Kinetic Determination of Selectivity Constants of Anion Extraction in Phase-transfer Catalytic Systems

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A kinetic method has been developed to measure selectivity constants of pairs of anions in phase-transfer catalytic systems. The method is based on the study of the poisoning effect produced by the presence of catalytic amounts of different salts in the kinetic behaviour of the phase-transfer-catalysed isomerization of 4-allylanisole to 4-methoxy-β-methylstyrene in basic medium. The kinetic profiles experimentally obtained for this reaction are numerically analysed and K^{sel} values for different anions are subsequently derived. Particular attention is given to alkoxide anions, formed *in situ* by contact of alcohols with concentrated NaOH. A selectivity constant parameter that includes the acidity of the alcohols is defined.

The selectivity constant $K^{\mathrm{sel}}_{X/Y}$ of pairs of anions is one of the main factors that determine the kinetic behaviour of phase-transfer-catalysed (p.t.c) reactions. It is defined[1] by equation (1) which is the equilibrium expression for the reversible reaction (2) that

$$K^{\mathrm{sel}}_{X/Y} = [QX][Y]/[QY][X] \qquad (1)$$

$$Q^+Y^-(\mathrm{org}) + X^-(\mathrm{aq}) \Longleftrightarrow Q^+X^-(\mathrm{org}) + Y^-(\mathrm{aq}) \qquad (2)$$

takes place in an organic–aqueous liquid biphase system; Q^+Y^- and Q^+X^- are quaternary ammonium salts and X^- and Y^- are anions that compete for the cation Q^+.

The p.t.-catalysed reaction may be, for example, an S_N2 reaction such as (3). Here, as the reaction proceeds, the ion X^-

$$RX + Y^- \xrightarrow{Q^+Y^-} RY + X^- \qquad (3)$$

is formed while RX disappears. The increasing concentration of X^- causes a gradual poisoning of Q^+ because of the formation of Q^+X^-. $K^{\mathrm{sel}}_{X/Y}$ Will determine how effective the p.t. catalysis for a given system is: the smaller its value, the higher the catalytic efficiency. The original counterion of the quaternary ammonium salt must also be taken into consideration, since it may partially neutralize the catalytic activity of the salt.[2]

K^{sel} Values for pairs of anions in different chemical systems do not abound in reports of p.t. reactions. To date, such values have been generally obtained through potentiometric measurements with the aid of ion-selective electrodes.[3,4] This method, although advantageous in many cases, suffers from some limitations. First, one would often like the relative selectivity properties of anions for the chemical system in which a reaction is actually being performed. The ion-selective electrode method requires a 'static' chemical system, one in which the different species (the anions and Q^+) have reached thermodynamic equilibrium. Secondly, the method is inconvenient when corrosive substances (mainly concentrated basic solutions) are involved, since the electrode membranes may be damaged. This eliminates anions which are not isolated and must be prepared *in situ* in strongly basic media, as for most alkoxide salts.

The study of profiles of p.t.-catalysed reactions is an alternative approach to elucidate K^{sel} values for different anions, given their influence on kinetic behaviour. There is difficulty in handling the kinetic data of a system that includes the catalysed reaction, equilibria among the different ionic species, and the Hofmann degradation that the quaternary ammonium catalyst suffers, which, together with its poisoning by foreign anions present, contributes to its gradual deactivation. We have undertaken this study and the method and results are presented here. Values of selectivity constants obtained for several anions, in particular alkoxides, are given.

Results and Discussion

The method makes use of the base-catalysed isomerization of 4-allylanisole to 4-methoxy-β-methylstyrene under p.t. conditions [equation (4)] as a probe for catalytic activity of Q^+OH^-

$$p\text{-}H_3C\text{–}O\text{–}C_6H_4\text{–}CH_2\text{–}CH{=}CH_2 \xrightarrow[\text{p.t.c.}]{Q^+OH^-} p\text{-}H_3C\text{–}O\text{–}C_6H_4\text{–}CH{=}CH\text{–}CH_3 \qquad (4)$$

species in the presence of various anions, either added to the system or formed *in situ*. The reaction profiles obtained were analysed and K values for the different anions derived.

