

ORGANOMETALLIC SALTS AS PHASE TRANSFER CATALYSTS

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Summary: Six organometallic compounds were tested to see if they could behave as phase transfer catalysts. All of the compounds appeared to catalyze the base hydrolysis of p-nitrophenylacetate in a 2 layer aqueous-organic system.

Research on phase transfer catalysis (PTC) has largely been focused on applications to a wide variety of reactions and more recently on the mechanism of catalysis.¹⁻⁷ Relatively few studies have been done on the analysis and development of new catalysts.^{8,9} Different phase transfer catalysts can vary widely in such things as their ability to extract counterions into nonpolar solvents, their cost, their stability in strong alkali or acid, and their thermal stability. Consequently, it would be well worth examining other classes of compounds (not previously identified as catalysts) to see if they can be used in PTC. In this work we show that several organometallic compounds are sufficiently stable in controlled conditions to act as phase transfer catalysts in the same manner as traditional "onium" catalysts.

The base catalyzed hydrolysis of p-nitrophenyl acetate in an aqueous-organic two layer system was analyzed. Six compounds (triphenylgermanium chloride, triphenyllead acetate, triphenyltin hydroxide, tricyclohexyltin bromide, tri-n-butyltin chloride and dibutyltin dichloride) were tested for PTC properties. The rates of hydrolysis of p-nitrophenyl acetate using traditional "onium" catalysts, organometallic salts and no catalyst were compared. The results are given in Table 1 (infra vide).

All six organometallic salts show PTC activity over the time scale of this reaction. A comparison of the triphenyl metal salts of the IV A elements (germanium, tin and lead) indicates that those metals with the larger ionic radius are slightly better catalysts. The aliphatic analogue (tricyclohexyltin bromide) was superior to all of the aryl catalysts. The most surprising result involved dibutyltin dichloride. This was the only disubstituted compound tested. Because it had fewer hydrophobic groups, it was not expected to be an effective phase transfer catalyst. Quite to the contrary, it proved to be the most effective catalyst of all the organometallic salts tested for this particular reaction.

Table 1. Pseudo First Order Rates of Hydrolysis of p-Nitrophenyl Acetate in a Two Layer Aqueous-Organic System Using Different Phase Transfer Catalysts.^a

Catalyst	Stirring Rate, rpm	Temperature, °C	$10^2 k_{\text{obsd}}$, sec. ⁻¹
none	800	20	0.33
tetraphenylphosphonium bromide	800	20	2.48
tetrabutylammonium bromide	800	20	2.66
triphenylgermanium chloride	800	20	1.50
triphenyllead acetate	800	20	1.83
triphenyltin hydroxide	800	20	1.62
tricyclohexyltin bromide	800	20	2.00
tri-n-butyltin chloride	800	20	1.28
dibutyltin dichloride	800	20	2.37

^aThe organic layer consisted of 30 ml of 0.025 M p-nitrophenyl acetate in cyclohexane. The aqueous layer consisted of 30 ml of 0.75 M NaOH. The concentration of the appropriate catalyst (in the aqueous layer) was always $1.1 \times 10^{-3} \text{M}$. The disappearance of p-nitrophenyl acetate (from the organic layer) was monitored spectrophotometrically at 265 nm.

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