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# Attempting to grade phase transfer catalysts

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ABSTRACT: Electrical potential oscillations across liquid–liquid interfaces in phase transfer catalytic systems were studied. The possibility of using the amplitudes of these oscillations as a criterion for grading the catalysts in order of their efficacies for a reaction was suggested. Gradation in the efficacies of the catalysts derived on the basis of the gradation in the amplitudes in the reactions of nucleophilic nature was shown to be in agreement with the gradation in the partition coefficients of the nucleophiles in the presence of the phase transfer catalysts. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: phase transfer catalysts; grading; electrical potential oscillations; relative efficacies; Aliquat 336; tetrabutylammonium chloride; cetyltrimethylammonium bromide; 18-crown-6

## INTRODUCTION

In phase transfer catalyst systems which are biphasic in nature, usually an aqueous phase containing one of the reactants is in contact with an organic phase containing other reactants. The phase transfer catalyst (PTC) may be dissolved in either of the two phases depending on its solubility. In the phase transfer catalytic reactions, a shuttling mechanism is known to operate.[1] The shuttling mechanism implies that if one inserts in the two phases two electrodes capable of sensing the ions, one should observe oscillations of electrical potential difference across the electrodes. In a recent study by our group, the existence of such oscillations has been demonstrated[2] in a few phase transfer catalytic reactions.

Although numerous reactions[3–5] have been carried out using phase transfer catalysts, very little comparative work is available which will enable one to grade the catalysts in order of their efficacies for a reaction. If such a gradation becomes available it will become easy to choose a proper catalyst for a reaction. An attempt made in this direction is described in this paper. Oxidation of benzaldehyde and benzyl alcohol and esterification of benzoic acid were chosen for study.

Since the amplitudes of electrical potential oscillations

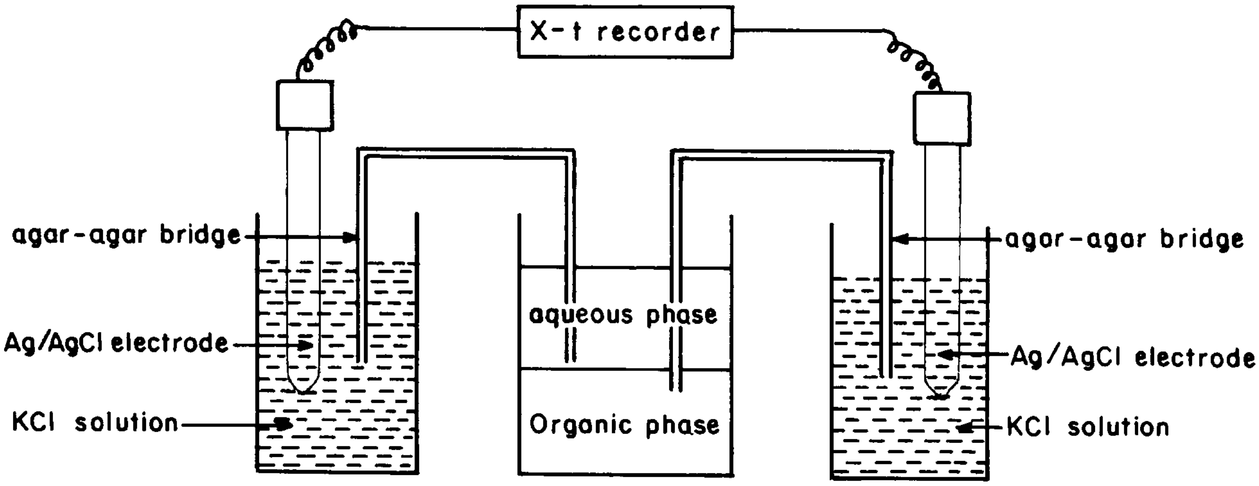

**Figure 1.** Schematic representation of the experimental set-up for monitoring electrical potential oscillations

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**Table 1.** Comparative study of oxidation and esterfication reactions using different PTCs[a]

