



Int. J. New. Chem., 2021, Vol. 8, Issue 3, pp 356-364.

International Journal of New Chemistry

Published online 2021 in <http://www.ijnc.ir/>.

Open Access

Print ISSN: 2645-7237

Online ISSN: 2383-188x



Original Research Article

Study on Catalytic Synthesis of Azodicarbonamide with Hydrogen Peroxide as a Green Oxidant

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Received: 2020-09-19

Accepted: 2021-06-04

Published: 2021-07-01

ABSTRACT

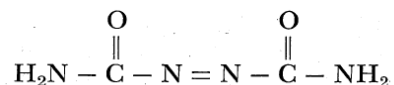
This study relates to an improved method for the preparation of azodicarbonamide, which is useful as a chemical blowing agent. Azodicarbonamide is prepared from the oxidation reaction of hydrazodicarbonamide (biurea) with hydrogen peroxide as a green oxidant in the presence of a potassium bromine as a catalyst. Biurea also is prepared by reaction of urea and hydrazine. The prepared products have been characterized by FTIR and TGA/DSC. By Series of comparative experiments, Factors of influencing the yield of azodicarbonamide are studied, such as the amount of oxidant and temperature of reaction solution. Under the optimum process conditions, the yield of azodicarbonamide can reach over 95%, with hydrogen peroxide oxidation process.

Keywords: Azodicarbonamide, Hydrazodicarbonamide, Green Oxidation, Hydrogen peroxide oxidation.

Introduction

Azodicarbonamide (ADCA) is a yellow powder and widely used in industry as a foaming agent [1-3] in the production of various products because its decomposition products are non-toxic, odorless and non-polluting. The gases from the ADCA decomposition are 65% nitrogen gas, 24% carbon monoxide, 5% carbon dioxide and 5% ammonia [4-6].

Azodicarbonamide has the following structure [7]:



The current process of ADCA is as follows: hydrazodicarbonamide (biurea) is synthesized from hydrazine hydrate and urea by means of acid condensation reaction [8], and ADCA is synthesized from biurea through oxidation reaction. There are several processes for producing azodicarbonamide by the oxidation of biurea, it can be divided according to different methods used dichromate oxidizing agent [9-11], chlorate method [12], chlorine method [13-15] and hydrogen peroxide process [16, 17]. The oldest and still commonly used process uses dichromate oxidizing agent. The dichromate method employed due to high cost and the pollution generated during chrome is eliminated. Further, the deep green color of the chromate ions masks the orange colored azo compound, to such an extent that it is difficult to determine the end point of the reaction. In addition, chromium compounds are skin irritants and cause health problems if any chromium residues remain in the product. Serious and expensive waste disposal problems also arise with use of chromium [9]. Hydrogen peroxide oxidation process is a new method to produce ADCA foaming agent. There is a current intense interest in using hydrogen peroxide as an environmentally friendly oxidant that produces water as a by-product [18-22]. The low oxidation power of hydrogen peroxide seems to be due to the poor leaving tendency of the hydroxide ions [23, 24]. With this method, the only by-product is water, no pollutants. The dosage of the H₂O₂ is easy to control. The product has stable quality and yield. So, the method has a lot of advantages, such as no danger of explosion, no pollutants, no by-products, high product quality and high yield.

In the present research, first of all biurea was synthesized from hydrazine and urea, after purification, ADCA was synthesized from biurea through oxidation with hydrogen peroxide

according to our reported procedure [25, 26]. The influence of factors such the amount of oxidant and temperature of reaction solution on product yield was investigated.

Experimental

Materials

Urea, hydrogen peroxide (30%) and sodium bromide were obtained from Merck. Other materials were of commercial reagent grade and were purchased from Sigma-Aldrich or FLUKA companies and treated when necessary.

General procedure for synthesis of biurea

4 g (0.03 mol) of hydrazine sulfate, 5.4 g (0.09 mol) urea and 100 ml of water was heated to the refluxing temperature under refluxing conditions and with agitation. After about two hours of boiling with adding some sulfuric acid that was added dropwise to hold the pH at a level between 2 and 2.5. The reaction was discontinued at the end of five hours total elapsed time. The reaction mixture was then cooled and filtered and the filtered precipitate was washed with water.

General procedure for the preparation of azodicarbonamide by oxidation of biurea with hydrogen peroxide.

2.3 g (0.02 mol) of the biurea was suspended in some water and 0.6 mmol of potassium bromide as a catalyst was added. The pH was down to less than 2 with adding some sulfuric acid. The suspension was heated to the chosen reaction temperature and, after the pH value had been adjusted, 0.09 mol of hydrogen peroxide was added. After the oxidation increase, the reaction mixture was stirred for 30 minutes in a stirred water bath to form yellow ADCA deposits. Then filtered the product and washed several times with distilled water.

