

NOTE**Phase Transfer Catalysis: Ester Bond Cleavage in Non-polar Medium with Hydroxyl Group**

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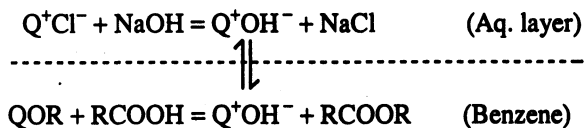
A benzene solution of the ester when subjected to reaction with aqueous sodium hydroxide in the presence of a small quantity of tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst (PTC), benzoic acid was formed in more than 70% yield in about 6 h. The saponification rates of benzyl benzoate in 60% (v/v) acetonitrile-water and 60% (v/v) dioxane-water solvents were measured and were found to be relatively less.

Key words: Phase transfer catalysis, Ester bond cleavage.

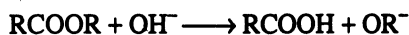
Studies on phase transfer catalysis for various reactions have assumed great importance during recent years. Even though aqueous protic or aprotic solvents can be used for studying the hydrolysis of water-soluble esters, the study of the hydrolysis of ester bond cleavage with hydroxyl group of water-insoluble esters in non-polar solvents remains in its infancy. The use of phase transfer catalysts offers immense hope in this field. Ester bond cleavage in non-polar solvents like benzene, carbon tetrachloride etc. with hydroxyl group cannot be ordinarily carried out due to the immiscibility of aqueous solutions of sodium hydroxide in the non-polar media. In such situations and in situations where use of toxic organic solvents like acetonitrile, dioxane etc. are to be avoided, the phase transfer technique can be applied for ester bond cleavage with hydroxide. The present paper is on the phase transfer catalyzed ester bond cleavage of benzyl benzoate with hydroxyl in benzene using tetrabutyl ammonium bromide (TBAB) and a comparative rate study of the saponification of the same ester in aqueous acetonitrile and aqueous dioxane solvents. The phase transfer catalyzed ester bond cleavage in the heterogeneous situation has technological importance.

It can be seen from Table-1 that the percentage yield of benzoic acid increased with increase in the concentration of the catalyst under identical conditions. The quantity of the catalyst used is a factor related to the yield of the acid. Larger amount of the catalyst is required for getting larger yield. The yield of benzoic acid is 70% when the substrate-catalyst ratio is 1 : 0.25 while a 1 : 0.01 ratio only yielded 25% of benzoic acid. The reaction appears to occur as a consequence of

the following phase transfer equilibrium. If Q represents the TBAB cation, then the following equilibria will be obtained:



It appears to proceed as a nucleophilic displacement of the OR group by the hydroxyl as given in the following chemical equation.



The tetrabutyl ammonium hydroxide formed in the aqueous layer gets phase transferred into the benzene layer where it provides very reactive hydroxide which easily reacts with the ester in a nucleophilic substitution reaction to produce benzoic acid. The tetrabutyl ammonium alkoxide formed, having a better organic structure, would like to be more partitioned into the benzene layer. Hence the fraction of QOR getting phase transferred into the water layer to exchange the anion with NaOH would be less and hence more of the catalyst is needed for bringing about greater percentage of the reaction by transferring more and more of the hydroxyl into the non-polar layer. The rate constant data for different temperatures for the classical saponification reaction of the same ester in the aqueous dipolar aprotic solvents presented in Table-2 shows that the reaction is very slow. The phase transfer catalysed heterogeneous reaction therefore is quite advantageous as far as ester bond cleavage of difficultly hydrolyzable esters are concerned.

TABLE-1
EFFECT OF THE QUANTITY OF TBAB ON THE YIELD OF BENZOIC ACID
(HETEROGENEOUS PTC REACTION)

Solvent : Benzene Temp : 60°C		Ester : 1 m NaOH : 5 m
Quantity of TBAB (g)	Duration (h)	Percentage yield (by weight)
0.5	6	25.6
1.0	6	46.5
1.5	6	71.0
2.0	6	71.0

Pure samples of benzyl benzoate and commercially available tetrabutyl ammonium bromide were used. Benzene was purified by the known standard method. AnalaR quality sodium hydroxide was used. The cleavage of the ester bond under phase transfer catalysis was carried out in a heterogeneous mixture of 5 g of benzyl benzoate in 20 mL of benzene mixed with 25 mL of a 5 N solution of sodium hydroxide containing 0.5 g of the catalyst. The mixture was stirred mechanically for about 6 h while keeping the mixture at 60°C. The experiments were repeated with different quantities of the catalyst and the results

are presented in Table-1. The rate studies in the aqueous dipolar media were carried out as typical ester saponification rate measurements. The rate data of such studies are presented in Table-2.

TABLE-2
SAPONIFICATION RATES OF BENZYL BENZOATE IN AQUEOUS DIPOLAR
APROTIC SOLVENTS (HOMOGENEOUS REACTION)

Ester : 0.04 m		NaOH : 0.05 m		
Temp. (°C)	10 k L mol min			
	60% aq. acetonitrile		60% aq. dioxane	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
31.5	5.19	6.39	7.89	8.72
36.0	7.33	8.21	8.87	9.29
40.0	9.05	10.02	10.90	11.84
45.0	12.71	14.00	12.05	15.00

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