| Description of the reaction system | Partition coefficient ($K_D$) | | | Product yield (%) | Amplitude of electrical potential oscillations (mV) | Traces of electrical potential oscillations shown in |
|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | P | | | |
| **I. Oxidation of benzaldehyde** | | | | | | |
| (a) $\frac{\text{benzene + benzaldehyde (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + TBAC (0.07 M)(aqueousphase)}}$ interface | 4.7840 | 0.0836 | 0.3165 | 51.0 | 7.2 | Fig. 2(a) |
| (b) $\frac{\text{benzene + benzaldehyde (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + 18-crown-6 (0.02 M)(aqueousphase)}}$ interface | 4.7992 | 0.0670 | 0.3342 | 45.2 | 6.4 | Fig. 2(b) |
| (c) $\frac{\text{benzene + benzaldehyde (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + CTAB (0.07 M)(aqueousphase)}}$ interface | 4.9783 | 0.0324 | 0.3550 | 11.3 | 0.40 | Fig. 2(c) |
| **II. Oxidation of benzyl alcohol** | | | | | | |
| (a) $\frac{\text{benzene + benzylalcohol (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + TBAC (0.07 M)(aqueousphase)}}$ interface | 2.348 | 0.0836 | 0.3165 | 58.8 | 8.0 | Fig. 3(a) |
| (b) $\frac{\text{benzene + benzyl alcohol (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + 18-crown-6 (0.02 M)(aqueousphase)}}$ interface | 2.5126 | 0.0670 | 0.3342 | 53.9 | 5.6 | Fig. 3(b) |
| (c) $\frac{\text{benzene + benzyl alcohol (organic phase)}}{\text{Acidic KMnO}_4\text{(0.01 M) + CTAB (0.02 M)(aqueousphase)}}$ interface | 2.551 | 0.0324 | 0.3550 | 50.5 | 4.8 | Fig. 3(c) |
| **III. Esterification reaction** | | | | | | |
| (a) $\frac{\text{benzoic acid(0.1 M) + NaOH (0.1 M) + TBAC (0.07 M)(aqueous phase)}}{\text{dichloromethane (organic phase)}}$ interface | 2.362 | 0.5524 | 0.5426 | 88.0 | 10.4 | Fig. 4(a) |
| (b) $\frac{\text{Benzoic acid(0.1 M) + NaOH(0.1 M) + CTAB(0.02 M)(aqueous phase)}}{\text{dichloromethane (organic phase)}}$ interface | 2.452 | 0.3932 | 0.5341 | 37.5 | 1.6 | Fig. 4(b) |
| (c) $\frac{\text{Benzoic acid(0.1 M) + NaOH(0.1 M)(aqueous phase)}}{\text{dichloromethane + Aliquat 336 (organic phase)}}$ interface | 2.8117 | — | 0.5311 | 28.5 | 0.40 | Fig. 4(c) |

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[a] In the control experiments where no PTCs were used (i) product yields were immeasurably low, (ii) no oscillations were observed and (iii) $K_D$ values for $R_2$ were immeasurably low.

in phase transfer catalytic reactions of a nucleophilic nature measure the relative concentrations of the nucleophile in the two phases, it appears logical to use them as criteria to grade the PTCs in order of their efficacies for a reaction. It has been shown that gradation in the efficacies of the PTCs derived on the basis of gradation in the amplitudes is consistent with the gradation in the partition coefficients of the nucleophiles between the two phases.

## EXPERIMENTAL

*Materials.* Aliquat 336 (Aldrich, Cat. No. 20,561.3), tetrabutylammonium chloride (TBAC) (Fluka, Cat. No. G5505), cetyltrimethyl ammonium bromide (CTAB) (Sigma, Cat. No. H5882) and 18-crown-6 (Sigma, Cat. No. C5515) were used. All other chemicals, e.g. benzene, benzyl alcohol, benzaldehyde and dichloromethane, were of analytical grade. Deionized water distilled twice in an all-Pyrex glass still was used for preparing aqueous solutions.

