

Molecular sieve behaviour in polymeric reagents

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A number of polystyrene supported pyridine reagents have been prepared with a wide range of cross-link ratio and degree of backbone substitution. Reaction of these with a number of alkyl halides gives rise to kinetic data which indicates the rate controlling step to be one of diffusion in the supports. As a result, larger halides are retarded more than smaller ones, in comparison to their corresponding homogeneous reactions, the supports, therefore, exhibiting molecular sieving properties. The effect of temperature and solvent has also been examined, and the diffusive nature of the reactions discussed in detail.

INTRODUCTION

Although many totally new chemical reactions and reagents are still being developed, there is an ever increasing effort aimed at improving well characterized processes, with the intention of enhancing yields, moderating conditions, increasing selectivity, simplifying work-up, introducing regenerable character, etc. In this context the arrival of a wide variety of polymer supported reagents^{1-9,43,44} has made some impact, especially in the latter two areas. However, the attractive feature of improving the selectivity of reagents for particular substrates, with a move towards enzyme-like behaviour, has still to meet with significant success in reactions other than simple esterolyses¹⁰. One rather naive approach which comes to mind is to synthesize reagents which might be capable of selecting potential substrates according to their size (molecular sieving), by introducing a diffusional barrier on the reaction pathway, prior to a chemical one. The philosophy behind this thinking has been expressed rather well recently in a short review¹¹.

Towards this end we have already examined some highly crosslinked polystyrenes as reaction supports which might be able to exercise thermodynamic and/or kinetic control of substrates attempting to gain access to a reactive site¹². However, our initial results have been clouded by the mechanistic complexity of the probe reaction chosen for study²¹. Consequently we have now moved to a much simpler system, the quaternization of polymer supported pyridine, using alkyl halides of varying molecular bulk.

This is particularly attractive for two main reasons. Firstly the homogeneous quaternizations of pyridine and its derivatives are well studied reactions, and known to be simple bimolecular processes¹³⁻¹⁷. In addition the corresponding reactions of linear homopolyvinylpyridines^{13,17,18} and linear copolymers of vinylpyridines with styrene¹⁷ have also been investigated and quantified. Secondly, 4-vinylpyridine (4-VP) is a relatively cheap and readily available monomer carrying an exploitable functional group. A wide variety of polystyrene based polymeric analogues of pyridine, with varying degrees of backbone substitution and crosslinked ratio, can therefore be produced by free radical

suspension copolymerization, with a minimum of effort. Furthermore, quite fortuitously, the reactivity ratios of styrene and 4-VP are sufficiently similar^{19,20} that for all practical purposes a random incorporation of pendant pyridine residues can be assumed throughout the various resin matrices.

EXPERIMENTAL

Materials

Pentan-2-one, toluene and n-heptane were dried by passing down a 1 m column of molecular sieves. Benzyl bromide, 2-(bromomethyl)naphthalene and various hydrocarbon gas-liquid chromatography (g.l.c.) standards were used without further purification. 1-Iodobutane and 1-iodooctadecane were prepared from 1-bromobutane and 1-chlorooctadecane, respectively, by the standard exchange reaction using an excess of sodium iodide in dry acetone. The former iodide was purified by fractional distillation and the latter by recrystallization from acetone.

Styrene and commercial divinylbenzene (~55% w/w divinylbenzene in ethylstyrene) were shaken with 1% sodium hydroxide solution to remove the stabilizer, twice with distilled water, and were dried over anhydrous calcium chloride. 4-VP was fractionated under vacuum from solid potassium hydroxide to remove water and inhibitor. Azobisisobutyronitrile (AIBN) and 99-100% hydrolysed poly(vinyl alcohol) (molecular weight ~100 000) were used as supplied.

Suspension copolymerizations

These were carried out essentially as described previously¹² though in the present work poly(vinyl alcohol) was the chosen suspension agent. In a typical reaction 4-VP (7.5 ml) was added to a styrene/divinylbenzene mixture (22.5 ml), and the whole volume suspended by rapid stirring (~800 rev/min) in a previously prepared solution of poly(vinyl alcohol) (2.5 g) in water (250 ml). After addition of the free radical initiator, AIBN (0.25 g), the reaction vessel was flushed with gaseous nitrogen and then stirred at 80°C for 6 h to effect virtually quantitative conversion to copolymer.

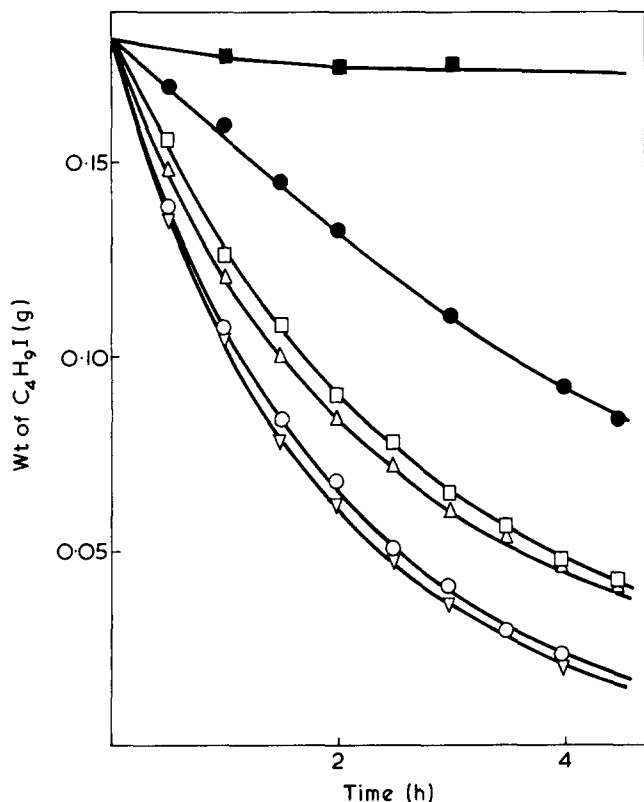


Figure 1 Reactions of 1-iodobutane with 15% pyridine substituted resins in pentan-2-one at 102°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine; \blacksquare , reaction with various neutral resins. $[C_4H_9I]_{\text{initial}} = 8.7 \times 10^{-2} \text{M}$. Molar ratio pyridine/ $C_4H_9I = 2/1$

The resulting polymer beads and small (by wt) quantity of amorphous product were collected by suction filtration and washed with acetone. Isolation of the required beads from contaminants was then achieved by stirring the mixture magnetically overnight in acetone, when the less dense fragments formed a separate upper layer. This was readily removed by careful pipetting. Where necessary the process was repeated to optimize separation. Finally the beads were dried at 50°C in a vacuum oven for 24 h to yield a dry product with particle size range 85–30 British Standard Mesh i.e. $\sim 185\text{--}500 \mu\text{m}$. Internal surface areas of dry beads were typically $<5 \text{ m}^2/\text{g}$ and pore volumes $\sim 0.01 \text{ ml/g}^*$.

