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ADSORPTION AT THE LIQUID–LIQUID INTERFACE: AN IMPORTANT FACTOR IN PHASE-TRANSFER CATALYSIS*

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A new rationalization of some phenomena in the phase-transfer catalysed processes promoted by concentrated aqueous alkali solutions, such as alkylations and β-eliminations, is proposed. It is predicted on the basis of adsorption theory and subsequently evidenced experimentally that the size of the interfacial area, controlled by the rate of stirring, affects the position of the extraction equilibrium of various anions with quaternary ammonium cations supplied by the phase-transfer catalysts.

INTRODUCTION

Phase-transfer catalysis (PTC) is a well established methodology in organic synthesis and its scope and mechanistic features have been the subjects of numerous studies and appear to be well recognized and understood.[2]

There are, however, some observations which do not conform fully with the framework of existing concepts and mechanistic interpretations. For example, alkylations of carbanions generated from weak CH acids,[3] some base-induced β-elimination processes[4] and isomerization reactions[5] often proceed more efficiently in two-phase systems containing concentrated aqueous alkali and a phase-transfer catalyst than one would expect on the basis of the ion-exchange equilibria, which in the former case is also associated with deprotonation of CH acids, the carbanion precursors.

Thus, for example, despite low or negligible concentrations of hydroxide or carbanion in the organic phase (as determined after separation of the phases), the degree of β-elimination or the alkylation of weak CH acids is often relatively high. For the β-elimination process these observations may be partially explained by the presence of minute amounts of alcohols, which are able to act as the co-catalysts in the PTC elimination.[6] They may exist as impurities in the starting alkyl halides or be formed in a competing hydrolysis process. Such an explanation is, of course, invalid for the alkylation and isomerization processes, in which an alcohol is neither introduced nor formed. Further, it appears insufficient also for the β-elimination reaction.

Since the crucial difference between systems in which the concentration of reacting anions can be determined and those in which reactions really take place is the size of the interfacial area, in this work we have analysed thoroughly effect of the stirring rate, which determines the size of the interfacial surface, on the concentration of reacting anions in the organic phase.

In many studies of the PTC mechanism, phenomena occurring in highly dispersed media, e.g. during vigorous agitation of two-phase systems, are rationalized on the basis of data acquired by analysis of the concentrations of the reacting species after complete separation of both phases.[7] Although in many cases this approach appears to be justified and gives a satisfactory correlation, the situation in systems being agitated and systems subjected to the separation of phases is substantially different, provided that these two phases are virtually immiscible. In systems in which vigorous agitation was followed by separation of the phases, which usually requires a few minutes because of the slow coalescence process, the interfacial phenomena play a marginal role because of the small value of the so-called ‘specific area’, measured in $m^2 m^{-3}$, expressing the ratio of surface area to volume. In such a situation, the position of the exchange equilibrium between two phases, determined by the measured concentration of ions in the separated phases, depends predominantly on the properties of the bulk phases. Let us consider that this is the ‘static’ situation.

On the other hand, in vigorously stirred two-phase systems, the size of the interface in relation to the volume of phases, i.e. the specific area, is usually

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several orders of magnitude greater than in static systems. In these cases interfacial phenomena can affect substantially the ion-exchange process.

It is necessary to stress that when in such vigorously agitated systems extracted or produced anions are subjected to a reaction, their concentration in the bulk phase differs from that expected on the basis of the extraction equilibrium constant, because of the reaction proceeding in the interfacial region.[8] Because of the large size of the interfacial region in such systems, the contribution of the effect of the interfacial reaction can be important. Let us consider that such highly dispersed, vigorously stirred systems are 'dynamic' systems.

There are many observations which suggest that the surface properties of the onium catalyst or reacting species play an important role in PTC reactions.[9-11] It appears that the rate of stirring, which determines the size of the interfacial area, not only influences the rate of ion exchange but can also have a more profound effect.

