

Obtaining Isocyanates Through Thermal Decomposition of Carbamates

Muxabbat Sattarovna Khatamova,

Sevara Gulmirzayevna Dosimbetova

Navoi State University, Navoi, Uzbekistan

	Abstract In this article, methods of synthesizing isocyanates through the thermal decomposition of carbamate compounds have been studied. The research focuses on the structure of various carbamates and their decomposition mechanisms under the influence of temperature. Additionally, the high reactivity of isocyanates and their industrial significance (for example, in the production of polyurethanes) are substantiated. Conditions of thermal decomposition, factors affecting the reaction (temperature, catalysts, pressure), and the analysis of the resulting products are presented. Based on the obtained results, the possibilities of obtaining isocyanates in an environmentally and economically efficient way are analyzed.
Keywords: carbamates, thermal decomposition, isocyanates, reactivity, polyurethanes, catalysts, temperature, pressure, environmental efficiency, industrial chemistry	

Introduction

Isocyanates are highly reactive organic compounds with the general formula RNCO . These compounds play a critical role in various organic synthesis reactions, particularly as key raw materials in the production of polyurethane materials. In recent years, the development of economically and environmentally efficient methods for the industrial-scale synthesis of isocyanates has become increasingly relevant. In this context, obtaining isocyanates through the thermal decomposition of carbamates offers a promising approach due to the possibility of using renewable and environmentally friendly feedstocks [1].

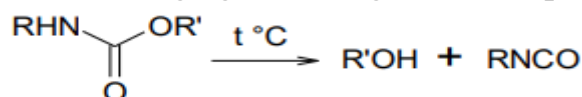
It is well established in the scientific literature that carbamates decompose thermally to produce isocyanates and CO_2 . This reaction is considered enthalpically favorable and exhibits high selectivity, making it one of the preferred routes for isocyanate synthesis. The efficiency of the process depends on several factors, including the nature of the carbamate, reaction temperature, pressure, the presence of catalysts, and reaction time.

In the Republic of Uzbekistan, research in the field of organic synthesis, particularly related to the production of isocyanates, is actively being carried out. Scientific institutions such as the Tashkent Institute of Chemical Technology, the National University of Uzbekistan, and the Institute of Chemistry have contributed to developing new synthetic approaches based on carbamates and to adapting existing technologies to more environmentally sustainable methods. Uzbek researchers have studied the thermal decomposition mechanisms of various alkyl and aryl carbamates and demonstrated the potential for obtaining high-purity isocyanates through this method [2].

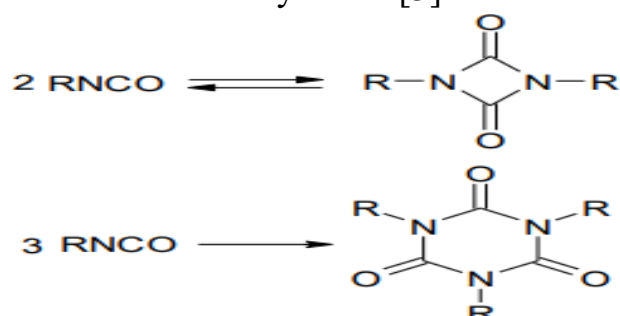
This article presents a scientific analysis of the mechanism of isocyanate formation via thermal decomposition of carbamates, evaluates the factors influencing the reaction conditions, and discusses the technological advantages of the process. Based on the obtained results, the feasibility of applying this method at an industrial level is also examined.

Experimental Part

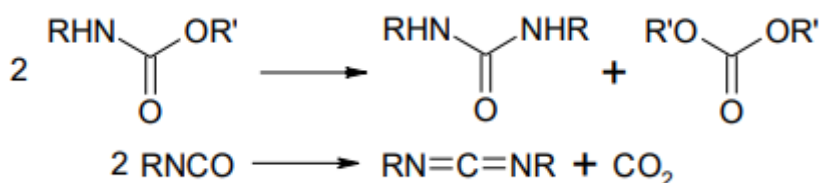
Producing isocyanates from carbamates by cleaving off alcohols using high temperatures and various activating agents is regarded as a promising approach



