Kinetics in Phase-transfer Catalysis: a Theoretical Study. Part 2.† The Method of Initial Rates

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A theoretical study of a phase-transfer-catalysed irreversible S_N2 reaction, $RY + X^- \longrightarrow RX + Y^-$, was undertaken in order to establish the necessary conditions for the application of the method of initial rates in phase-transfer catalysis. The system studied consists of a slow chemical reaction coupled to a fast anion exchange *via* an organic quaternary 'onium salt. An error in measuring the initial reaction rate was shown to be inherent in a system in which the released anion Y^- is initially absent. This error is negligibly small when the selectivity extraction constant $K_{x/y}^{sel} \geqslant 1$ for equal reactant concentrations and when $K_{x/y}^{sel} \geqslant 0.1$ for a five-fold or more molar excess of concentration of the ionic reactant.

Most previous kinetic studies in phase-transfer catalysis (p.t.c.) have made use of integral kinetic analysis.[1,2] The differential method has been only occasionally applied.[3,4] The method of initial rates is particularly suited to phase-transfer-catalysed reactions whose mechanism is complex, as in metal-catalysed reactions in the organic phase,[5] or to a reaction inhibited after a limited conversion[6] as when $K_{x/y}^{sel} < 0.1$, or to a phase-transfer system in which $K_{x/y}^{sel}$ varies with the concentration ratio of the ionic reactant.[7] However, phase-transfer systems may exhibit a drastic change in reaction rates at the very beginning, as reported by Brandstrom.[8] The application of the initial rate method to such systems is bound to create large errors in experimental initial rates, leading possibly to a false kinetic analysis. The purpose of this study was to establish the conditions where the initial rate method should not be applied to p.t.c. and to evaluate the expected experimental error. The chosen model reaction for this study was, as in the preceding paper,[9] the irreversible S_N2 reaction of organic substrate RY with the aqueous nucleophile X^-, catalysed by a lipophilic organic 'onium (Q^+) salt added in the reacting anion form Q^+X^- or in the inactive foreign anion form Q^+Z^- with $K_{x/y}^{sel} \leqslant 1$.

Kinetic Treatment

Development of Analytical Rate Equations.—The heterogeneous reaction is formulated as (1) and is assumed to take

$$RY(org) + X^-(aq) \longrightarrow RX(org) + Y^-(aq) \quad (1)$$

place under the conditions described in the preceding paper. Adding the p.t. catalyst in Q^+Z^- form ($K_{x/y}^{sel} \leqslant 1$) is practically equivalent to its addition in Q^+X^- form[9] and therefore all catalyst is initially in the organic phase in Q^+X^- form. Since the catalytic amount of Z^- is negligible, it follows that at every moment equation (2) applies, where $[Q]_0$ is the

$$[Q]_0 = [QX]_{org} + [QY]_{org} \quad (2)$$

initial concentration of the p.t. catalyst added in either Q^+X or Q^+Z^- form. In a system of equal volumes of organic and aqueous phases, in which Y^- is initially absent, the reaction rate in the organic phase at $t = 0$ is given by equation (3), where

$$-r_0 = k[RY]_0[Q]_0 \quad (3)$$

$[RY]_0$ and k are the initial substrate concentration and the intrinsic reaction rate coefficient in the organic phase, respectively. At a subsequent moment, the rate is given by equation (4), where $[QX]_{org}$ is determined by the instantaneous

$$-r = k[RY][QX]_{org} \quad (4)$$

establishment of the anion-exchange equilibrium (5). Equations (6) and (7) define $[X^-]_{aq}$ and $[Y^-]_{aq}$, and x and $[X^-]_0$ are the

$$K_{x/y}^{sel} = \frac{[QX]_{org}[Y^-]_{aq}}{[QY]_{org}[X^-]_{aq}} \quad (5)$$

$$[X^-]_{aq} = [X^-]_0 - x[RY]_0 + [QY]_{org} \quad (6)$$

$$[Y^-]_{aq} = x[RY]_0 - [QY]_{org} \quad (7)$$

conversion fraction and the initial X^- concentration in the aqueous phase, respectively. Substitutions of equation (6) and (7) into (4) will not lead to an explicit expression of the rate as a function of x. However, neglecting the catalytic amounts of $[QY]_{org}$ in equations (6) and (7) leads to an analytical rate equation (8), which is condensed into the form (9).

