Phase-transfer catalysis: kinetics and mechanism of dichlorocyclopropane formation in liquid/liquid and solid/liquid systems

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Abstract

The kinetics and mechanism of dichlorocarbene addition to C=C bond under liquid/liquid (l/l) and solid/liquid (s/l) phase-transfer catalysis conditions are discussed. In the s/l system reaction kinetics is strongly influenced by the formation of a crust of solid NaCl on the NaOH surface. In the l/l system the reaction is significantly slower and occurs in a liquid border film. The influence of physical factors in both s/l and l/l systems is shown.
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1. Introduction

Phase-transfer catalysis (PTC) is presently a mature and well-established method. Soon it will be 35 years since Makosza published his paper on two-phase catalytic dichlorocarbene addition [1]. However, the kinetics of this reaction had never been investigated. Moreover, there still exist a variety of arguments in the literature concerning the mechanisms of a solid/liquid (s/l) and liquid/liquid (l/l) PTC in general and PTC in the presence of strong inorganic bases in particular [2–5]. For the l/l system, the most ardent arguments concern the point whether there takes place an actual anion exchange (the "extraction" mechanism) or the role of the hydroxide is limited to the interfacial deprotonation of the substrate followed by the extraction of the organic anion into the bulk of the organic phase where the subsequent reaction occur (the "interfacial" mechanism). As concerns the PTC reactions in s/l systems, the differences in the mechanisms proposed are even bigger. Some authors [2] use analogies with enzyme kinetics disregarding different assumptions used in the development of the PTC and enzyme kinetic models, others apply arbitrarily taken equations and invent mechanisms to fit them [6].

We attempted to obtain mechanistic data for OH-promoted phase-transfer catalysed reactions studying the kinetics of chloroform reaction with styrene (Makosza reaction) in s/l and l/l systems (TEBA is triethyl benzyl ammonium chloride) (Scheme 1).

This reaction runs smoothly giving only one product, so its monitoring is quite simple. This allowed us to obtain fairly accurate kinetic data.

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PhCH=CH₂ + CHCl₃ —TEBA/NaOH→ Ph△(Cl)(Cl)
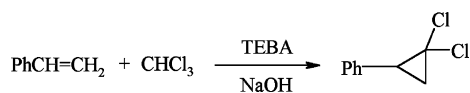
Scheme 1.

2. Results and discussion

2.1. Kinetics in the liquid/liquid system

To avoid diffusion-limited reaction realm it was necessary to determine the dependence of the initial reaction rate on the stirring speed. In a l/l system, the reaction rate becomes stirring-independent at about 1000 rpm, in a s/l system this threshold is attained at 1250–1300 rpm. All further experiments were carried out at a stirring speed exceeding 1500 rpm. The results are shown in Fig. 1. It is seen that in opposite of what was observed by Yufit and Zinovyev [2] for the nucleophilic displacement this reaction runs significantly faster in a s/l system.

It should be noted that apparent rate–stirring speed profiles are the same for both s/l and l/l systems, although for the nucleophilic displacement in a s/l system a linear relationship was observed [7]. The

obtained profiles are strikingly similar to the dependence of a specific interfacial area versus stirring speed obtained by Starks [8] who derived the following equation:

$$a = \frac{5.3862\rho\phi\omega^2 L^2}{\gamma} \tag{1}$$

where a is the interfacial tension, ρ the specific gravity, ϕ the volume fraction of a dispersed phase in a continuous phase, ω the rotation speed, and L the reactor radius. Although he assumed that this equation should not be necessarily valid at stirring speeds exceeding 500 rpm, it seems he was overly cautious. Also, according to his model the ratio of chemical reaction rate constant and ion-transfer rate constant lies in the range 10^3–10^5.