Crosslink ratios were adjusted by choice of the styrene/divinylbenzene mixture and in one case a macroporous resin was obtained by including toluene in the reaction mixture, in the ratio 1/2 relative to the total monomer volume employed (in this instance the nominal crosslink ratio was 37%). The degree of functionalization of resins was varied by adjustment of the ratio of 4-VP used in the monomer mixture. Microanalyses of the products always showed a lower incorporation of pyridine residues than expected from monomer mixtures, though this was expected because of the known partial solubility of 4-VP in hot water. After appropriate experimentation, however, resins carrying between 15–50% pendant pyridine groups could be readily prepared.

Quaternization reactions

Reaction mixtures were prepared by first dissolving an alkyl halide (1 mmol) in the appropriate solvent, usually pentan-2-one (2 ml), along with a hydrocarbon, suitable as an internal standard for quantitative analysis by g.l.c.

* Measurements kindly made by the British Petroleum Company.

(Perkin–Elmer F11, flame ionization detector). Simultaneously polymer beads containing 2 mmol of pyridine residues (estimated from nitrogen microanalysis) were added to another sample of solvent (5 ml) and allowed to equilibrate at room temperature ($\sim 15 \text{ min}$) while the alkyl halide mixture was assayed. The latter solution was then added quantitatively to the wetted beads by washing with three volumes of solvent (each 1 ml) to yield an overall volume of 10 ml. The resulting mixture was then placed in an oil bath at the required temperature, normally 102°C, and stirred magnetically using a small follower. Every 15 min a $1 \mu\text{l}$ sample was withdrawn for g.l.c. analysis. Alkyl halide loss was calculated in the usual way from the recorder output and plotted as a function of time (see Figures 1–4).

Solvent imbibition measurements

Solvent imbibition by the various resins was determined using the centrifuge method²². A sample of resin ($\sim 1 \text{ g}$) was placed in a glass sinter stick (porosity 3) and the latter immersed in a solvent for 1 h. The stick was then transferred to a centrifuge tube where it was held in position using a 'suba' seal. Excess solvent was removed by centrifuging for 15 min, and the stick and contents weighed. Immersion in the solvent was then repeated (5 min), followed by centrifugation (15 min) and weighing. These operations were carried out until a constant weight increase was achieved. Finally a similar blank experiment was performed using the empty sinter stick. The data was expressed as a weight of solvent absorbed by unit weight of dry resin (g/g). In addition the volume occupied by unit weight of dry resin in its solvent swollen state (ml/g) was measured by noting the volume arising when a known weight of dry resin was added to known volume of solvent in a small measuring cylinder

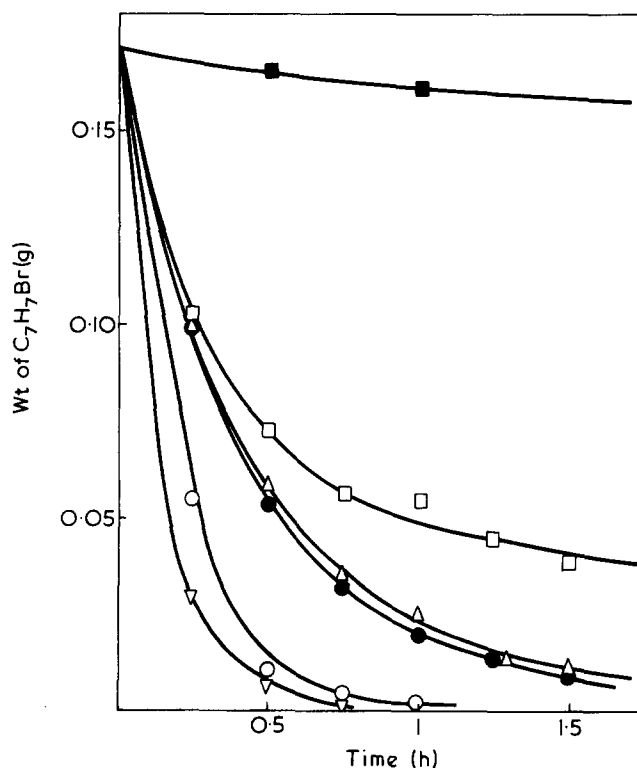


Figure 2 Reactions of benzyl bromide with 15% pyridine substituted resins in pentan-2-one at 102°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine; \blacksquare , reaction with various neutral resins. $[C_7H_7Br]_{\text{initial}} = 8.7 \times 10^{-2} \text{M}$. Molar ratio pyridine/ $C_7H_7Br = 2/1$

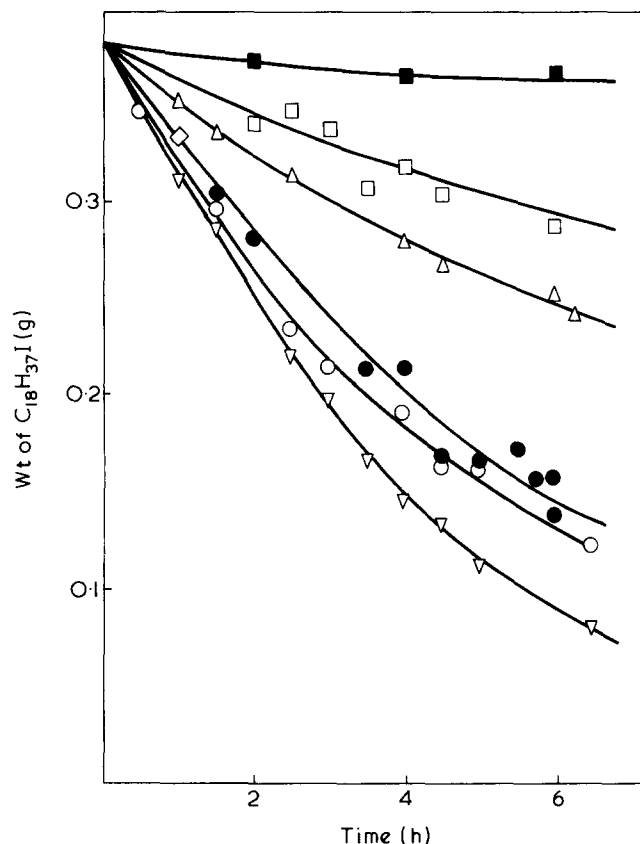


Figure 3 Reactions of 1-iodooctadecane with 15% pyridine substituted resins in pentan-2-one at 102°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine; \blacksquare , reactions with various neutral resins. $[C_{18}H_{37}I]_{\text{initial}} = 8.7 \times 10^{-2} \text{ M}$. Molar ratio pyridine/ $C_{18}H_{37}I = 2/1$

(see Table 1). From both sets of data it is then possible to establish the effective total volume occupied by solvent swollen resin plus excess solvent, in any particular reaction. Effective alkyl halide concentrations were calculated on the assumption that the halide is distributed throughout this volume.