In this paper we direct attention to some physicochemical aspects of the interfacial phenomena that are instrumental in the PTC reactions and apply a quantitative approach to this problem. Let us analyse the problem of the extraction of basic anions, such as hydroxide anions or carbanions, in the form of ion pairs with quaternary ammonium cations (Q^+), which are usually applied as catalysts in PTC reactions, carried out in the presence of a concentrated aqueous solution of sodium hydroxide.[12] When a small amount of tetrabutylammonium bromide (Bu_4NBr) was equilibrated between a non-polar solvent and concentrated aqueous alkali, analysis of the organic phase in the static systems (as defined above) revealed a negligible concentration of hydroxide anions. When the tetrabutylammonium cation (Bu_4N^+) was accompanied by the more hydrophilic chloride anion, the concentration of HO^- in the organic phase was somewhat higher, but still below 4% of the total concentration of the quaternary ammonium salt.[13] It fell to a negligible value on addition of some amount of NaCl or NaBr to the system, despite the fact that some reactions effected by extracted HO^- anions, in course of which halide anions are produced, proceeded satisfactorily when such two-phase systems were vigorously stirred. The apparent controversy between these observations may be clarified on the basis of an analysis of the interfacial phenomena. There are several ways in which the interfacial phenomena may be responsible for such effects: (a) because of the high rate of chemical reactions the overall process may be diffusion controlled, so it is accelerated by an increase in the rate of ion exchange via vigorous stirring; (b) the process proceeds between molecules and ions adsorbed at the interface; or (c) the ion exchange equilibrium is affected by the size of the interface, hence the speed of stirring influences the concentration of the reacting anions in the organic phase. The first two are well documented,[14-16] but (c) the dependence of the ion-exchange equilibrium on the rate of stirring, at first glance appears unreasonable and needs theoretical justification and experimental verification.

In order to formulate this idea in a quantitative way, it is necessary to express the described phenomena in terms of equations and to introduce certain notions. First, it is necessary to state that both phases are immiscible. Organic compounds are completely insoluble in concentrated aqueous NaOH solution, and there are only traces of sodium cations and water in a moderately polar organic phase.[17] Next, it is necessary to assign adsorption properties to the interface. This concept is frequently used in many electrochemical or physicochemical studies of quaternary ammonium salts or long-chain alkyl esters or salts, which adsorb at the interface.[15,18,19] This may be understood, for instance, as a much longer residence time for a certain volume of liquid situated at the interface than the residence time for a similar volume of liquid chosen anywhere in the bulk of the phase (far from the interface). Such a situation corresponds to physical adsorption on solids. This phenomenon may be enhanced by chemical bonding across the interface (e.g. due to deprotonation of weak organic CH acids) and in such cases it may be related to the idea of chemisorption on solids. For a quantitative treatment it is possible to apply the formalism used for adsorption on solids to adsorption on the liquid/liquid interface, keeping in mind its different physical sense.

At the interface there is a typical acid–base equilibrium between adsorbed molecules of CH acids and the corresponding carbanions $\geqslant C^-$, anchored at the interface (on one side of the phase boundary) and hydroxide anions together with water molecules on the other side of it:

$$\geqslant CH_i + HO_i^- \underset{k_p}{\overset{k_d}{\rightleftarrows}} \geqslant C_i^- + H_2O \qquad (1)$$

where the subscript i refers to the interface.

Hence we may write the equation for the rate of the carbanion (C_i^-) formation:

$$\frac{d[C_i^-]}{dt} = k_d S_{CH_i} a_{OH_i} - k_p S_{C_i^-} a_{H_2O_i} \qquad (2)$$

where $d[C_i^-]/dt$ (moles/time) = rate of $\geqslant C^-$ formation at the interface; k_d = rate constant of the deprotonation reaction of the CH acid; k_p = rate constant of the protonation reaction of the $\geqslant C^-$ anion; a_{OH_i} = activity of HO^- in the aqueous phase at the interface; $a_{H_2O_i}$ = activity of H_2O in the aqueous phase at the interface; $S_{CH_i}(m^2)$ = area of the interface occupied by the adsorbed CH acid molecules; $S_{C_i^-}(m^2)$ = area occupied by $\geqslant C^-$ carbanions adsorbed at the interface.

In the equilibrium we have

$$\frac{d[C_i^-]}{dt} = k_d S_{CH_i} a OH_i - k_p S_{C_i^-} a_{H_2O_i} = 0 \qquad (3)$$

Hence

$$\frac{k_d}{k_p} = \frac{S_{C_i^-} a_{H_2O_i}}{S_{CH_i} a_{OH_i}} = \frac{S_{C_i^-}}{S} \times \frac{S}{S_{CH_i}} \times \frac{a_{H_2O_i}}{a_{OH_i}}$$

$$= \frac{\Theta_{C^-}}{\Theta_{CH}} \times \frac{a_{H_2O_i}}{a_{OH_i}} \qquad (4)$$

where $S(m^2)$ = total interfacial area; Θ_{C^-} = fraction of a total interfacial area occupied by the $\geqslant C^-$ anions; Θ_{CH} = fraction of a total interfacial area occupied by CH molecules.

