



PHASE TRANSFER CATALYSIS FOR GREEN CHEMISTRY

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Abstract: *The problem of “Green Chemistry” using like example phase transfer catalysis has been discussed in the present paper. Nowadays catalysis plays a very important role in the new green chemical industry. Catalysis can reduce the environmental impact of processes and therefore can reduce the costs of these processes. Application of new catalysts and catalytic systems aim to achieve both environmental protection and economical benefits. The PTC technology has been chosen and is used in these applications, because it provides many compelling benefits, primarily related to the cost reduction of organic manufacture chemicals and secondly because it prevent the environmental pollution.*

Keywords: *Green chemistry, sustainable development, phase transfer catalysis PTC, pollutions.*

1. Introduction

Globalization and countries industrial development creates fast changes on environment fact that conduct to the opportunity of occurrence of new principles for definition of tasks of a society. Moreover, the increases changes of the extreme climatic phenomena are worsening more and more the situation on a global scale.

It is widely acknowledged that there is a increase need of the human society for a more environmentally acceptable processes in the chemical industry. In the present paper the idea of green chemistry develops as a philosophy of chemical research that tried to minimize the use and the production of dangerous substances. The focus is to minimize the substance

chemical danger and to maximize the efficiency of any chemical choose.

Catalysis has played such a vital role in the success of the chemical industry in the 20th century, the application of this process ranging from pharmaceuticals to petroleum processing fields. More than 90% of all industrial processes are based on catalysis process. The widespread utilization by industry of catalytic processes has a positive influence on the economic and environmental safety [1].

One of the best way to realize of chemical processes, specially in organic reactions is the phase transfer catalysis - PTC [2,3]. Cost reduction and pollution prevention are the two most powerful driving forces in the chemical industry today, and they match precisely the strengths and benefits provided by phase transfer catalysis.

Phase transfer catalysis conduct to high productivity, increase environmental performance, improved safety environment, and increase plant operability in hundreds of commercial manufacturing processes for organic chemicals in dozens of reaction categories [2, 3].

2. Materials and methods

Green chemistry and the principles

The developing of green chemistry methodologies is a challenge that can be presented through the framework of the “Twelve Principles of **Green Chemistry**” [4].

The principles of **Green Chemistry** [4] compared with the advantages of PTC are presented in table 1.

The principle number 9 identifies the catalysis as one of the most important tools for implementing green chemistry.

Nowadays, organic synthesis, especially fine chemicals and pharmaceuticals use “stoichiometric” technologies.

Some of these reactions types were transformed in phase transfer catalytic (**PTC**) system.

PTC is one of the most efficient methodologies in organic synthesis and therefore it. It was widely used for the synthesis of organic compounds. **PTC** uses as phase transfer catalyst onium salts (as quaternary or phosphonium ammonium salts /**Quat**/, **crown ethers** and others/, who facilitate the transport of one reactant into the other and interaction between reagents in two immiscible phases. **PTC** is widely used in the organic chemicals synthesis for both two and tri- phase systems. The use of **PTC** can be combined with other rate enhancement techniques like microwaves, sonochemistry and others.

PTC has made possible to use cheaper and easily available alternative raw materials, avoiding in these way the need of using severe anhydrous conditions, expensive

solvents, and dangerous bases such as metal hydrides and organo-metallic reagents. **PTC** uses much fine organic chemistry instead of toxic alkali metal alkoxides, amides, and hydrides.

Table 1
A comparison of the principles of Green Chemistry and PTC advantages

N	Principles of Green Chemistry
1.	Waste prevention instead of remediation
2.	Atom efficiency
3.	Less hazardous and toxic chemicals
4.	Safer products by design
5.	Innocuous solvents and auxiliaries
6.	Energy efficient by design
7.	Preferably renewable raw materials
8.	Shorter syntheses
9.	Catalytic rather than stoichiometric reagents
10.	Design products for degradation
11.	Analytical methodologies for pollution prevention
12.	Inherently safer processes
N	Advantages of PTC
1.	Minimization of industrial wastes
2.	High reactivity and selectivity
3.	Less dangerous, inconvenient and expensive reactants
4.	High yields and purity of products
5.	Less inconvenient and expensive organic solvents
6.	Low energy consumption
7.	Simplicity of technology
8.	Possibility to mimic counter-current process

An important issue in organic chemistry technology is the use of organic solvents. The principle of PTC also proposes the use of usual and environmental friendly solvent that coincides with the number 5 principle for green chemistry. For both of them it necessary to use the solvents with different characteristics like: low toxicity, easy recyclability (no disposal) and further desirable characteristics - easy removal from the product and. In this case some solvents should never be used: *tetrachlorocarbon*, *1,2-dichloroethane*, *1,1-dichloroethane* and some solvents are preferred like *water*, *CO₂*, *heptane*, *tert-butyl methyl ether*, *ethyl acetate*, *tert-butyl alcohol*, *ethanol*.