RESULTS

Effect of substrate size

Quaternization of four resins, of increasing crosslink ratio, each carrying 15% pendant pyridine groups were carried out in pentan-2-one at 102°C using 1-iodobutane, benzyl bromide, 1-iodooctadecane and 2-(bromomethyl)naphthalene. The results are shown in Figures 1–4 respectively, and include blank reactions with non-functionalized resins, and the corresponding equimolar homogeneous reactions with pyridine itself. In all cases the disappearance of alkyl halide with neutral polystyrene resins is negligible. With 1-iodobutane (Figure 1) the rate of quaternization is relatively insensitive to the crosslink ratio of the polymeric reagent. However, such dependence becomes increasingly apparent in the sequence benzyl bromide (Figure 2), 1-iodooctadecane (Figure 3) and 2-(bromomethyl)naphthalene (Figure 4). The effect is most significant with the latter halide which combines two factors, large molecular bulk, and high intrinsic reactivity.

Kinetics

Kinetic studies were carried out using 2-(bromomethyl)

naphthalene, initially with a polymer of 10% crosslink ratio carrying 25% pyridine groups. The usual technique was employed of varying the initial concentration of one component while keeping the other fixed. In the case of the

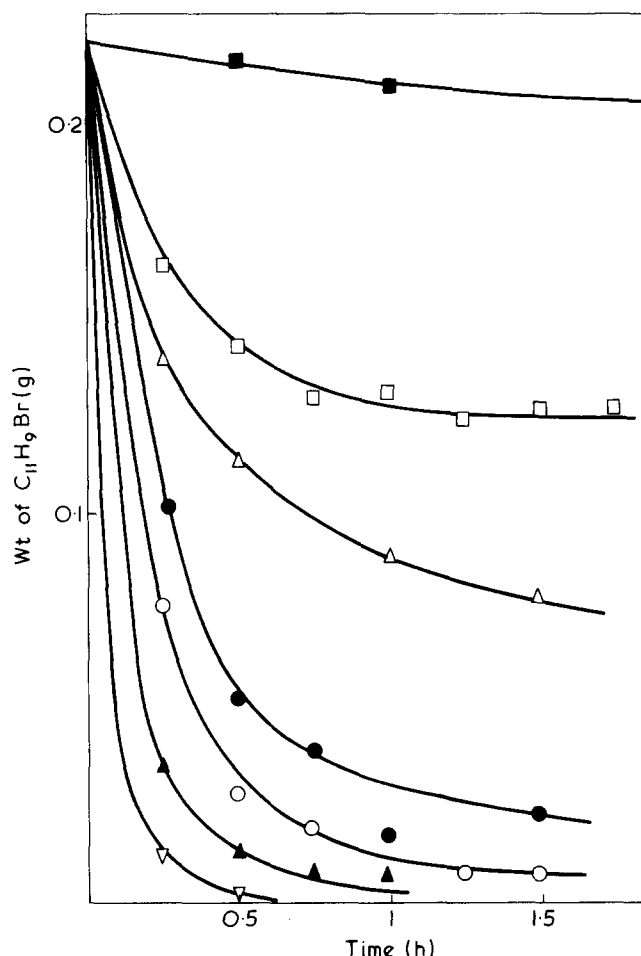


Figure 4 Reactions of 2-(bromomethyl)naphthalene with 15% pyridine substituted resins in pentan-2-one at 102°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine; \blacktriangle , molar equivalent homogeneous reaction with 4-ethylpyridine; \blacksquare , reactions with various neutral resins. $[C_{11}H_9Br]_{\text{initial}} = 8.7 \times 10^{-2} \text{ M}$. Molar ratio pyridine/ $C_{11}H_9Br = 2/1$

Table 1 Solvent imbibition by polystyrene supported pyridine reagents*

Solvent	Crosslink ratio of resin (%)	Solvent inhibition† (g/g)	Volume of swollen resin† (ml/g)
Pentan-2-one	5	0.590	1.69
	5‡	0.558	1.67
	10	0.412	1.48
	20	0.296	1.36
	37§	0.190	1.11
Toluene	37	0.457	1.45
	5	1.04	2.11
	10	0.604	1.67
	20	0.348	1.38
n-Heptane	37	0.195	1.19
	5	0.0519	1.05
	10	0.0514	1.05
	20	0.0412	1.04
	37	0.0379	1.02

* 15–25% pendant pyridine residues; † see text for definition; ‡ 50% pendant pyridine residues; § macroporous support

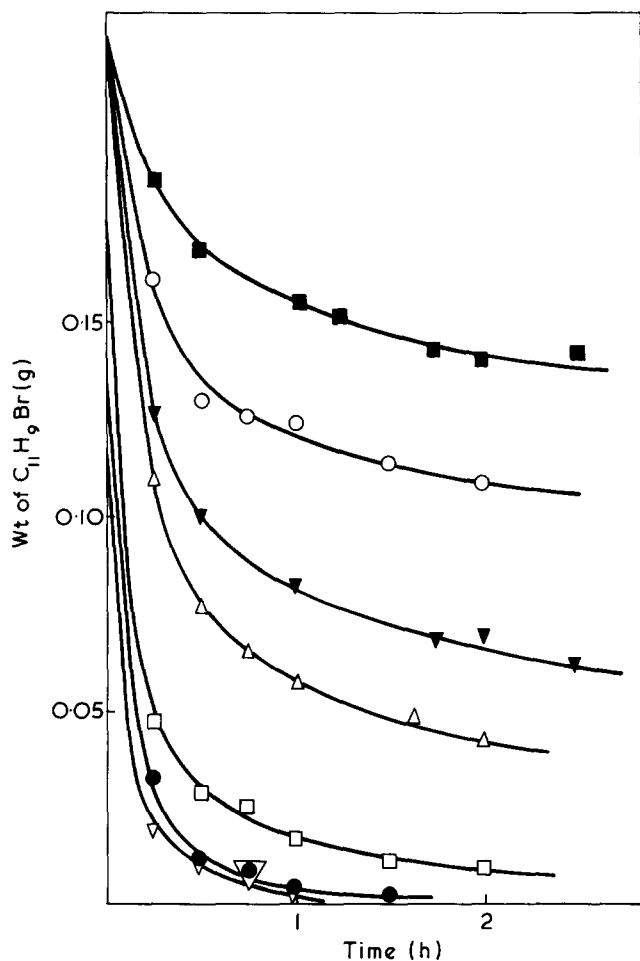


Figure 5 Reactions of 2-(bromomethyl)naphthalene with a 25% pyridine substituted, 10% crosslinked resin in pentan-2-one at 102°C. Molar ratio pyridine/C₁₁H₉Br: ■, 0.5/1; ○, 1/1; ▼, 1.5/1; △, 2/1; □, 2/0.8; ●, 2/0.6; ▽, 2/0.5. [C₁₁H₉Br]_{initial} = 9.2 × 10⁻² M in pyridine dependence studies

pyridine residue dependence, different weights of the same polymer were employed with a given initial concentration of halide. The results are shown in Figure 5.

