicheskaya Tekhnologiya [General Chemical Technology]*. Vysshaya Shkola; Moscow, 1990; 169–204 (in Russian); (c) Frank-Kamenetsky DA. *Diffuziya i Teploperedacha v Khimicheskoy Kinetike [Diffusion and Heat-Transfer in Chemical Kinetics]*. Nauka: Moscow, 1987 (in Russian).
- Weiner H, Snee RA. *J. Am. Chem. Soc.* 1965; **87**: 287.
- (a) Starks CM. *Tetrahedron* 1999; **55**: 6261–6274; (b) Starks CM. *ACS Symp. Ser.* 1997; **659**: 10–28.
- (a) Starks CM, Owens RM. *J. Am. Chem. Soc.* 1973; **95**: 3613; (b) Starks CM. *J. Am. Chem. Soc.* 1971; **93**: 195.
- (a) Danilova OI, Yufit SS. *Mendeleev Commun.* 1993; 165–166; (b) Savelova VA, Vakhitova LN, Rybak VV, Kosmynin VV. *Russ. J. Org. Chem.* 1996; **32**: 729. (in Russian); (b) Antoine JP, De Aquirre I, Janssens F, Thyron F. *Bull. Soc. Chim. Fr.* 1980; **5**–6: II–207.