This isomerization has been found to be first order in both substrate and quaternary salt.[5] Further study[6] revealed that the Hofmann decomposition of the salt was important. This decomposition which, for instance, in the case of tetrabutylammonium hydroxide yields the corresponding tertiary amine, the olefin but-1-ene, and water [equation (5)] was also found to proceed as a first-order reaction.

$$(C_4H_9)_4N^+OH^- \longrightarrow (C_4H_9)_3N + C_4H_8 + H_2O \qquad (5)$$

The presence of Na^+X^- salts causes partial poisoning of the catalyst because of competition of the X^- anions with OH^- for Q^+. Thus a fast equilibrium (6) is achieved.

$$(C_4H_9)_4N^+OH^- + Na^+X^- \Longleftrightarrow (C_4H_9)_4N^+X^- + Na^+OH^- \qquad (6)$$

Equations (4)—(6) may be written as (7)—(9). k, k_d, and K are

$$A + QOH \xrightarrow{k} B + QOH \qquad (7)$$

$$QOH \xrightarrow{k_d} P \qquad (8)$$

$$QOH + X \xleftrightarrow{K} QX + OH \qquad (9)$$

the isomerization reaction constant, the decomposition constant for the ammonium salt, and the selectivity constant $K^{\mathrm{sel}}_{X/Y}$, respectively.

Two assumptions are made about species QX. First, their Hofmann decomposition rate is very small compared with that of the quite unstable species QOH and thus may be disregarded.

Second, their catalytic effect on the isomerization reaction compared with that of the strongly basic QOH form is nil.

The above considerations lead us to the set of equations (10)—(12) for our system where x is the conversion of A into B,

$$dx/dt = k[\mathrm{QOH}](1 - x) \quad (10)$$

$$d[\mathrm{QOH}]/dt = k_d[\mathrm{QOH}] \quad (11)$$

$$K = [\mathrm{QX}][\mathrm{OH}]/[\mathrm{QOH}][\mathrm{X}] \quad (12)$$

[QOH] and [QX] correspond to the molar concentrations of Q^+OH^- and Q^+X^- respectively in the organic phase, [OH] and [X] to the molar concentrations of OH^- and X^-, respectively, in the aqueous phase, and t is time.

If the salt NaX is absent from the system, equation (12) is irrelevant and the system is regulated only by equations (10) and (11). As shown previously,[6] these two differential equations can be integrated analytically to give expression (13) to which

$$\ln\left[\ln\left(\frac{1 - x}{1 - x_e}\right)\right] = \ln\left(\frac{k[\mathrm{Q}]_0}{k_d}\right) - k_d t \quad (13)$$

data for conversion *versus* time may be fitted by linear regression in order to find values of k and k_d. Here x_e is the conversion at the end of the reaction (time infinity), and $[\mathrm{Q}]_0$ is the initial concentration in the organic phase.

The first step of our method consists in determining values of k and k_d for a given temperature, with no salt present. In the next step, reactions are carried out in the presence of different salts Na^+X^-. The poisoning effect of anion X^- decreases the amount of available Q^+OH^-, and thus the observed rate of both isomerization and decomposition. The intrinsic rate constants k and k_d stay the same. Their known values, obtained in the first step, are utilized in the analysis of the profiles in this second step to derive values of $K^{\mathrm{sel}}_{\mathrm{X/Y}}$.

When a salt Na^+X^- is present in the system, equation (12) must be taken into consideration since the Q^+OH^- concentration is then determined not only by its decomposition rate, but also by being partially poisoned by X^-. The decomposition rate itself is influenced by such poisoning. We derived from equation (12) an expression for Q^+OH^- concentration as a function of the overall concentration, deduced its differential form, and substituted these two expressions into equations (10) and (11), arriving at a set of two differential equations which, although they cannot by any means be solved analytically, can be dealt with numerically. In such equations, $K^{\mathrm{sel}}_{\mathrm{X/OH}}$ is an unknown whose value is assigned from the best fit to experimental data.

The mathematical development leads to the final differential equations (14)—(16) at time t where $[\mathrm{Q}]_t$ is the total

$$[\mathrm{Q}]_x = [\mathrm{Q}]_t - [\mathrm{QOH}] \quad (14)$$

$$[\mathrm{OH}] = [\mathrm{OH}]_0 - [\mathrm{QOH}] \cong [\mathrm{OH}]_0 \quad (15)$$

$$[\mathrm{X}] = [\mathrm{X}]_0 - [\mathrm{QX}] = [\mathrm{X}]_0 - ([\mathrm{Q}]_t - [\mathrm{QOH}]) \quad (16)$$

concentration of Q^+X^- and Q^+OH^- together and $[\mathrm{OH}]_0$ and $[\mathrm{X}]_0$ are the initial concentrations of OH^- and X^-, respectively. The approximation (15) is justified by the fact that the concentrations of quaternary ammonium salt utilized were always very small compared with those of NaOH (in general <0.1%).

