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Solid–Solid–Liquid Reaction Systems. A Mechanistic Study

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The mechanism of the alkylation of phenoxide with benzyl bromide, catalysed by polymer-bound phase-transfer catalysts, has been studied as a model for solid–solid–liquid reaction systems. A 'typical triphase catalyst' has been compared with a commercial ion-exchange resin. The reactions proceed by a mechanism which is similar to the extraction mechanism of classical phase-transfer catalysis. Depending on the reaction conditions, the reaction rates are either mass-transfer controlled or chemical-reaction controlled. In some cases the *C*/*O*-alkylation ratio is found to depend on the water content of the system. The possible mechanisms for the transport of the phenoxide ion to the catalytic site are discussed.

Triphase catalysis, in which a solid, polymer-supported catalyst promotes reactions involving two immiscible liquid phases, has drawn much attention during the last 15 years.[1–3] Unfortunately this liquid–solid–liquid (L–S–L) technique has not found widespread application in organic synthesis owing to the relatively low catalytic activity of the catalysts,[4,5] their low physical stability[4,6] and their high price.†

To overcome this problem we have searched for cheap and commercially available catalysts for these triphase systems. We found that the expensive hydrophobic resins generally used can be substituted effectively by commercial ion-exchange resins of the strongly basic type (Cl^- form), provided the inorganic reagent is applied as a solid rather than in aqueous solution.[7] More recently we have demonstrated the use of tetramethylammonium halides impregnated onto silica, as solid catalysts in such solid–solid–liquid (S–S–L) reactions.[8] S–S–L reactions have been reported previously,[9] but little is known about their mechanism. In a study of displacement reactions with solid iodide salts catalysed by polymer-bound polyethylene glycol it was suggested that dissolution of the inorganic salt in the organic phase is required.[10] However, in other work with the same type of catalyst and solid potassium phenoxide this assertion was denied; rather it was found that the intimate contact between the catalyst and the inorganic reagent is critical for the success of the reaction.[11] Mechanistic investigations of reactions with other types of catalysts have not been reported.

The *C*/*O*-alkylation ratio of phenols is known to be a reliable indicator for the nature of the medium surrounding the reactive site.[12] *C*-Alkylation has been shown to occur only with solvents capable of strong hydrogen-bond formation such as water or phenol[12] or in a 'truly heterogeneous' solid–liquid reaction.[13] Therefore the application of soluble phase-transfer catalysts (PTC) in non-polar aprotic solvents leads to selective *O*-alkylation.[14] Similar results have been recently obtained in triphase catalytic (L–S–L) systems using hydrophobic tetraalkylphosphonium ions anchored to a polystyrene resin.[15]

In the present work we set out to identify the mechanism of solid–solid–liquid reactions of the kind described. We studied the alkylation of phenoxide with benzyl bromide in toluene [eqn. (1)] with two different catalysts: a commercial ion-exchange resin (Amberlyst A27,[16] referred to as A27) and a 'typical triphase catalyst'[1–6] (microporous polystyrene-bound benzyltributylammonium bromide, referred to as **P-BTBABr**). We used this reaction not only to determine the catalytic site environment, but also as a tool with which to investigate the transport phenomena in S–S–L reactions.‡

$$\mathrm{PhONa(s)} + \mathrm{PhCH_2Br} \longrightarrow \mathrm{PhCH_2OPh} + o\text{- and } p\text{-}\mathrm{HOPhCH_2Ph} + \mathrm{NaBr(s)} \quad (1)$$

Results

The alkylation of phenoxide with benzyl bromide was examined in four different reaction systems, each with variable amounts of water: (*i*) with sodium phenoxide without addition of a catalyst; (*ii*) with sodium phenoxide and **P-BTBABr** as catalyst under triphasic reaction conditions; (*iii*) with sodium phenoxide and a catalytic amount of A27 (Br^- form) under triphasic reaction conditions; and (*iv*) with A27 (PhO^- form) as stoichiometric reagent under biphasic reaction conditions [eqn. (2)].

$$\mathrm{A27\text{-}PhO^-} + \mathrm{PhCH_2Br} \xrightarrow{\text{toluene}} \mathrm{A27\text{-}Br^-} + \mathrm{PhCH_2OPh} + o\text{- and } p\text{-}\mathrm{HOPhCH_2Ph} \quad (2)$$