$$\frac{dx}{dt} = \frac{k\,K_{x/y}^{sel}[Q]_0(1-x)([X^-]_0 - x[RY]_0)}{K_{x/y}^{sel}([X^-]_0 - x[RY]_0) + x[RY]_0} \quad (8)$$

$$\frac{dx}{dt} = \frac{a + bx + cx^2}{A + Bx} \quad (9)$$

where

$a = k\,K_{x/y}^{sel}[Q]_0[X^-]_0$
$b = -k\,K_{x/y}^{sel}[Q]_0([X^-]_0 + [RY]_0)$
$c = k\,K_{x/y}^{sel}[Q]_0[RY]_0$
$A = K_{x/y}^{sel}[X^-]_0$
$B = (1 - K_{x/y}^{sel})[RY]_0$

When $[X^-]_0 = [RY]_0$, equation (9) is integrated to (10), and when $[X^-]_0 \neq [RY]_0$, to (11), where $q = 4ac - b^2$.

Evaluation of Initial Rate Error.—The initial reaction rate is commonly measured by a graphical method from an experimental plot of reactant concentration *vs.* time. In fact, the drawn tangent is not strictly a tangent to the single point at $t =$

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† Part 1, ref. 9.

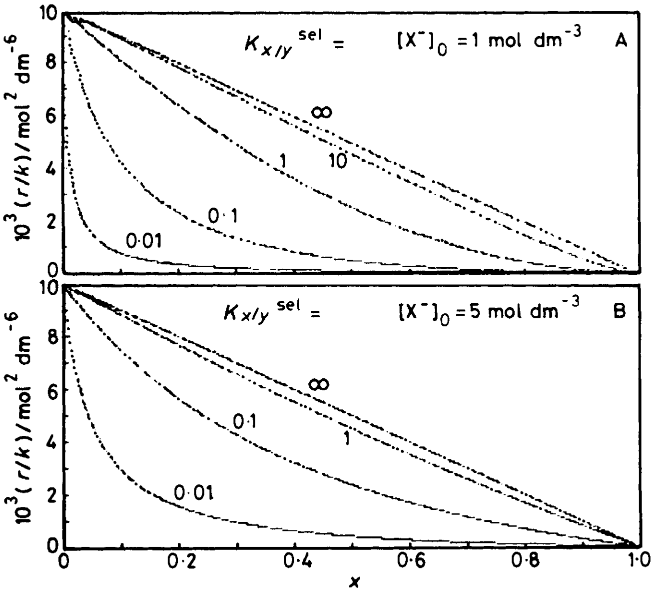

Figure 1. Generalised instantaneous reaction rate coefficient, r/k, as a function of the fractional conversion x and $K_{x/y}{}^{sel}$ for $[RY]_0 = 1$ mol dm^{-3};A : $[X^-]_0 = 1$, B : $[X^-]_0 = 5$ mol dm^{-3}

$$\left(\frac{4Ac}{b} - 2B\right)\left(\frac{x}{b + 2cx}\right) + \frac{B}{c}\ln\left(\frac{b + 2cx}{b}\right) = t \quad (10)$$

$$\frac{B}{2c}\ln\left(\frac{a + bx + cx^2}{a}\right) + \frac{1}{\sqrt{-q}}\left(A - \frac{Bb}{2c}\right)\ln\left(\frac{(b + \sqrt{-q})(2cx + b - \sqrt{-q})}{(b - \sqrt{-q}))(2cx + b + \sqrt{-q})}\right) = t \quad (11)$$

0 but rather covers a finite range of time values or alternatively, of fractional conversions, during which the rate is constant. This range of a few fractional conversions (*ca.* 0.01—0.05) depends on the experimental and graphical accuracy. If we assume that the experimental kinetic reaction profile is identical with the theoretical one obtained from equation (10) or (11), the application of the graphical method leads to an initial rate $r_g = [RY]_0\, x/t$ where x and t are the ranges of conversion and time covered by the tangent line. This graphically measured rate is compared with the known theoretical one [equation (3)] by the error $(r_0 - r_g)\ 100\%/r_0$. Using an Apple II+ computer, reaction rates, kinetic profile, and initial errors were computed and plotted for phase-transfer systems in which $[RY]_0$ and $[Y^-]_0$ are 1 mol dm^{-3} and 0, respectively.