If equations (14)—(16) are substituted into (12), expression (17) is obtained. This is a second-degree equation in [QOH],

$$K = \frac{([\mathrm{Q}]_t - [\mathrm{QOH}])[\mathrm{OH}]_0}{[\mathrm{QOH}]([\mathrm{X}]_0 - [\mathrm{Q}]_t + [\mathrm{QOH}])} \quad (17)$$

and algebraic manipulation leads to its roots [equation (18)] where $a = ([\mathrm{OH}]_0 + K[\mathrm{X}]_0)/2K$, $b = 1/2$, and $c = 1/2K$, and $i = K^2$, $j = 2K([\mathrm{OH}]_0 - K[\mathrm{X}]_0)$, and $m = ([\mathrm{OH}]_0 + K[\mathrm{X}]_0)^2$. It was found that the positive root in equation (18) was the relevant one.

$$[\mathrm{QOH}] = a + b[\mathrm{Q}]_t \pm c\sqrt{i[\mathrm{Q}]_t^2 + j[\mathrm{Q}]_t + m} \quad (18)$$

The derivation of equation (18) with respect to $[\mathrm{Q}]_t$ leads to the differential equation (19). If we substitute equation (18) into

$$d[\mathrm{QOH}] = \left[b + \frac{c(2i[\mathrm{Q}]_t + j)}{2\sqrt{i[\mathrm{Q}]_t^2 + j[\mathrm{Q}]_t + m}}\right] d[\mathrm{Q}]_t \quad (19)$$

(10), and equations (18) and (19) into (11), and rearrange, we obtain the definitive differential equations (20) and (21).

$$dx/dt = k(1 - x)\{a + b[\mathrm{Q}]_t + c\sqrt{i[\mathrm{Q}]_t^2 + j[\mathrm{Q}]_t + m}\} \quad (20)$$

$$d[\mathrm{Q}]_t/dt = \frac{-k_d\{a + b[\mathrm{Q}]_t + c\sqrt{i[\mathrm{Q}]_t^2 + j[\mathrm{Q}]_t + m}\}}{\{b + c(2i[\mathrm{Q}]_t + j)/(2\sqrt{i[\mathrm{Q}]_t^2 + j[\mathrm{Q}]_t + m})\}} \quad (21)$$

It is quite obvious that equations (20) and (21) cannot be solved analytically. Still, complicated as they may seem, they are essentially two differential equations in two dependent variables, x, and $[\mathrm{Q}]_t$ and an independent variable t [functions f1 and f2 in equations (22) and (23),

$$dx/dt = \mathrm{f1}\,(x, [\mathrm{Q}]_t) \quad (22)$$

$$d[\mathrm{Q}]_t/dt = \mathrm{f2}\,([\mathrm{Q}]_t) \quad (23)$$

respectively]. If values of the different constants in the equations are known, then the system can be solved numerically by a number of methods, among them the initial-value fourth-order Runge–Kutta method.[7]

This allows us to simulate profiles of our system, making use of the known values of t_0, x_0, $[\mathrm{Q}]_0$, $[\mathrm{X}]_0$, and $[\mathrm{OH}]_0$, and k and k_d (or any desired set of values of all such parameters), and arbitrarily defined values of K. This permits us to obtain families of profiles for different K values, such as those shown in Figures 1 and 2, given different initial conditions. Here, the two families correspond to two different values of the initial foreign ion concentration $[\mathrm{X}]_0$, all other parameters being equal.

It can be inferred from Figures 1 and 2 that the simulation capability permits a search for appropriate experimental conditions, that is those in which a wide range of K values can be differentiated. In our case it can be seen that working with the given set of conditions and $[\mathrm{X}]_0$ 0.07M, a greater spread of the family of curves is obtained than with $[\mathrm{X}]_0$ 0.04M. A very small or large $[\mathrm{X}]_0$ will give families of poorly differentiated curves.