In the catalytic reactions [(*ii*) and (*iii*)] formation of benzyl chloride according to eqn. (3) must be avoided, since it can

$$\mathbf{P}\text{-}\mathrm{R_3N^+Cl^-} + \mathrm{PhCH_2Br} \longrightarrow \mathbf{P}\text{-}\mathrm{R_3N^+Br^-} + \mathrm{PhCH_2Cl} \quad (3)$$

participate in the alkylation reaction. We therefore used the catalysts in their bromide form. The kinetics of the reactions were determined by following the formation of the three possible products [eqn. (1)] by GC analysis. The ratio of *O*- and *C*-alkylation products remains constant during any given reaction. We chose the initial rates of the reactions (total rates = sum of *O*- and *C*-alkylation) as a basis for comparison for the various systems. With one exception the initial rates represent the relative reaction rates during the course of the reaction. The reproducibility of the results, which was determined by triplicate runs, was within a relative error of

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† Fluka Chemie AG-Suisse offers polymer-bound benzyltributylammonium chloride at a price of 110 SFr per 25 g, which is *ca.* 50 times the price of Amberlyst A 27.

‡ The influence of the particle size of the resin on the reaction kinetics is of great help in determining reaction mechanisms and rate-determining steps. It was not investigated in the present study, since in our system the particles are disrupted after a short time of any kind of conventional agitation.[7] The reaction conditions with ultrasonic agitation, which prevents this particle dissociation, could not be accurately controlled.

Table 1 Initial rates and product distributions of the uncatalysed reactions[a]

Type of reaction	Volume of water/ mm^3	Product distribution[b]			Initial rate/10^{-6} mol dm^{-3} s^{-1}
		O-Alkylation	*ortho*-*C*-Alkylation	*para*-*C*-Alkylation	
S–L[c]	*e*	10%	90%	—	2.01
	25	17%	83%	—	1.6
	50	25%	75%	—	1.1
	100	53%	47%	—	1.0
	150	70%	29%	1%	5.2
L–L[c]	250[f]	75%	24%	1%	5.3
	1 000	78%	13%	9%	5.2
L–L[d]	16 000	82%	7%	11%	5.6

[a] Reaction conditions: 10 cm^3 of a 0.2 mol dm^{-3} solution of benzyl bromide in toluene was magnetically stirred at 55 °C with sodium phenolate (1.6 mol equiv., 0.371 g). [b] The reactions were stopped at conversions >90%. [c,d] The inorganic reagent was applied either as the dried solid reagent (*c*) or as an aqueous solution (0.2 mol dm^{-3}) (*d*). [e] No water was added; the water content was *ca.* 5 mm^3. [f] Saturated solution at 55 °C.

Table 2 *O*-Alkylation of sodium phenoxide catalysed by polymer-bound benzyltributylammonium bromide[a]

Type of reaction	Volume of water/mm^3	Reaction order	Initial rate[b]/10^{-6} mol dm^{-3} s^{-1}
S–S–L	*c*	0	16.0
	25–100	?	—
	150	1	52.0
L–S–L	500	1	50.0
	1 000	1	53.0
	16 000	1	50.5

[a] Reaction conditions: 10 cm^3 of a 0.2 mol dm^{-3} solution of benzyl bromide in toluene was magnetically stirred at 55 °C with sodium phenolate (1.6 mol equiv.) in the presence of polymer-bound benzyltributylammonium bromide (0.1 mol equiv.). The inorganic reagent was applied as a solid or in aqueous solution as described in Table 1. [b] Since *O*-alkylation is the sole reaction pathway, the initial rate represents the total and the *O*-alkylation rate. [c] No water was added and the water content was *ca.* 6 mm^3.

Table 3 Effect of water on the alkylation of sodium phenoxide catalysed by Amberlyst A27[a]

Number	Volume of water/mm^3	Reaction order	Initial rate/10^{-6} mol dm^{-3} s^{-1}	*ortho*-*C*-Alkylation (%)
1	*c*	0	7.8	2.1
2	50	0	9.9	5.8
3	100	0	13.4	6.8
4	150	1	17.4	10.6
5	200	1	2.6	15.3

[a] Reaction conditions: solution of benzyl bromide in toluene (0.2 mol dm^{-3}; 10 cm^3) was magnetically stirred at 55 °C with sodium phenoxide (1.6 mol equiv.) in the presence of Amberlyst A27–Br$^-$ (0.2 mol equiv., 0.4 mequiv.). [b] Percentage of total alkylation; *C*-alkylation in the *para* position did not occur. [c] No water was added, the water content was *ca.* 6 mm^3.