Analysing the initial rates in the normal way gave a kinetic exponent of 0.60 for the alkyl halide and 1.2 for pyridine. Identical experiments with 5 and 37% crosslinked resins gave corresponding figures of 0.55 and 0.95, and 0.66 and 0.93. The overall initial rate of disappearance of alkyl halide may therefore be expressed:

$$\frac{-d[\text{RX}]_0}{dt} = k_1 [\text{RX}]_0^{0.6} [\text{Py}]^{1.0}$$

It is apparent that in deriving the pyridine dependence, while the total number of moles of pyridine was varied in each experiment, the local concentration in each reactive polymer bead remained the same. Consequently the above result may be interpreted simply as showing a linear dependence on the weight of polymeric reagent used. In order to distinguish between these possibilities, a series of experiments were performed using four reagents all of 5% crosslink ratio with different degrees of pyridine substitution. In all cases the ratio of total moles of pyridine residue to alkyl halide concentration was fixed, though the local concentration of pyridine varied by a total factor of 3.33. Figure 6 shows the decay curves obtained. Rather remarkably the curves do not superimpose, and indeed the poly-

mer with the highest local concentration of pyridine units produces the slowest initial rate of halide disappearance. Close analysis shows that the initial rate is in fact virtually linearly dependent on the weight of polymeric reagent taken. This result was confirmed by taking equal weights of 5% crosslinked reagents each with quite different pyridine contents, and carrying out reactions with a given concentration of halide. Figure 7 shows that reaction rates are very similar and it is difficult to draw separate profiles through the points, hence confirming the linear rate dependence on the weight of polymeric reagent, and only a minor dependence on the local concentration of supported functional group. The experimental rate law is therefore most appropriately expressed as:

$$\frac{-d[\text{RX}]_0}{dt} = k_{\text{expl}} [\text{RX}]_0^{0.6}$$

per g of polymer resin.

The results of all the experiments have been analysed according to this experimental relationship, and the values of k_{expl} obtained, along with the bimolecular constants for the homogeneous reactions, are summarized in Table 2. Rate constants have been calculated similarly for those experiments displayed in Figure 6, employing resins with different pyridine contents, and these results appear in Table 3.

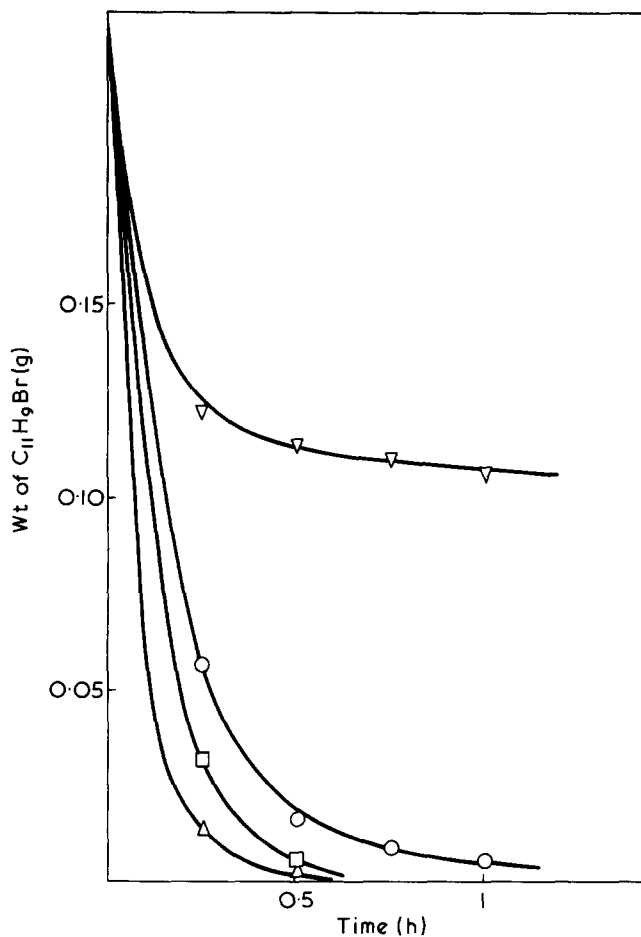


Figure 6 Reactions of 2-(bromomethyl)naphthalene with supported reagents of varying pyridine contents, in pentan-2-one at 102°C. Pyridine substitution (%) (weight of polymer used): ▼, 50 (0.43 g); ○, 25 (0.87 g); □, 20 (1.04 g); △, 15, (1.51 g). [C₁₁H₉Br]_{initial} = 9.2 × 10⁻² M. Fixed molar ratio pyridine initial/C₁₁H₉Br = 2/1

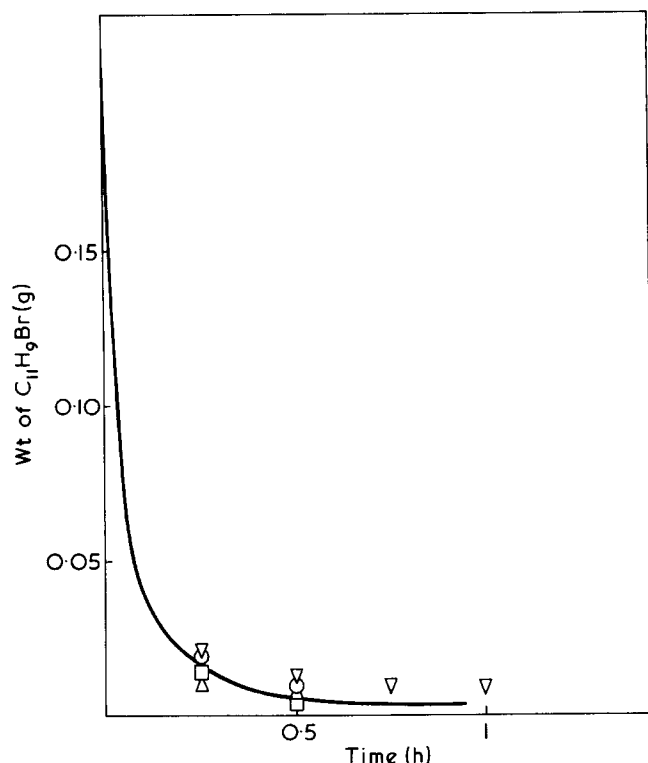


Figure 7 Reactions of 2-(bromomethyl)naphthalene with equal weights of supported reagents of varying pyridine contents, in pentan-2-one at 102°C. Pyridine substitution (%): ∇ , 50; \circ , 25; \square , 20; \triangle , 15. $[C_{11}H_9Br]$ initial $\sim 9.2 \times 10^{-2}$ M. Weight of polymer in each reaction = 1.51 g

Table 2 Experimental rate constants for reactions of alkyl halides with polymer supported pyridine reagents and for the corresponding homogeneous systems in pentan-2-one at 102°C

Crosslink ratio of support (%)	$10^5 k_{\text{expl}}$ from $-\frac{d[RX]}{dt} = k_{\text{expl}}[RX]_0^{0.6}$ per g of polymer resin			
	C_4H_9I	C_7H_7Br	$C_{18}H_{37}I$	$C_{11}H_9Br$
5	4.01	22.8	1.13	25.0
10	3.34	19.5	0.933	20.0
20	2.35	11.2	0.438	9.79
37	1.70	9.69	0.278	6.04
Pyridine*	15.1	242	18.1	298
4-Et pyridine*	—	—	—	462

*Homogeneous bimolecular rate constants $\times 10^5$ ($M^{-1} \text{sec}^{-1}$)

Effect of particle size

A sample of a 5% crosslinked polymer with 20% pyridine groups was meshed to yield two samples one with particle diameters in the range 185–250 μm and the other 422–500 μm . Identical weights of each of these were taken and reacted under the same conditions with 2-(bromomethyl)naphthalene. Figure 8 shows the curves obtained. From the initial slopes of these curves k_{expl} was calculated for each, and in the case of the smaller particles this had a value ~ 1.4 times that of the larger. The average ratio of external geometric surface areas of these samples is of course ~ 4 .

