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Use of Polymer Supported Catalysts and Reagents for Organic Reactions

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Abstract - Phase-transfer catalysis (PTC) is an efficient method for the synthesis of organic reactions involving two immiscible-phased substances. The objective of the study is the creation of diverse soluble and insoluble phase-transfer catalysts for the synthesis of various chemical compounds under heterogeneous circumstances using ultrasonic energy. For chemical identification and analysis, the following instrumental characterizations were utilized: GC, NMR, FTIR, Mass spectrum, Ultrasonification, TLC, Column chromatography, and SEM examination. In heterogeneous conditions, the kinetic analysis of these organic processes was conducted using soluble and insoluble phase-transfer catalysts (PTCs). For each organic reaction, the thermodynamic parameters activation energy (Ea), enthalpy of activation (H#), entropy of activation (S#), and free-energy of activation (G#) were determined. We postulated a plausible mechanism for each system based on the kinetic findings obtained. The comparison analysis demonstrates that the ultrasonic aided phase-transfer catalyst exhibited more reactivity increases than the standard phase-transfer catalyst(s) alone. The current phase-transfer catalysis is thus concluded to be a key synthetic tool, valued not only in diverse disciplines of organic chemistry, but also in several industrial applications.

Keywords - Phase Transfer Catalysis (PTC), Phase Transfer Catalyst, Immiscible Phase, NMR, FTIR, Activation Energy, Ultrasonification, Enthalpy of Activation, Free-energy Activation, Entropy of Activation

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INTRODUCTION

The increasing significance of "green chemistry" in the synthesis of organic compounds has prompted the development of environmentally friendlier synthetic techniques. Green chemistry is an approach that tries to alleviate pollution and sustainability issues by producing environmentally friendly chemical processes. For organic synthesis to be called eco-friendly or green, it must satisfy at least some of the following criteria: Important steps in developing sustainable chemical processes include avoiding waste, being atom efficient, avoiding the use and production of toxic and dangerous chemicals, producing compounds that perform as well as or better than existing ones and are biodegradable, avoiding auxiliary substances (such as solvents), reducing energy requirements, utilising renewable materials, and using catalysts in place of stoichiometric reagents. Less desirable are chemical processes that produce considerable volumes of byproducts and waste in addition to the intended output.

Careful design of chemical processes may reduce the quantity of embodied energy, including physical, metabolic, and other kinds of energy, as well as the environmental consequences of excessive energy use. In the pharmaceutical and agricultural sectors, where bioactive molecules are often too fragile to withstand bulk chemical conditions, the need for selective transformations is at an all-time high. During a synthetic transformation, it is essential to study the potentially hazardous properties of all molecules that must be synthesised, as well as the potentially hazardous properties of all starting materials and reagents. In several processes utilized today, selective transformations using catalytic processes assist reduce the quantity of stoichiometric auxiliary chemicals needed, which may ultimately result in reduced waste production. In addition, they can perform the crucial synthetic transition in a manner that is less harmful to the natural environment.

Since environmental and economic concerns have developed in recent years, chemists are now compelled to seek out as many environmentally friendly catalytic reactions as is technically practicable. Despite the similarity of the basic concepts behind diverse forms of catalysis, heterogeneous catalysis, homogeneous catalysis, and bio catalysis have grown into three distinct scientific fields. This dispersion is a consequence of the diverse procedures and research methods used by the many disciplines. These methods and techniques provide the majority of the input for catalyst development and process design. Catalysis, which played such an important part in the expansion of industry in the 20th century, will also play an important role in the creation of a more environmentally friendly industry in the 21st century. Not only can catalysis help green chemical processes (by substituting reagents or allowing for more efficient processes, for instance), but the demonstration of their value will accelerate the greening of chemistry by minimizing the negative environmental impact of processes and reducing the costs associated with those effects. (6) In 1835, the word "catalysis" was used to describe a situation in which the addition of a tiny quantity of a foreign substance accelerated the rate of a chemical reaction without consuming the foreign component. At that time, catalysis was recognized as a fascinating phenomenon, and continuous attempts have been undertaken to better comprehend it and identify its practical applications. This has led to the creation of many technologies that have improved the level of life for humanity in this century. Almost every part of the chemical industry relies on catalysis, and its direct and indirect contributions account for more than 20% of the gross domestic product of industrialized countries.

