

Clay-Supported Quaternary Ammonium and Phosponium Cations in Triphase Catalysis and the Effect of Cosolvent in Catalytic Activity

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In this research, a naturally occurring clay mineral, hectorite, was used as the support for several quaternary ammonium and phosphonium cations to measure and compare their catalytic activity in a triphase catalytic system. The intercalation of the catalysts in the clay has the advantage of easy catalyst recovery; the catalyst can be removed by a simple separation technique, such as filtration or centrifugation, upon completion of the reaction. The rate of conversion of *n*-butyl bromide to *n*-butyl chloride was measured in the presence of two classes of phase transfer catalyst: Quaternary ammonium and quaternary phosphonium cations. The rate of the reaction was measured for the biphasic reactions (no supporting clay) and for the triphase catalytic system (with supporting clay). The results have shown that quaternary phosphonium catalysts are somewhat more reactive than the corresponding quaternary ammonium catalysts. It was also found that the intercalated catalysts could be used several times before losing their catalytic activity. Also, a remarkable increase in catalytic activity has been observed using a co-solvent. However, it appears that there is a limit for the co-solvent concentration to be effective.

INTRODUCTION

The application of Phase-Transfer Catalysis (PTC) in the past few decades has become prevalent in academic research, as well as in commercial processes [1-4]. Some of the advantages that this technique offers are increased reaction yield, requirement of only mild reaction conditions, safety, requirement of inexpensive solvents and reagents and the ability to conduct reactions on a commercial scale. However, the recovery and recycling of relatively expensive phase transfer catalysts from the liquid phase has been a challenge for this technique. The treatment of the reaction mixture associated with soluble catalysts imposes limitations on the applicability and usefulness of PTC as an industrial technique of synthesis. Recently, Triphase Catalysis (TC) has been introduced by Regen [5-8] as a unique type of heterogeneous catalysis, in which the catalyst and each of a pair of reactants are located in different

phases. Based on this technique, synthetic methods have been developed for aqueous-organic phase reactions using solid catalysts, such as synthetic polymers or various clay minerals. TC shows considerable potential for commercial application. Several commercially available ion-exchange resins, such as Dowex resins, containing quaternary ammonium groups, have been studied as triphase catalysts [9]. Also, quaternary ammonium salts immobilized on insoluble polymers and inorganic oxides, such as silica and alumina, have been extensively explored in TC. However, silica, alumina and polymers are relatively unstable in strong acidic or alkaline environments and they normally suffer from poor physical strength. In contrast, clays have better physical strength, better resistance towards alkali treatment and are relatively inexpensive. Recently, some investigations have appeared on the application of clays as solid supports for quaternary salts [10-16].

In the present investigation, a study on the use of clay of the smectite family, hectorite, is reported as support for quaternary ammonium and phosphonium salts. Smectite clay minerals are among members of various layered silicates with 2:1 mica-like layer lattice structures. Naturally occurring negative charges on the clay layers are balanced by interlayer cations that occupy intercalated positions between the interlayers.

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Naturally occurring alkali and alkaline earth cations in the pristine clay minerals can be replaced by almost any desirable cation. Cation exchange in this type of clay mineral is relatively rapid. Smectite or swelling clay has a great affinity towards water, as well as organic reagents. This unique wetting property makes the clay quite attractive for catalysis. Earlier work [17,18] has demonstrated that alkyl ammonium ions intercalated in smectite clay produce ordered structures, in which the alkyl chains and the ammonium groups form a specific orientation, with respect to the clay layers. Thus, these structures depend on the length of the alkyl chains and the charge density of the clay layers. Chi-Li Lin et al. [19] have indicated that onium ions within the clay have an emulsion-forming ability, which, most likely, is related to the amphiphilic nature of onium ions on the external surfaces of the clay tactoids. Thus, by adopting parallel or perpendicular orientations at the clay-liquid interface, the onium ions may show hydrophilic or organophilic wetting properties.

The rate of conversion of *n*-butyl bromide to *n*-butyl chloride was measured in the presence of two classes of phase transfer catalysts: Quaternary ammonium and quaternary phosphonium salts. The rate of the reaction was measured for the biphasic catalytic system (no supporting clay) and for the triphase catalytic system (with supporting clay). The results have shown that quaternary phosphonium catalysts are more effective than the corresponding quaternary ammonium catalysts. It was also found that the intercalated catalysts could be recycled several times without significantly losing their activities.