It is widely assumed in works on PTC kinetics that in the plateau segment (>1000–1500 rpm in our case) the phase-transfer process is reaction rate limited. This is not necessarily true. It was shown above [8] and elsewhere [9] that the specific interfacial area increases linearly with the stirring speed till the stage is reached where it does not increase any more. The reaction rate may be independent of the stirring speed just because the mass-transfer rate has reached a limiting value for
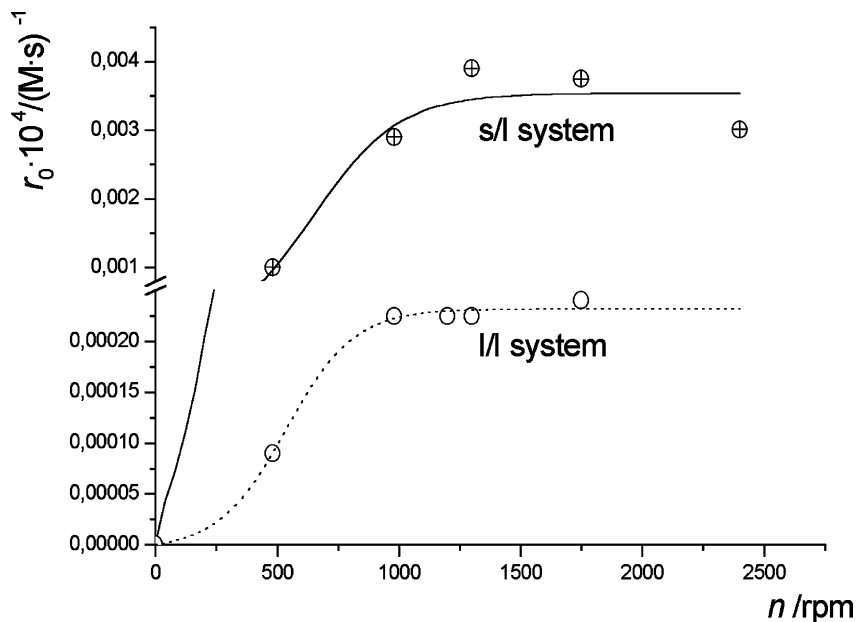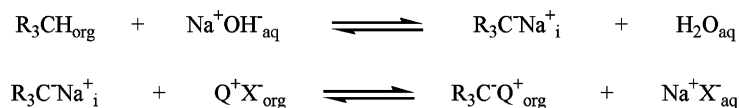

Fig. 1. Initial rates vs. stirring speed.

$$R_3CH_{org} + Na^+OH^-_{aq} \rightleftharpoons R_3C^-Na^+_i + H_2O_{aq}$$

$$R_3C^-Na^+_i + Q^+X^-_{org} \rightleftharpoons R_3C^-Q^+_{org} + Na^+X^-_{aq}$$
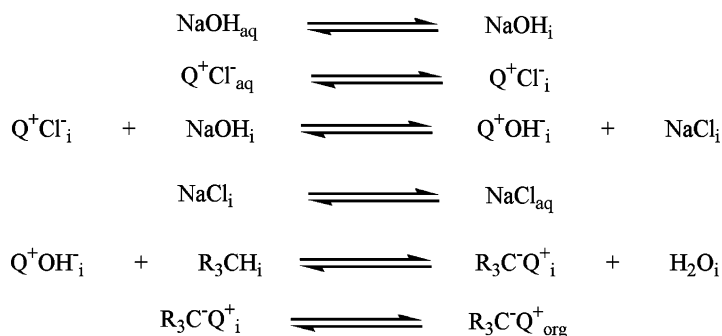
Scheme 2.

this reactor and stirrer configuration. Only a value of the activation energy allows to determine whether the reaction is mass-transfer limited or not. Makosza proposed [10] the following interfacial mechanism for his reaction (Scheme 2; subscripts i, org, and aq denote the interface, organic and aqueous phases, respectively).

According to this mechanism, the crucial step, i.e. the deprotonation, proceeds at the liquid/liquid interface and a catalyst forms the lipophilic ion pair $R_3C^-Q^+_{org}$ that migrates into the organic phase. This mechanism is supported by the data on the extraction of OH^- anion into the organic phase obtained by Dehmlow et al. [11]. It was shown that the extractability of OH^- anions into the organic phase is negligibly small even at high alkali and catalyst concentrations. According to Makosza, just this mechanism operates in all l/l PTC reactions with the participation of alkalis and not the Starks original extraction mechanism [12]. Also, the interface is understood as the two-dimensional plane. In the monograph [5] the Makosza mechanism was considered inadequate on the basis of the interpretation of the results obtained in the studies of deuterium exchange of fluorene [13], and reaction of chloroform-d with phenylacetonitrile [5]. The authors [5] proposed the "modified interfacial mechanism". According to this mechanism, in the presence of the quaternary ammonium salt in the
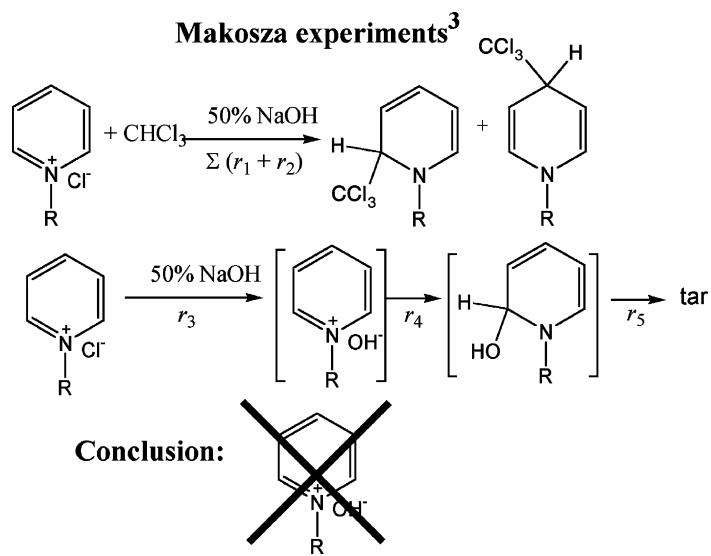
interfacial region, the third phase is formed where the reaction proceeds. Indeed, the formation of this third phase as a light-yellow layer can be visually observed, when to the two-phase system of benzene/50% NaOH the Makosza catalyst, i.e. $Et_3N + CH_2PhCl^-$ is added even in a small amount. The authors [5] formulated the "modified interfacial mechanism" in the following way (Scheme 3).

