Mechanism of Phase-transfer Catalysis

By Dario Landini,* Angelamaria Maia, and Fernando Montanari*
(Centro C.N.R. e Istituto di Chimica Industriale dell' Università, Via C. Golgi 19, *Milano* 20133, *Italy)*

Summary Using liquid membranes it was shown that in phase-transfer catalysis the transport of anions from one phase into the other does not require the concomitant transfer of the organic cation; kinetic measurements indicate that the effectiveness of the catalyst depends essentially on its organophilicity.

The mechanism of phase-transfer catalysis in anion-promoted reactions, proposed by Starks[1] and supported by other authors,[2-4] implies that the catalyst transports the anion from the aqueous into the organic phase, where the reaction occurs, and then returns the leaving group into the aqueous phase. The efficacy of the catalyst, usually a tetra-alkylammonium or phosphonium salt, largely depends on its solubility in the organic phase.[2]

$$\begin{tikzcd}
RX + Q^+Y^- \arrow[r] & RY + Q^+X^- \arrow[d] & \text{(organic phase)} \\
X^- + Q^+Y^- \arrow[u] \arrow[r, shift left] & Y^- + Q^+X^- \arrow[l, shift left] & \text{(aqueous phase)}
\end{tikzcd}$$

Such a mechanism seems to involve the partitioning of the catalyst between the two phases, even if its solubility in water is so small as to be undetectable by the usual analytical techniques.

To solve this problem we employed liquid membranes.

In a 'U' system two independent organic phases (A) and (B) were connected through an aqueous solution of potassium bromide. When a quaternary ammonium or phosphonium bromide was dissolved in organic phase (A) and the system was stirred, equilibrium was achieved in a few hours, with partition of the quaternary salt between the two organic phases (A) and (B), provided that it was partially soluble in water (Table, nos. **1**, **3**, **4**, **6**, and **7**). In contrast, with quaternary salts which appear to be insoluble in water (nos. 2 and 5), no transfer from (A) to (B) could be detected even after several days.

$$C_8H_{17}OSO_2Me(org.) + Br^-(aq.) \xrightarrow{Q^+Br^-} C_8H_{17}Br(org.) + MeSO_3^-(aq.) \qquad (1)$$

When catalyst nos. 2 or 5 and the substrate were dissolved in phase (A) of the 'U' system and the inorganic salt in the aqueous phase, reaction (1) followed regular pseudo-first-order kinetics.[4] In analogous experiments in the presence of the other quaternary salts (nos. 1, 3, 4, 6, and 7), the rate of the reaction diminished with time until partition equilibrium of the catalyst between (A) and (B) was achieved. As expected, when the latter catalysts and the substrate were dissolved into the two separated organic phases (A) and (B), respectively, the rate of the reaction increased with time from zero up to a constant value. Under these same conditions no reaction occurred with catalysts (nos. 2 and 5) not soluble in the aqueous phase.

This indicates clearly that the activity of a phase-transfer catalyst does not necessarily imply its partial solubility in water, and thus that transfer of the anion can occur without a concomitant transfer of the organic cation from one phase to the other.

In the Table are reported the rate constants for reaction (1), carried out under the usual two-phase conditions in $PhCl-H_2O$,[4] in the presence of onium catalysts (nos. 1—7).

The observed pseudo-first-order rate constants differ by factors up to two powers of ten. However, the second-order rate constants, which take into account the actual concentration of the catalyst in the organic phase, are in a very narrow range, the maximum difference being a factor of 2·5.

TABLE. Influence of the catalyst on the rate constant in the reaction of n-octyl methanesulphonate with bromide ion in a $PhCl-H_2O$ two-phase system.[a]

No.	Catalyst[b]	% Catalyst in the organic phase	$10^5 k_{obs}/s^{-1}$	$10^3 k_{obs}/[cat]_{org}/(l\ mol^{-1}\ s^{-1})$
1	$Bu_4P^+Br^-$	97	10·4	2·7
2	$Bu_3(C_{16}H_{33})P^+ Br^-$	100	12·8	3·2
3	$Pr_4N^+Br^-$	2·5	0·24	2·4
4	$Bu_4N^+Br^-$	83	12·0	3·6
5	$(C_8H_{17})_4N^+Br^-$	100	20·4	5·1
6	$Pr_3(CH_2Ph)N^+$-Br^-	17	1·3	1·9
7	$Bu_3(CH_2Ph)N^+$-Br^-	95	8·2	2·1

[a] At 60 °C; 20 ml of a chlorobenzene solution of substrate (0·6 M) and 15 ml of an aqueous solution of KBr (4·2M). Kinetics were measured by following the disappearance of the methanesulphonate, in the presence of $PhOCH_2Ph$ as internal standard (^1H n.m.r. analysis). [b] 0·8 mmol in the system $PhCl-H_2O$.

This quantitatively confirms that the effectiveness of a phase-transfer catalyst depends mainly on its organophilicity, with other structural factors, such as the nature of the heteroatom, being much less important.

(*Received*, 2*nd December* 1976; *Com.* 1318.)

---

[1] C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195; C. M. Starks and R. M. Owen, *ibid.*, 1973, **95**, 3613.

[2] A. W. Herriott and D. Picker, *J. Amer. Chem. Soc.*, 1975, **96**, 2345.

[3] A. Brändström and H. Kolind-Andersen, *Acta Chem. Scand.* (*B*), 1975, **29**, 201.

[4] D. Landini, A. M. Maia, F. Montanari, and F. M. Pirisi, *J.C.S. Chem. Comm.*, 1975, 950.