Kinetics in Phase-transfer Catalysis: a Theoretical Study. Part 1. Poisoning Effect by Catalyst Foreign Ion

Raphael Bar, Jaime de la Zerda, and Yoel Sasson *
Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

The kinetics of phase-transfer-catalysed reversible or irreversible S_N2 substitution of an organic substrate RY by an aqueous electrolyte X^- has been studied theoretically, in order to analyse the poisoning effect due to a foreign counter ion Z^- of the phase-transfer catalyst. The foreign ion, although introduced in catalytic amount, deactivates a portion of the phase-transfer catalyst. This results in a slower reaction, although it may go to completion or to equilibrium conversion. However, the poisoning effect is negligibly small when the selectivity extraction constant $K_{z/x}^{sel} \leqslant 1$ at equal initial reactant concentrations and when $K_{z/x}^{sel} \leqslant 10$ at a ten-fold electrolyte concentration. Under these conditions, the reaction rates depend linearly on the overall 'onium salt concentration in the organic phase.

Phase-transfer catalysis[1,2] (p.t.c.) brings about a reaction between two immiscible reactants with the aid of a catalytic amount of an agent capable of transferring one reactant into the other phase. This may be achieved *via* complexation, *e.g.* by crown ethers, polyethylene glycols, or cryptates, or *via* ion-pair formation, *e.g.* by organic quaternary 'onium salts (quat). A common phase-transfer system consists of an electrolyte and an organic substrate, dissolved in water and an organic solvent, respectively, in the presence of a tetra-alkylammonium halide as p.t. catalyst. P.t.c. has been extensively used for synthetic purposes,[3] but has rarely been subjected to a thorough kinetic study.[4] Such an investigation is difficult because of the heterogeneity of the system. There may be an interfacial reaction as well as one in the bulk organic phase. The nature and degree of hydration of the extracted ionic reactant may be uncertain. The selectivity extraction constant of the ions involved may not be a true constant, and the p.t. catalyst may be poisoned. This article is devoted to the phenomenon of catalyst poisoning by a foreign ion and its effect upon the kinetics of the reaction catalysed by a quat cation (Q^+). We limit consideration to second-order reactions and illustrate the phenomenon by the S_N2 reaction of a substrate RY with the nucleophile X^-, catalysed by a p.t. catalyst added in the form Q^+Z^-, where Z^- is a chemically inactive foreign ion. A p.t. catalyst with a foreign anion Z^- different from the reacting anion X^- must frequently be used when the latter is unavailable (*e.g.* sulphide,[5] hydrogen sulphite,[6] nitrite,[7] or hypochlorite[8]), or when it is generated *in situ* as in the Williamson ether synthesis[9] or in alkylation reactions.[10] Furthermore, difficulties in preparation and handling,[11] as in the cases of tetra-alkylammonium carboxylates, fluorides, or hydroxides, as well as catalyst cost, often justly encourage the use of catalysts which are relatively easy to prepare and handle as bromides or chlorides, even if these anions differ from the reactive ones. The anion Z^-, although introduced in catalytic amount, interferes with the reaction kinetics by creating a poisoning effect. This effect has heretofore received only scant attention and in many instances [4,12–14] was totally disregarded. Gordon and Kutina[15] as well as Starks,[16] consider solely the cationic part of the p.t. catalyst (Q^+) competing only for the exchanging ions X^- and Y^-.

Kinetic Treatment

The heterogeneous reaction is formulated as (1), and is assumed to take place under the following conditions:

(*a*) the reaction occurs in the bulk of the organic phase;

(*b*) the cationic part of the p.t. catalyst resides totally in the organic phase and is added to the reaction system in the form of Q^+Z^-;

(*c*) The anion exchange through the interface is fast, thus making the process a chemically controlled one.

$$\mathrm{RY(org)} + \mathrm{X^-(aq)} \rightleftharpoons \mathrm{RX(org)} + \mathrm{Y^-(aq)} \qquad (1)$$