Because the left-hand side of equation (4) may well be related to the thermodynamic acidity constant K_a of a CH acid, and omitting subscripts i, we obtain finally

$$\Theta_{C^-} = K_a \times \frac{a_{OH}}{a_{H_2O}} \times \Theta_{CH} \qquad (5)$$

Ion exchange takes place at the interface and because of the immiscibility condition we may use the same formalism to describe the exchange equilibrium:

$$\geqslant C_i^- + Q^+A_i^- \xrightleftharpoons{K_{ex}} Q^+C_i^- + A_i^- \qquad (6)$$

Hence:

$$K_{ex} = \frac{\Theta_{QC} a_A}{\Theta_{C^-} \Theta_{QA}} \qquad (7)$$

where Θ_{QC} = fraction of a total interfacial area occupied by the ion pair QC; Θ_{QA} = fraction of a total interfacial area occupied by the ion pair QA; a_A = activity of the catalyst parent anion at the interface.

Combining equations (5) and (7), we obtain

$$\Theta_{QC} = K_a K_{ex} \times \frac{a_{OH}}{a_A a_{H_2O}} \times \Theta_{QA} \Theta_{CH} \qquad (8)$$

In order to relate interfacial parameters to the parameters in the bulk phases, it is necessary to assume a certain model of the adsorption. We decided to use the Langmuir adsorption isotherm, although its applicability to salt systems is still under discussion,[15,19,20] for the sake of simplicity of the mathematical description and because of an insufficient general knowledge of adsorption processes with highly concentrated salt solutions. Moreover, the Langmuir isotherm has a good theoretical explanation and to a first approximation may be much more correctly applied than any other semi-empirical correlation. Let us assume that molecules of CH acid, and also ion pairs QA and QC, adsorb at the interface. Hence, according to the Langmuir isotherm, we can write

$$\Theta_{QC} = \frac{K_{QC} C_{QC}}{1 + K_{CH} C_{CH} + K_{QC} C_{QC} + K_{QA} C_{QA}} \qquad (9)$$

$$\Theta_{QA} = \frac{K_{QA} C_{QA}}{1 + K_{CH} C_{CH} + K_{QC} C_{QC} + K_{QA} C_{QA}} \qquad (10)$$

$$\Theta_{CH} = \frac{K_{CH} C_{CH}}{1 + K_{CH} C_{CH} + K_{QC} C_{QC} + K_{QA} C_{QA}} \qquad (11)$$

where K_{CH}, K_{QC}, K_{QA} = constants of adsorption equilibrium of CH acid molecules, ion pair QC and ion pair QA, respectively; C_{CH}, C_{QC}, C_{QA} = bulk concentrations in the organic phase of CH acid, ion pair QC and ion pair QA, respectively.

Substitution of equations (9),(10) and (11) into equation (8) gives

$$C_{QC} = K_a K_{ex} \times \frac{K_{CH} K_{QA}}{K_{QC}} \times \frac{a_{OH}}{a_A a_{H_2O}} \times \frac{C_{CH} C_{QA}}{1 + K_{CH} C_{CH} + K_{QC} C_{QC} + K_{QA} K_{QA}} \qquad (12)$$

Finally, it is necessary to make a Q^+ cation inventory in the organic phase. Taking into account the surface activity of quaternary ammonium salts, we can write

$$V_{org} C_{QA}^0 = V_{org}(C_{QA} + C_{QC}) + (\Gamma_{QA} + \Gamma_{QC}) S n \qquad (13)$$

where $C_{QA}^0(\text{mol dm}^{-3})$ = initial concentration of QA salt in the organic phase; V_{org} = volume of the organic phase; $\Gamma_{QA}(\text{mol m}^{-2})$ = interfacial excess of the ion pair QA, i.e. surplus of QA molecules on a plane situated close to the interface in comparison with any plane lying in the bulk of the organic phase; $\Gamma_{QC}(\text{mol m}^{-2})$ = interfacial excess of the ion pair QC; $S(m^2)$ = interfacial area; n = number of adsorption layers; in general the value of n need not be an integer.