EXPERIMENTAL

Unless stated otherwise, all reagents were obtained commercially and used without further purification.

Natural Hectorite

Naturally occurring sodium hectorite, with particle size $< 2 \mu\text{m}$, was obtained in the precentrifuged and spray-dried form. The idealized anhydrous unit-cell formula of hectorite is $\text{Na}_{0.66} [\text{Li}_{0.66} \text{Mg}_{5.34}] (\text{Si}_{8.00})\text{O}_{20} (\text{OH}, \text{F})_4$; the experimentally determined cation-exchange capacity is about 73 meq/100 g and the surface area is about $750 \text{ m}^2/\text{g}$ of air-dried clay. The clay contains two major impurities that may interfere with the catalytic reactions. These are calcium carbonate and free (non-lattice) iron oxides, which can inhibit intercalation of the clay, because they act as cementing agents, which prevent flocculation from occurring. The impurities also interfere with the determination of the Cation-Exchange Capacity (CEC) of the clay. These two major impurities are removed prior to intercalation, in order to promote flocculation of the freeze-dried clay.

Adding sodium acetate buffered to pH 5 with acetic acid converts calcium carbonate to carbon dioxide, which is removed when heated to 70°C . 10 g samples of clay were used to remove carbonates and soluble salts. First, 100 mL of 1 N sodium acetate buffered to pH 5 with acetic acid was added to the clay in a blender. The clay suspension was then heated for 1 hour at 70°C with occasional stirring. The solution was then centrifuged and the supernatant was analyzed on an atomic absorption spectrophotometer (Varian Spectra AA-10) for the amount of calcium. Standards were prepared from 1000 ppm Fisher standards. The previous steps were repeated until the amount of calcium was less than 2 ppm.

Free iron oxides are removed by the addition of a sodium citrate/sodium bicarbonate solution and with treatment by sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$). 80 mL of 0.3 N sodium citrate and 10 mL of 1N NaHCO_3 were added to the clay suspension in water. The mixture was then heated to $75\text{--}80^\circ\text{C}$ and 2 g of sodium hydrosulfite was slowly added. Care was taken not to heat above 80°C to prevent FeS precipitation. The clay suspension was heated for 15 minutes. The resulting solution was centrifuged and the supernatant was analyzed for the amount of iron. A typical atomic absorption calibration curve was constructed to measure the amount of iron in ppm.

Hydrogen peroxide was employed to digest organic matter in the clay. A 30% solution of hydrogen peroxide (150 mL for 10 g clay) was mixed with the clay slurry for 15 minutes at room temperature. Then, the clay was saturated with sodium by addition of sodium chloride (10% solution, 200 mL). The mixture was stirred for another 15 minutes, then centrifuged. The clay was then washed four to five times until free of chloride ions (test with silver nitrate solution). After this process, the clay was freeze-dried using a VirTis bench top freeze-dryer. Typically, the freeze-drying is done overnight.

Preparation of Clay Intercalates

Intercalation reactions of all cations were performed under similar conditions, since all the quaternary onium salts were quite stable and also soluble in water. In a typical experiment, a 1.0 wt% aqueous suspension (e.g. 0.1 g of the mineral in 10 mL H_2O) was added to a vigorously stirred aqueous solution of the quaternary onium salt containing about 1.2 meq/meq of clay. The reaction mixture was stirred for over an hour. After an equilibration time of 24 hours, the clay was repeatedly washed with deionized water and then collected by centrifugation. The resulting homoionic quaternary onium cation-exchanged forms of the minerals were air-dried or freeze-dried, as desired, and stored in desiccators over anhydrous CaCl_2 .

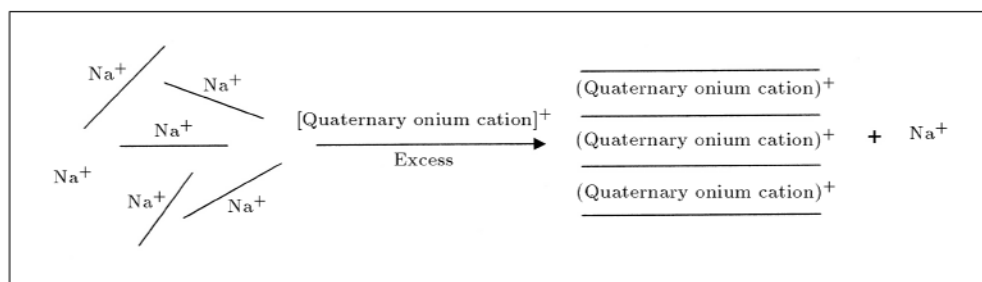


Figure 1. Schematic representation of onium cation exchange reaction. Lines represent the negatively charged clay layers.