Assumption (*a*) implies the formulation of the reaction rate as (2), where k_1 and k_{-1} are the intrinsic forward and backward

$$-r = k_1[\mathrm{RY}]_{org}[\mathrm{Q^+X^-}]_{org} - k_{-1}[\mathrm{RX}]_{org}[\mathrm{Q^+Y^-}]_{org} \qquad (2)$$

reaction rate coefficients, respectively, and $[\mathrm{RY}]_{org}$, $[\mathrm{RX}]_{org}$, and $[\mathrm{Q^+Y^-}]_{org}$ are the respective concentrations of reactants in the organic phase. The equilibrium constant of the reaction in the organic phase is $K_{org} = k_1/k_{-1}$. The concentrations of the organic salts are determined, as assumption (*c*) implies, by the instantaneous establishment of the equilibria (3) and (4), where

$$\frac{[\mathrm{Q^+Z^-}]_{org}[\mathrm{X^-}]_{aq}}{[\mathrm{Q^+X^-}]_{org}[\mathrm{Z^-}]_{aq}} = K_{z/x}^{sel} \qquad (3)$$

$$\frac{[\mathrm{Q^+X^-}]_{org}[\mathrm{Y^-}]_{aq}}{[\mathrm{Q^+Y^-}]_{org}[\mathrm{X^-}]_{aq}} = K_{x/y}^{sel} \qquad (4)$$

$K_{z/x}^{sel}$ and $K_{x/y}^{sel}$ are the selectivity extraction constants between the anions Z^- and X^-, and between X^- and Y^-, respectively.

Assumption (*b*) implies the material balance equation (5), where $[\mathrm{Q^+Z^-}]_0$ is the initial concentration of the p.t. catalyst in the organic phase.

$$[\mathrm{Q^+Z^-}]_0 = [\mathrm{Q^+Z^-}]_{org} + [\mathrm{Q^+X^-}]_{org} + [\mathrm{Q^+Y^-}]_{org} \qquad (5)$$

Simultaneous solution of the equation system (3)—(5) by the Newton–Raphson method[17] and integration of (2) by Euler's method[17] enable the determination of the instantaneous composition of the organic salts Q^+Z^-, Q^+X^-, and Q^+Y^- as a function of the fractional conversion x and the kinetic profiles for both the irreversible and the reversible reactions. All computations were performed on an Apple II computer with the constant initial concentrations of $[\mathrm{Y^-}]_0 = 0$, $[\mathrm{RY}]_0 = 1$, $[\mathrm{Q^+Z^-}]_0 = 0.01$ mol dm^{-3} and an intrinsic rate coefficient $k_1 = 1$ dm^3 mol^{-1} s^{-1} in equal volumes of the aqueous and organic phases.