*Methods.* Electrical potential oscillations in different phase transfer catalytic systems were monitored using a set-up similar to that described earlier[2] (Fig. 1). The volume of both aqueous and non-aqueous phases was 25 ml. In all oxidation reactions, $KMnO_4$ solution was made acidic by adding a drop of concentrated hydrochloric acid. To monitor electrical potential oscillations, the sensing electrodes (Ag/AgCl electrodes obtained from ELICO, Hyderabad, India) were placed as close to the interface as possible and connected to an *x–t* recorder (Omniscribe Series 5000, Digital Electronics, Bombay, India). While monitoring electrical potential oscillations, the solutions were not stirred. Products were identified spectroscopically. The product benzoic acid formed in the oxidation reactions and bismethylene benzoate formed in the esterification reaction under unstirred conditions were estimated using methods described in the literature.[6,7]

All reactions were carried out for 4 h at constant temperature using a thermostat set at $30 \pm 0.1\,^{\circ}C$. In order to compare the yield in the case of different PTCs it was necessary to conduct all reactions for the same duration and at the same temperature.

## RESULTS AND DISCUSSION

Two oxidation reactions and one esterification reaction using different PTCs were investigated; the reaction systems are described in Table 1. Traces of electrical potential oscillations which are a consequence of the shuttling mechanism as shown previously[2] are shown in Figs 2–4. The amplitudes of electrical potential oscillations and also the product yields for each reaction system are also recorded in Table 1. It may be mentioned that since very little comparative work on phase transfer catalytic reactions is available, it is not possible to obtain from literature reports the values of the product yields under uniform conditions. The values of the product yields in Table 1 are for the reactions conducted for 4 h under unstirred conditions. Product yields in the control experiments where no PTC was used were immeasurably low.

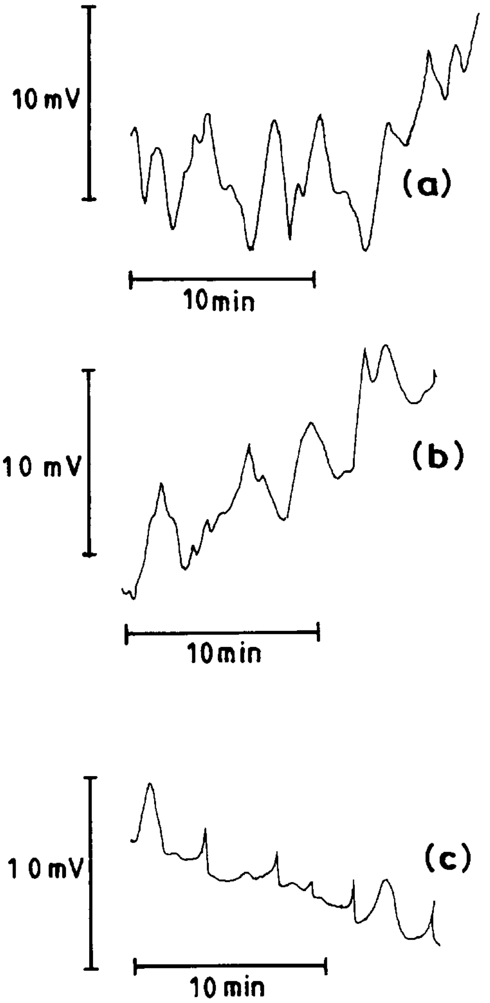

**Figure 2.** Traces of electrical potential oscillations in the oxidation of benzaldehyde using different PTCs: (a) TBAC; (b) 18-crown-6; (c) CTAB

The data in Table 1 reveal that gradation in the values of the amplitudes of the electrical potential oscillations in the case of different PTCs is the same as the gradation in the values of the product yields which should also be the gradation in the efficacies of the PTCs. Thus, (i) for the oxidation of benzaldehyde and benzyl alcohol, TBAC > 18-crown-6 > CTAB; and (ii) for the esterification reaction TBAC > CTAB > Aliquat 336. In fact, the product yields increase linearly with increase in amplitude (Fig. 5).