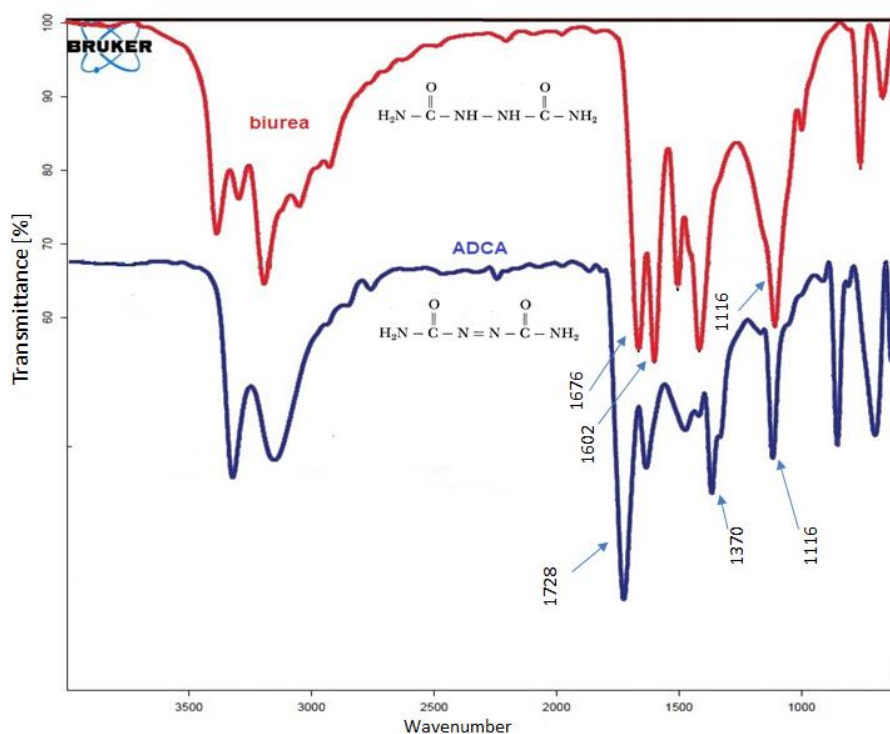
Results and discussion

IR spectra of ADCA and biurea

As shown in Figure. 1, the IR of ADCA and biurea have been compared. The IR band assignments of ADCA and biurea are listed in Table 1.

Table 1. Comparison of IR spectra in frequency and assignments of ADCA and biurea.

IR-ADCA (cm ⁻¹)	Assignments
636	$\delta\text{N}-\text{C}=\text{O} + \delta\text{NCN} + \delta\text{C}-\text{N}=\text{N}$
752	$\delta\text{C}=\text{O} + \delta\text{H}-\text{N}-\text{H} + \delta\text{N}=\text{N}$
856	$\delta\text{N}-\text{H}$
1116	$\delta\text{H}-\text{N}-\text{H} + \nu\text{C}=\text{O} + \nu\text{C}-\text{N}$
1370	$\delta\text{H}-\text{N}-\text{H} + \nu\text{C}-\text{N} + \delta\text{N}-\text{C}=\text{O}$
1633	$\delta\text{N}-\text{H} + \nu\text{C}=\text{O}$
1728	$\nu\text{C}=\text{O} + \nu\text{C}-\text{N}$
IR-biurea (cm ⁻¹)	Assignments
559	$\delta\text{N}-\text{C}=\text{O}$
613	$\delta\text{N}-\text{C}=\text{O} + \delta\text{N}-\text{C}-\text{N} + \delta\text{C}-\text{N}-\text{N}$
1116	$\delta\text{NH}_2 + \nu\text{C}-\text{N} + \nu\text{C}=\text{O}$
1425	$\nu\text{C}-\text{N} + \nu\text{N}-\text{N} + \delta\text{N}-\text{H}$
1602	$\nu\text{C}-\text{N} + \delta\text{N}-\text{H} + \nu\text{C}=\text{O}$
1676	$\nu\text{C}-\text{N} + \delta\text{N}-\text{H} + \nu\text{C}=\text{O}$

**Figure 1.** IR spectra of azodicarbonamide (ADCA) and biurea.

FTIR spectras agree with the standard spectra of biurea and azodicarbonamide [27, 28], indicating that the products are biurea and azodicarbonamide.

Thermal Analysis of ADCA

TG and DSC curves for ADCA are presented in Figure 2. Pure ADCA has three peaks corresponding to three mass loss steps in the TG curve [29, 30].

There is a sharp endothermic peak (220 °C) in the DSC curve, with a mass loss of about 75% in the TG curve. At the end of analysis, the sample mass reaches to zero [31].