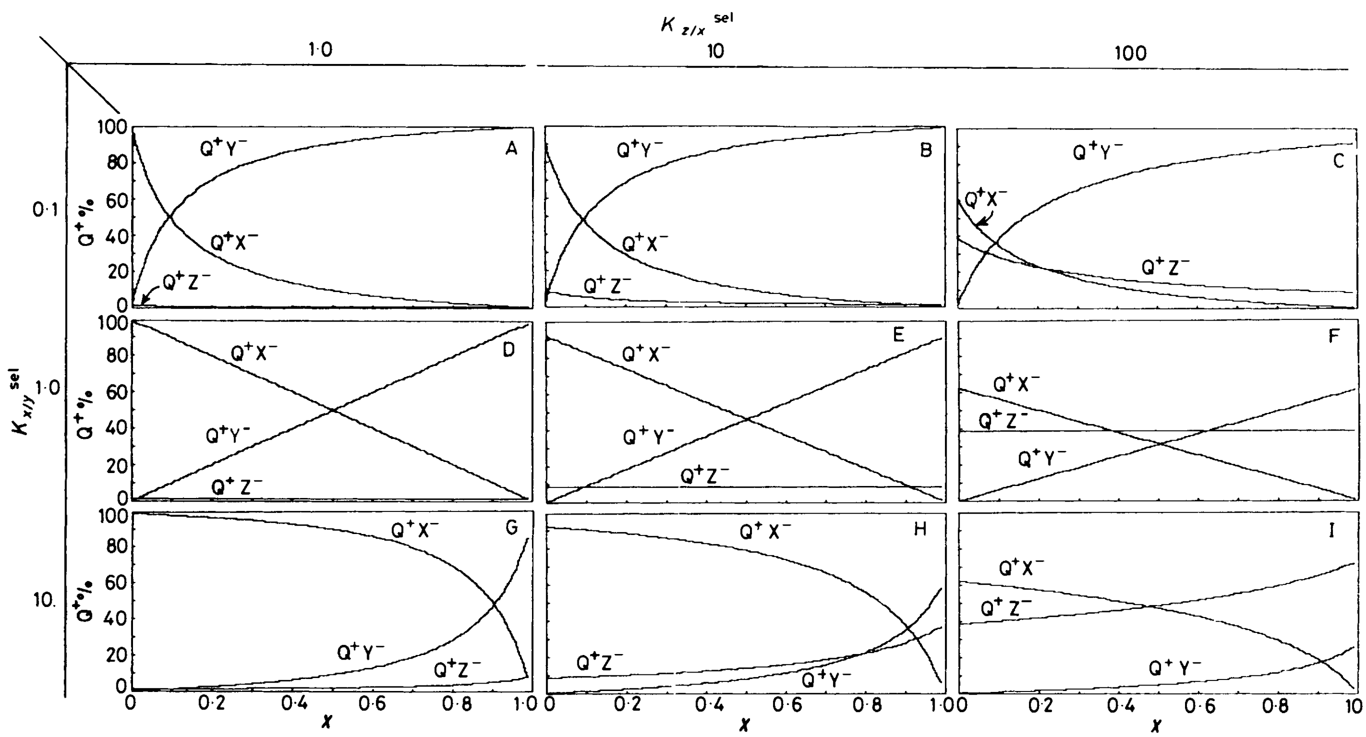

Figure 1. Composition of a lipophilic quat (Q^+) in Q^+X^-, Q^+Y^-, and Q^+Z^- forms for various $K_{z/x}^{sel}$ and $K_{x/y}^{sel}$ *versus* reaction conversion x. $[Q^+Z^-]_0 = 0.01$ mol dm^{-3}, $[X^-]_0 = 1$ mol dm^{-3}, $[Y^-]_0 = 0$

Results

Equilibrium Quat Distribution.—Figure 1, which shows the concentration profiles of the three quats (Q^+X^-, Q^+Y^-, Q^+Z^-) *versus* reaction conversion is a matrix of subfigures. Each column corresponds to three different $K_{x/y}^{sel}$ values at constant $K_{z/x}^{sel}$ and each row corresponds to three different $K_{z/x}^{sel}$ at constant $K_{x/y}^{sel}$.

(a) *Effect of $K_{z/x}^{sel}$ on quat distribution at constant $K_{x/y}^{sel}$.* This is illustrated in each row of Figure 1. Since $[Y^-]_0 = 0$, each $K_{z/x}^{sel}$ value determines a different initial quat distribution between X^- and Z^-. The lower the $K_{z/x}^{sel}$ value, the less is the amount of quat held by the foreign ion Z^-, as expressed by the lower integral area under the curve of Q^+Z^-. The Q^+Z^- concentration is negligibly small at $K_{z/x}^{sel} = 1$ and vanishes as $K_{z/x}^{sel}$ tends to 0.

(b) *Effect of $K_{x/y}^{sel}$ on quat distribution at constant $K_{z/x}^{sel}$.* This is illustrated in each column of Figure 1. The higher $K_{x/y}^{sel}$, the greater is the integral area under the Q^+X^- curve. However, the increase in area occurs by a change in form of the curve from convex to concave *via* a straight line. The concavity of the curve for high $K_{x/y}^{sel}$ values implies an approximately constant Q^+X^- concentration over a wide range of conversions. This behaviour is the reason for the pseudo-first-order kinetics previously reported.[15] Interestingly, each column shows a different trend in the Q^+Z^- curve upon change of $K_{x/y}^{sel}$ from 0.1 to 10. Figure 2 reveals that this change occurs at $K_{x/y}^{sel} = 1$, irrespectively of $K_{z/x}^{sel}$. For this value, Q^+Z^- concentration remains constant with conversion, while for larger and smaller values, it exhibits a moderate increase and a steep decrease, respectively.