Kinetics of Biphasic and Triphase-Catalyzed Displacement Reactions

The reactions of alkyl bromides with NaCl under triphase conditions were carried out as follows: Air dried [hectorite] [(onium head cation)⁺][X⁻] (0.037 meq of quaternary onium salt as catalyst) was dispersed in 3.0 mL aqueous 3.3 M NaCl in a 15 × 150 mm Pyrex culture tube fitted with a Teflon-lined screw cap and magnetic stir bar. The mixture was stirred for a few hours until a homogeneous suspension was obtained. To the suspension was added 1.0 mmol of the appropriate alkyl bromide in 2 mL of toluene. The tubes were sealed with a Teflon-lined screw cap and vigorously shaken for a minute. The kinetics experiment was then started by placing the tube in an oil bath maintained at the desired temperature, while the reaction mixture was constantly stirred using a stir bar. No significant change in the rate of reaction was observed due to change in the stirring rate. Perhaps mass transfer is not a limitation for this reaction.

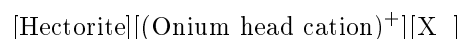
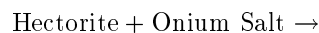
The reaction was followed by withdrawing 1- μ L samples of the organic phase at different times (no less than 30 minute intervals) and monitoring the disappearance of the reactant by gas chromatography. For sampling, the tube was removed from the oil bath, shaken, quickly cooled by ice water to below room temperature, opened, resealed and returned to the bath after sampling with a small syringe. The overall process took less than one minute. The temperature of the oil bath used for the kinetic experiments was controlled to $\pm 1^\circ\text{C}$ with the aid of a temperature controller. The product mixture was analyzed by gas liquid chromatography.

RESULTS AND DISCUSSION

Comparing Catalytic Reactivity of two Different Onium Ion Hectorite Intercalates

Naturally occurring sodium within the smectite clay interlayer is rapidly replaced by onium salt cations in aqueous solution. The exchange reaction may be

represented as follows:



Hectorite clay intercalate.

These types of intercalates were used to study triphase catalysis. To prepare the triphase catalysts, onium salts were added in excess of the clay Cation Exchange Capacity (CEC) and the clay intercalates were washed several times with water to remove the excess onium salts (see Figure 1). Earlier investigations [17,19] have shown that, depending on the type and size of the alkyl chain of the onium salt, the thickness of the clay layer expands beyond a monolayer of onium ions. This results in a basal spacing of about 18 \AA or more by x-ray powder diffraction, depending on the size of the alkyl group, since the van der Waals thickness of the clay layer is only about 9.6 \AA . Since the quaternary onium cations are sandwiched between the clay interlayers, a larger cation will create a larger lateral surface. In general, a cation that creates a larger lateral surface area is expected to result in higher catalytic activity.

In the present study, various quaternary ammonium and phosphonium salts have been used as biphasic, as well as triphase, catalysts for side by side comparison. Schematic representations of biphasic and triphase catalytic systems are given in Figures 2 and 3. All the catalysts are used in nucleophilic displacement reactions converting *n*-butylbromide to *n*-butylchloride. This halogen ion displacement was

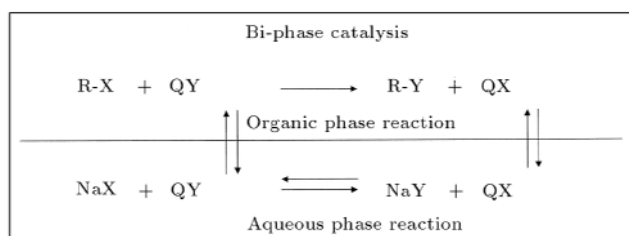


Figure 2. Schematic representation of biphasic displacement reaction.