±5% for the reaction rate and ±3% for the product distribution.

Reaction System 1: *Uncatalysed Reactions*.—The results of the uncatalysed control reactions are in good agreement with previous work. Thus, the S–L reaction with dried solid reagent results in 90% *ortho*-*C*-alkylation.[12] The addition of water to the S–L reaction causes a shift towards *O*-alkylation (Table 1). Up to 100 mm^3 of added water leads to a decrease in the overall rate, but at 150 mm^3 both reaction pathways (particularly the *O*-alkylation) are dramatically accelerated. At 250 mm^3 the sodium phenoxide is completely dissolved and a homogeneous aqueous phase is formed. The liquid–liquid (L–L) reaction with dilute aqueous sodium phenoxide (0.2 mol dm^{-3}) follows pseudo-first-order kinetics with respect to benzyl bromide and affords 82% of the *O*-alkylation product.[15] Although the reaction rates remain constant above 150 mm^3 water content, the product distributions of the reactions continue to change (Table 1).

Reaction System 2: *Reactions Catalysed by Polymer-bound Benzyltributylammonium Bromide*.—Polymer-bound benzyltributylammonium bromide catalyses the alkylation of sodium phenoxide with benzyl bromide. With a catalyst:alkylator molar ratio of 0.1 the initial rate increases by a factor of 8–20, depending on the water content of the system (compare Tables 1 and 2).

Similar to results previously reported by Montanari *et al.*,[15] the liquid–solid–liquid reaction results in selective *O*-alkylation and follows first-order kinetics with respect to benzyl bromide up to at least 70% conversion.

In the solid–solid–liquid reactions *O*-alkylation is also the sole reaction pathway, independent of the amount of water present. The 'dry' reaction (5 mm^3 water) follows zero-order kinetics, and has an activation energy of 7.2 kcal mol^{-1}. On addition of up to 100 mm^3 of water the reaction profile becomes rather strange, with a comparatively high initial rate (*ca.* 75 × 10^{-6} mol dm^{-3} s^{-1}), which drops by an order of magnitude after a few minutes. The various possible reasons for this phenomenon will not be discussed in this paper, since they do not contribute to the understanding of the reaction mechanism. With $\geqslant$ 150 mm^3 of water the reaction has the same profile as the L–S–L reaction (Table 2).

Reaction System 3: *Reactions Catalysed by Amberlyst* A27.—Similar to the catalysis of the same reaction by polymer-bound linear polyethers,[11] the reaction catalysed by A27 resin shows a strong dependence on the water content of the reaction system (Table 3). The proportion of *C*-alkylation, which occurs in the *ortho* position only, is very small in the dry reaction system but increases steadily with the addition of water, up to 15% in the presence of 200 mm^3 (Fig. 1).

The reaction rate increases with the addition of up to 150 mm^3 water and is *ca.* 4–10 times greater than the uncatalysed rate. Above this amount of water reaction order changes from zero to first order in benzyl bromide and the rate drops sharply, to below the uncatalysed reaction rate observed with the same water content (Fig. 2). The activation energy of the reaction also depends on the water content of the system. In the dry reaction system it is 10.0 kcal mol^{-1} but in the presence of 100 mm^3 of water it increases to 15.6 kcal mol^{-1}.

Reaction System 4: *Reactions with Stoichiometric Amberlyst* A27 *as Reagent*.—Application of Amberlyst A27 (PhO$^-$ form) as a reagent results in selective *O*-alkylation, independent of the

Table 4 *O*-Alkylation of phenoxide with Amberlyst A27 as stoichiometric reagent[a]

Number	Water		Initial rate/ 10^{-6} mol dm^{-3} s^{-1} (0.2 mol equiv. A27)[c]	Product ratios	
	cm^3 g^{-1} resin	mm^3 per 0.4 mequiv. A27[b]		*O*-Alkylation	*ortho*-*C*-Alkylation
1	*d*	—	286	100%	—
2	0.12	20	58.5	100%	—
3	1.0	165	11.6	100%	—
4	1.0	165[e]	Not determined	96%	4%
5[f]	—	—	Not determined	100%	—

