Kinetic Studies and Simulation of Cyanobutylation Between Butanol and Acrylonitrile

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Abstract— **Cyanobutylation is one of the most important reactions in chemical industry which is followed to produce butyl acrylate. Butyl ester of acrylic acid is used in paints, sealants, coatings, adhesives, fuel, textile, plastics. This work completely covers the kinetic study of cyanobutylation reaction. Acrylonitrile and butanol are reacted with suitable solid ion exchange IRA-400 catalyst for certain time to produce butyl acrylate. Different mole ratio of acrylonitrile to butanol and by varying mass of solid catalyst the effects on conversion, yield and other parameters is studied. Product formed is analyzed to cheak its physical and chemical properties. Some features of this cyanobutylation are observed which are important from design, operational and control point of view, are presented.**

Index Terms— **Cyanobutylation, Michael addition, basic catalyst, butyl acrylate**

I. INTRODUCTION

The catalytic addition of alcohols or amines to a carbon-carbon double bond provides a useful method for the preparation of ethers and amines. Cyanoethylation, the addition of alcohols or amines with active hydrogen to acrylonitrile, has attracted significant interest for the synthesis of drug intermediates, plasticizers, insecticides, emulsifiers, additives for synthetic rubber, and physiologically active compounds. The resulting nitriles can be converted to different types of amines after hydrogenation or can form the related carboxylic acid. Usually, cyanoethylation can be promoted in the presence of a base. The homogeneous basic catalysts so far reported for the cyanoethylation of alcohols are alkali hydroxides, alkali alkoxides, and tetraalkylammonium hydroxides, alkyl mercaptans, cresols, and partial pyrophosphate esters. Neutralization of these soluble catalysts prior to purification of the product generates waste and reduces the product yields. In most cases, bleaching steps are necessary for the removal of color arising from impurities. Low selectivity is an additional problem [1].

As chemical education has evolved, it has seen numerous trends become mainstay modes of teaching in the classroom. The use of computational chemistry is one example. Until the turn of the 21st century, the use of computational chemistry to explain phenomena in organic chemistry was reserved for individuals or institutions with access to specialized software. The use of computations and the visually stunning three-dimensional output from these calculations is now available to students in a growing number of textbooks. Two other prevalent trends in chemistry education are the emphasis on chemistry's relationship to the fields of biology and medicine, and the incorporation of research data and results into lectures and laboratory experiments. As students become more accustomed to these methods of presenting chemical concepts, instructors will need to find more examples that allow them to incorporate these modes of presentation into their daily lectures [2].

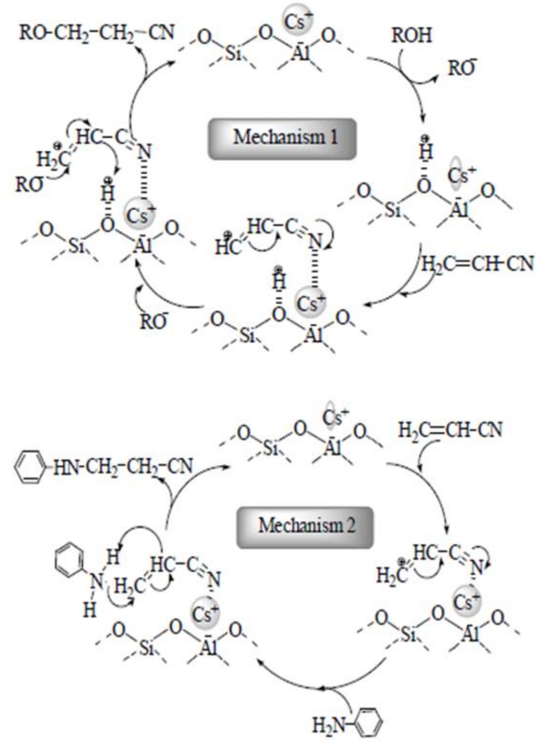
The Michael addition of carbon nucleophiles is one of the most important carbon carbon bonds forming reactions in organic synthesis. However, the base catalyzed reactions often suffer from the formation of side products. These include nucleophilic attack of the base, re- arrangements, polymerization of the Michael acceptor or secondary condensation reactions of the intermediate enolate, transesterifications, cyclocondensations and above all retro Michael reactions. To circumvent these problems several catalysts such as phase transfer catalysts, alumina, alkali metal halides or transition metal complexes have been successfully used [3].

In the last few decades great attention has been paid to the development of polymer blends. Blends offer the possibility of combining the properties of available materials to produce new materials with better properties. Polycarbonate (PC) is an amorphous polymer with good mechanical properties, but it can result in brittle failure, depending on the environmental factors. On the other hand, acrylonitrile–butadiene–styrene (ABS) is widely used as a thermoplastic with good physical properties, but the overall mechanical properties of ABS are lower than those of other engineering plastics. PC and ABS can be blended to improve their applications these blends have been reported to have a useful balance of toughness, heat resistance, and ease of processing. Nevertheless, the properties of this blend could be affected if commercial polymers contain low molecular weight species such as monomers, oligomers, and others additives that accumulate at the interface. These effects can be reflected in changes in their calorimetric, mechanical, or dielectric properties. PC and ABS are immiscible, and the blend presents phase separation. Two glass-transition and two main dynamic mechanical relaxation processes appear in the blend. ABS is a copolymer containing a block of polybutadiene to which styrene–acrylonitrile (SAN) random copolymer has been grafted. Thus, in the PC/ABS blend the interface between the two phases present is in fact a PC/SAN, which has also been reported to be immiscible [4].