Kinetic Profiles.—(a) *Reversible reactions.* Figures 3A and B compare the concentration profiles of the substrate RY in the organic phase for two different $K_{x/y}^{sel}$ values at the same set of $K_{z/x}^{sel}$ values, while $K_{org} = 1$. It is seen that the two $K_{x/y}^{sel}$ values determine two different equilibrium conversions although the equilibrium constants of the reaction in the organic phase are identical. A different kinetic behaviour for the same parameters is shown in Figures 3C and D but for a ten-fold initial molar concentration of X^-.

(b) *Irreversible reactions.* The influence of $K_{z/x}^{sel}$ upon the kinetic behaviour of an irreversible reaction ($k_{-1} = 0$) is shown in Figures 4A and B for two different $K_{x/y}^{sel}$ values at the same set of $K_{z/x}^{sel}$ values. Once again, a different kinetic behaviour for the same parameters is shown (Figures 4C and D) but for a ten-fold initial concentration of X^-.

Discussion

Knowing the actual concentration of the reacting species Q^+X^- and Q^+Y^- at each instant is of primary importance for understanding the progress of the reaction. The quat composition is determined by the ratio of the reacting anions in the aqueous phase, *i.e.* the reaction conversion, and by the different K^{sel} values. The latter are known to vary with the anion concentrations,[12] but for a quat acting as 'liquid anion exchanger'[15] they tend to vary only moderately,[18] thus supporting the assumption of constant K^{sel}. Such a quat resides wholly in the organic phase owing either to a high lipophilicity or to a salting-out from a concentrated aqueous phase.

The presence of Q^+Z^- reduces the amount of Q^+ available for phase transfer of the two reacting anions and consequently partially poisons the p.t. catalyst. This of course implies a chemical inertness of the foreign ion. Otherwise, reaction rates may be enhanced as observed by Herriot and Picker,[19] who studied the reaction of bromo-octane with sodium benzenethiolate catalysed by the reactive tetrabutylammonium iodide. Figure 1 shows such a poisoning at different extents all along the reaction path, which almost vanishes when $K_{z/x}^{sel}$ is very small, as seen in Figures 1A, D, and G. A high hydrophilicity of