The gradation in the efficacies of the PTCs, which is

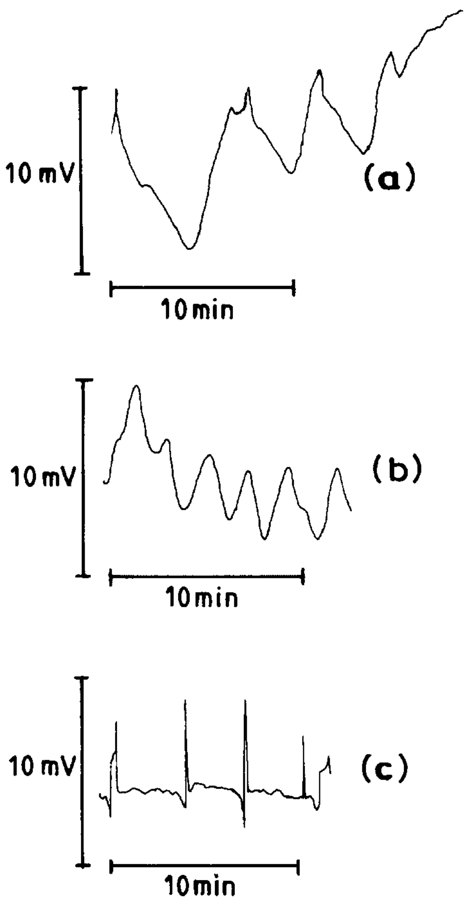

**Figure 3.** Traces of electrical potential oscillations in the oxidation of benzyl alcohol using different PTCs: (a) TBAC; (b) 18-crown-6; (c) CTAB

based on the gradation in the values of the amplitudes of electrical potential oscillation, is supported by the considerations of partition coefficients in the presence of PTCs. Consider a phase transfer reaction system schematically depicted as

$$\frac{\mathrm{R_1, P(organicPhase)}}{\mathrm{R_2(aqueousPhase)}}\text{interface}$$

where $R_1$ and $R_2$ represent the reactants present in the organic and the aqueous phase, respectively, and P represents the product formed. Let us consider the situation where the organic phase is the seat of reaction, which it is in case of all reactions studied here. Defining the partition coefficient $K_D$ as the ratio of the concentration $C_{org}$ in the organic phase to the concentration $C_{aq}$ in the aqueous phase, i.e. $K_D = C_{org}/C_{aq}$, it would be expected that product formation will be favored by (i) high values of $K_D$ for the reactants $R_1$ and $R_2$ and (ii) low values of $K_D$ for the product P.

The experimentally determined values of $K_D$ for oxidation and esterification reactions in the presence of different PTCs are recorded in Table 1. For oxidation of both benzaldehyde and benzyl alcohol, $R_2$ and P represent $KMnO_4$ and benzoic acid, respectively, whereas $R_1$ represents benzaldehyde in the oxidation of benzaldehyde and benzyl alcohol in the oxidation of benzyl alcohol. Similarly, in the esterification reaction $R_1$ represents dichloromethane which, in addition to being a reactant, is also the medium for the reaction, $R_2$ is the benzoate ion formed in the aqueous phase and P is the product bismethylene benzoate.