In his recent paper [3], Makosza strongly opposed this mechanism on the following grounds. First of all, he justly argues that in the homogeneous phase there should be no distinction between the OH^- anion associated with Na^+ or Q^+. Thus, the deprotonation by QOH would be indistinguishable from the same deprotonation by NaOH. So, he concluded [3] that modified interfacial mechanism is possible but not necessary. In order to substantiate these conclusions, he studied the reaction of N-2,4,6-trimethylbenzyl and N-benzyl pyridinium chlorides with chloroform in the presence of concentrated NaOH with the formation of stable CCl_3 adducts in 2- and 4-positions (Scheme 4).

The addition of NaOH to these pyridinium chlorides in the absence of chloroform resulted in their rapid decomposition. He interpreted these results as the strong evidence that N-alkyl pyridinium hydroxides are not involved in the $CHCl_3$ deprotonation and that CH acids, such as chloroform, prevent the

$$NaOH_{aq} \rightleftharpoons NaOH_i$$

$$Q^+Cl^-_{aq} \rightleftharpoons Q^+Cl^-_i$$

$$Q^+Cl^-_i + NaOH_i \rightleftharpoons Q^+OH^-_i + NaCl_i$$

$$NaCl_i \rightleftharpoons NaCl_{aq}$$

$$Q^+OH^-_i + R_3CH_i \rightleftharpoons R_3C^-Q^+_i + H_2O_i$$

$$R_3C^-Q^+_i \rightleftharpoons R_3C^-Q^+_{org}$$

Scheme 3.

Makosza experiments[3]

Scheme 4.

formation of $R_3C^-Q^+$ ion pair. In our opinion, it may or may not be so dependent on the relative rates of the decomposition and deprotonation. If the rate of the deprotonation is higher than the rate of decomposition, then the formation of *N*-alkyl pyridinium hydroxides is quite possible (Scheme 5).

As the deprotonation is a very fast process, this is quite viable.

It is quite curious that virtually the same phenomenon, i.e. the decomposition of a quaternary ammonium salt by NaOH was interpreted by Sasson and coworkers [4] as the evidence in proof of the extraction mechanism. In the authors' opinion, the Hoff-

mann degradation reaction is "a direct probe and evidence of the existence of the extraction mechanism" [4]. The absence of the Hoffmann degradation served as the evidence of the interfacial mechanism.

The problem of reactions in the fluid/fluid system is well known to chemical engineers and is discussed in much detail in the Levenspiel monograph [9]. The gas/liquid system was discussed, but all the reasoning can be applied to the system of two immiscible liquids as well. The aqueous phase plays the role of the gas phase (phase 1 in Figs. 2 and 3) and the organic phase plays the role of the liquid phase (phase 2).

It was shown that for the second-order reaction $A + B \rightarrow R$, the observed reaction order depends on the topology of the reaction. If the reaction proceeds in the film, then the second-order rate law is observed.

An alternative explanation:

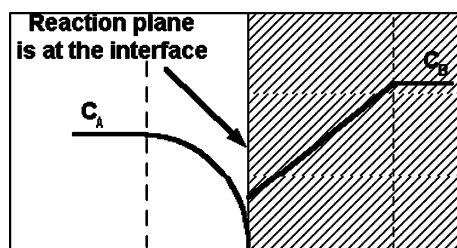If $r_6 > r_4$, then QOH exists
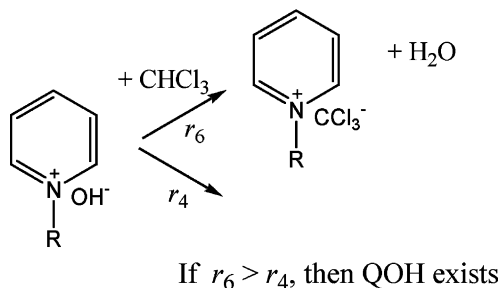
Scheme 5.