[a] Reaction conditions: solution of benzyl bromide in toluene (0.2 mol dm^{-3}; 4 cm^3) was magnetically stirred with Amberlyst A27 resin (PhO^- form, 1.0 mol equiv.) at 55 °C. [b] For comparison with the catalytic reaction, in which 0.4 meq. A27 has been applied (Table 3). [c] The measured initial rate (obtained with 1 mol equiv. A27) was divided by a factor of 5 in order to facilitate the comparison with the catalytic reactions, which were performed with 0.2 mol equiv. of A27. [d] When no water was added the reaction system contained *ca.* 6 mm^3 of water. [e] Saturated aqueous sodium phenoxide was used instead of water. [f] Phenol (0.1 mol dm^{-3}) was added to the organic phase in addition to the benzyl bromide (0.2 mol dm^{-3}).

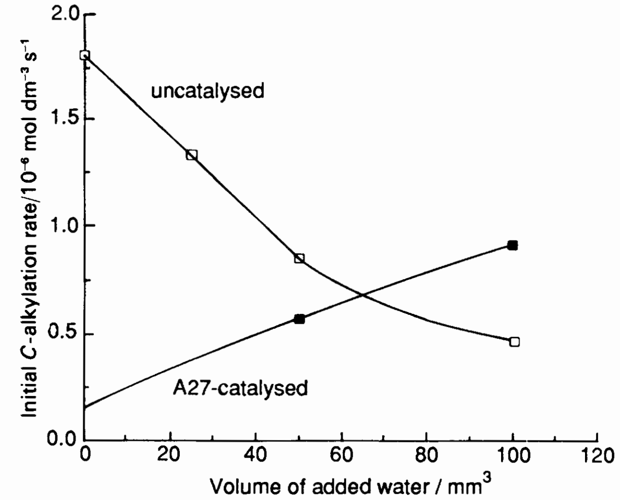

Fig. 1 *C*-Alkylation rates in control and A27-catalysed reactions. The initial *C*-alkylation rates 10^{-6} mol dm^{-3} s^{-1} have been calculated from the results presented in Tables 1 and 3.

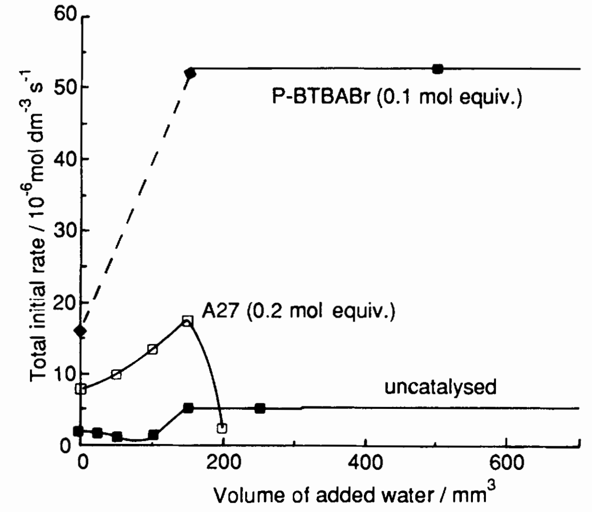

Fig. 2 Effect of water on the initial rates of the catalysed and uncatalysed reactions. Initial rates are expressed as 10^{-6} mol dm^{-3} s^{-1}; for reaction conditions, see Tables 1–3.

amount of water imbibed into the resin before the reaction (up to 1 cm^3 g^{-1}). Addition of phenol to the organic phase does not induce any *C*-alkylation. However, some *C*-alkylation does occur when, instead of water, a saturated aqueous solution of sodium phenoxide is added to the resin. The results are summarised in Table 4.

All the reactions follows second-order kinetics, up to at least 70% conversion. The reaction rate is strongly affected by the addition of water, and reduces to a mere 4% of the anhydrous rate in the presence of 1 cm^3 of water per gram of catalyst (Table 4, reaction No. 3). The anhydrous reaction has an activation energy of 16.1 kcal mol^{-1}.