Cyanobutylation reaction of alcohols and amines to related nitriles [1].

$$\underset{\text{ALCOHOL}}{\text{R-OH}} + \underset{\text{ACRYLONITRILE}}{CH_2\text{=CH-CN}} \xrightarrow{\text{BASE CATALYST}} \underset{\text{ACRYLATE}}{\text{R-O-}(CH_2)_2\text{-CN}}$$

Reaction mechanism [1]



II. LITERATURE REVIEW

1. Sara Zamanian, Ali Nemati Kharat: Studied that Zeolite Y modified by cesium and magnesium ions was prepared by ion-exchange and impregnation methods, and its activity in the cyanoethylation of aliphatic and aromatic alcohols and amines was investigated. During the preparation of some samples, the transformation of zeolite Y into a pollucite- type phase occurred. This phase exhibited good activity in the cyanoethylation of aliphatic alcohols. The prepared solids modified by the impregnation method were more active than the ion-exchanged solids. The activities of the catalysts, in contrast to other basic solids, were scarcely affected by the presence of air or moisture. A correlation between catalyst basicity and catalytic activity is discussed. The catalysts were characterized by X-ray diffraction, volumetric nitrogen adsorption surface area measurement, and CO2 temperature-programmed desorption. Scanning electron microscopy revealed that the particles of the modified nanocatalysts were < 40 nm. The reaction of acrylonitrile with linear alcohols in the presence of the catalysts was accelerated by microwave irradiation.

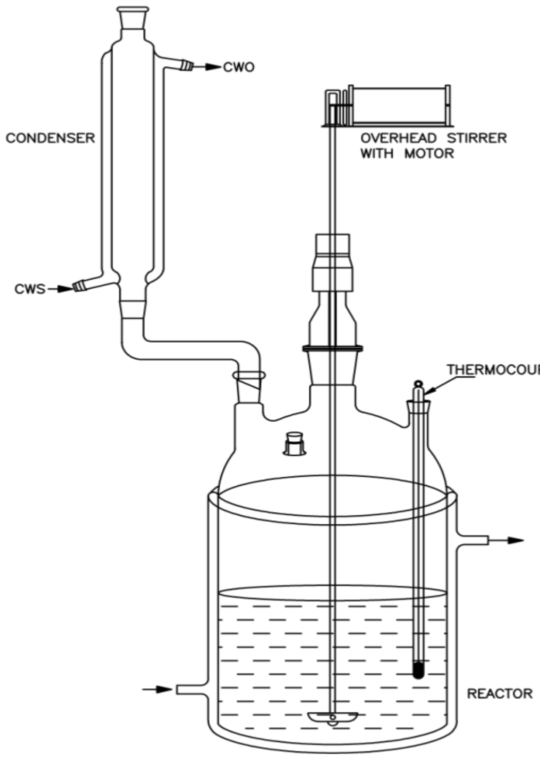


Fig 1: Total reflux arrangement for cyanobutylation.

2. Thomas Poon: Reported that in this short account we have provided computational insight for the observed conjugate addition associated with the Michael reaction, presented significant examples of the reaction in synthesis, and shown its relevance in the activity a new type of drug. While introductory organic chemistry possesses a fair number of topics that have already benefited from computational treatments, biologically and medicinally relevant stories, and significant research examples, there are many topics yet to be enriched by such approaches. We present herein a concise review of a staple reaction in the organic chemistry curriculum, the Michael reaction. Included are examples of its use in chemical research, an illustration of its biological and medicinal relevance, and detailed instructions for educators who wish to use a computational approach to present this reaction to their students.

3. Fülöp, F., Mattinen, J., Pihlaya: Copper (II) Schiff base complex catalysed Michael additions of methyl 1-oxoindanecarboxylate with methyl vinyl ketone (MVK) were performed in water. Several a-amino acid and a-amino alcohol derived water-soluble Schiff base copper (II) complexes were investigated as chiral, water stable Lewis's acids. Although an increase of the rate of the 1, 4-addition could be accomplished, no enantio selectivity was found when the reaction was performed in water. The reaction suffered from ligand-substrate exchange which prevented the possibility to get high asymmetric induction.