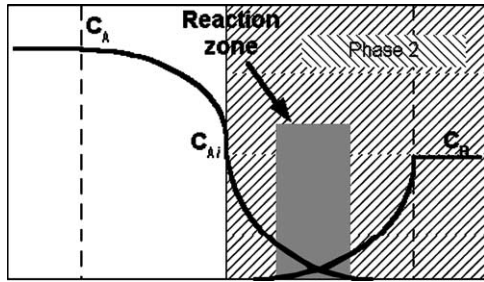Fig. 2. Reaction at interface (l/l system).

Fig. 3. Reaction in a border film (l/l system).

However, if the reaction proceeds on the plane, then the rate obeys the first-order law. It is best illustrated by the graphs reproduced from [9] (Figs. 2 and 3).

For the above case, the general rate expression [9] is shown below (Eq. (2)), where S is an interfacial area, N_A is a number of component A moles.

$$-r = -\frac{1}{S}\frac{dN_A}{d\tau} = kC_A \qquad (2)$$

The general rate Eq. (3) for this case was derived in [9], where p_A is the partial pressure of component A, k_{A1}, and k_{A2} are the resistances of the films of phases 1 and 2, respectively, H_A is the Henry's law constant, and E the liquid film enhancement factor. Although this equation was derived for gas/liquid reactions it also can be adapted to liquid/liquid ones

$$-r = \frac{p_A}{1/k_{A1}a + (H_A/k_{A2}C_A aE)} \qquad (3)$$

The reaction was run using large excess of $CHCl_3$ under pseudo first-order rate conditions (Fig. 4).

We carried out the experiments at different molar ratios $CHCl_3$/styrene. The results are presented in the Fig. 5. It is seen that the overall reaction order (excluding catalyst) is 2. Thus, it seems that the reaction proceeds in the film and not on the plane after all. However, it is a mistake to think that a liquid/liquid interface is a two-dimensional plane. It was shown [14] that it is an intricate voluminous formation. According to the calculations [14], the effective thickness of the phase boundary in the water/CCl_4 system is about 9–10 Å due to the formation of the capillary waves. At the end, it may not be such a big difference between the two mechanisms after all.

The reaction is also first-order on the catalyst (Fig. 6). The rate-limiting step of the reaction is
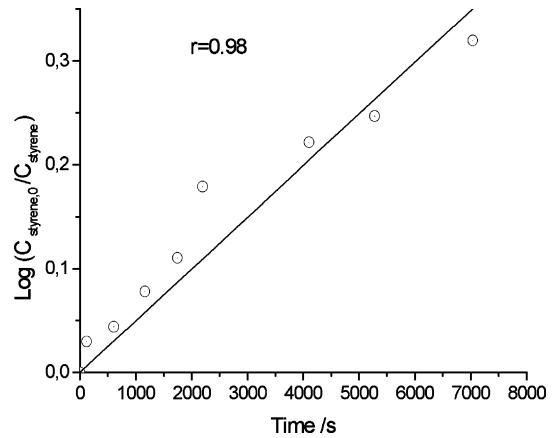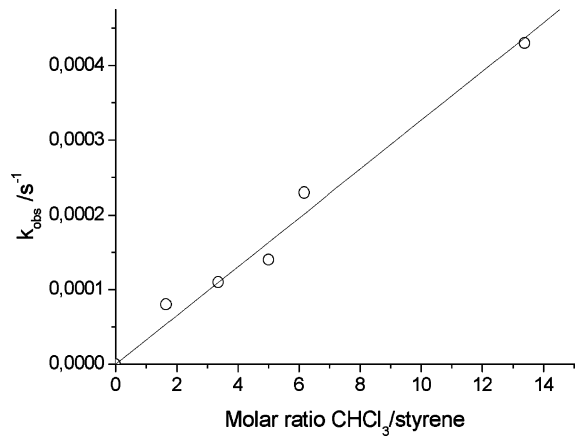

Fig. 4. Linearisation of a kinetic curve.

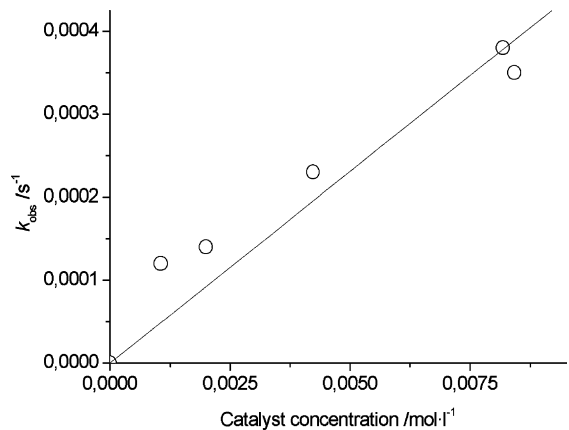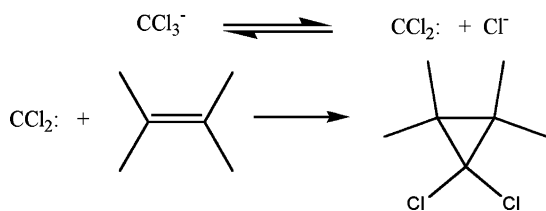Fig. 5. Dependence of the observed rate constant on molar ratio chloroform/styrene.