Temperature studies

Reactions were carried out over the temperature range 50°–102°C using pentan-2-one as solvent and 2-(bromomethyl)naphthalene as substrate. The initial rates were used to calculate data for k_{expl} and the Arrhenius plots

constructed as shown in Figure 9. Table 4 shows the activation parameters calculated using the normal transition state expression for solutions, and for comparison the experimentally derived activation data for the corresponding homogeneous reaction is included.

Solvent studies

In a further attempt to demonstrate the role of the support in these reactions quaternizations using 2-(bromomethyl)naphthalene were carried out in toluene at 110°C and n-heptane at 98°C. Figures 10 and 11 respectively show the results obtained using resins carrying 25% pyridine groups. Analysis of the initial rates as before produced the data for k_{expl} shown in Table 5.

Table 3 Experimental rate constants for reactions of 2-(bromomethyl)naphthalene and polymer supported reagents with varying pyridine contents in pentan-2-one at 102°C

Pyridine pendant group (%)	$10^5 k_{\text{expl}}^*$	Relative values of k_{expl}
15	26.1	1.00
20	35.2	1.35
25	37.7	1.44
50	43.1	1.65

*See Table 2 for mathematical description

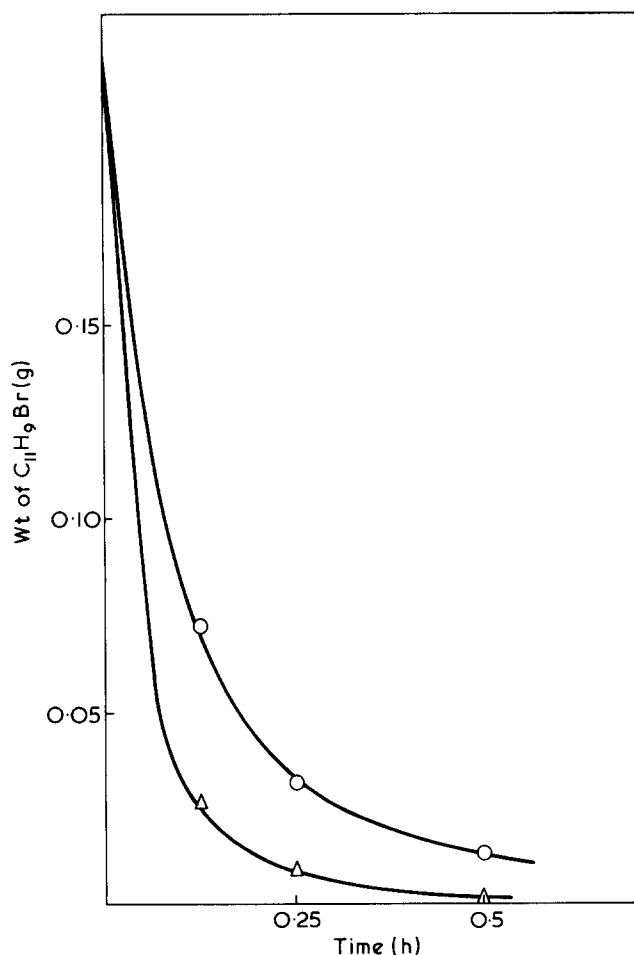


Figure 8 Effect of particle size on reactions of 2-(bromomethyl)naphthalene with supported reagents in pentan-2-one at 102°C. Bead size: \circ , 422–500 μm ; \triangle , 185–250 μm ; 5% crosslinked polymers, 20% pyridine substitution. $[C_{11}H_9Br]$ initial = 9.1×10^{-2} M. Ratio pyridine/ $C_9H_{11}Br$ = 2/1

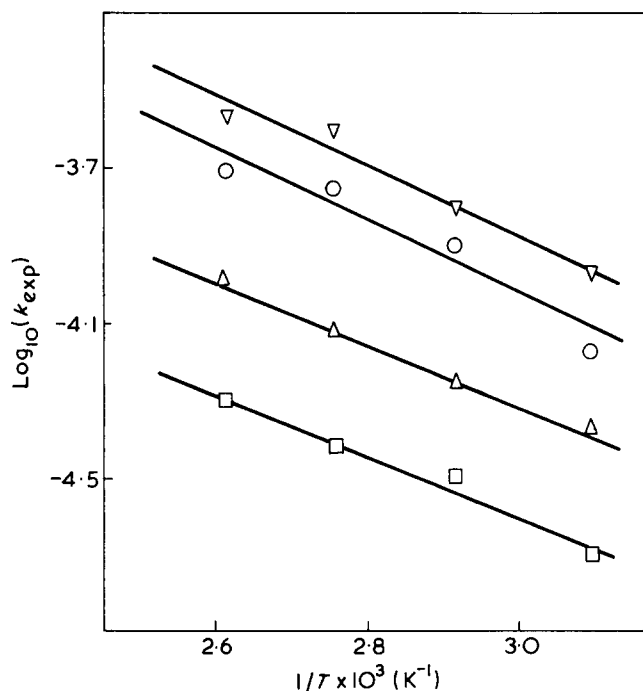


Figure 9 Arrhenius plots for reaction of 2-(bromomethyl)naphthalene with polymeric reagents in pentan-2-one. Crosslink ratio of support (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. 25% Pyridine substitution

Table 4 Activation parameters for the reaction of 2-(bromomethyl)naphthalene with pyridine and polymer supported reagents in pentan-2-one

Crosslink ratio of support (%)	E_{act}^a (kJ/mol)	ΔS^\ddagger a, b (J/K mol)
5	19.8	-268
10	20.9	-268
20	16.7	-286
37	16.9	-291
Pyridine	29.0	-226

a Calculated from $k_{expl} = \frac{ekT}{h} \exp(\Delta S^\ddagger/R) \exp(-E_{act}/RT)$;

b quoted for 102°C

Effect of copolymerization diluent

In the production of crosslinked polymers it is known that the inclusion of a solvent or diluent during preparation results in a more porous network. Indeed it is possible to produce structures with macropores and large internal surface areas^{23-25,45}. Such a reagent was prepared with a crosslink ratio of 37% in the presence of toluene, in a volume ratio of 1/2 relative to that of the comonomers. Quaternization of this resin, carrying 25% pyridine groups, proceeded very much more rapidly than the equivalent reagent prepared in the total absence of diluent as shown by Figure 12. From the initial slopes data for k_{expl} was obtained as before and was a factor of ~ 3 larger in the case of the diluent modified polymer.