In many instances, the creation of medications, insecticides, pigments, photosensitive chemicals, monomers, and other similar compounds requires the use of a multi-stage chemical process that requires the use of a broad range of chemicals, catalysts, solvents, and other similar things. In order to complete the reaction, it is essential that the chemicals interact with one another to the greatest extent possible. On the other hand, these processes are often seen as intrinsically irreversible. To bypass the immiscibility issue, it is necessary to move a moisture anion exchange reactant into an organic-soluble reactant or organic phase. Using protic and aprotic solvents, rapid stirring rates, and high temperatures are some of the more typical approaches (7) for overcoming this immiscibility. These methods, on the other hand, are not without their downsides, which include a high energy consumption, the creation of byproducts, purifying challenges, and environmental harm. Thus, these practices are undesirable, inadequate, and contribute to industrial pollution.

- **History of PTCs:**

Late in the 1960s, a practical method referred to today as "phase transfer catalysis" (PTC) (8) was developed to overcome the encounter issue produced by the mutual insolubility of aqueous and organic phases. This key green method (9) that reduces waste utilizes water as a solvent and is applicable to a wide range of processes in which chemical & chemical metal ions, typically three to five, mix with organic substrates. Utilizing unequal two separate solutions, one component (water) is a storehouse of responsive anions or base for the creation of organic anions, while the second phase (organic) consists of sustainably cultivated reactants and catalysts. Combinations of lipophilic ions with lipophilic cations provided by the catalyst continuously release reactive anions into the organic phase. Starks et al. (8) proved that the immiscibility of a combination of sodium chloride cyanide and 1-chlorooctane prevents nucleophilic aliphatic substitution. Minutes after the addition of 1% hexadecyl tributyl phosphonium bromide, cyanide ions are transported into the organic phase, and 1-cyanooctane is produced quantitatively.

- **Steps involved in PTCs:**
  1) The stage in the transfer reaction in which the reactant anion is transferred from the aqueous or solid phase into the organic phase and the product anion is transferred from the organic phase into the aqueous or solid phase.
  2) The phase of the reaction known as the intrinsic reaction, during which the product is generated in the organic phase. The optimization of each of these phases is dependent on a number of factors, the most important is the phase transfer catalyst's physical structure.
- **Mechanism of PTC:**

In general, LLPTC involving simple displacement reactions is described by Stark's Extraction mechanism (8, 18) / Brandstorm-Montanari modification (19, 20), while hydroxide-initiated reactions have been represented by either Stark's Extraction mechanism (8, 18) or Makossa's Interfacial Mechanism. (21).

Stark's Reaction:

In this specific process, the Quaternary salt (Q+ X^-) is amphilic, i.e., it has both organophilic and hydrophilic properties, and is thus dispersed across stages organic and aqueous (Figure: 2). The intact phase transfer cation-anion pairs are transferred to the organic phase through the interfacial area. (8, 17, 18, 22).

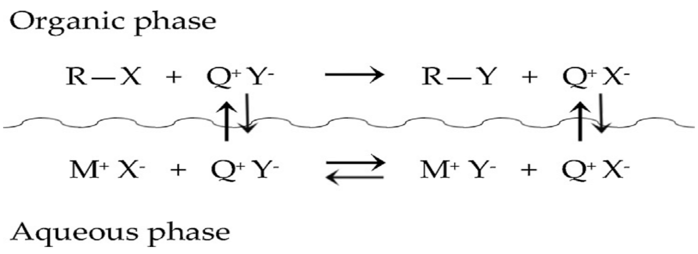

Figure 2: Stark's Reaction

Source: https://www.researchgate.net/

Brandstorm-Montanari Modification:

The catalyst in this refined procedure is so organophilic that it cannot survive in the inorganic phase of the reaction. In this case, the reactant as well as the product, anions, are transferred into the organic phase by a two-step process that begins with an exchange of species at the interface in the vicinity of the cationic complexation reagent. (20)

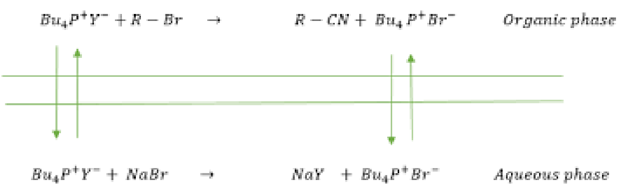

Figure 3: Brandstorm-Montanari Modification

Source: http://ethesis.nitrkl.ac.in/6836/1/PHASE_Sethi_2015.pdf

Interfacial Mechanism:

The "interfacial mechanism," as proposed by Makosza (23), is a second potential mechanism. First, in contradiction to the extraction method, the interfacial OH- interacts with both the organic acid R-H to produce the corresponding solvated carbanion. In the second stage, the carbanion is coordinated well with phase transfer cation and moves from the interfacial region through into bulk organic phase.