Fig. 6. Catalyst influence.

Scheme 6.

the interaction of the dichlorocarbene with olefin (Scheme 6).

The reaction with an activated olefin such as α-methylstyrene runs faster (Fig. 7).

Nevertheless, we think that Makosza arguments concerning deficiencies of the "modified interfacial mechanism" are quite reasonable. In a separate experiment using large concentrations of TEBA, it was shown that the formed third layer also contains Na^+ cation. The first order on the catalyst concentrations means that the catalyst does participate in the rate-limiting step as an ion pair with CCl_3^- anion. It seems that both the deprotonation and dichlorocarbene addition occur inside the thin border film.

2.2. Kinetics in the solid/liquid system

The reaction in the s/l system proceeds much faster than in the l/l one (Fig. 1). In our opinion, it is explained by the higher activity of the hydroxide anion in the s/l system.
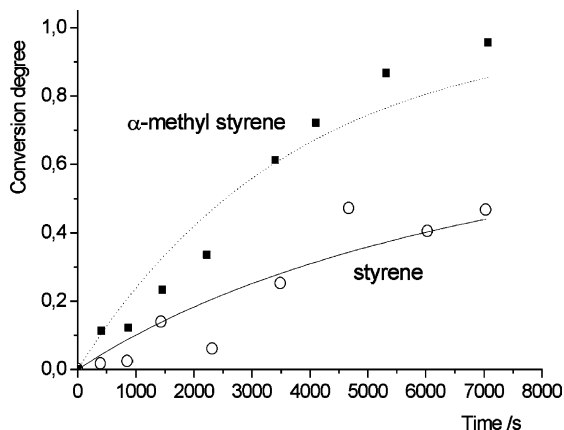

Fig. 7. Olefin structure influence.

Earlier [15], we had published the work discussing various models of phase-transfer catalysed reactions in the different solid/liquid systems. It was shown that Makosza reaction in this system is hindered by the formation of the crust of NaCl.

A suggestion was put forward that phase-transfer catalysed reactions in these systems closely resemble the so-called topochemical processes (solid/fluid) described elsewhere [9]. We applied the quite obscure Erofeev Eq. (4) [16] for the description of the reaction kinetics:

$$x = 1 - \exp(-k\tau^n) \tag{4}$$

where k is the rate constant, x the conversion degree and n the parameter depending on the properties of the solid phase. The obtained results were satisfactory.

However, the Erofeev Equation (Eq. (4)) was derived starting from molecular statistics without the use of the mass action law and is quite general. It also includes the semi-empirical parameter n. In our opinion, the closest analogy to the OH-promoted phase-transfer catalysed reactions in a s/l system in the terms of physical processes that occur there, is the decomposition of apatite by sulphuric acid. During this reaction, a crust of $CaSO_4$ is formed on the surface of apatite particles, inhibiting their further dissolution. Just like this, during the Makosza reaction in the s/l system, the crust of the solid NaCl is formed on the surface of the solid NaOH hindering further reaction. The mathematical model of the apatite decomposition was developed in large detail by Beskov et al. [17]. The basic assumptions of this model are the following: (i) Concentration of H^+ ions is uniform and constant. That corresponds to our conditions: $CHCl_3$ is in large excess, so its concentration can be roughly considered constant. (ii) $[Ca^{2+}][SO_4^{2-}] > SP$, where SP is the solubility product of $CaSO_4$. That also corresponds to our conditions, as NaCl is virtually insoluble in $CHCl_3$. Starting with these assumptions, one can write down following equations:

$$C_{Na}C_{Cl^-} \geq s_{NaCl} \tag{5}$$

The crust of NaCl covers the surface of NaOH particle, thus, decreasing the active surface and, consequently, the reaction rate. Assuming that specific rate of NaCl crust formation is constant, we obtain:

$$\frac{dn}{d\tau} = \lambda\varphi \tag{6}$$

where n and λ are specific amount and rate of NaCl formation, φ is the fraction of the free surface of NaOH particle, and