4. J. Mas, A. Vidaurre, J. M. Mesegue: Studied that Blends of polycarbonate (PC) and poly (acrylonitrile-co-butadiene-co-styrene) (ABS) with different compositions are characterized by means of dynamic mechanical measurements. The samples show phase separation. The shift in the temperatures of the main dynamic mechanical relaxation shown by the blend with respect to those of the pure components is attributed to the migration of oligomers present in the ABS toward the PC in the melt blending process. A comparison with other techniques (dielectric and calorimetric analysis) and the application of the Takayanagi three block model confirm this hypothesis. In all the studied blend compositions (ABS weight up to 28.6%) the PC appears as the matrix where a disperse phase of ABS is present. The scanning and transmission electron microscopy micrographs show that the size of the ABS particles increases when the proportion of ABS in the blend increases. The FTIR results indicate that the interaction between both components is nonpolar in nature and can be enhanced by the preparation procedure

5. Ismail Mathakiya, Veena Vangani, Animesh Kumar Rakshit: Studied that Free-radical solution terpolymerization of acrylamide, acrylic acid, and acrylonitrile was carried out in a mixture of dimethylformamide and water (60: 40, v/v) at 857C using benzoyl peroxide as the initiator. The polymers were characterized by elemental analysis, IR, 1H-NMR, TGA, and viscosity measurements. Elemental analysis data were used to evaluate the terpolymer composition. The reactivity ratios were determined by Fineman–Ross and Kelen–Tudos methods. The reactivity ratios (r) for the copolymerization of (1) acrylic acid / acrylonitrile with (2) acrylamide was found to be r1 0.86 {0.09 and r2 1.93 {0.03, respectively, by the Kelen–Tudos method. The Fineman–Ross method yielded a value of r1 0.86 {0.05 and r2 1.94 {0.09, respectively. The activation energy values for various stages of decomposition

were calculated from TGA analysis. Voluminosity (VE) and the shape factor (n) were also computed from the viscosity measurements in different ratios of the solvent mixture.

6. Michael Baumann, Gudrun Schmidt-Naake: This paper studied that the influence of acetic anhydride on the controlled radical copolymerization of styrene and acrylonitrile was studied. If benzoyl peroxide/2, 2, 6, 6-tetramethylpiperidine- N-oxyl (BPO/TEMPO) are used the addition of acetic anhydride up to a molar ratio of additive/TEMPO =2:1 result in a twelve times higher rate of polymerization. Molecular weights are increased and the molecular weight distributions are slightly broadened. A further increase of this molar ratio did not accelerate the polymerization rate further, but broadened the molecular weight distributions. Contrarily, the influence of acetic anhydride on the PS-TEMPO controlled radical copolymerization is less pronounced. By means of UV-VIS spectroscopy the reduction of the concentration of free TEMPO through reaction with acetic anhydride at 1258C in ethyl benzene was demonstrated.

7. Athipettah Jayakrkhnan, Venkatanarayana Mahadevan: Reported that the kinetics of polymerization of acrylonitrile initiated by the redox systems cyanoacetic acid/Mn (III) and 2-butanone/Mn III) were investigated in the temperature range of 30 - 50°C in aqueous sulphuric acid. The kinetics are consistent with the formation of a 1: 1 complex between the reducing agent and Mn (III), its unimolecular decomposition yielding the initiating radical. Extensive oxidation of the primary radical with exclusively mutual termination of growing radicals accounts for the kinetics of the polymerization. Rate and equilibrium constants as well as thermodynamic parameters were evaluated and their significance is discussed.

8. M. Bartenev, N.I. Shut', S. V. Baolyuk, V. V. Tulikova: The author had reported the majority of relaxation transitions in poly (butadiene-co-acrylonitrile) that are observed above the glass transition temperature are connected with the butadiene component. The acrylonitrile component affects the glass transition temperature and the temperature of chemical decomposition of the polymer, and it leads also to the occurrence of the relaxation process connected with the mobility of local dipole-dipole cross bonds. Copolymers are seldom characterized by a pure statistical distribution of units in the polymer chain; Therefore, the individuality of A and B units is supposed to appear in the relaxation processes in copolymers. The purpose of this paper is to ascertain the contribution of the butadiene and acrylonitrile units to the relaxation processes observed by means of relaxation spectrometry in butadiene-acrylonitrile copolymers.

III. CONCLUSION

Review of cyanobutylation between n-butanol and acrylonitrile with different mole ratio of n-butanol to acrylonitrile and varying solid catalyst is discussed in the paper. Butyl acrylate is the important product used in different chemical industries as raw material. Also, it having wide applications in polymer and paint industries. Butyl acrylate is produced by single Michael addition reaction but quality of acrylate may be hampered due to equal molar ratios of n-butanol and acrylonitrile, hence by changing mole ratios of the n-butanol and acrylonitrile pure acrylate will achive. Cyanobutylation is carried out in total reflux condenser fitted in round bottom flask. Cyanoethylation is studied by many researchers with various changes involved in it, similar to that cyanobutylation is now challenging task to evolve new research methodology. From all this studies it can see that by keeping constant moles of acrylonitrile and varying moles of n-butanol, butyl acrylate can be produced with maximum purity with minimum amount of waste or byproduct.

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