Ultrasonic Agitation of Sodium Phenoxide and Amberlyst A27.—As previously reported,[7] application of ultrasonic agitation to S–S–L systems leads to reaction rates similar to those obtained with conventional agitation, but in contrast with these systems, not only is the resin easily separated from the organic product, but also the three dimensional structure of the resin is preserved, and the resin can be recovered intact.[7]

In the course of our mass-transfer studies, ultrasound was also applied to mixtures of sodium phenoxide (4.8 mequiv.), catalyst (0.6 mequiv. $A27^+$ Br^-), water (none or 100 mm^3), and toluene. Since the mixtures were lacking any organic alkylator, the possible processes in these systems are limited to mass transfer between phases and ion-exchange reactions.

Irradiation of the 100 mm^3 water-containing system for 1 h causes almost total 'disappearance' of the inorganic solid phase. Determination of the bromide, phenoxide and sodium ion content of the recovered A27 reveals, that most of the sodium salts (3.1 mequiv.) are now located inside the resin. This finding was also confirmed by the weight loss of this dried recovered resin, when it was washed with water and dried again: the weight loss is greater than the resin's own weight.

On the other hand, the resin recovered from the dry system has a phenoxide ion content of only 0.06 mequiv. and does not contain any sodium at all. The separate inorganic phase can be easily isolated. It contains 0.058 mequiv. of bromide ions.

Recovered resin particles from both systems do not disclose any external changes, when examined under an optical microscope at × 400 magnification.

Discussion

The discussion aims to investigate the following: (*a*) the steps that comprise the reaction mechanism; (*b*) the rate-limiting factor; and (*c*) how the transport of the inorganic reagents from the solid phase to the catalytic site is accomplished.

Reaction Mechanism.—Two reaction mechanisms have been suggested for triphase catalytic reactions. L–S–L triphase catalysis has been found[2,15] to proceed by a mechanism analogous to the classical extraction mechanism of phase-transfer catalysis[17] [eqns. (4) and (5)].

$$\text{P-}R_3N^+Br^- + NaOPh(aq.) \longrightarrow \text{P-}R_3N^+PhO^- + NaBr(aq.) \quad (4)$$

Table 5 Activation energies for the alkylation of phenoxide in various reaction systems[a]

Catalyst	Molar amount of catalyst	Volume of water added/mm^3	E_a/kcal mol^{-1}
P-BTBABr	10% (catalytic)	—	7.2
A27 (Br$^-$)	20% (catalytic)	—	10.0
A27 (Br$^-$)	20% (catalytic)	100	15.6
A27 (PhO$^-$)	100% (stoichiometric)	—	16.1

[a] Reaction conditions: according to the type of reaction, refer to Tables 2–4.

$$\mathbf{P}\text{-}R_3N^+PhO^- + PhCH_2Br \longrightarrow \mathbf{P}\text{-}R_3N^+Br^- + PhCH_2OPh + o\text{- and } p\text{-}HOPhCH_2Ph \quad (5)$$

Reaction at the aqueous–organic interface inside the resin, formed by extensive pool–pool phase boundaries, has been suggested by Regen *et al.* as an alternative pathway for triphase catalysts with high catalytic site density.[18,19] According to this second pathway, which we will refer to as the 'interfacial pool mechanism', the product distribution should be similar to that obtained in the appropriate uncatalysed reaction. Since in S–L–S systems any aqueous pools would be saturated with sodium phenoxide, the appropriate uncatalysed reaction is the reaction with a saturated aqueous phase, which yields 25% *C*-alkylation (Table 1). Therefore complete *O*-alkylation will be obtained only by the first mechanism.

Thus, since *O*-alkylation is the sole product in all the **P-BTBABr** catalysed reactions, they clearly proceed according to the classical extraction mechanism, and, since **P-BTBABr** and A27 have a similar chemical structure, one would expect both catalysts to function according to the same mechanism. This does not, however, account for the *C*-alkylation occurring in the A27 catalysed reactions and its increase on addition of water (Table 3). Three explanations are possible. (*a*) The phenoxide ions associated with the catalytic sites in the highly polar A27 resin can be assumed to be strongly solvated by molecules of water or phenol, the latter being formed during the reaction by partial hydrolysis of the phenoxide. Although such solvation by hydrogen bonds is known to induce partial *C*-alkylation,[12] this possibility can be ruled out in the present case, since the stoichiometric reaction does not produce any *C*-alkylation even when the resin is saturated with water, or when phenol is added to the reaction mixture (Table 4). (*b*) A partial contribution by the S–L uncatalysed reaction pathway, *i.e.* a pathway which does not involve the A27 catalyst, can also be ruled out as such a contribution is not observed in the **P-BTBABr**-catalysed reaction. Also the *C*-alkylation rate of the uncatalysed reaction decreases upon the addition of water, compared to the increasing *C*-alkylation on addition of water to the A27-catalysed reaction (Fig. 1). (*c*) Therefore, the observed *C*-alkylation in the A27-catalysed reaction must be attributed to a certain contribution of the interfacial pool mechanism to the overall reaction. This is strongly supported by the fact that the reactions with stoichiometric A27 (PhO$^-$ form) exhibit some *C*-alkylation only when aqueous sodium phenoxide is imbibed into the resin instead of water (Table 4).