$$\varphi = 1 - \frac{n}{\rho_m \Delta} \tag{7}$$

where ρ_m is the molar density of a NaCl crust, Δ is an average crust thickness. Integrating Eq. (6) we obtain

$$\varphi = \exp(-\lambda_1 \tau) \tag{8}$$

where $\lambda_1 = \lambda / \Delta \rho_m$

Because NaOH reacts only where the surface is not closed by NaCl crust the mass balance for NaOH particle is as follows:

$$\frac{dr}{d\tau} = \frac{\varphi \beta (C_{NaOH}^s - C_{NaOH})}{R_0 N_0} \tag{9}$$

where r is a dimensionless particle radius, β is the NaOH mass-transfer coefficient, R_0 the initial size of NaOH particle, N_0 the molar density of solid NaOH (mol/l). Conversion degree of NaOH particle is

$$X = 1 - r^3 \tag{10}$$

Integrating Eq. (9), one obtains

$$X = 1 - \left[1 - \left(\frac{1}{k\tau_\infty} \right) 1 - \exp(-k\tau) \right]^3 \tag{11}$$

where k is the rate constant of the crust formation (s^{-1}), τ the time (s), τ_∞ the time of a complete particle dissolution. The results of the treatment of the kinetic data are shown in Fig. 8. It was found that the Eq. (11) fits the observed kinetics significantly better than the first-order rate law. The reaction was also first-order on catalyst concentrations (Fig. 9) as in the l/l system.

It should be noted that all the experiments were carried out in the region where the stirring speed did not influence the rate of the reaction as shown in Fig. 1.

The influence of water in this reaction was of utmost interest because it could be considered a crucial test on the validity of the model. The results are presented in Fig. 10.

It is seen that the reaction rate is maximal (the rate of the crust formation minimal) at the concentrations of water in the range of 0.2–0.6 M, where the so-called "omega phase" [5] is formed providing for the partial renovation of the solid surface. At higher concentrations, the reaction rate is lowered as the particles of NaOH are visibly aggregated.
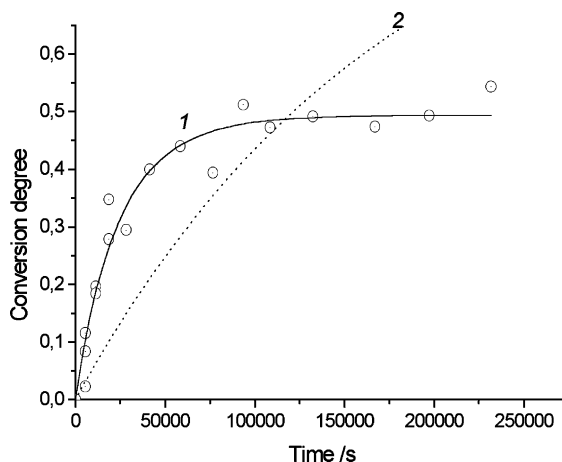

Fig. 8. Typical kinetic curve in a s/l system: (1) treatment according to the Eq. (11); (2) first-order rate law.

The reaction with α-methylstyrene in this system also runs faster (Fig. 11) and proceeds nearly to completion. It means that dichlorocarbene addition to olefin is the rate-limiting step.

The activation energy is quite high: 88.80 ± 15 kJ/mol, thus confirming the absence of diffusion-related inhibition (Fig. 12). It is interesting to note that the obtained value of activation energy for the same reaction in a l/l system is somewhat lower: 50 ± 8 kJ/mol. It is an additional proof that in the l/l system the reaction occurs in a border film.

When assessing the reaction mechanism in a s/l system, one should take into account the following facts:
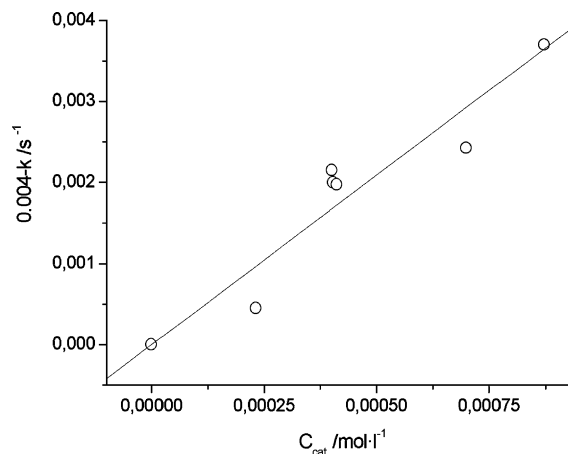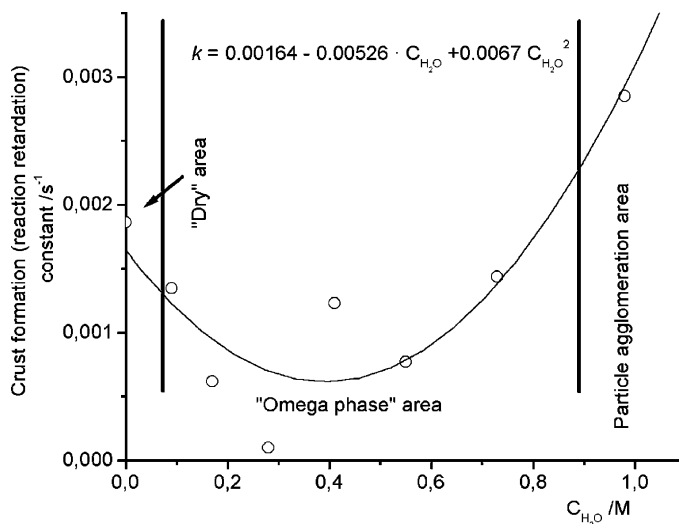