Results

Effects of $K_{x/y}{}^{sel}$ upon Reaction Rate.—The instantaneous theoretical reaction rates [equation (8)] in generalised terms of r/k as a function of the fractional conversion are shown in Figure 1 for various selectivity extraction constants $K_{x/y}{}^{sel}$. The p.t. catalyst concentration is 1% of that of the organic substrate, but the initial X^- concentrations is 1 and 5 mol dm^{-3} in Figures 1A and B, respectively. Values of $K_{x/y}{}^{sel}$ higher than 100 yield the same straight line as for $K_{x/y}{}^{sel} = 100$.

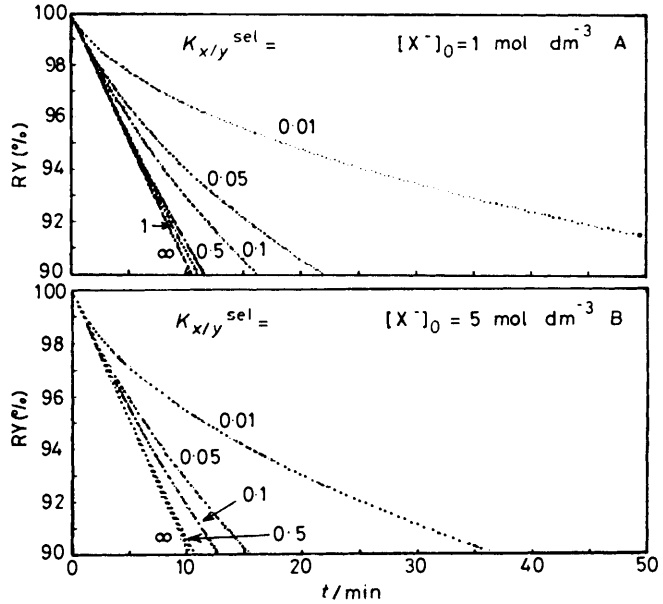

Figure 2. Kinetic profiles of the remaining RY *vs.* time for different $K_{x/y}{}^{sel}$, $[RY]_0 = 1$ mol dm^{-3}, $k = 1$ dm^3 mol^{-1} min^{-1}, A : $[X^-]_0 = 1$ mol dm^{-3}, B : $[X^-]_0 = 5$ mol dm^{-3}

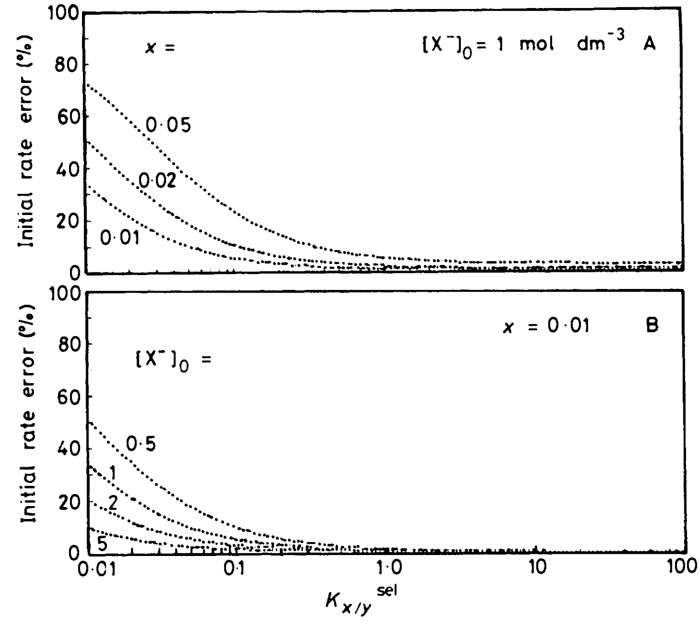

Figure 3. Initial rate error as a function of $K_{x/y}{}^{sel}$ for $[RY]_0 = 1$ mol dm^{-3}, A : $[X^-]_0 = 1$ mol dm^{-3} and several x values and B : x = 0.01 and several $[X^-]_0$ values