The last step in an alkylation process that takes place in an organic phase. In contrast, the phase transfer cation is not engaged in the interfacial mechanism where deprotonation of the organic acid happens at the aqueous-organic interface. The phase transfer cation's one and only purpose is to combine with the produced carbanion and transfer it to the organic phase, where it may react with either an organic electrophile. Here is a schematic of the Makosza interfacial phenomenon (24):

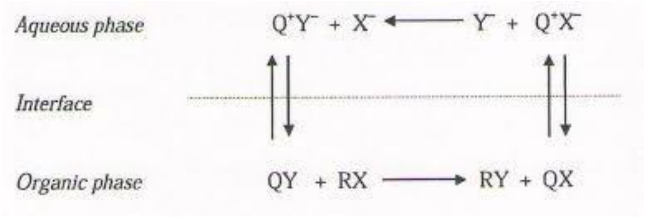

Figure 4: Makosza's Interfacial Mechanism

Source: https://www.ijstr.org/final-print/april2012

- **Selecting Phase Transfer Catalysts:**

The following are two conditions that are absolutely necessary for a PTC (17):

1. The phase transfer agent must be cationic and include sufficient organic structure to partition the nucleophilic anion into the organic phase. This is only possible if the agent has sufficient organic structure.
2. To ensure that there is a high amount of anionic reactivity, the cation-anion bond must be suitably loose.
3. When selecting a phase transfer catalyst, the stability of the catalyst under the reaction conditions, the ease of its separation or recovery, the convenience with which it can be made or acquired, its activity, and its toxicity are all relevant factors.

- **Applications of PTCs:**

PTC is used in several chemical processes. Its principal uses in the presence of bases are nucleophilic substitution reactions and deprotonation of moderately and weakly acidic organic molecules. PTC-catalyzed reactions include oxidations, reductions, polymerizations, transition metal co-catalyzed reactions, synthesis of carbenes and further reactions of carbenes, addition reactions, condensations, etc., which are performed frequently in multi-step synthesis processes for the production of fine chemicals. Alkylations of mildly acidic organic molecules mediated by bases. This eliminates the need for harsh anhydrous conditions, costly solvents, and hazardous bases such as metal hydrides and organometallic reagents (27).

In biphasic systems, instead of dangerous alkali metal alkoxides, amides, and hydrides, simple, inexpensive, and mild bases such as NaOH and K2CO3 may be utilized in the presence of a phase transfer catalyst. Makosza (9), for instance, was a pioneer in the C-alkylation of active methylene compounds, such as activated benzylic nitriles, activated hydrocarbons, and activated ketones, under PTC/OH- conditions, which is extensively employed in a variety of essential chemical processes. In certain instances, according to Dehmlow, enhanced selectivity is an additional benefit of these reactions. In the presence of 50% NaOH, phase separation prevents the hydrolysis of the organic substrate during carbene reactions. In commercial applications, the necessity to separate the catalyst from the organic phase of the product is one of the most important drawbacks of PTC. At the end, several generic separation approaches are explored. Immobilizing the PTC on a stable substrate is another way to sidestep the difficulties connected with catalyst recovery. This is further covered in the section about ultrasonography in PTC systems (28).

METHODOLOGY

The research technique for this study was determined based on a literature review, an industry survey, and statistical methodologies, with possible sub-sections containing several parameters, different tables and figures, and data collection and analysis. For chemical identification and analysis, the following instrumental characterizations were used: GC, NMR, FTIR, Mass spectrum, Ultrasonification, TLC, Column chromatography, and SEM analysis.