Combining equations (12) and (13) in order to calculate the ratio of both ion pairs in the bulk of the organic phase, we obtain finally

$$[C_{QA}^0 - (\Gamma_{QC} + \Gamma_{QA}) a n] \times \frac{K_{QC} + K_{QA} \times \frac{C_{QA}}{C_{QC}}}{1 + \frac{C_{QA}}{C_{QC}}}$$

$$= K_a K_{ex} \times \frac{K_{CH} K_{QA}}{K_{QC}} \times \frac{a_{OH}}{a_A a_{H_2O}} \times C_{CH} \times \frac{C_{QA}}{C_{QC}} - (1 + K_{CH} C_{CH}) \qquad (14)$$

where $a \equiv S/V_{org}(m^2\, m^{-3})$ = specific area of a dispersed organic phase. This equation may be rearranged in order to obtain the form of a quadratic equation:

$$\alpha \left(\frac{C_{QA}}{C_{QC}} \right)^2 + \beta \left(\frac{C_{QA}}{C_{QC}} \right) + \sigma = 0 \qquad (15)$$

where α, β and σ are constants. This equation can easily be solved to obtain the ratio C_{QA}/C_{QC} as a physically real single root, the other one bearing a negative sign. The form of this solution, however, is complicated and hence difficult to discuss. Nevertheless, when the CH compound is really a weak CH acid, we can readily discuss a special case of the above solution, i.e.

$$\frac{C_{QA}}{C_{QC}} \gg 1$$

Now we can simplify equation (14), taking into account that

$$1 + \frac{C_{QA}}{C_{QC}} \approx \frac{C_{QA}}{C_{QC}}$$

$$\text{and } K_{QC}\left(1 + \frac{K_{QA}}{K_{QC}} \times \frac{C_{QA}}{C_{QC}}\right) \approx K_{QA} \times \frac{C_{QA}}{C_{QC}} \quad (16)$$

On introduction of the above conditions into equation (14), we obtain

$$\frac{C_{QA}}{C_{QC}} = \frac{1}{K_a} \times \frac{1}{K_{ex}} \times \frac{K_{QC}}{K_{CH}K_{QA}} \times \frac{a_A a_{H_2O}}{a_{OH}} \times \frac{1}{C_{CH}}[1 + K_{CH}C_{CH} + K_{QA}C^0_{QA} - K_{QA}(\Gamma_{QC} + \Gamma_{QA})an] \quad (17)$$

This equation represents a straight-line relationship of the kind $C_{QA}/C_{QC} = \Omega - \phi a$, where Ω and Φ are constants, and the specific area a can be related to the speed of stirring in the form of numerous correlations.[21] The remaining parameters in equation (17) bear the character of physico-chemical constants and may be determined experimentally or be considered invariable in a given system.

Now we can clearly see that in the case of a static system ($a \to 0$) ratio of anions C_{QA}/C_{QC} extracted into the organic phase is not much affected by interfacial parameters Γ_{QA} and Γ_{QC}. On the other hand, in a dynamic system, when the area of phase contact (hence the value of a) is large, the ratio C_{QA}/C_{QC} decreases, which means that in the bulk of droplets of the organic phase the concentration of the $—C^-$ increases. This effect exists only when quaternary ammonium ion pairs QA and QC show interfacial properties, in other words when $\Gamma_{QC} \gg 0$ and $\Gamma_{QA} \gg 0$; on the other hand, when $\Gamma_{QC} = \Gamma_{QA} = 0$, even very large values of the specific area a (i.e. a very high agitation speed) cannot influence the ratio of anions C_{QA}/C_{QC}, which remains the same as in the static system. In such cases stirring only accelerates the extractive equilibrium between the phases. On the other hand, in the case of the dynamic system, in which reacting species show interfacial properties, stirring first creates a large value of the interfacial area, where the equilibration in fact takes place, and also, as stems from the above equations, influences all interfacial equilibria in the system. This reasoning seems to be adequate to explain at least some of the experimental observations found earlier.[22]

It is necessary to stress also that the decrease in the ratio C_{QA}/C_{QC} with increasing specific area a is not restricted to the aforementioned special case [equation (17)] of the general equation (14). This dependence still exists in the solution of the general equation (14), although it is no longer linear.

The effect of the rate of stirring on the extraction equilibrium between two phases was reported earlier; the starting point was a serendipitous observation. For rationalization of this phenomenon, the calculations were made on the basis of the Gibbs adsorption isotherm.[23] In our work, initial theoretical, physico-chemical considerations were followed by attempts to confirm the conclusions experimentally.

The main difficulty in the experimental verification of the presented reasoning is connected with a lack of direct methods of determining concentrations in the organic phase of two-phase systems under dynamic conditions, i.e. while keeping the agitation vigorous all the time. In the above-mentioned case it was possible to measure the concentration of extracted species directly during stirring.[23] In order to overcome this obstacle, it was necessary to employ a chemical reaction as the internal sensor of a base concentration. Such a reaction should fulfil rigorously several requirements: (1) its rate should be dependent only on the homogeneous base concentration in the organic phase; (2) it should not consume the base in order to avoid a shift of the equilibrium in the organic phase; (3) substrates and products of the reaction should not undergo any other reactions with species present in the system (hydrolysis, addition, oxidation, etc) and (4) the course of the reaction should not involve a continuous mass transfer between phases, which might be able to impose mass transfer effects on a homogeneous reaction kinetics.