We are mentioned below the solvents are more convenient to be used for green chemistry technologies:

2.1. Water as a reaction medium

Economically and Environmentally attractive

- Inexpensive and abundantly available
- Non-inflammable and non-toxic
- Odorless and colorless

Highly polar reaction medium

- Facile product separation
- Reduced product contamination.

2.2. Supercritical CO₂ as a reaction medium

T_c 31.0 °C, p_c 73.8 bar, d_c 0.477 kg L⁻¹

- Low viscosity (more like a gas than like a liquid); hence, fast mass transfer
- Cheap and abundantly available
- Easy to remove
- Non-toxic, non-inflammable, inert.

PTC tries to use no toxic reagents, solvents and other materials as we seen in the number 3 principle for green chemistry.

One of the other advantages of **PTC** is it lower energy and simplified technology – as we can see from the number 6 principle. However, the main disadvantages of **PTC**, especially in commercial applications, are the necessity to separate the catalyst from the organic phase. Further, is important to show the difference between homogenous and heterogeneous catalysis.

Phase transfer catalysts can be either homogeneous (soluble in one or both solvents) or heterogeneous. The place **PTC** in catalytic systems between homogenous and heterogeneous, because of its catalytic system allowed to transfer heterogeneous system into the homogenous one – as in **PTC** liquid-liquid system. In this case appeared the possibility to use the advantages of homogenous catalysis. Quaternary ammonium and similar onium salts (**Quat**), **crown ethers** with alkaline metal cation and other provide a source of

singly charged lipophilic cations. Generally, catalyst efficiency is influenced by the large number of carbon atoms and the symmetry of the carbon atom chains around the heteroatom that provide high lipophilicity [2,3]. Homogenous **PTC** is based on the mechanism proposed [2].

Table 2
Advantages and disadvantages of catalytic systems

Catalytic system	Advantages	Disadvantages
Homogeneous	Mild reaction condition, High activity and selectivity, Efficient heat transfer	Cumbersome separation and recycling of catalyst
Heterogeneous	Facile separation of catalyst Continuous processing Product contamination	Heat transfer problems Low activity and selectivity products Not readily adapted

Biphasic homogeneous catalysis integrates reaction and products and catalyzes separation into one single operation:

- Other possible solutions;
- Supported liquid phase catalysis;
- Thermo-regulated biphasic catalysis supported liquid phase catalysis.

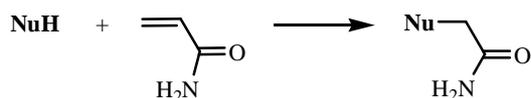
PTC is used also in solid-liquid system, which is coming more as a heterogeneous system and even more heterogeneous when we have tri-phase system. **PTC** linked to a polymer or inorganic matrix are described as heterogeneous catalysis. In this system the catalysts play role as like a third system, for instance, the immobilized on alumina / and other inorganic material/ or polymers quaternary ammonium salts or crown ethers. Here can include also polyethyleneglicols (**PEG**) [2, 3] and polypropargyl alcohols [2].

For **Quat** and **crown ethers** the situation is: catalyst is bonded to a matrix forming a third immiscible solid phase between the organic and aqueous ones involving a swelling, mixing and diffusion during the reaction. Due to diffusion retardation, reactions with slow intrinsic reaction rates are much slower with a tri-phase catalyst than with its homogeneous counterpart [2,3]. The use of tri-phase **PTC** simplifies the removal of the catalyst after the reaction which can be re-used until they lose their mechanical stability.

Here we discussed about C–C Bond formation as **Michael** condensation in **PTC** system.

3. Results and discussions

PTC is efficiently applicable for base-induced reactions of organic anions as Michael reaction. This reaction mentioned concern the chemists from the perspective point of view. Unsaturated compounds (acceptor groups), and compounds with donor group (**CH**-acid) receive new connections with the most different groups [5, 6].