Effects of $K_{x/y}{}^{sel}$ upon Kinetic Profiles.—As the initial rate method is primarily concerned with the first stages of the reaction, Figure 2A plots the percentage of the remaining RY in the organic phase *vs.* time as obtained from equation (10). Similarly, equation (11) is used to plot the kinetic behaviour in Figure 2B for various $K_{x/y}{}^{sel}$ values but for a five-fold initial molar concentration of X^-. The p.t. catalyst is 1% of $[RY]_0$ and $k = 1$ dm^3 mol^{-1} min^{-1}. A different magnitude of k will not alter the form of the curves if the time co-ordinate is proportionally changed.

Effect of $K_{x/y}{}^{sel}$ upon the Initial Rate Error.—The initial rate error (%) as a function of $K_{x/y}$ is shown in Figure 3A for various

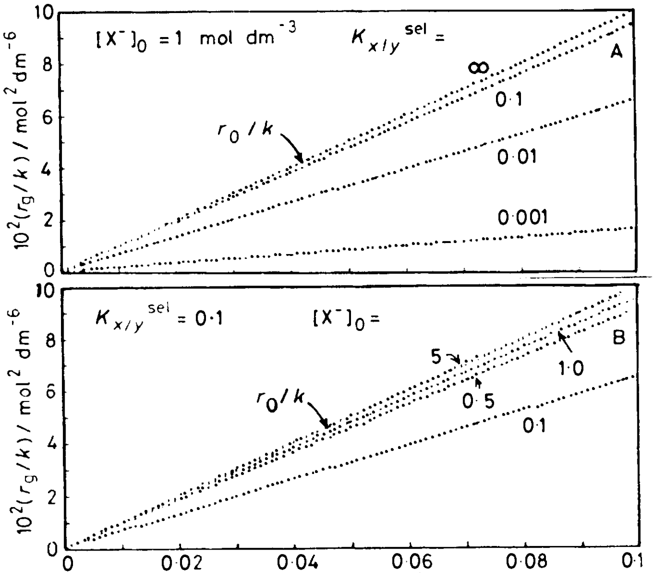

Figure 4. Generalised graphical initial rates *vs.* p.t. catalyst concentration $[Q]_0$ for $[RY]_0 = 1$ mol dm^{-3}, $x = 0.01$; A : $[X^-]_0 = 1$ mol dm^{-3} and different $K_{x/y}^{sel}$; B : $K_{x/y}^{sel} = 0.1$ and different $[X^-]_0$

ranges of x, upon which the graphical computation of the initial rate r_g is based. Figure 3B is a similar plot for a constant conversion range of 0.01 and various initial X^- concentrations. The p.t. catalyst concentration is again 1% of $[RY]_0$. The magnitude of k does not alter the computed errors.

Effect of $K_{x/y}^{sel}$ upon the Relationship between r_g and $[Q]_0$.—The linear dependence of the graphical rate r_g upon the initial p.t. catalyst concentration $[Q]_0$ is shown in Figure 4A in generalised terms of r_g/k for various $K_{x/y}^{sel}$, but for constant x and $[X^-]_0$ of 0.01 and 1 mol dm^{-3}, respectively. The line for $K_{x/y}^{sel} = 1$ merges with the one for an infinite value, which is identical with the error-free line (r_0/k) obtained from equation (3). Figure 4B shows that for the low $K_{x/y}^{sel}$ value of 0.1, increasing the initial X^- concentration increases the slope of the line towards the error-free line. The maximum quaternary salt concentration is restricted to 10% of [RY] in order to maintain a catalytic amount and to keep valid the simplifying assumption necessary for obtaining an analytical rate.