Taking all this into account, we chose the double bond migration reaction in substituted allylarenes, which apparently meets these criteria.[5,24] Amongst allylarenes, neither unsubstituted allylbenzene nor its *p*-methoxy derivative were found to be sufficiently acidic compounds to undergo the rearrangement at an acceptable rate at room temperature. For availability reasons we concentrated on *o*-allylanisole derivatives, which can be readily prepared via allylation of appropriately substituted phenols, the Claisen rearrangement and methylation of the *o*-allylphenols produced. However, 2-allyl-4-bromoanisole (**1**) also did not undergo the rearrangement reaction at room temperature at an acceptable rate. On the other hand, introduction of two or three halogen atoms into the aromatic ring, as in 2-allyl-3,4,6-trichloroanisole (**2**) or in 2-allyl-4,6-dibromo-anisole (**3**), increased the rate of the rearrangement reaction sufficiently, but the substituted propenylbenzenes produced underwent a further addition reaction with carbanions present in the system, so they could be used only for the investigation of the extraction of hydroxide anions. Finally, 2-allyl-4-cyanoanisole (**4**) and 1-methoxy-2-allyl-4-chloronaphthalene (**5**) were selected as suitable model substrates, which covered the full range of the problems studied. They rearrange at a sufficient rate under the action of either the hydroxide anions extracted as Q^+HO^- into the organic phase or phenylacetonitrile carbanion formed at the interface and extracted in the form of the ion pair with the Q^+ cation into the organic phase, giving stable products under the reaction conditions. Catalysts used in this work included tetrabutylammonium bromide (Bu_4NBr) (**6**), tetramethylammonium bromide (Me_4NBr) (**7**) and tetrabutylammonium hydrogensulphate (Bu_4NHSO_4) (**8**).

EXPERIMENTAL

All the quaternary ammonium catalysts were commercial products of purity more than 95%. Bu_4NHSO_4 (**8**) may occasionally contain some tributylammonium hydrogensulphate, which does not interfere with the reaction. 1,2-Dichlorobenzene was of 99% purity and was used without further purification. Commercially pure benzyl cyanide was distilled before use and its purity was above 99% (GC). Sodium hydroxide was of analytical-reagent grade; all its solutions were prepared using distilled water and were subjected to prolonged sedimentation in order to obtain clear, transparent solutions without solids. Allylarenes were synthesized from the corresponding hydroxyarenes via allylation, Claisen rearrangement and methylation reactions. Details of the synthesis of these compounds and the identification of the isomerization products are described elsewhere.[1]

Dynamic experiments were carried out in a three-necked, round-bottomed flask, equipped with a mechanical stirrer, consisting of a glass helical ribbon impeller (providing coaxial circulation of liquid down the impeller, which resulted in good mixing without splashing and aeration), a thermometer and a thick PTFE sampling tube, attached directly to a 10 ml polypropylene syringe. A solution of organic substrates was prepared in a separate, small Erlenmeyer flask: benzyl cyanide (2.5 ml, 21.45 mM) and *o*-dichlorobenzene (18 ml) were added to 1 mM of a suitable allylarene (**1**–**5**). In cases when the extraction of hydroxide was investigated, 2.5 ml of *o*-dichlorobenzene instead of benzyl cyanide were applied in order to keep the volume of organic phase constant. When Bu_4NBr (**6**) was used as the catalyst, it was dissolved in the organic reagent solution.

The flask was charged with a saturated aqueous (19.32 M) sodium hydroxide solution (40 ml), then the solution of the organic reagents was carefully poured on to it. When Me_4NBr (**7**) or Bu_4NHSO_4 (**8**) was applied as the catalyst, they were added in the form of well ground, fine powder directly on to surface of the organic phase.

After loading the flask with reagents, agitation was applied at about 1300 rpm at room temperature for the times indicated in Tables 1 and 2. After certain time intervals small (*ca* 1.5 ml) aliquots of the mixture were drawn off, poured immediately into 10 ml of distilled water and shaken well. After the separation, a drop of organic phase was sucked off with a pipette, dried via filtration through anhydrous Na_2SO_4 and used directly for GC analysis. Results of dynamic experiments are given in Tables 1 and 2.