This contribution of the interfacial pool mechanism occurs only in reactions catalysed by highly polar resins such as A27, and is not observed with hydrophobic catalysts (such as **P-BTBABr**) which do not form aqueous pools.[2,15] Its importance increases with higher water content of the system as shown by the increasing degree of *C*-alkylation (Fig. 1).

In the presence of 200 mm^3 of water, the catalysed reaction becomes slower than its uncatalysed counter part (Fig. 2). Thus, in contrast with the original proposal,[18,19] the interfacial pool mechanism in this reaction system is non-catalytic, but rather a modified uncatalysed reaction occurring inside the resin. This limits the contribution of the interfacial pool mechanism to reactions with a significant uncatalysed reaction rate, and reactions with a negligible control reaction rate should proceed only *via* the classical extraction mechanism, even when catalysed by a hydrophilic ion-exchange resin such as A27.

The Rate-determining Step.—The next point to be discussed is the rate-limiting step of the reaction and its dependence on the water content of the system, which is generally similar to the dependence observed in S–L PTC with soluble catalysts.[20]

When the system is short of water, mass transfer of the inorganic ions to and from the catalytic site is problematic, and therefore rate limiting. This is demonstrated by the small amount of polymer-associated bromide ions exchanged for phenoxide in a dry system without alkylator: 10% after 1 h of ultrasonic agitation. It is further supported by the low rate of the 'dry' A27 catalysed reaction, which is only 3% of the catalytic potential indicated by the respective stoichiometric reaction (compare reactions Nos. 1 in Tables 3 and 4) and by the steep increase in the reaction rates with both catalysts on addition of water (Fig. 2).

With the addition of water the reaction rate increases until mass transfer is fast enough, for the chemical reaction to become rate determining. This shift in the rate-determining step is indicated by a change in the reaction order from zero to first order in benzyl bromide with both catalysts. The activation energies, which are quite low in the dry reactions (Table 5),[21] also increase on addition of water. In the presence of 100 mm^3 water the activation energy of the A27 catalysed reaction becomes very similar to that of the stoichiometric reaction, and to values reported for L–S–L reactions limited by intrinsic catalytic site reactivity.[2,22]

The effect of surplus water depends on the type of catalyst (Fig. 2). In cases where further addition of water is accompanied by a rise in the hydration of the catalytic site, as with the polar A27 resin, the rate decreases, because of the decreasing nucleophilicity of the hydrated phenoxide. This effect is especially pronounced in the biphasic reactions with the PhO$^-$ form of the A27 resin (Table 4). On the other hand the rates of the **P-BTBABr** catalysed reactions reach a plateau (Fig. 2), owing to the limited water uptake of such catalysts.[2,15]

Transportation of the Inorganic Reagent.—The last, and probably the most interesting question, is concerned with the mechanism responsible for the transport of the inorganic ions to the catalytic site. In L–S–L triphase catalysis, inorganic substances are transported through the polymer matrix by the aqueous phase,[2,23] but when the water content of the system is reduced, the contribution of a competing mechanism may increase. Two alternatives can be suggested.

(a) *Direct penetration of solid particles into the resin.* This possibility can be rejected simply because the smallest inorganic particles are *ca.* 100 times larger than the largest pores (1200 Å for A27).