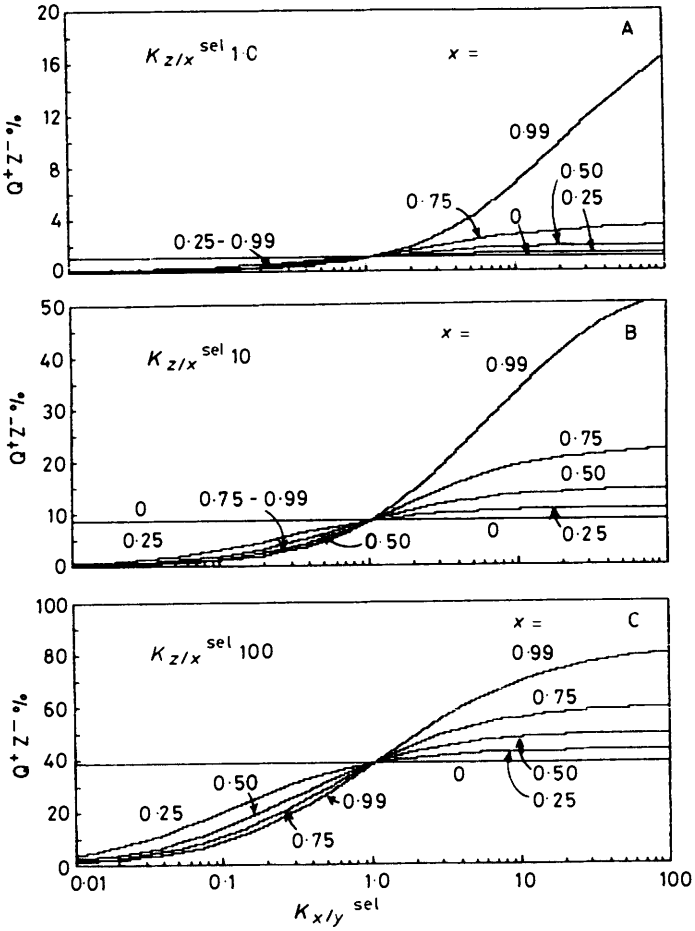

Figure 2. Percentage of Q^+Z^- in the organic phase as a function of $K_{x/y}^{sel}$ for various reaction conversions and $K_{z/x}^{sel}$ values. $[Q^+Z^-]_0 = 0.01$ mol dm^{-3}, $[X^-]_0 = 1$ mol dm^{-3}, $[Y^-]_0 = 0$

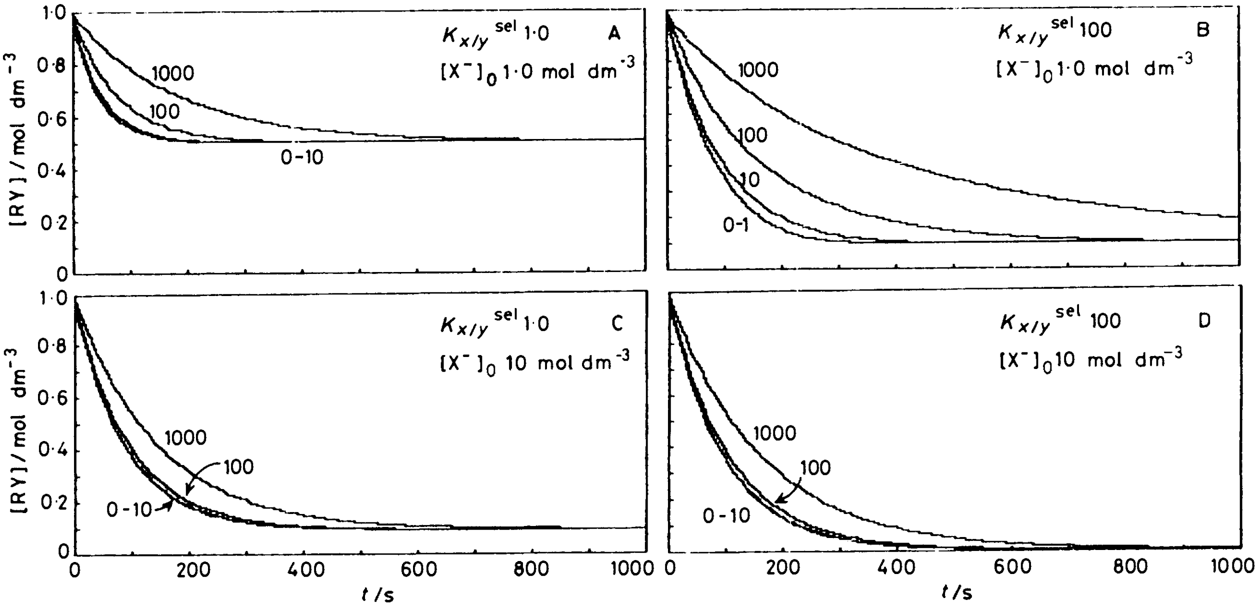

Figure 3. Kinetic profiles of a phase-transfer-catalysed reversible S_N2 reaction of substrate RY at several $K_{z/x}^{sel}$, $K_{x/y}^{sel}$, and reactant concentrations. $[Q^+Z^-]_0 = 0.01$ mol dm^{-3}