Static experiments were carried out in a similar three-necked, round-bottomed flask, equipped with the same mechanical stirrer, thermometer and a narrow PTFE tube attached to a polypropylene syringe by means of a stainless-steel needle. A separately prepared solution of Bu_4NBr (**6**) (0.85 mM) and benzyl cyanide (4.9 ml, 42.45 mM) in 38 ml of *o*-dichlorobenzene was added to a saturated aqueous (19.32 M) sodium hydroxide (85 ml). When the extraction of hydroxide was examined, *o*-dichlorobenzene (4.9 ml) instead of benzyl cyanide was added in order to keep the volume of the organic phase constant. When Bu_4NHSO_4 (**8**) was used as the catalyst it was added in the form of a fine powder directly on to the surface of the organic phase (0.85 mmol). Vigorous stirring was maintained for 3 min, then the dispersion was allowed to separate into two layers. After 10–30 min of separation, a *ca* 20 ml sample of the organic phase was drawn off and additionally subjected to a centrifugal separation for 3 min. Finally, the well separated organic phase was divided into 4–6 parts and each was weighed, mixed with 3 ml of distilled water and titrated with 0.01 M HCl with *o*-nitrophenol as the indicator. The basicity determined was ascribed to extracted hydroxide anion or phenylacetonitrile carbanion and their share in binding the quaternary ammonium cation in the case of complete separation of phases was calculated. Results of these static experiments are summarized in Table 3.

RESULTS AND DISCUSSION

The concentration of hydroxide anions in the organic phase of the dynamic systems which gave the value of the ion-exchange equilibrium:

$$Q^+Br^-_{org} + NaOH_{aq} \rightleftarrows Q^+HO^-_{org} + NaBr_{aq} \qquad (18)$$

was estimated in the following way. First, the rate of isomerization of **1**, **2**, **3**, **4** and **5** in the two-phase system [equation (19)], catalysed by Q^+Br^- (**6**), was measured:

$$ArCH_2CH{=}CH_2 \xrightarrow{Q^+Br^-/Q^+HO^-} ArCH{=}CHCH_3 \qquad (19)$$

Next, a series of analogous experiments were carried out in which the isomerization reaction (19) was catalysed by **8**. Since **8** is known to be able to exchange HSO_4^- anions for HO^- completely, the concentration of hydroxide anions extracted into the organic phase should therefore be equal to the current concentration of **8** as the catalyst.[25,26] This behaviour was independently confirmed by separate experiments. Using **8** in an amount which ensures a rate of isomerization close to that observed for the process catalysed by **6**, the concentration (amount) of HO^- anions in the organic phase of dynamic systems can be estimated with a sufficient degree of confidence. These results are presented in Table 1.

Entry 2 gives result of the isomerization of **2** when **6** was used as the catalyst (1 mmol). Entries 3 and 4 give the results of analogous experiments in which **8** was applied in amounts ensuring the closest similarity of the kinetics of the isomerization to that observed in entry 2. From these data, taking into account complete conversion of **8** into Q^+HO^-, one can conclude that the concentration of Q^+HO^- in entry 2 is *ca* 2–3% of the concentration of **6**.

Similar reasoning applied to the isomerization of **3**, **4** and **5** (data presented in entries 7, 8, 9 for **3**, and 10, 11, 12 for **4** and 15, 16, 17 for **5**) gives variable results, but the discrepancies are not substantial. Participation of the possible interfacial process in the global outcome of the isomerization reaction was excluded by experiments without any quaternary ammonium catalyst, when no isomerization was observed (entries 5, 13 and 18). Moreover, no isomerization was detected when it was attempted in the presence of a much less lipophilic quaternary ammonium salt, i.e. tetramethylammonium bromide (Me_4NBr) (**7**). This salt accumulates at the interface; obviously the process does not proceed at such a modified interface.

In another series of experiments the influence of the size of the interfacial area on the concentration of carbanions in the form of the ion pairs Q^+C^- in the organic phase of dynamic systems was studied. Here the situation is more complicated, because the observed concentration is a result of an acid–base equilibrium at the interface (deprotonation process), followed by ion-exchange equilibrium between the carbanions adsorbed at the interface and the parent catalyst anions. In these experiments phenylacetonitrile was used as the model carbanion precursor because its acidity is within a convienient range and the carbanions formed were able to catalyse the isomerization and appeared to be sufficiently stable.