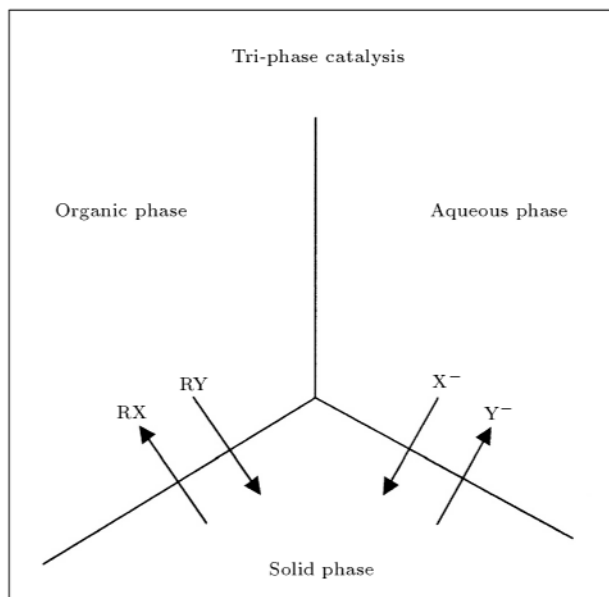


Figure 3. Schematic representation of the triphase system using quaternary onium clay intercalates as solid phase.

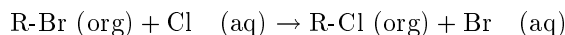
conducted in 50 mL culture tubes, using the procedures described in the experimental section. Sodium chloride was added in high concentration (several times more than alkyl bromide) to remove the dependency of the observed rate constant (K_{obs}) for the displacement reaction on the chloride concentration. Also, no significant change in the rate constant was observed by the rate of stirring. Rates of reaction were monitored by following the disappearance of the starting alkyl halides from the organic phase, using gas liquid chromatography, every half hour.

In the clay catalytic system, alkyl halide and halide anion from the organic phase and the aqueous phase, respectively, are transferred to the interface of the solid clay intercalate where they can react. These quaternary onium ion hectorite intercalates help to stabilize emulsification of the organic aqueous mixture and, as a result, help to improve the reactivity and

catalytic reactions at the aqueous liquid/organic liquid interface. In fact, the emulsification being facilitated by the clay intercalates helps to bring the nucleophile from the aqueous phase into contact with the substrate, which is contained in the organic phase. It is anticipated that a higher degree of emulsification leads to higher catalytic activity. It is important to mention that the emulsion formation is not a limitation for this triphase system, since the emulsions can be easily broken through a simple separation technique, such as filtration or centrifugation. It seems that the degree of emulsification depends on the nature of the onium cation and the characteristics of the intercalates, as well as the organic solvents.

It is interesting to note that once the onium cations are intercalated, their exchange with sodium ions in the aqueous layer is not favored, due to the great affinity that clay exhibits for these kinds of catalyst. Therefore, this phenomenon prohibits biphasic catalytic reactions within the solution, since little or no leaching of quaternary onium cations out of the clay intercalates occurs, despite the high concentration of sodium ions within the reaction mixture (sodium chloride concentration in the aqueous phase is about ten times higher than *n*-butylbromide).

Several quaternary onium catalysts have been used (see Table 1) for intercalation, to investigate the effects of alkyl chain length, size and shape of these catalysts and, also, to observe a difference between ammonium and phosphonium catalysts, according to the equation below. For all of the catalysts used, a pseudo first order reaction was observed. Since $[Cl^-] \gg [1\text{-bromobutane}]$, the complete kinetic equation can be written in the following form. The reaction rate constants are given in Table 1.



$$d[1\text{-bromobutane}]/dt = k_{obs}[1\text{-bromobutane}]$$

In comparison, somewhat lower catalytic activity has been observed for tetrabutylammonium or phospho-

Table 1. Pseudo first-order rate constants at 90°C for the chlorination of *n*-butyl bromide in the presence of a quaternary onium cation-hectorite intercalates as triphase catalysts and also under biphasic reaction conditions.

Type of Quaternary Onium Salt Used in the Catalytic Reactions	Unsupported Biphasic Catalytic System k_{obs}, hr^{-1}	Clay Supported Triphase Catalytic System k_{obs}, hr^{-1}
Tridodecylmethylammonium chloride	0.420	0.260
Hexadecyltributylphosphonium bromide	0.600	0.550
Tetrabutylammoniumchloride	0.065	0.032
Tetraoctylphosphoniumchloride	0.260	0.057
Tetraoctylammonium bromide	0.740	0.430
Tetraoctylphosphonium bromide	0.880	0.610

nium intercalates, while somewhat higher catalytic activity has been observed in the biphasic reactions (see Table 1). Due to the relatively large size of onium ions, it is fair to assume that there are no interlayer surfaces available for catalytic reactions. Thus, the reactions are occurring only at the lateral surfaces of the clay intercalates rather than inside the interlayers. When the onium catalysts are small, such as tetrabutyl ammonium or phosphonium bromide, they are unable to separate the clay layers to a great extent and, as a result, the lateral surfaces decrease considerably. This may directly affect the rate of the reactions.