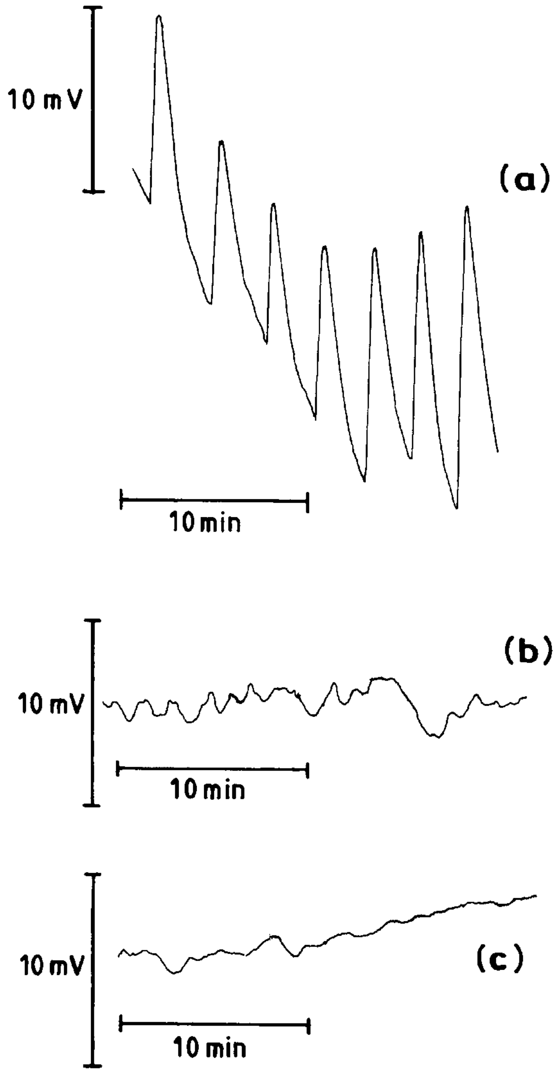

**Figure 4.** Traces of electrical potential oscillations in the esterification of benzoic acid using different PTCs: (a) TBAC; (b) 18-crown-6; (c) CTAB

It can be seen from Table 1 that the values of $K_D$ for $R_1$ and P in the case of all reactions studied do not show any significant variation with the choice of PTC, whereas the value of $K_D$ for $R_2$ does show a gradation. The value shows that the higher is the value of $K_D$ for $R_2$ in the presence of a PTC, the higher is the product yield. The gradation in the values of $K_D$ for $R_2$ in the presence of

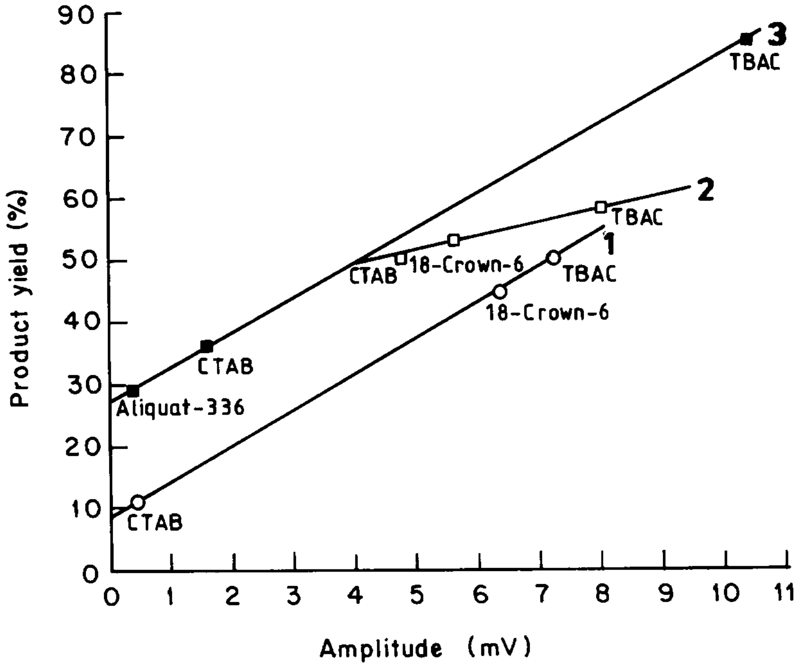

**Figure 5.** Variation of product yields with the amplitudes of oscillations in different phase transfer catalytic reactions. Curves 1 and 2 are for the oxidation of benzaldehyde and benzyl alcohol and curve 3 is for the esterification reaction

different PTCs is also the gradation in the product yields, which is as follows: (i) for the oxidation reactions, TBAC > 18-crown-6 > CTAB; and (ii) for the esterification reaction, TBAC > CTAB > Aliquat 336.

Thus the agreement between the gradation in the amplitudes of electrical potential oscillations with that in the value of the partition coefficient of the nucleophile appears to indicate that the former may be used as a criterion for grading phase transfer catalysts in order of their efficacies for a particular reaction.

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