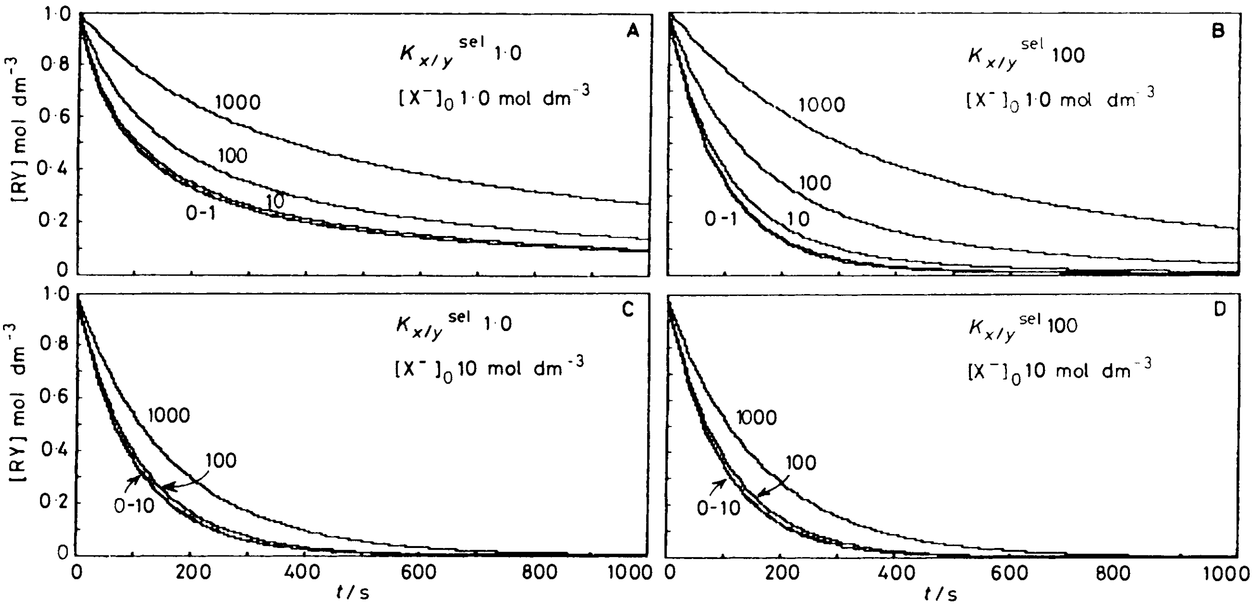

Figure 4. Kinetic profiles of a phase-transfer-catalysed irreversible S_N2 reaction of substrate RY at several $K_{z/x}^{sel}$, $K_{x/y}^{sel}$, and reactant concentrations. $[Q^+Z^-]_0 = 0.01$ mol dm^{-3}

the foreign ion ensures a low $K_{z/x}^{sel}$ value and consequently a low degree of poisoning. In the latter case, adding the p.t. catalyst in Q^+Z^- form is practically equivalent to adding it in Q^+X^- form. For this reason, the hydrophilic anions HSO_4^- and Cl^- are very common as counterions in p.t. catalysts.

The degree of quat poisoning by Z^- decreases relative to the initial state ($x = 0$) when $K_{x/y}^{sel} < 1$. Multiplying equation (3) by (4) leads to (6). For a given $K_{z/x}^{sel}$, $K_{x/y}^{sel} < 1$ entails a lower

$$K_{z/x}^{sel} K_{x/y}^{sel} = \frac{[Q^+Z^-]_{org}[Y^-]_{aq}}{[Q^+Y^-]_{org}[Z^-]_{aq}} = K_{z/y}^{sel} \qquad (6)$$

$K_{z/y}^{sel}$, which implies that Y^- competes better for Q^+ than does Z^-. Consequently, the concentration of Q^+Z^- decreases from the inital one as the reaction proceeds and more Y^- is liberated. The reverse is true for $K_{x/y}^{sel} > 1$. However, when the quat affinity is the same towards X^- and Y^-, as occurs at $K_{x/y}^{sel} = 1$, Q^+Z^- remains constant with conversion, and consequently the degree of poisoning by the foreign ion Z^- is also constant. The aforementioned behaviour is well illustrated in Figure 2 which shows the initial poisoning degree varying with $K_{z/x}^{sel}$.