Estimation of the carbanion concentration in the organic phase of the dynamic systems was performed in

Table 1. Dynamic extractability of hydroxide by Bu_4NBr[a]

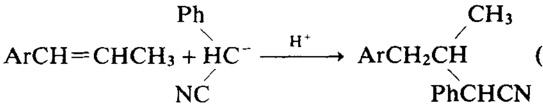
Entry	Substrate[b]	Catalyst		Average temperature (°C)	Total reaction time (min)	Time interval between sampling (min)	Conversion after			
		Type used	Amount (mM)				1st interval	2nd interval	3rd interval	Last interval
1	**1**	**6**	1	19·3	180	30	0·064	0·258	0·451	0·783
2	**2**	**6**	1	19·4	28	4	0·093	0·293	0·453	0·792
3	**2**	**8**	0·026	19·9	28	4	0·202	0·374	0·499	0·654
4	**2**	**8**	0·017	19·2	28	4	0·077	0·119	0·222	0·359
5	**2**	None	—	18·7	120	30	0	0	0	0
6	**2**	**7**	1	19·5	120	30	0	0	0	0
7	**3**	**6**	1	17·5	6	1	0·138	0·389	0·622	0·797
8	**3**	**8**	0·026	17·5	6	1	0·113	0·152	0·177	0·223
9	**3**	**8**	0·042	17·6	6	1	0·353	0·437	0·481	0·560
10	**4**	**6**	1	21·1	120	20	0·437	0·768	0·905	1·000
11	**4**	**8**	0·085	20·4	120	20	0·657	0·775	0·845	0·928
12	**4**	**8**	0·042	18·8	120	20	0·204	0·280	0·335	0·455
13	**4**	None	—	23·8	240	120	0	0	0	0
14	**4**	**7**	1	20·1	225	45	0	0	0	0
15	**5**	**6**	1	20·6	35	4	0·175	0·409	0·585	0·905
16	**5**	**8**	0·043	19·2	35	4	0·537	0·754	0·864	0·91
17	**5**	**8**	0·017	20·1	35	4	0·126	0·240	0·300	0·54
18	**5**	None	—	18·7	120	30	0	0	0	0
19	**5**	**7**	1	19·0	120	30	0	0	0	0

[a] Kinetic picture of each parent run, recorded with Bu_4NBr as thte catalyst (entries 2, 7, 10 and 15) (amount of Bu_4NOH extracted unknown) is approximated by the upper (entries 3, 9, 11 and 16) and the lower (entries 4, 8, 12 and 17) limiting kinetic pictures, corresponding to known amounts of Bu_4NHSO_4 (full equivalence to Bu_4NOH), which determine the limits of concentration of Bu_4NOH extracted by Bu_4NBr in the parent run.

[b] **1** = 2-Allyl-4-bromoanisole; **2** = 2-allyl-3,4,6-trichloroanisole; **3** = 2-allyl-4,6-dibromoanisole; **4** = 2-allyl-4-cyanoanisole; **5** = 1-methoxy-2-allyl-4-chloronaphthalene.

a similar manner to that for HO$^-$ anions. In this way, the isomerization of some allylarenes into propenylarenes was first catalysed by the system: Bu_4NBr (**6**)–$PhCH_2CN$, the latter taken in excess, followed by analogous experiments in which Bu_4NHSO_4 (**8**) instead of **6** was used in an amount such as to provide similar kinetics of the isomerization reaction.

For this study, however, not all allylarenes employed in the previous series of experiments (i.e. extraction of hydroxide) were suitable; some propenylarenes produced in the isomerization process reacted further with the phenylacetonitrile carbanion according to the Michael addition pathway:



$$\mathrm{ArCH{=}CHCH_3} + \overset{\mathrm{Ph}}{\underset{\mathrm{NC}}{\mathrm{HC^-}}} \xrightarrow{H^+} \mathrm{ArCH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{PhCHCN}}{\mathrm{CH}}} \qquad (20)$$

This process was particularly significant for allylarenes **2** and **3** and is discussed elsewhere.[1]

From the data in Table 2, the degree of conversion of the original Q^+Br^- into Q^+C^-, determined on the basis of the isomerization reaction of **4** (entries 3–5) and **5** (entries 7–12), was *ca* 40% with a small discrepancy. The same conversion determined in the static system, as shown in Table 3, gives value of *ca* 27%. Also in this series of experiments it was shown that in absence of the catalyst no isomerization occurred; hence interfacially located carbanions are unable to promote the isomerization. Similarly, no reaction was observed when Me_4NBr (**7**) was used as the catalyst. The tetramethylammonium cation is insufficiently lipophilic to form with phenylacetonitrile carbanion an ion pair that is soluble in the organic phase.

From the results presented we may draw the following main conclusions. Ion-exchange equilibria between two immiscible liquid phases are a function of the size of the interfacial area, and therefore they are affected by the stirring rate. This is why in all the static systems exchange of bromide for hydroxide in Bu_4NBr (**6**) dissolved in the organic phase is negligible, whereas in the dynamic systems, during vigorous stirring, it attains a value of *ca* 3–4% of the original amount of **6**.