DISCUSSION

Molecular sieve effect

Both the form of the experimental rate law, and the pattern of the activation parameters (Table 4) for the polymer reactions compared to the homogeneous data, suggest that the rate controlling step for the supported systems is

quite different from the normal bimolecular collisional process of solution reactions. It seems most reasonable to deduce therefore that diffusion limiting phenomena arise within the supporting matrices. The visually obvious variations which occur with increasing crosslink ratio and which become highlighted on increasing the size and reactivity of the alkyl halide employed, (Figures 1-4) are quantified in the data for k_{expl} shown in Table 2. Clearly for all substrates the effective reactivity falls with increasing crosslink ratio (5 \rightarrow 37%) the overall factor increasing from ~ 2.3 in the case of 1-iodobutane, to ~ 4.2 in the case of 2-(bromomethyl)naphthalene. A parallel reduction in the complexing ability of crosslinked polyvinylpyridines has been observed before³⁰.

While it is not possible to make a direct numerical comparison between the homogeneous rate constants and values of k_{expl} because of the quite different units, it is possible to compare relative reactivities of halides. Whereas 2-(bromomethyl)naphthalene is ~ 20 times more reactive towards pyridine in solution than is 1-iodobutane, with a 37% crosslinked reagent the factor is reduced to around 3. With benzyl bromide and 2-(bromomethyl)naphthalene the relative reactivity is actually reversed in going from the homogeneous system to resins with crosslink ratio of 20% or more. Closely related observations have been reported previously in ion exchange kinetics, where retardation effects usually increase with increasing size of the diffusing ion³³.

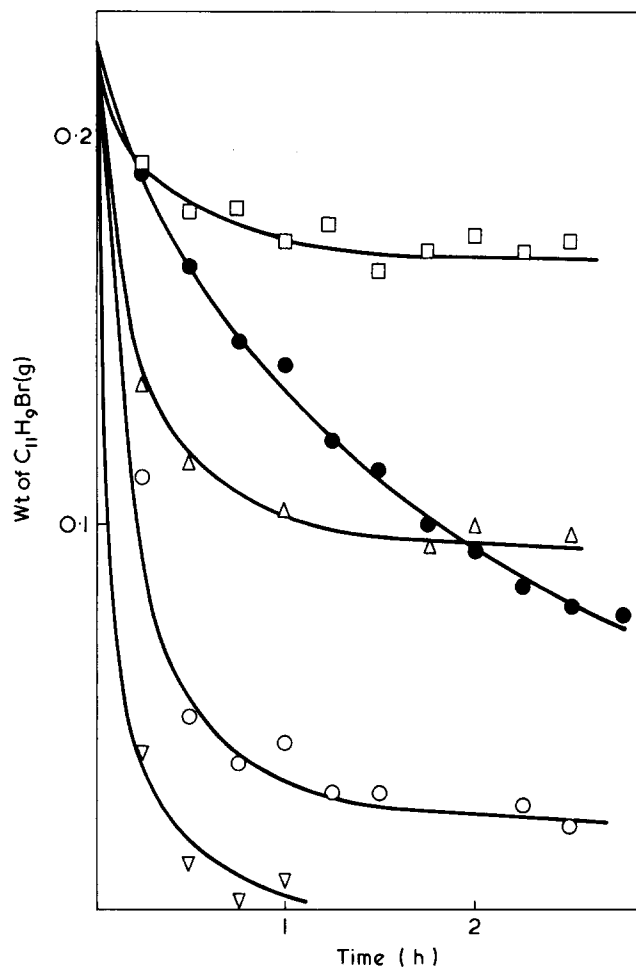


Figure 10 Reactions of 2-(bromomethyl)naphthalene with 25% pyridine substituted resins in toluene at 110°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine. $[C_{11}H_9Br]_{initial} = 9.2 \times 10^{-2} M$. Molar ratio pyridine/ $C_{11}H_9Br = 2/1$

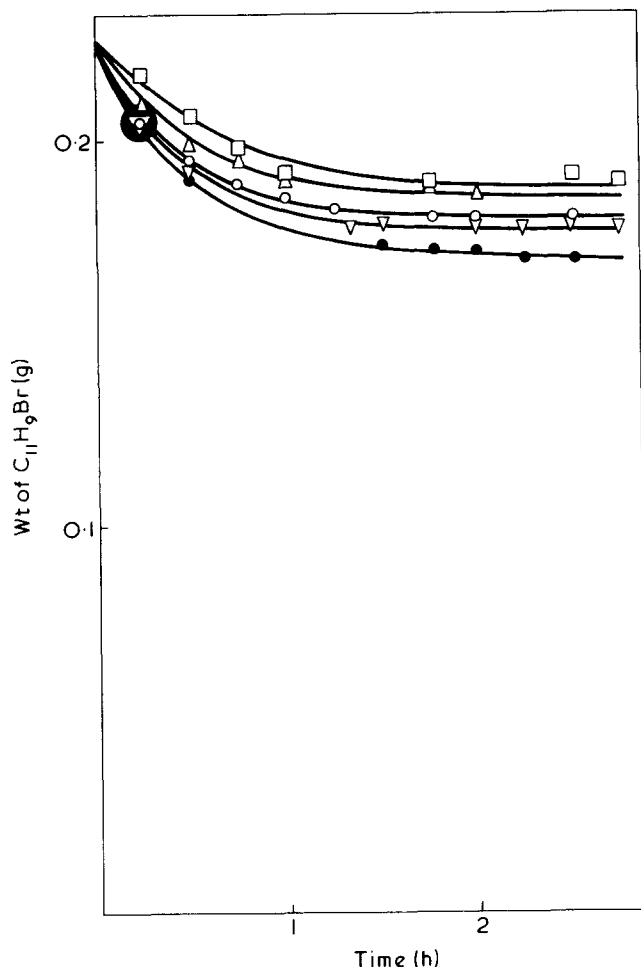


Figure 11 Reactions of 2-(bromomethyl)naphthalene with 25% pyridine substituted resins in n-heptane at 98°C. Crosslink ratio (%): ∇ , 5; \circ , 10; \triangle , 20; \square , 37. \bullet , Molar equivalent homogeneous reaction with pyridine $[C_{11}H_9Br]_{\text{initial}} = 9.2 \times 10^{-2} \text{ M}$. Molar ratio pyridine/ $C_{11}H_9Br = 2/1$

Quite clearly therefore even such random structures as these are capable of producing significant molecular sieving effects, even with substrates whose molecular volumes do not differ by excessively large amounts.

Homogeneous comparison

In this work pyridine is the low molecular weight model compound with which comparison has been made. From an electronic point of view its 4-ethyl derivative would be more appropriate, however, since in our hands this was only ~ 1.5 times as reactive as pyridine itself (Table 2) the latter was deemed to be satisfactory.