The competition of the three anions for the quat cation Q^+ influences the observed kinetic profile. For a reversible reaction only Q^+Z^- is inactive and a higher $K_{z/x}^{sel}$ causes a slower reaction towards the same equilibrium conversion (Figure 3). Comparison of Figures 1D, E, and F with Figure 3A reveals that the foregoing observation parallels a larger integral area below the Q^+Z^- curve. However, one can see from Figure 3 that at equal initial concentrations of reactants, similar kinetic profiles are observed when $K_{z/x}^{sel} \leqslant 1$. Upon increasing the electrolyte concentration, it is seen that $K_{z/x}^{sel}$ may be less than 10 for an identical kinetic behaviour. Figures similar to Figure 3 but for higher catalyst concentrations confirm these observations. The higher equilibrium conversion for $K_{x/y}^{sel} = 100$ in Figure 3 is explained by equation (7), which is easily derived.[20]

$$\frac{[RX]_{org}[Y^-]_{aq}}{[RY]_{org}[X^-]_{aq}} = K_{org}K_{x/y}^{sel} \qquad (7)$$

A higher $K_{x/y}^{sel}$ increases the chemical equilibrium constant of the heterogeneous reaction and consequently its equilibrium conversion.

In an irreversible reaction, both Q^+Z^- and Q^+Y^- are inactive. Despite the previously mentioned dependence of the trend of Q^+Z^- concentration upon $K_{x/y}^{sel}$ (Figure 2), it is the sum of Q^+Z^- and Q^+Y^- which determines the poisoned proportion of the p.t. catalyst. Alternatively, a large or small integral area under the Q^+X^- curve (Figure 1) determines a correspondingly fast or slow reaction as observed by comparison of Figures 1D, E, and F with 4A. Contamination of the reaction system by the foreign ion Z^- always deactivates a portion of the p.t. catalyst and slows the reaction (Figure 4).

Figure 4 reveals that at equal initial concentrations of reactants, identical kinetic profiles are obtained for $K_{z/x}^{sel} \leqslant 1$. At a ten-fold initial X^- concentration, even $K_{z/x}^{sel} = 10$ does not appreciably alter the kinetic profile obtained when $K_{z/x}^{sel} = 0$, *i.e.* Z^- is absent. As in the case of the reversible reaction, adding the catalyst under these conditions in Q^+Z^- form is again practically equivalent to its addition in Q^+X^- form.

So far, we have used the term poisoning in the sense of holding the p.t. catalyst and preventing it from transferring the reactive anion from the aqueous to the organic phase. In much of the p.t.c. literature, it is used in the sense of a complete reaction inhibition as found experimentally.[13,21,22] According to Gordon and Kutina, who consider solely the exchanging anions, $K_{x/y}^{sel} < 0.1$ leads to a virtual standstill of the reaction after a small conversion fraction. This condition remains valid even when the p.t. catalyst is used in Q^+Z^- form. However, a phase-transfer reaction with a favourable $K_{x/y}^{sel}$ may be inhibited if $K_{z/x}^{sel}$ is very high or if the system is enriched with Z^-. Reactions with intermediate $K_{z/x}^{sel}$ are subject to a partial catalyst poisoning even though they proceed to completion or to equilibrium conversion. The need for a simultaneous solution of equations (2)—(5) reveals that the reaction rate is not a simple linear function of the total quat concentration as it is when Z^- is absent.[15] Disregarding this effect, which in fact reduces the effective catalyst concentration, results in an incomplete kinetic analysis. Such a case is reported by Starks and Owens[12] who studied the kinetics of 1-chloro-octane substitution with aqueous NaCN in the presence of hexadecyltributylphosphonium bromide. In this system, CN^-, Cl^-, and Br^- correspond to X^-, Y^-, and Z^- respectively, and $K_{z/x}^{sel}$ is estimated to be[15] *ca.* 20. These authors were surprised to find that the plot of the pseudo-first-order rate coefficients *versus* quat concentration had a negative intercept rather than passing through the origin. However, use of the reduced effective quat concentrations, resulting from catalyst poisoning by the foreign ion bromide, would no doubt have shifted the line towards the origin. Only when $K_{z/x}^{sel}$ ensures negligible poisoning (see before) is a linear dependence with zero intercept of reaction rates against the overall quat concentration in the organic phase expected.