Fig. 9. Catalyst influence.

$$k = 0.00164 - 0.00526 \cdot C_{H_2O} + 0.0067\, C_{H_2O}^{2}$$

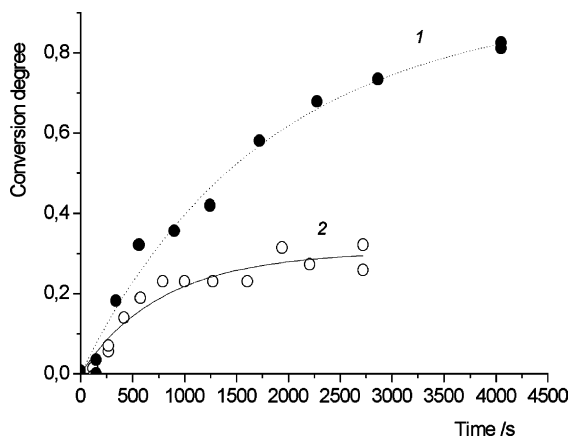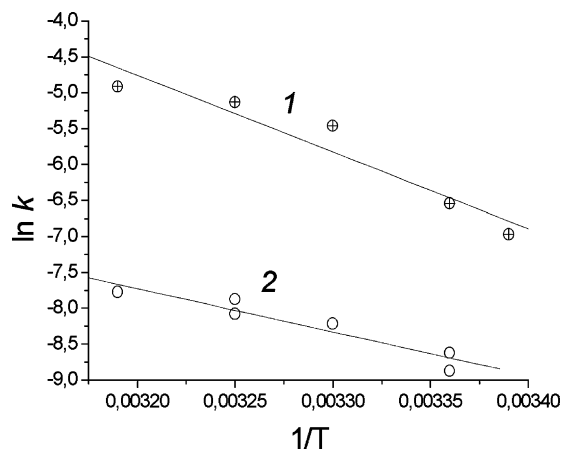Fig. 10. The water influence in the s/l system.

Fig. 11. Reaction of CHCl$_3$ with α-methylstyrene (1) and styrene (2) in a s/l system.

Fig. 12. Determination of the activation energy in s/l (1) and l/l (2) systems.

(i) inhibition of the process by the crust formation with less reactive olefins; (ii) linear dependence of the observed rate constant on the catalyst concentration; (iii) influence of water content confirming the crucial role of the surface; (iv) high value of the activation energy proving the absence of diffusion limitations; (v) prominent solvent influence [15].

It allows supposing that the crust formation and addition of dichlorocarbene are concurrent-independent processes. Also, the following equilibria are strongly

$$Q^+Cl^-_b \;\rightleftharpoons\; Q^+Cl^-_{ad}$$

$$Q^+Cl^-_{ad} \;+\; NaOH_s \;\rightleftharpoons\; Q^+OH^-_{ad} \;+\; NaCl_s$$
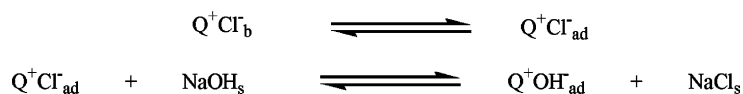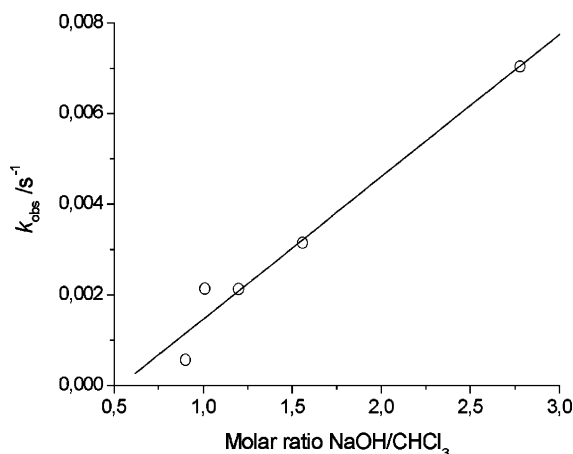
Scheme 7.