Until this point we have simulated reaction profiles by using arbitrary values of K^{sel}, and we have not obtained such values, our final goal. The simulation program must be expanded to perform regression analysis, *i.e.* to make available a program in which the numerical Runge–Kutta differentiation method is interwoven with a numerical regression method for fitting data to a curve. We have developed such a program, and analysed with it experimental data for profiles of the isomerization in the presence of several salts Na^+X^-. Good correlations obtained in most cases suggest that the mathematical–computational model

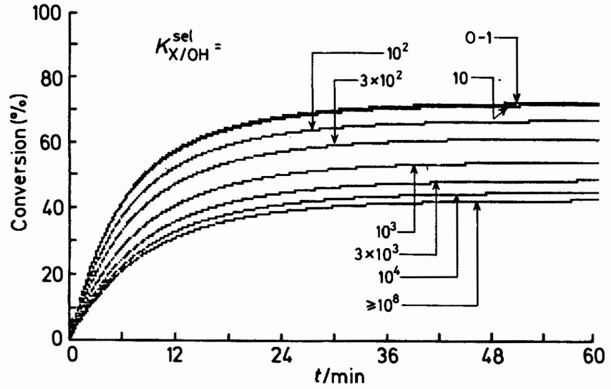

Figure 1. Computer-simulated kinetic profiles for the p.t.-catalysed isomerization of 4-allylanisole to 4-methoxy-β-methylstyrene in the presence of a foreign ion X^- ($[X^-]$ 0.04M) for different $K^{sel}_{X/OH}$ values, at 41 °C (k 1.615 l mol^{-1} min^{-1} and k_d 0.0902 min^{-1}); $[4\text{-allylanisole}]_0$ 0.0864M, $[TBAHSO_4]_0$ 8 mol%, $[NaOH]_0$ 19.06M (50% w/w)

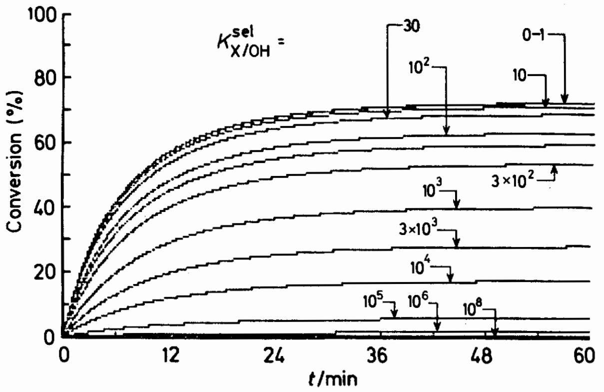

Figure 2. As Figure 1, with $[X^-]$ 0.07M

is satisfactory. The determination of $K^{sel}_{X/OH}$ for several anions X^- illustrates its capabilities. In particular, values corresponding to alkoxide anions were found after a slight modification to the model (see below), their elucidation being of particular interest.

Our biphase system consisted of equal volumes (10 ml each) of chlorobenzene as solvent, and 50% w/w NaOH as the source of OH^-. 4-Allylanisole was added at a concentration of 0.864M to the organic phase (0.01 mol). Tetrabutylammonium hydrogen sulphate was used which in the presence of 50% w/w NaOH is completely converted into the corresponding hydroxide and totally resides in the organic phase.[8] Its working concentration was 8 mol% (relative to the substrate). The temperature was always 41 °C.

The values of k and k_d were 1.615 l mol^{-1} min^{-1} and 0.0902 min^{-1}, respectively, from the E_a values found for the system.[6] These were utilized in further analysis.

$K^{sel}_{X/OH}$ Values were determined for MnO_4^-, ClO_4^-, SCN^-, I^-, ClO_3^-, NO_3^-, Br^-, $C_6H_5COO^-$, Cl^-, CH_3COO^-, F^-, $(COO^-)_2$, SO_4^{2-}, and CO_3^{2-}. The initial concentration of added salt Na^+X^- in the aqueous phase was either 0.04 or 0.07M, depending on the degree of solubility of the salt in the aqueous phase.

Since p.t.c. reactions in which alcohols are present as reactants are of particular importance (etherification, esterification, *etc.*), special attention was given to alkoxide anions. Such systems are more complex than those described above, since alkoxide anions are usually formed *in situ* by an equilibrium between alcohols and base present in the system, and are not simply added as such. Thus, the acidity of the different alcohols plays a role in the system, determining the equilibrium concentrations of ROH and OR^-, and consequently, of QOH and QOR. The analytical model described above was correspondingly expanded to take account of this factor.