(b) *Transportation of molecular sodium phenoxide through the toluene solution.* This proposition has previously been ruled out for reactions with polymer-bound polyethylene glycol and potassium phenoxide[11] and further evidence for this conclusion is shown as follows. (*i*) As stated above, in 'dry' systems mass transfer of the phenoxide is rate determining. If it occurs by dissolution in the organic solvent, then the catalyst with the larger pores, *i.e.* the macroporous A27 resin, should be the more efficient catalyst. This is, however, clearly contradicted by the observed results (Fig. 2). (*ii*) In a 'dry' system, only 10% of the catalytic sites exchanged anions with the inorganic solid after 1 h of ultrasonic irradiation. This can hardly be called a transport of inorganic molecules into the polymer matrix, but is rather a phenomenon limited to the outer region of the resin. (*iii*) The dissolution rate of the inorganic reagent in toluene is not affected by the presence or absence of the catalyst. Therefore, in order to account for the mass transfer in the catalysed reaction, the dissolution rate must be at least as high as the catalysed reaction rate itself, *i.e.* much faster than the uncatalysed reaction rate (compare reactions Nos. 1 in Tables 1–3). Since dissolved, non-hydrated ion-pairs of sodium phenoxide react with benzyl bromide faster than the solid phenoxide salt,[13] and since this encounter results in *O*-alkylation,[13] this would be expected to be the major product in the uncatalysed S–L reaction. Instead 90% *C*-alkylation is observed (Table 1).

Thus it seems that the 'classical' transportation by aqueous solutions is the sole significant pathway of mass transfer. Therefore, in systems without added water the reaction is limited to sites close to the surface of the catalyst particle. Minute amounts of water, which are always present, form a saturated aqueous phase (the fourth phase in the system), without which the ion-exchange reaction cannot proceed.[20] Addition of water increases the volume of the aqueous solution. With hydrophobic catalysts this solution is attached to the surface of the remaining solid inorganic reagent, but with the hydrophilic catalyst most of it is soaked into the resin. If enough water is available, then all the inorganic reagent is drawn into the resin. This constitution is thermodynamically preferable, since it provides hydration for both the catalytic sites and the inorganic salt.

Conclusions

The present study provides strong evidence that solid–solid–liquid displacement reactions catalysed by polymer-bound quaternary onium ions proceed *via* the same mechanism as phase-transfer catalysis and L–S–L triphase catalytic reactions. As expected, the reaction system is very sensitive to variations in its water content. The only mass-transfer mechanism consistent with the observations in this study is the transport of the inorganic reagent by small amounts of water.

Experimental

General Methods.—All reagents were analytical grade. Amberlyst A27[16] (polystyrene-bound benzyltrimethylammonium chloride, ring substitution 40%, macroporous resin, pore radius 210–1200 Å, porosity 51%, total pore volume 0.91 cm^3 g^{-1}, surface area 45 m^2 g^{-1}) was purchased from Fluka AG and extracted with *o*-dichlorobenzene.[7] **P-BTBACl** (gel-type, 2% DVB, 8% ring substitution) was prepared from commercially available chloromethylated polystyrene (Aldrich Chemical Co.) and tributylamine by standard procedures as previously described.[7] The catalysts were exchanged with aqueous solutions of sodium bromide (and washed exhaustively), until no benzyl chloride could be detected when the resin was treated with benzyl bromide. Sodium phenoxide was prepared from phenol and sodium hydroxide.[13] All the solids were dried overnight at 90 °C and 1 mmHg.

GC analyses were performed on a 10% SP 2100 on Chromosorb P column, installed in a Perkin-Elmer 8410 instrument, equipped with an FID detector. The results were evaluated according to the disappearance of the alkylator, and the formation of the various product peaks. The integrator was calibrated using analytical reference substances.

The water content of the solid reagents and of the reaction mixture (at the end of the reaction) were determined by Karl–Fisher analysis, using the standard reagents obtained from Riedel de Haen AG.

General Reaction Conditions.—A solution of benzyl bromide in toluene (0.2 mol dm^{-3}; 10 cm^3), sodium phenoxide (3.2 mequiv., 0.371 g, sieved through 0.1 mm openings), catalyst (**P-BTBABr**, 0.2 mequiv., 0.32 g; A27–Br, 0.4 mequiv., 0.190 g) and water (0–1000 mm^3) were placed in a vial (Thomas Scientific Co., No. 9170 D61, internal diameter 18 mm, volume 14 cm^3), equipped with a Teflon-lined (Pierce Chemical Co., No. 12716) screw cap and a 15 × 7 mm Teflon-lined magnetic stirring bar. The vial was placed in an oil bath thermostatted at 55 ± 0.5 °C, and stirred vigorously. Eight samples (at *ca.* 5, 10, 15, 20, 25, 30, 50 and 70% conversion, 0.1 cm^3 each), were withdrawn at appropriate time intervals and immediately diluted, filtered through cotton and analysed by GC. To determine the final product distribution all the reactions were continued until >95% conversion. The very common catalyst conditioning prior to the reaction[1,2,15] was avoided, since mass-transfer-controlled reactions were strongly altered. L–S–L reactions were performed similarly, in 30 cm^3 vials using an appropriate stirring bar, and adding 16 cm^3 of a 0.2 mol dm^{-3} aqueous solution of sodium phenoxide instead of the solid reagent. The samples for GC analysis were immediately dried ($MgSO_4$) and filtered.