Fig. 13. The effect of a molar ratio sodium hydroxide/chloroform in a s/l system.

shifted to the right (Scheme 7; the subscripts b, ad and s denote bulk of organic phase, adsorbed state and solid state, respectively).

Judging from the results shown in Figs. 11 and 13, it is reasonable to suppose that under the reaction conditions, the rate of olefin consumption while the surface of NaOH is free is controlled solely by its reactivity. In the studied s/l system the concentration of TEBA ca. 10^{-4} M provides the existence of a small excess of dichlorocarbene that is relatively slow consumed by reaction with styrene till the surface of NaOH particles is coated with NaCl and the reaction is inhibited. At TEBA concentrations ca. 10^{-3} M, we observed intensive tar formation due to dichlorocarbene polymerisation as at these catalyst concentrations the rate of dichlorocarbene generation strongly exceeds the rate of its consumption. Thus, the rate of dichlorocarbene generation is the function of the catalyst concentration. These results also provide the viable explanation for the somewhat unusual solvent influence that we obtained earlier (see Fig. 10 in [15]). On one hand, a solvent can facilitate surface renovation increasing NaCl solubility (MeCN, THF). On the other hand, a solvent can provide for better solvation of the transition state (benzene and halobenzenes). One can predict that with reactive olefins the latter group of solvents would cause much more significant increase in the reaction rate than the former.

Summing up the findings, it is evident that physical factors (the formation of a liquid film in a l/l system and formation of crust of a product on particles of a solid reactant in a s/l system) make a prominent contribution to the observed kinetics and sometimes can make it quite difficult to elucidate the intrinsic reaction mechanism.

3. Experimental

3.1. Materials

Commercially available chloroform, styrene, toluene, benzene, were purified in the standard manner and distilled prior to use. TEBA and NaOH were of p.a. grade and used without further purification. Bidistilled water was used for NaOH solutions.

3.2. Dichlorocarbene addition to styrene in the l/l system

The reactor, controlled at a constant temperature, was a 250 ml four-necked water-jacketed cylindrical Pyrex flask fitted with baffles, thermometer, reflux condenser, and mechanical stirrer with tachometer. The concentration of the reagents was changed in the range 0.4–6 M, concentration of TEBA in the range 0.004–0.01 M, and temperature from 25 to 45 °C in intervals of 10 °C. In a typical run styrene (3 ml, 0.025 mol), CHCl$_3$ (14 ml, 0.18 mol), 40 ml toluene (solvent and internal standard), TEBA (0.075 g, 3.3×10^{-4} mol) and 8 ml of 50% aqueous NaOH (0.15 mol) were introduced into the reactor at the desired temperature. The reaction was carried out at 2000–2500 rpm. An aliquot sample was withdrawn from the organic phase after stopping the stirrer, and analysed quantitatively by GLC using the method of internal standard. For the analysis on GLC (TSWETT model 100 chromatograph with thermoconductivity detector, Khimavtomatika, Russia), the conditions were: stainless steel column (2 m × 4 mm) packed with 5% SE-30 on Chromaton N-AW-DMCS (0.125–0.16 mm), injector temperature 250 °C, starting column temperature 110 °C, final column temperature 300 °C, temperature growth rate 20 °C/min, carrier gas (He) flow 33.3 ml/min, sample volume 0.4 μl. Specially staged experiments proved that in

the absence of agitation no reaction was observed. Also no reaction was observed without the catalyst.

3.3. Dichlorocarbene addition to styrene in the s/l system

Suspension of NaOH in benzene was prepared by milling 100 g NaOH for 10–14 h in a ball mill KM-25 with 100 ml benzene. The resulting concentration of NaOH in a suspension was determined by titration. The concentration of reagents was changed in the range 0.14–2.8 M, concentration of TEBA in the range 2×10^{-4}–0.004 M, and temperature from 25 to 45 °C in intervals of 10 °C. In a typical run, styrene (1 ml, 8.7×10^{-3} mol), CHCl$_3$ (3 ml, 0.035 mol), toluene (internal standard, 2 ml), 5 ml of NaOH suspension in benzene (2 g, 0.05 mol), TEBA (5.2×10^{-3} g, 2.3×10^{-5} mol) and benzene (45 ml) were introduced into the above-described reactor and the reaction was carried out as described. Samples were withdrawn at predetermined times, quenched with distilled water and analysed as above.

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