The acidity of alcohols in aqueous medium is not of much interest, since alcohols (probably with the exception of methanol) do not reside in the NaOH phase, and the acidity of alcohols in an organic medium is usually different. This compels us to search for an overall extraction selectivity constant that may include both acidity and lipophilicity effects. For the system (24) and (25) we may define a new parameter $K^{s}_{OR/OH}$,

$$ROH + OH^- \xleftrightarrow{K_a} OR^- + H_2O \qquad (24)$$

$$QOH + OR^- \xleftrightarrow{K^{sel}_{OR/OH}} QOR + OH^- \qquad (25)$$

the acidity-selectivity constant, equal to $K_aK^{sel}_{OR/OH}$, which is the equilibrium constant for the overall reaction (26) and is given by equation (27).

$$QOH + ROH \xleftrightarrow{K^{s}_{OR/OH}} QOR + H_2O \qquad (26)$$

$$K^{s}_{OR/OH} = [QOR][H_2O]/[QOH][ROH] \qquad (27)$$

It seems that K^s could have greater experimental significance than K^{sel} alone, since it would include both abovementioned factors that determine the partition of the ammonium salt between OR^- and OH^-.

From the mathematical point of view, the analytical treatment of the system is completely analogous to that developed above for the case of a salt added to the system. Equations (14)—(17) would become (28)—(31) where $[Q]_0$,

$$[QOR] = [Q]_t - [QOH] \qquad (28)$$

$$[H_2O] = [H_2O]_0 + [Q]_0 - [QOH]_t \cong [H_2O]_0 \qquad (29)$$

$$[ROH] = [ROH]_0 - ([Q]_t - [QOH]) \qquad (30)$$

$$K^s = \frac{([Q]_t - [QOH])[H_2O]_0}{[QOH]([ROH]_0 - [Q]_t + [QOH])} \qquad (31)$$

$[H_2O]_0$, and $[ROH]_0$ are the initial concentrations of ammonium salt, water, and alcohol in the system, respectively. Since we worked with catalytic amounts of alcohol, the change produced in the water concentration by reaction (24) was always very small (of the order of 0.1%), and thus the approximation (29) is reasonable. From this point we reach two differential equations similar to (20) and (21), which are the basis for numerical analysis of our data. The results in Table 2 are those found for K^s.

K^s Values were obtained for the series of primary alcohols, methanol to octanol, s- and t-butyl alcohol, benzyl alcohol, and ethane-1,2-diol, propane-1,3-diol, pentane-1,5-diol, and 2,5-dimethylhexane-2,5-diol. The added alcohol was always 0.0016 g equiv., in 1:1 ratio with quaternary salt. Thus, in the case of monoalcohols, the ratio of alcohol to quaternary salt was 2:1, and in the case of the diols 1:1.

Two representative sets of data and corresponding kinetic profiles are in Figures 3 and 4. Complete K^{sel} and K^s values for the different anions X^- are in Tables 1 and 2.

The values in Table 1 may be easily compared with those compiled by other authors for different systems. The general trend of K^{sel} values of anions obtained in this work is similar in most cases to that in the literature.[4,9,10] The selectivity of

Table 1. $K^{sel}_{X/OH}$ Values for X^- in chlorobenzene–aqueous NaOH

Anion X^-	$K^{sel}_{X/OH}$
$(COO^-)_2$	10
CO_3^{2-}	20
SO_4^{2-}	30
F^-	50
CH_3COO^-	120
Cl^-	950
$C_6H_5COO^-$	2×10^3
Br^-	3×10^3
NO_3^-	8×10^3
ClO_3^-	9×10^3
I^-	1×10^4
SCN^-	5×10^4
ClO_4^-	1×10^5
MnO_4^-	$>1 \times 10^5$

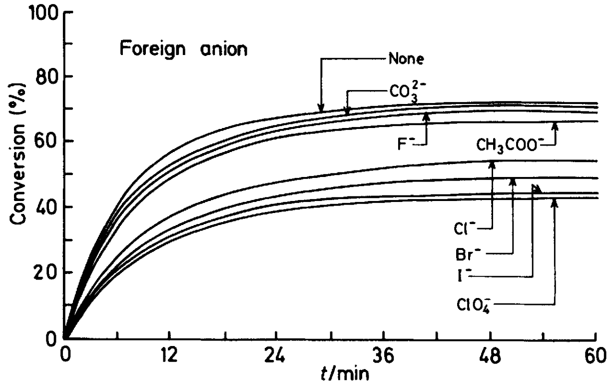

Figure 3. Actual kinetic profiles of the isomerization reaction studied, in the presence of 0.0004 equiv. of different salts at 41 °C; [4-allylanisole]$_0$ 0.0864M, [TBAHSO$_4$]$_0$ 8 mol%, [NaOH]$_0$ 19.06M