The same situation occurs in the formation of Q^+C^- ion pairs. In the static systems, as defined above, under the conditions specified in this paper with phenylacetonitrile as the carbanion precursor, 27% of $Bu_4{}^+NBr^-$ is converted into $Bu_4N^+C^-$, whereas in the dynamic systems, during vigorous stirring, *ca* 40% of the Bu_4NBr applied forms $Bu_4N^+C^-$ ion pairs.

The kinetics of the isomerization process over a wide time scale was not well behaved. One reason for this could be partial decomposition of the tetrabutylammonium cations, especially when they were accompanied by HO$^-$ anions.[27,28] Although the stability of the tetrabutylammonium cation is relatively high, estimations based on published data showed that at room temperature the decrease in the concentration of Bu_4NOH due to its decomposition is negligible only for a relatively short reaction time. The results of the static experiments (Table 3, entries 5 and 6) appear to confirm that some decomposition indeed takes place.

In all experiments with **6**, the decomposition of the catalyst in the form of Bu_4NOH is perhaps continuously compensated for by the excess of Bu_4NBr present in the system, whereas when **8** is used, the decomposition, although slow, results in a continuous decrease in the concentration of Bu_4NOH, which affects the

Table 2. Dynamic extractability of phenylacetonitrile carbanion by Bu_4NBr

Entry	Substrate[b]	Catalyst Compound	Catalyst Amount (mM)	Average temperature (°C)	Total reaction time (min)	Time interval between sampling (min)	Conversion after 1st interval	Conversion after 2nd interval	Conversion after 3rd interval	Conversion after Last interval	Remarks
1	**2**	**6**	1	22·8	80	10	0·296	0·413	0·496	0·744	a
2	**3**	**6**	1	19·0	30	6	0·464	0·652	0·746	0·815	a
3	**4**	**6**	1	21·0	210	30	0·188	0·311	0·407	0·592	
4	**4**	**8**	0·34	20·1	210	30	0·187	0·302	0·379	0·505	
5	**4**	**8**	0·40	22·0	210	30	0·214	0·332	0·409	0·528	
6	**4**	**7**	1	20·0	180	60	0	0	0	0	
7	**5**	**6**	1	20·9	120	15	0·283	0·439	0·538	0·782	
8	**5**	**8**	0·38	19·3	120	15	0·257	0·417	0·546	0·743	
9	**5**	**8**	0·43	19·1	120	15	0·277	0·438	0·557	0·777	
10	**5**	**8**	0·48	19·5	120	15	0·304	0·48	0·627	0·82	
11	**5**	**8**	0·17	18·0	120	15	0·125	0·213	0·283	0·44	
12	**5**	**8**	0·34	19·8	120	15	0·239	0·383	0·497	0·719	
13	**5**	None	—	17·6	120	30	0	0	0	0	
14	**5**	**7**	1	18·4	120	30	0	0	0	0	

[a] Product is an intermediate species and undergoes further transformations; conversion determined from the substrate consumption.

Table 3. Static extractability of basic anions by $Bu_4N^+X^-$

Entry	Average temperature (°C)	X^-	Titration	Benzyl cyanide	Basicity	Average Basicity
					Bu_4NX (mol%)	Bu_4NX (mol%)
1	19·7	Br	1	Yes	25·3	26·9
			2		26·0	
			3		23·7	
2	20·5	Br	1	Yes	26·3	
			2		28·0	
3	23·6	Br	1	Yes	25·6	
			2		29·1	
			3		31·3	
4	20·2	Br	1	No	0	0
			2		0	
			3		0	
5	22·9	HSO_4	1	No	92·7	94·1
			2		94·2	
			3		95·4	
6	23·8	HSO_4	1	Yes	97·8	93·6
			2		89·3	

observed kinetics. For this reason only the first sampling intervals may provide reliable approximations for both catalysts. In the isomerization of **4**, the observed discrepancies are more pronounced, perhaps because of partial hydrolysis of the CN group.

It appears, however, that these rationalizations of observed discrepancies are still insufficient. Perhaps the adsorption–extraction picture is more complicated than the model presented here.

Hence the determination of the concentration of reacting species in two-phase systems with quaternary ammonium halides as catalysts, after separation of the phases, often does not reflect the real concentrations of these species in the organic phase of these systems during agitation (i.e. before separation).[22,29]

Phenomena at the interface undoubtedly play a much more important role than was supposed in the course of PTC reactions. This situation should be taken into account in suggested mechanistic pictures of PTC and related processes.

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