Kinetic Evaluation.—The initial rate was computed from a best-fit linear plot through the first 5–6 sample points ($\leqslant$25% conversion). In reactions with catalytic amounts of A27, induction periods of up to 30 min were observed (positive intercept on the time axis). The reaction order was determined using all sample points. The activation energies were determined as usual by Arrhenius plot of the initial rates obtained between 37 and 85 °C (30 and 55 °C for reaction system 4).

Preparation of A27 (*PhO$^-$ form*).—A27 (Cl$^-$ form) was ion-exchanged repeatedly with aqueous solutions of sodium phenoxide, until titration of the chloride content of the resin gave a constant value (84% PhO$^-$ and 16% Cl$^-$). The resin was washed with water until it was free of sodium ions, and dried as before. The remaining chloride ions did not interfere with the kinetic evaluation of the stoichiometric reactions, since their reaction with benzyl bromide [eqn. (3)] is much slower than the reaction studied [eqn. (2)].

Reactions with Stoichiometric A27 (*PhO$^-$ form*).—To 0.8 mequiv. (0.49 g) of the reagent in the reaction vial was added water, (or saturated aqueous NaOPh) (for details refer to Table 4), and the mixture was shaken at room temperature for 3 h to ensure uniform distribution of the water throughout the resin. A stirring bar and 4 cm^3 of a 0.2 mol dm^{-3} solution of benzyl bromide in toluene were added to the ice-cooled mixture, which was immediately placed in a thermostatted oil bath and stirred. In the very fast reactions the vials were not closed in order to facilitate the sampling.

Ion-exchange Reactions with Ultrasonic Agitation.—An ultrasonic generator (W-375, Heat Systems – Ultrasonics Inc.) with a flat tip (1 cm^2) was used at an output level of 40 W. A 28 cm^3 (65 × 30 mm) open vial was used as reaction vessel. Since the ultrasonic tip has to be immersed in the reaction solution, the amount of all the components in the system (except for the missing alkylator) was increased by 50%. Prior to the reactions, the absence of small resin particles was assured by screening the catalyst on a 0.315 mm sieve.

Catalyst Recovery from Reactions with Ultrasonic Agitation.—(a) *Dry systems.* The reaction mixture was passed through a 0.1 mm sieve. The retained resin particles were washed twice with dichloromethane (50 cm^3), dried, and screened on a 0.315 mm sieve to remove any residual small particles. The passing fraction from the 0.1 mm sieve (organic solution and inorganic salts) was filtered. The solids were washed twice with dichloromethane and dried.

(b) *System with* 100 mm^3 *water*. Because of its stickiness, the catalyst had to be recovered by a modified procedure which could also be applied to the dry mixture with no influence on the results. The solids were filtered off, washed with dichloromethane and dried. The solid aggregates which formed during the drying procedure were then crushed gently. The detached resin particles were isolated by taking advantage of their high sphericity; they were rolled down a slightly inclined plane, leaving the residual solid mixture behind.

Halogen Determination.—Inorganic solids were dissolved in dilute aqueous HNO_3 (50 cm^3). Resin samples were stirred for 2 h in 20% HNO_3, after which time water (50 cm^3) was added. The solutions were titrated with $AgNO_3$ (0.01 mol dm^{-3}), using a combination silver-ring electrode (Mettler DM 141).

Phenoxide Determination.—The resin sample was stirred for 15 min with excess NaBr solution and titrated with HCl (0.01 mol dm^{-3}) in the presence of Bromocresol Blue indicator (colour change at pH 4). 1 cm^3 HCl was added to excess, the mixture was stirred for another 15 min, and then back-titrated with NaOH (0.01 mol dm^{-3}).

Sodium Determination.—The resin samples were burned. The residue was dissolved in dilute HCl and determined by atomic absorption spectroscopy.

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