Quite often, a choice has to be made between Q^+Y^- and $Q^+ Z^-$ forms of a p.t. catalyst. Kinetic profiles such as those of Figures 3 and 4 are practically identical in systems in which Q^+Y^- and Q^+X^- are initially used. However, the initial rates (at $t = 0$) in a phase-transfer system differ appreciably according to the form of the catalyst. While Q^+X^- yields the highest initial rate, $K_{z/y}^{sel}$ determines the preferred counterion Y^- or Z^-. When $K_{z/y}^{sel} = 1$ [equation (6)], which implies an identical quat affinity towards Z^- and Y^- as in Figures 1B and D, both Q^+Y^- and Q^+Z^- exhibit the same initial rate. However, $K_{z/y}^{sel} < 1$ ensures a higher initial Q^+X^- concentration in the organic phase, and consequently a higher initial rate when the catalyst is used in the Q^+Z^- form. The reverse is true when $K_{z/y}^{sel} > 1$.

Conclusions

The following conclusions arise from this study. (1) A phase-transfer reaction is best catalysed when the catalyst is initially used in the form of the reacting anion Q^+X^-. (2) When the p.t. catalyst contains a chemically inactive foreign ion (Q^+Z^-), the poisoning effect due to this anion is negligibly small when $K_{z/x}^{sel} \leqslant 1$. A ten-fold excess of electrolyte over the organic substrate concentration raises this lower limit to 10. (3) Under these conditions, the reaction rates depend linearly on the total quat concentration in the organic phase. (4) When $K_{z/y}^{sel} < 1$, the initial rate is higher when the p.t. catalyst is added as Q^+Z^- rather than as Q^+Y^-. The reverse holds when $K_{z/x}^{sel} > 1$.

References

1 E. V. Dehmlow and S. S. Dehmlow, 'Phase-Transfer Catalysis,' Verlag Chemie, Weinheim, 1983.

2 C. M. Starks and C. Liotta, 'Phase-Transfer Catalysis. Principles and Techniques,' Academic Press, New York, 1978.

3 W. P. Weber and G. W. Gokel, 'Phase-Transfer Catalysis in Organic Synthesis,' Springer Verlag, Berlin, 1977.

4 G. Lamaty, M. H. Riviere, and J. P. Roque, *Bull. Soc. Chim. Fr.*, 1983, 33.

5 D. Landini and F. Rolla, *Synthesis*, 1974, 565.

6 R. Lantzsch, A. Murkhold, and K. F. Lehment, Ger. Pat., 254644/1977.

7 C. Kimura, K. Murai, Y. Ishikawa, and K. Kashiwaya, *Sekigu Gukkai Shi*, 1976, **19**, 49 (*Chem. Abstr.*, 1977, **87**, 133781.)

8 G. A. Lee and H. H. Freedman, *Tetrahedron Lett.*, 1976, 1641.

9 H. H. Freedman and R. A. Dubois, *Tetrahedron Lett.*, 1975, 3251.

10 P. H. Hassanaly, H. Dou, and M. Ludwihow, *Bull. Soc. Chim. Belg.*, 1982, **91**, 661.

11 E. V. Dehmlow and S. S. Dehmlow, ref. 1, p. 15.

12 C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, 1973, **95**, 3613.

13 D. Landini, F. Montanari, and F. Rolla, *Synthesis*, 1974, 428.

14 S. S. Lele, R. R. Bhave, and M. M. Sharma, *Chem. Eng. Sci.*, 1983, **38**, 765.

15 J. E. Gordon and R. E. Kutina, *J. Am. Chem. Soc.*, 1977, **99**, 3903.

16 C. M. Starks and C. Liotta, ref. 2, ch. 2.

17 B. Carnahan, H. A. Luther, and J. O. Wilkes, 'Applied Numerical Methods,' Wiley, New York, 1969, p. 319.

18 R. Bar, L. K. Bar, Y. Sasson, and J. Blum, *Anal. Chim. Acta*, 1983, **154**, 313.

19 A. W. Herriot and D. Picker, *J. Am. Chem. Soc.*, 1975, **97**, 2345.

20 C. M. Starks and C. Liotta, ref. 2, p. 120.

21 C. M. Starks, *J. Am. Chem. Soc.*, 1971, **93**, 195.

22 Y. Sasson and H. A. Zahalka, *J. Chem. Soc., Chem. Commun.*, 1983, 1347.

Received 24*th November* 1983; *Paper* 3/2090