- **Synthesis of Soluble and Insoluble PTCs:** To be synthesised are one insoluble PSPTC, one di-sites (PSDSPTC-II), and one tri-site (PSTPTC-III), as well as one soluble single-site (SSPTC), three di-sites (SDSPTC-II), and one tri-site (STPTC-III).
- **Confirmation of structure of onium salts:** In order to verify the structures of the onium salts, spectroscopic techniques such as FT-IR, 1 H-NMR, 13C-NMR, scanning electron microscopy, and mass spectrometry will be used.
- **Examination of comparative catalytic efficiencies of PTCs:** Under identical pseudo-first order conditions, the relative catalytic efficiencies of all of these PTCs will be compared as they undergo a variety of organic reactions, including O-allylation, O-alkylation, and O-arylation; C-cinnamylation, C-arylation, and C-spirolation; S-alkylation, S-alkylation, and S-arylation of various alkyl and aryl halides; and dichlorocyclopropan
- **Examination of Superiority of MPTCs:** It will be determined using constants of a pseudo-first order in the rate of change of four different chemical processes whether or not the MPTCs are better.
- **Effect of various Experimental Parameters:** Analyses of the thermodynamic parameters activation energy (Ea), enthalpy of activation (ΔH#), entropy of activation (ΔS#), and free-energy of activation (ΔG#) have to be performed for each organic process. Each of the experimental factors, in addition to sonication, ought to have a direct influence on the rate at which the reaction is proceeding. On the basis of the findings, appropriate mechanisms will be provided for each of the responses.

RESULTS

- The first time that eight distinct soluble and insoluble PTCs were analysed. This contains one soluble single site (SSPTC), three di-sites (SDSPTC-II), and one tri-site (STPTC-III); one PSPTC, one di-sites (PSDSPTC-II), and one tri-site; and one insoluble single site (PSPTC), one di-site (PSDSPTC-III) (PSTPTC-III).
- The structures of these onium salts were verified using a range of spectrum techniques, including FT-IR, 1H-NMR, 13C-NMR, SEM, and mass spectroscopic examinations, among others.
- It has been found that the inclusion of a multi-active site in each MPTC (a molecule) should always boost the molecule's catalytic efficacy to a larger degree than single-site PTCs; hence, the new MPTCs should reduce the cost of the reaction process.
- Examined were the relative catalytic efficiencies of these PTCs in a variety of organic reactions, including O-Allylation, O-Alkylation, and O-Arylation; C-Cinnamylation, C-Arylation, and C-Spirolation; S-Alkylation, S-Alkylation, and S-Arylation of various alkyl and aryl halides; and dichlor (40 KHz, 300W).
- In order to determine the effect that different experimental parameters, such as stirring speed, [substrate], [NaOH], [MPTC's], and temperature, have on the rate of the reaction, detailed kinetics were performed for each of the four different organic reactions while maintaining pseudo first-order reaction conditions and varying experimental parameters. This was done to determine the influence that these various experimental settings had on the rate of the reaction.
- The rate of the response is directly influenced by all experimental variables, including ultra-sonication.
- In addition, the value of 'Ea' and other thermodynamic parameters such as DS1, DG1, and DH1 are calculated and presented for each of the four processes. On the basis of this kinetic data, we have constructed a mechanism applicable to each of these reactions.

CONCLUSION

The process of phase-transfer catalysis, often known as PTC, is an effective approach for the synthesis of chemical reactions that involve two compounds that cannot mix phases. The production of a wide variety of phase-transfer catalysts, both soluble and insoluble, for the synthesis of a wide variety of chemical compounds under heterogeneous conditions is the purpose of the research. Ultrasonic energy will be used in the process. The following instrumental characterizations were utilized for the purposes of chemical identification and analysis: gas chromatography, nuclear magnetic resonance, Fourier transform infrared, mass spectrum, ultrasonification, thin-layer chromatography, column chromatography, and scanning electron microscopy. The kinetic investigation of these organic processes was carried out utilising both soluble and insoluble phase-transfer catalysts under circumstances characterised as being heterogeneous (PTCs). The values of the thermodynamic parameters activation energy (Ea), enthalpy of activation (H#), entropy of activation (S#), and free-energy of activation (G#) were calculated for each organic process. On the basis of the kinetic observations that were obtained, we hypothesised a mechanism that may explain each system's behaviour. According to the findings of the comparative study, the phase-transfer catalyst with ultrasonic assistance displayed greater gains in reactivity than the regular phase-transfer catalyst(s) did on their own. The conclusion that can be drawn from this is that the present phase-transfer catalysis is an essential synthetic tool. This tool is valuable not only in several subfields of organic chemistry, but also in a variety of applications in industry.

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