As a general rule in making an absolute comparison between a given homogeneous reaction and its supported counterpart it is necessary to make the bases for the comparison as nearly identical as is possible. Unfortunately there are a number of instances in the literature where authors refer to supported reactions being of higher or lower reactivity than the homogeneous equivalent, when the effective reaction conditions are so different that a fair assessment is not possible. In the present work the closest approach to making such a direct quantitative comparison would be to estimate a pseudo-bimolecular rate constant for the supported reaction, based on the local concentrations of pyridine residues and alkyl halide within a reacting bead.

In terms of order of magnitude, alkyl halide concentrations are $\sim 10^{-1} \text{ M}$ in both the homogeneous and supported reactions, whereas local concentrations of pyridine in the resins are $\sim 2 \text{ M}$, compared with $\sim 2 \times 10^{-1} \text{ M}$ in the solution reactions. Initial rates of reactions are within the same order of magnitude, so that the pseudo-bimolecular rate constants for the supported reactions would be an order of magnitude less than the corresponding constants for the homogeneous systems. Since in practice the supporting matrices inhibit the normal random collisional behaviour of these molecules, a significant fall in the effective reactivity is not unexpected. The rather misleading

Table 5 Experimental rate constants for the reaction of 2-(bromomethyl)naphthalene with pyridine and polymer support pyridine reagents in various solvents

Crosslink ratio of support (%)	$10^5 k_{\text{expl}}^a$		
	Pentan-2-one ^b	Toluene ^c	Heptane ^d
5	36.8	39.4	4.03
10	24.4	24.6	3.67
20	12.9	17.5	2.99
37	6.35	5.47	2.03
Pyridine ^e	298	84.4	45.5

^aSee Table 2 for mathematical description; ^b102°C; ^c110°C; ^d98°C; ^ehomogeneous bimolecular rate constants $\times 10^5 \text{ (M}^{-1} \text{ sec}^{-1}\text{)}$

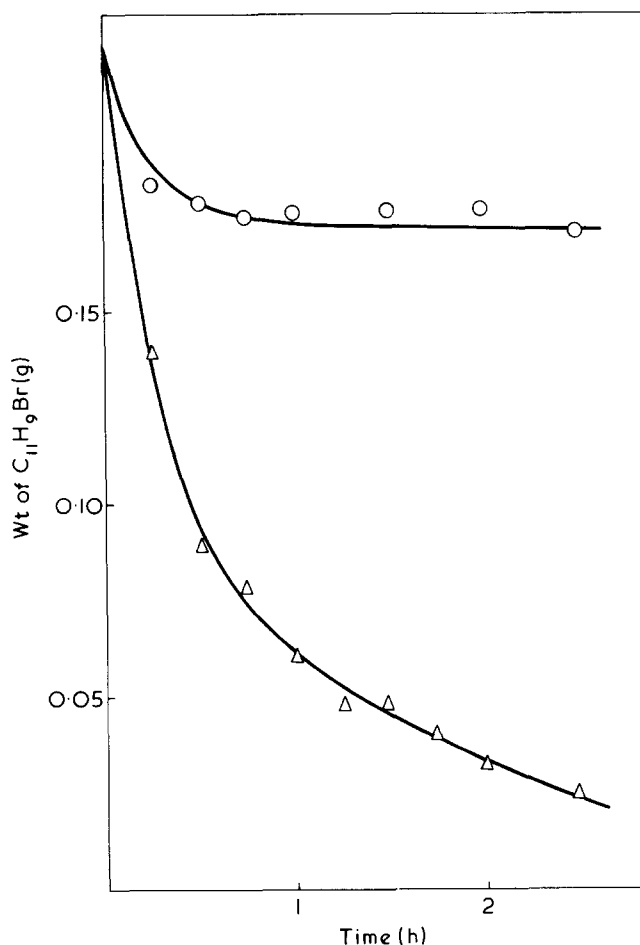


Figure 12 Effect of copolymerization diluent on the reactions of 2-(bromomethyl)naphthalene with 25% pyridine substituted, 37% crosslinked resins in pentan-2-one at 102°C. \circ , resin prepared with no diluent; \triangle , resin prepared in the presence of toluene in a volume ratio of 1/2 relative to that of the comonomers. $[C_{11}H_9Br]_{\text{initial}} = 9.2 \times 10^{-2} \text{ M}$. Molar ratio pyridine/ $C_{11}H_9Br = 2/1$

experimental observation that halides disappear sometimes more quickly in resin reactions than in the homogeneous situation, arises simply from the local concentration effects.

Model for reactions

We can represent these supported reactions schematically by imagining the pyridine functions located on some hypothetical reaction surface with alkyl halides diffusing down a concentration gradient, finally to undergo chemical reaction at the surface (Figure 13). The rate of disappearance of halide from the bulk solution would take the form:

$$\frac{-d[\text{RX}]_{\text{bulk}}}{dt} = k_{\text{diffusion}}([\text{RX}]_{\text{bulk}} - [\text{RX}]_{\text{internal}})$$

per unit reaction surface area. $k_{\text{diffusion}}$ would itself be a function of the effective diffusion coefficient, D , and inversely dependent on the diffusion layer thickness, d , (both being statistical averages). D would vary with the size of the alkyl halide and the crosslink ratio of the polymer matrix, and would account for the experimental observations. In addition both D and d would be functions of the initial concentration of alkyl halide, because of the resulting variations in polymer solvent interaction, and this would account for the fractional dependence on alkyl halide concentration in the experimental rate law (i.e. effectively accounting for substrate solubility effects in the resin). The value of $[\text{RX}]_{\text{internal}}$ would depend on the rate of reaction at the surface. For inherently very rapid reactions $[\text{RX}]_{\text{internal}}$ would be very small, the concentration gradient would be maximized, and the likelihood of observing the influence of crosslink ratio of the support and molecular bulk of the alkyl halide also maximized (see Figure 4). The value of $[\text{RX}]_{\text{internal}}$ would rise for increasingly slower chemical reaction, and would approach $[\text{RX}]_{\text{bulk}}$ when the chemical process becomes comparable in speed to the diffusional one. Under these circumstances any matrix influence or dependence on alkyl halide size would vanish.

$[\text{RX}]_{\text{internal}}$ would also vary to some extent with the concentration of pyridine residues on the reaction surface, the effective concentration gradient being larger for higher pyridine contents in the resins. It would be expected therefore that k_{expl} would not be totally independent of pyridine content, in spite of the diffusive nature of the rate controlling step, and this appears to be so in practice (Table 3). The dependence is, however, considerably lower than the linear one of a simple bimolecular process.