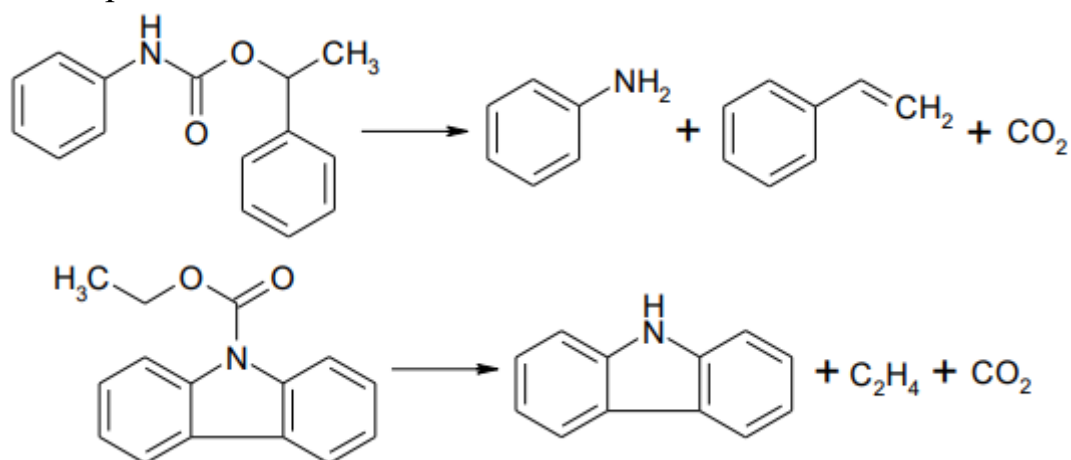
In industry, the application of this method is significantly complicated, and since the reaction is reversible, the separation of isocyanates from alcohols is quite difficult. At high temperatures of 200–300°C, a number of side reactions also occur — dimerization and trimerization of isocyanates [3].



formation of ureas and carbodiimides:



The degradation of isocyanates proceeds through C–N or C–C bonds to form intermediate products.



In the synthesis of initial carbamates, metals and non-metal hydroxides such as calcium, cadmium, silicon, phosphorus, and alkali metal alkoxides—along with catalysts like dibutyltin dilaurate—are commonly employed. These catalysts play a crucial role in facilitating the reaction by enhancing the reactivity and selectivity during carbamate formation [4-5].

It is important to highlight that O-aryl carbamates dissociate at lower temperatures compared to O-alkyl carbamates, primarily due to the higher acidity of phenols. This higher acidity stabilizes the transition state, making the dissociation process more favorable under milder conditions.

Additionally, the choice of catalyst can significantly influence the reaction kinetics and product distribution. For instance, dibutyltin dilaurate is known for its high efficiency in catalyzing carbamate formation through activation of the carbamoyl intermediate, leading to improved yields. On the other hand, metal hydroxides such as calcium or cadmium hydroxide can provide milder reaction conditions and better control over side reactions.

Moreover, the structural nature of the starting materials affects the overall synthesis pathway. O-aryl carbamates, derived from phenols, tend to exhibit greater thermal sensitivity due to the resonance stabilization of the aryl group, which facilitates cleavage of the carbamate bond at relatively lower temperatures. In contrast, O-alkyl carbamates, formed from aliphatic alcohols, generally require higher temperatures for dissociation due to the lack of such stabilization.

Understanding these factors is critical for optimizing industrial processes, where controlling reaction conditions and catalyst selection can improve efficiency, reduce by-products, and ensure safer operational parameters.

Conclusion

Research shows that the efficiency of thermal decomposition of carbamates depends on multiple factors, including the type of carbamate, temperature, pressure, presence of catalysts, and reaction duration. Notably, catalyst selection and their effect on reaction kinetics play a crucial role in optimizing the process. Organotin catalysts such as dibutyltin dilaurate effectively promote carbamate formation, while metal hydroxides offer more controllable reaction conditions.

The lower dissociation temperature of O-aryl carbamates compared to O-alkyl carbamates—due to the higher acidity of phenols and thermal sensitivity—is an important consideration when determining synthesis conditions.

Furthermore, in industrial settings, separating isocyanates from carbamates is challenging because the reaction is reversible, and side reactions such as dimerization and trimerization can occur at high temperatures. Therefore, selecting appropriate catalysts and carefully controlling reaction conditions are essential to improve process efficiency and product quality.

Overall, the thermal decomposition of carbamates represents an economically and environmentally promising method for isocyanate production, with significant potential for industrial-scale application. Further in-depth study and control of the influencing factors are critical for advancing and optimizing this technology.

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