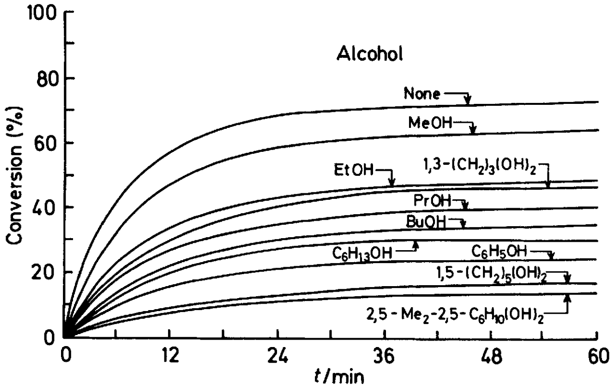

Figure 4. As Figure 3, with 0.0016 equiv. alcohol

bivalent anions is usually considered to be smaller than that of OH^-.[4,9] We found values somewhat greater than 1 for K^{sel} for such cases. Previous work[11] confirms the fact that in the case of SO_4^{2-}, K^{sel} is greater than expected.

The values of $K^{s}_{OR/OH}$ for monoalcohols increase as the size of the alcohol increases. This is expected, since the higher the alcohol, the higher its lipophilicity. The differences in K^s among the lower alcohols are, also as expected, greater than those among the higher ones.

Table 2. $K^{s}_{OR/OH}$ Values for RO^- formed *in situ* in chlorobenzene–aqueous NaOH

Alcohol ROH	$K^{s}_{OR/OH}$
MeOH	70
EtOH	420
PrOH	710
BuOH	960
Bu^{s}OH	970
Bu^{t}OH	980
$C_5H_{11}OH$	1 150
$C_6H_{13}OH$	1 300
$C_7H_{15}OH$	1 380
$C_8H_{17}OH$	1 380
$C_6H_5CH_2OH$	1 900
Ethane-1,2-diol	210
Propane-1,3-diol	450
Pentane-1,5-diol	4 100
2,5-Dimethylhexane-2,5-diol	4 900

Earlier work[10] proposed that an intramolecular hydrogen-bonding contribution to the stability of the ion pair formed between the ammonium salt and the alkoxide anion derived from a diol increased the affinity of the dialcohols to the salt relative to the corresponding monoalcohols. It can be seen from Table 2 that pentane-1,5-diol and 2,5-dimethylhexane-2,5-diol do have higher K^s values than pentanol and octanol, respectively.

For ethane-1,2-diol and propane-1,3-diol, Table 2 shows that their K^s values are smaller than that of ethanol and propanol, respectively, as opposed to the trend described above. As these alcohols are quite hydrophilic, they could be present partly in the aqueous phase, despite the high NaOH concentration, thus combining with the ammonium salt in a lower proportion than the corresponding amount of ethanol and propanol, respectively.

It is clear that our method could be used to find selectivity constants for practically any desired anion and for any solvent; even though the actual value of K^{sel} for a given anion in a particular system, for example, benzoate anion in a p.t.-catalysed solid–liquid esterification, would probably differ in some measure from the value obtained from the 'clean' isomerization reaction, the latter figure would approximate to the former.

Experimental

Reactions were performed at 41 ± 0.5 °C. Mechanical stirring at 500 r.p.m. was with a Heidolph stirrer. Typically, NaOH (0.2 mol) from a 50% w/w aqueous solution (10 ml) was stirred with chlorobenzene (10 ml), TBAHSO$_4$ (0.0008 mol) and Na^+X^- (0.0004 mol) for 5 min at room temperature to allow for equilibration. 4-Allylanisole (0.01 mol) was added, and the reaction proceeded for 1 h. Samples were taken at intervals, quenched with dilute HCl, dried (MgSO$_4$), and analysed for 4-allylanisole and 4-methoxy-β-methylstyrene with a Packard 427 flame detector gas chromatograph column a 2 m × 0.25 in, 15% OV-17 on acid-washed Chromosorb W, 130 °C, N_2 as carrier gas, flow rate 30 ml min^{-1}.

Salts and alcohols were analysed for water content by the Karl Fisher method with a Mettler DL 40 RC MemoTitrator.

Acknowledgements

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