Comparing tetraoctylammonium bromide with tetraoctylphosphonium bromide catalysts, somewhat higher activity has been observed with tetraoctylphosphonium, both in biphasic and triphase catalytic systems. Despite the fact that the non-symmetrical quaternary onium salts of ammonium and phosphonium have different alkyl chain length and anion, Hexadecyltributylphosphonium bromide has still shown higher activity than Tridodecylmethylammonium chloride. The higher catalytic activity of phosphonium ion in comparison with the ammonium ion counterpart, has been observed for biphasic catalytic reactions [20]. It is interesting that a similar trend has been observed for the triphase catalytic system, using clay-supported phosphonium and ammonium cations.

A few of these clay intercalates have been recycled several times after being washed with distilled water and no significant catalytic activity loss has been observed. This indicates that these types of catalyst are quite stable and robust. However, all of the quaternary onium cations used in this study, when intercalated, show lower activity than in a biphasic system. A loss of catalytic activity upon onium ion intercalation is a general feature of triphase catalysis and is not an uncommon phenomenon [19].

Effect of Cosolvent in Triphase Catalytic System

In a triphase catalytic system, reagents from two immiscible liquid phases are transferred to the interface of a solid (in this case, intercalated clay catalyst), where the reaction occurs. The reaction products at the interface are then returned to the liquid phases, in

which they are soluble. Smectite clays have dual characteristics, both hydrophilic and hydrophobic. This exceptional property is even enhanced when the clay is intercalated with onium ions and helps to stabilize small droplets of three-phase emulsion, which serve as an aid to the rate of the catalytic reaction. To further stabilize the emulsion formation of the clay intercalates, a relatively polar cosolvent (ethylene glycol) was introduced into the triphase catalytic system. The expectation was to observe an enhancement in the catalytic activity. In this study, tetraoctylammonium clay intercalate was used as the solid phase to carry out nucleophilic displacement reactions converting *n*-butylbromide to *n*-butylchloride. The results of this study are given in Table 2, where three different concentrations of the cosolvent are used. As the results indicate, catalytic activity is increased more than three times when only 5% of water is replaced by ethylene glycol as a cosolvent. This remarkable increase in catalytic reactivity due to cosolvent may be related to better emulsion formation in the triphase system. However, it is interesting to note that when the amount of cosolvent was subsequently increased by two- and four-fold, the catalytic activity somewhat dropped rather than increased. This reaction was repeated a few times to make sure that the decrease in the observed reaction rate, upon increasing the cosolvent concentration, were not an experimental error.

In this investigation, it seems that certain concentration mixtures create a metastable solution that helps the demulsibility rather than the emulsification enhancement of the system, which is necessary to increase interfacial surfaces available for reaction. Thus, it appears that there is an optimum concentration of co-solvent that can contribute to emulsion stability. This results in a maximum catalytic activity in the clay-supported triphase catalytic system. Since clay has hydrophobic, as well as hydrophilic, characteristics, it appears that a fine concentration balance needs to be kept to stabilize emulsion formation within the catalytic reaction mixture. Thus, the choice of a proper solvent or cosolvent is critical to the catalytic activity of the clay-supported triphase system. In this regard, perhaps the Henson Solubility Parameter [21] can be a proper guide in choosing a right solvent mixture to achieve the maximum catalytic activity. Investigations

Table 2. Effect of co-solvent in the rate of nucleophilic displacement reaction.

Solvent System	% Co-Solvent (Ethylene Glycol)	Rate of Reaction at 90°C k_{obs} , hr ⁻¹
Toluene/water	0	0.43
Toluene/water/ethylene glycol	5	1.20
Toluene/water/ethylene glycol	10	0.56
Toluene/water/ethylene glycol	20	0.44

of various solvent polarities in the triphase system and their effect on catalytic activity are in progress.

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