This description would also predict a linear rate dependence on the weight of polymeric reagent, as found experimentally, or more accurately on the effective surface area over which diffusion can occur. If the diffusional process was one from the geometric exterior of polymer beads to functional groups within its bulk, as observed in rapid solvent imbibition²⁶, and in some ion exchange processes²⁷ and catalyses²⁸, then initial rates should be a linear function of the square of particle diameters. In this instance increasing the particle size by a factor of ~ 2 increased the rate by only ~ 1.4 . Additionally, microtomed sections of both 5 and 37% crosslinked beads having reacted with ~ 60 and $\sim 30\%$, respectively, of added 1-iodooctadecane, showed the characteristic pyridinium iodide charge transfer colour across the whole of their surfaces. There was no evidence for a shrinking essentially unreacted, core as observed in other reactions²⁹. It must be concluded therefore that the diffusional process being observed is one taking place

throughout the entirety of polymer particles, more or less from the outset of reactions, and almost certainly involves movement of alkyl halide molecules from relatively readily accessible volumes in the resin beads to more tangled environments i.e. from internal surfaces to buried sites.

This is confirmed to some extent with the diluent modified polymer where the effective internal surface is much increased, and therefore the observed rate of reaction per g of polymer considerably enhanced.

Nature of diffusion

It is rather interesting to note that compared with the homogeneous reactions the rates of reaction of the supported systems are controlled significantly more by entropy, or statistical factors, than by energy considerations, (see Table 4). The order of magnitude of activation energies is appreciably lower than that for segmental rotation of high molecular weight polystyrene chains, which in solvents such as toluene³¹ and carbon tetrachloride³⁴ is ~ 30 – 35 kJ/mol, and is likely to be similar in pentan-2-one. The diffusional motion of alkyl halides therefore does not require cooperative movements of large sections of polymer chains. On the other hand the activation energy for self-diffusion in pure pentan-2-one as measured from the temperature dependence of its viscosity is only ~ 7 kJ/mol³² so that the diffusional processes in the resins are energetically more hindered than would be simple migration through rigid solvent filled channels. It would appear, therefore, that a more realistic picture would be one of motion through narrow winding solvent channels, the boundaries of which are continually shifting due to polymer backbone motion, and the cross-sections of which are frequently intersected by solvated polymer chains.

There is even a tentative indication that the activation energy falls with increasing crosslink ratio of the support, and this could be interpreted as being a trend towards a more rigid support with more well defined solvent channels. However, the number of channels available for successful reactions would be reduced relative to more lightly crosslinked networks, and would be reflected, as it is, in a less favourable entropy factor. Low crosslink resins might therefore be regarded as having a larger number of less well defined solvent channels, which individually possess higher activation barriers than those in the more rigid networks, but which collectively provide a faster route for diffusion to take place.

Solvent effect

In the case of the homogeneous reactions the effect of

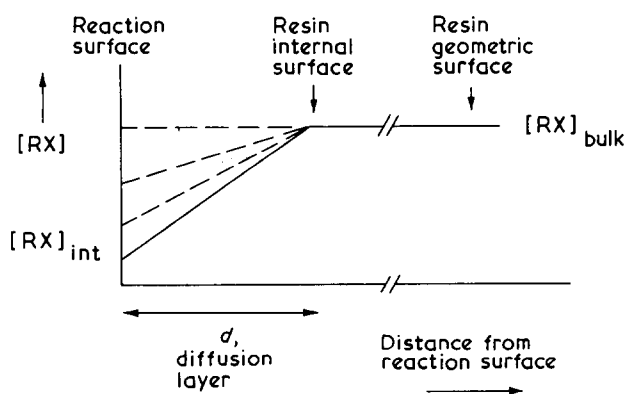


Figure 13 Schematic representation of supported reactions

changing the solvent conforms to the usual pattern associated with solvation phenomena in processes involving charge generation in forming the transition state. As the polarity of solvent is reduced in the sequence pentan-2-one, toluene and n-heptane, the transition state is relatively destabilized and this is reflected in a fall in the magnitude of the bimolecular rate constant (*Table 5*).

In contrast to this the effect of solvent on the supported reactions should in the main reflect their interactions with the polystyrene backbone. The latter has a solubility parameter, δ , of ~ 9.0 the corresponding values for pentan-2-one, toluene and n-heptane being 8.7, 8.9 and 7.4³⁵, respectively. These values are totally consistent with the solvent imbibition data in *Table 1* where a close parallel exists between the behaviours of pentan-2-one and toluene, which in turn differ markedly from that of n-heptane. The amount of the latter taken up by the various resins is on average only $\sim 5\%$ by weight, compared with a range of $\sim 17\text{--}50\%$ with the other two solvents. Not surprisingly therefore the kinetic data for supported reactions in pentan-2-one and toluene shown in *Table 5* are very similar, with a dramatic fall in reactivity in moving to n-heptane.

The zero frequency measured glass transition temperature, T_g , for polystyrene is $\sim 100^\circ\text{C}$, so that all the experiments were performed at temperatures around or below this value. With crosslinked samples there is even some indication that T_g rises with the degree of crosslinking^{40,41}. However, the resins in this work are solvent swollen to varying extents and there exists a number of ways of estimating the effective T_g of such mixtures³⁶⁻³⁸. Application of one of these³⁶ to the pentan-2-one and toluene imbibed resins yields T_g values well below the temperature range of the reactions carried out, even in the case of 37% crosslinked matrices. However, with n-heptane the predicted change in T_g from the value for pure polystyrene is not sufficiently large to assume that the polymer supports are not glass-like in reactions involving this solvent. Indeed the large difference in behaviour with n-heptane would be in keeping with diffusion in a glassy polymer compared with motion in the rubbery state³⁹.

With solutions of linear polymers (molecular weight $\sim 100\,000$ s), the diffusion coefficient of the solvent rises dramatically even with relatively small mass fractions of solvent (0.1-0.2), and becomes indistinguishable from the self-diffusion value in pure solvent with mass fractions of ~ 0.5 ⁴². As far as solvent molecules are concerned therefore the presence of polymer species in these concentrations has no effect. This is quite different to the situation in the present work where even swollen resins consisting of $\sim 50\%$ solvent show a significant influence from the polymeric network. Clearly, therefore, it is misleading to consider resins as totally analogous to concentrated polymer solutions, the additional effect of linking each polymer molecule to the next, with its attendant complications of permanent entanglement, is a significantly large one.

CONCLUSIONS

The description of these supported reactions presented here, is, we feel, the most satisfactory way of explaining the experimental results. We believe it lays down the principles upon which more useful substrate selective reagents may be developed. We recognize that a number of approximations have been made at various stages. In particular the description is based upon initial periods for the reactions,

and quite clearly additional complications arise with higher conversions. The polarity of the resins change markedly and almost certainly would influence the diffusive processes; the presence of quaternized groups may modify the inherent reactivity of nearby unreacted groups^{13,17,18}; the available pore volume would be reduced etc. In spite of these factors however, the overall picture remains intact, and the application of these supports, perhaps with additional properties built in e.g. substrate binding sites, provides exciting possibilities for enhancing the specificity of reactions.

The general applicability of the results to copolymerized resins prepared with other functional groups may also be in question, but while there may be a number of detailed differences, the principles and trends described here should be universal.

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