NuH – the molecule of conforming **CH** - acid (see table 3).

This reaction one of two major categories of **PTC** reaction, when anion generated *in situ*/there is an anion from acetoacetic acid ethyl ether that reacts with **acrylamide**. Here is studied the interaction of **acrylamide** with some accessible classic **CH** - acids – malonic ester or diethylmalonate (**ME**), acetoacetic ester or ethyl acetoacetate (**AAE**), ethyl ether of cyanoacetic acid (**ECA**) and acetylacetone or pentanedione-2,4 (**AA**).

All these reagents react with **acrylamide** as the type of 1,4-addition for **Michael** reaction.

The conversion of **acrylamide** with **CH** - acids is implemented in a water-alkaline medium, in conditions of **PTC** as catalyst of phase transfer carry were applied with different **Quats**.

Table 3
The molecule of conforming **CH** - acid

NuH	Nu ⁻
malonic ester (ME)	
ethyl ether of cyanoacetic acid (ECA)	
acetoacetic ester (AAE)	
Acetylacetone (AA)	

Influencing of **CH** - acids structure and catalysts on a reaction rate constant and yields of product is studied.

It is visible from the results in table 4 **ME** and **ECA** in conditions of Michael addition to **acrylamide** are very close on reactivity. The **AAE** reacts with **acrylamide** a little bit more slowly, than **ECA** or, in particular **ME**. The reaction for **AA** is more slowly. At the same time, outgoing from values of dissociation constants of this **CH** acids, diverse sequence of reaction speeds was expected: **ME** (pK~13) < **CAE** (pK~11) < **AAE** (pK~11) < of an **AA** (pK~9). Probably, the main role in the control of reaction speed is played by solvation of **CH**-acids or their complexes with catalyst in aqueous phase, where an addition reaction flows past. In this case, the anion of more strong acid and slowing down for

reacting, because of solvation effects is most solvated for that is also more.

The speed of **Michael addition** in **PTC** conditions depends not only on a **CH-acid**, but also, at largely, from used catalyst (table 4).

Table 4
The yield of addition products of **CH-acids** to **acrylamide**

Catalysts	The yield Michael addition product (%)			
	ME	CAE	AAE	AA
Without catalyst	4.0	3.0	3.75	1.75
TMACI	60	40	75	28
TMHACI	80	58	80	40
TMBACI	85	70	80	45
TMDHACI	90	85	90	60

Outgoing from an extreme length of radical alkyl chain of 1, the best catalytic activity shown trimethylhexadecylammonium or trimethylcetyl-ammonium chloride (**TMDHACI**), is objective, as well as least, shown by tetramethylammonium chloride. To activity of chlorides trimethylhexyl and trimethylbenzylammonium (**TMBACI**) are rather close, despite of a little bit large length hexyl radical, as contrasted to benzyl. Despite of a little bit smaller, than for **TMDHACI** catalytic activity, (**TMDHACI**), nevertheless, is perspective catalyst because of the availability that can have crucial importance, in case of organization for a commercial production.

On our point of view, in a reduced example of **Michael addition**, the important organic reaction, **PTC** demonstrates actual chance for an approaching to principles **Green Chemistry**.

It is necessary to mark also, that here for the first time is described new reaction of **acrylamide** for synthesis of the very relevant products, in particular for synthesis physiologically and bacteriological active compounds. In this

paper have not gone deep into mechanistic estimations of the conducted reaction, as it implements in called of an inverse **PTC**.

4. Conclusion

The experiments were conducted in the reactor of ideal mixture at 300C. Initial concentrations of a **CH-acid** and **acrylamide** at 1,5-1,75 mol/L; it was compared yields of experiments by confrontation constants of reaction speeds in the supposition, that at enough high concentration of catalyst - 0,1 mol/L, what, for utilized of **Quat**, in 1,7- 5 times for above critical concentration micelle formation (**CMF**) - change of concentration for catalyst cease is appreciable to have an effect for reaction speed. Current concentration of the conforming **CH-acid** determined (**GLCh**) through 10 minutes from a beginning of reaction.

The yields of addition reaction product was determined on expiration of an estimated time of reacting indispensable for achievement of 95% transformation for reagents (receiving conditionally selectivity for reacting equal 100 %). In tab. 4 the yields of addition products for investigated **CH-acids** to **acrylamide** are described.

Due to the features and advantages of **PTC** here was considered as an efficient for green chemistry.

5. References

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