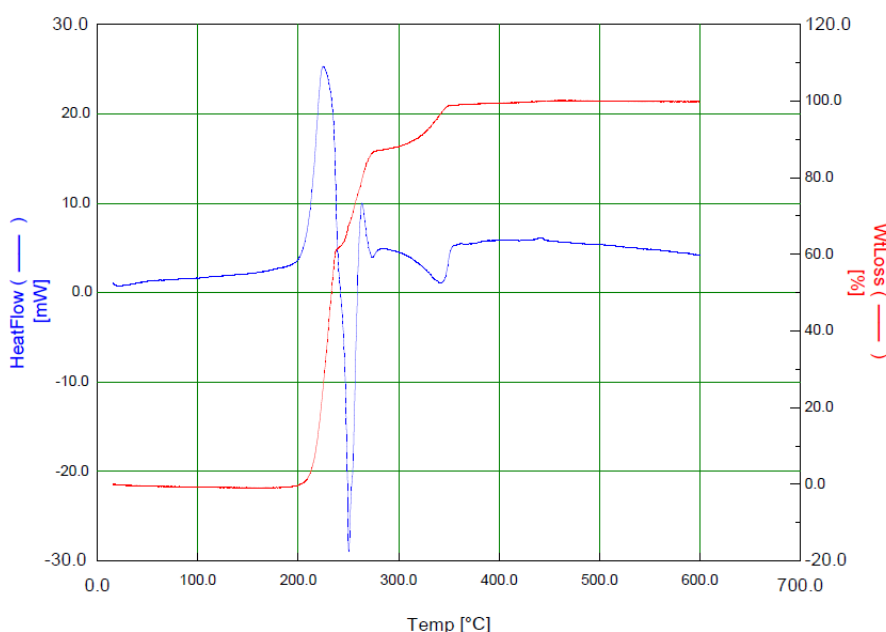


Figure 2. TG and DSC curves for ADCA.

Catalytic oxidation of biurea to ADCA with hydrogen peroxide

In order to find the suitable reaction conditions, the effect of the various reaction parameters that may affect the yield of the reaction were studied. The amount of oxidant and temperature of reaction solution are the factors that have been evaluated.

The effect of H_2O_2 concentration on the oxidation of biurea has also been studied (Table 1). The H_2O_2 concentrations used were 0, 0.06 and 0.09 mol, while the amount of biurea was kept fixed. It is clear from Table 1 that the percentage of ADCA yield increases with increasing the H_2O_2 content. In general, it is appropriate to use H_2O_2 in excess of the stoichiometrically required amount of one mol per mol of biurea.

Table 1. The effect of oxidant amounts on the oxidation of biurea catalyzed by potassium bromide^{a,b}.

Entry	Oxidant (mol)	amount	Yield of ADCA ^c (%)
1	none		0
2	0.06		75
3	0.09		96

^aReaction conditions: the molar ratio for catalyst:biurea: H_2O_2 (30%) are 1:33:X. ^b Reaction time: 30 min. ^cIsolated yield.

Examine the effect of temperature on the yield of the product, the experimental results are shown in figure 3. The figure 3 shows that with the increase of temperature, the yield of ADCA increasing, when after reacting for 60°C and further increments of temperature can slightly decrease the yield. This may be due to thermal decomposition of H_2O_2 .

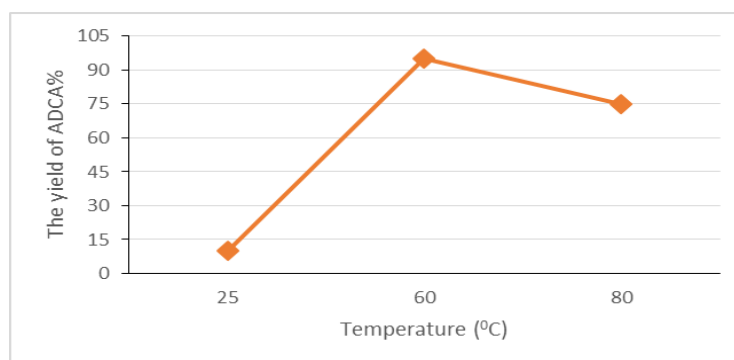


Figure 3. Effect of temperature on the yield of azodicarbonamide

Conclusion

It can be concluded that this catalytic system is highly efficient for oxidation of biurea to ADCA with hydrogen peroxide as an environmentally friendly oxidant. Addition of KBr as a catalyst to the biurea/hydrogen peroxide systems led to a remarkable increase in the yield of ADCA. In this work, by optimization of reaction conditions, factors of influencing the yield of azodicarbonamide were studied. Under the optimum process conditions, the yield of azodicarbonamide reached over 95%, with hydrogen peroxide oxidation process.

Acknowledgments

The financial support of this work by ACECR is acknowledged.

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How to Cite This Article

Elaheh Bohloulbandi, Parviz Ahmadi Aval, “Study on Catalytic Synthesis of Azodicarbonamide with Hydrogen Peroxide as a Green Oxidant” *International Journal of New Chemistry.*, 2021; DOI: 10.22034/ijnc.2020.136525.1129.