Discussion

The analysis of the initial rate error is performed on a theoretical kinetic profile rather than on an experimental one since this study is aimed at revealing the error inherent to p.t.c. and not the error due to the experimental inaccuracy and precision. Of course, the latter adds statistically to the former. Furthermore, the analysis is based on the graphical method of calculating the initial rate, since we believe it to be a very common procedure and as accurate as a method based on mathematical modelling.[10] The range of conversion fractions (0.01—0.05) throughout which the rate is taken as constant is the one usually employed in kinetic analysis of continuous systems in a differential reactor.[10]

In the absence of the released anion Y^-, all p.t. catalyst resides initially in the organic phase in the reacting anion form Q^+X^- and consequently yields the highest initial rate, irrespective of the magnitude of $K_{x/y}^{sel}$ and the initial X^- concentration [equation (3)]. After an infinitesimal fractional conversion, yielding correspondingly some amount of Y^-, the subsequent concentration Q^+X^- is determined by the non-linear relationship [equation (5)] of anion-exchange equilibrium. Therefore, $[Q^+X^-]$ may either remain high or suddenly drop, thus entailing a corresponding change in the reaction rate. The drastic decrease in rate at low $K_{x/y}^{sel}$ is clearly demonstrated in Figure 1A, and the moderating effect of the presence of high initial X^- concentration is shown in Figure 1B. The drastic transition from a high rate to a lower one occurs instantaneously at the very beginning and therefore is not detected by the graphical method, which measures concentration changes from kinetic profiles (Figure 2) during a finite lapse of time. The resulting error in measurement of the initial rate may consequently be as high as 70% for $K_{x/y}^{sel} = 0.01$ (see Figure 3A). One can see from Figure 3A that for $K_{x/y}^{sel} \geqslant 1$, the error is low and reasonably acceptable for systems of equal initial concentration of the organic and aqueous reactants. A large $K_{x/y}^{sel}$ value brings about an almost constant Q^+X^- concentration, thus reducing the sudden change of reaction rate and the inherent initial rate error. In fact, an infinite $K_{x/y}^{sel}$ establishes pseudo-first-order kinetics with respect to RY, as seen by the straight line in Figure 1, thus eliminating the error.

Similarly, pseudo-first-order kinetic behaviour is approached by increasing $[X^-]_0$, resulting in a decreasing initial rate error as shown in Figure 3B. This Figure, and others drawn for an x value of up to 0.05, reveal a small initial rate error of 2—6% when $K_{x/y}^{sel}$ and $[X^-]_0/[RY]_0$ are 0.1 and 5, respectively.

The plot of the initial rate *vs.* the p.t. catalyst concentration is commonly sought in order to ascertain the order of $[Q]_0$ and to calculate the intrinsic reaction rate coefficient k. In our case, such a plot is a straight line (see Figure 4), as expected from equations (3) and (8) upon which the computation of r_g is based. The magnitude of the slope for low $K_{x/y}^{sel}$ is smaller than the true one, for which $K_{x/y}^{sel}$ is infinite. The higher $K_{x/y}^{sel}$, the closer the slope is to the correct value. A similar behaviour is observed by increasing $[X^-]_0$, as seen in Figure 4B.

So far, we have considered a phase-transfer system in which Y^- is initially absent. When it is initially present, Q^+X^- concentration at $t = 0$ and at any subsequent moment is determined by equation (5) and consequently no drastic change in either [QX] or r occurs. In such a system, the initial rate method is satisfactory but the measured reaction rates may be too low, especially when $K_{x/y}^{sel} < 1$, as a result of an enhanced catalyst poisoning effect.[6]

Conclusions

The following conclusions arise from this study. (1) The application of the method of initial rates to a phase-transfer-catalysed reaction may be subject to a substantial error when the released anion Y^- is initially absent. (2) Establishment of pseudo-first-order conditions eliminates the initial rate error. (3) When $K_{x/y}^{sel} \geqslant 1$ and $[X^-]_0/[RY]_0 = 1$, and when $K_{x/y}^{sel} \geqslant 0.1$ and $[X^-]_0/[RY]_0 \geqslant 5$, the error is negligibly small.

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Received 24*th November* 1983; *Paper* 3/2091