



# K<sub>3</sub>PO<sub>4</sub>-catalyzed carboxylation of amines to 1,3-disubstituted ureas: A mechanistic consideration



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## ABSTRACT

K<sub>3</sub>PO<sub>4</sub> was found to effectively catalyze the carboxylation of amines by CO<sub>2</sub>, producing corresponding 1,3-disubstituted ureas in high yields and selectivities. X-ray diffraction and FT-IR spectroscopic analysis of the solid mixture, recovered from the carboxylation of *n*-butylamine, revealed that K<sub>3</sub>PO<sub>4</sub> was completely transformed into KH<sub>2</sub>PO<sub>4</sub> and KHCO<sub>3</sub>. Mechanistic and computational studies suggested that the high activity of K<sub>3</sub>PO<sub>4</sub> could be attributed to the synergy effect exerted by the co-presence of KHCO<sub>3</sub> and KH<sub>2</sub>PO<sub>4</sub>, generated from the interaction of K<sub>3</sub>PO<sub>4</sub> with CO<sub>2</sub> and water.

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## 1. Introduction

The synthesis of 1,3-disubstituted ureas via the direct carboxylation of amines with CO<sub>2</sub> has received increasing interest with regard to the utilization of carbon dioxide, a greenhouse gas [1,2]. 1,3-Disubstituted ureas are widely used as intermediates of fine chemicals such as pesticides, herbicides, medicines, and pigments [3–9]. Recently, much effort has also been devoted to using 1,3-disubstituted ureas as precursors of isocyanates and raw materials of polyurethanes [10,11].

The most commonly used industrial process for manufacturing 1,3-disubstituted ureas is the phosgenation of amines to isocyanates followed by the reaction with corresponding amines [12–14]. However, the synthetic process involving phosgenation has inherent drawbacks such as the use of highly toxic phosgene and the generation of hydrogen chloride [15,16]. As alternative processes, oxidative and reductive carbonylation of amines have been extensively investigated [17–19], but none

of the carbonylation processes have been commercialized yet, possibly due to the failure to find inexpensive catalysts with high activity and stability. In this regard, the synthesis of 1,3-dibutylureas from carboxylation reaction of amines by CO<sub>2</sub>, as shown in Scheme 1, is highly attractive in terms of economic and environmental points of view as long as suitable catalysts can be developed. A number of carboxylation catalysts have been reported, including metal salts [20], triphenylstibine oxide [21,22], *N*-phosphonium salts of pyridine [23,24], rare-earth metal complexes [25], sulfur trioxide–trimethylamine complex [26], dicyclohexyl carbodiimide and tertiary amine [27], and ionic liquids (ILs) [28–31]. Of these, ILs have received particular interest because some IL-based catalysts have been found to exhibit activities higher than those of other catalysts and catalytic systems.

While the advances made so far in the direct carboxylation of amines have been significant, there remains much to be improved for the practical application of the carboxylation process, particularly in terms of the activity of catalysts.

In a continuous effort to develop active catalysts for the carboxylation of amines by CO<sub>2</sub>, we now report that potassium phosphate (K<sub>3</sub>PO<sub>4</sub>) can be used as an efficient catalyst for the carboxylation of amines. The mechanistic aspect of catalysis is also discussed on the basis of experimental and spectroscopic results.

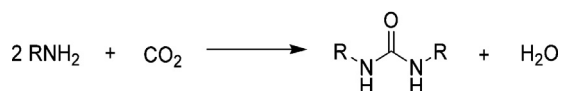
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**Scheme 1.** Carboxylation of amine to 1,3-disubstituted urea.

## 2. Experimental

### 2.1. General

All of the chemicals used for the synthesis of 1,3-dialkylureas were purchased from Aldrich Chemical Co. Solvents were distilled over appropriate drying agents prior to use. CO<sub>2</sub> with a purity of 99.9% was obtained from Shin Yang Gas Co. Korea. To remove water, all the catalysts were dried before use at elevated temperatures under vacuum.

The elemental analysis of fresh and used catalysts was made on a CHNOS Elemental Analyzer (Model: Fisons EA 1108) for C, H, and N, and on an inductively coupled plasma optical emission spectroscopy ICP-OES instrument (Varian 720/730-ES series) for P. The X-ray diffraction patterns (XRD) were recorded on a Shimadzu X-ray diffractometer (XRD-6000) using nickel-filtered Cu K $\alpha$  radiation with a 2 $\theta$  angle from 10° to 40°. FT-IR spectra of catalyst samples were obtained using a Nicolet FT-IR spectrometer (iS10, USA) equipped with a SMART MIRACLE accessory.

The product mixture was analyzed using an Agilent 6890 gas chromatograph (GC) equipped with an FID and a DB-5 capillary column. Product characterization was performed on a 400 MHz Bruker NMR spectrometer and on an Agilent 6890-5973 MSD GC-mass spectrometer equipped with an HP-MS capillary column.

### 2.2. Carboxylation of amines

A typical carboxylation reaction is as follows: *n*-butylamine (BuNH<sub>2</sub>, 50 mmol), *N*-methylpyrrolidinone (NMP, 20 mL), K<sub>3</sub>PO<sub>4</sub> (0.5 mmol), and toluene (2.00 g) as an internal standard were loaded into a 100 mL stainless steel bomb reactor. The reactor was pressurized with 1.0 MPa CO<sub>2</sub> and then heated to 170 °C with vigorous stirring. The pressure in the reactor at 170 °C was maintained at 5.0 MPa throughout the reaction using a gas reservoir equipped with a high pressure regulator and a pressure transducer. After the completion of the reaction, the product mixture was analyzed by GC. For the isolation of 1,3-dibutylurea, water (100 mL) was added to the product mixture to precipitate 1,3-dibutylurea as a white solid, which was then collected by filtration and dried in a vacuum oven overnight.

### 2.3. Synthesis of CO<sub>2</sub> adduct of K<sub>3</sub>PO<sub>4</sub>, K<sub>3</sub>PO<sub>3</sub>(OCO<sub>2</sub>)

A CO<sub>2</sub> adduct, K<sub>3</sub>PO<sub>3</sub>(OCO<sub>2</sub>) was prepared from the reaction of K<sub>3</sub>PO<sub>4</sub> with CO<sub>2</sub> in NMP or CH<sub>3</sub>CN at room temperature for 4 h. The same compound was also produced from the carboxylation of K<sub>3</sub>PO<sub>4</sub> (2 g) conducted at 170 °C in NMP (30 mL) for 4 h in the absence of BuNH<sub>2</sub>. After the reaction was completed, the solid precipitates were collected by filtration, washed with CH<sub>2</sub>Cl<sub>2</sub>, and then dried under a N<sub>2</sub> atmosphere at room temperature. Elemental analysis calcd. (%) for CK<sub>3</sub>O<sub>6</sub>P: C, 4.69; K, 45.77; O, 37.46; P, 12.09. Found: C, 4.66; K, 45.82; O, 37.41; P, 12.11. <sup>31</sup>P NMR (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 3.51, -5.08, <sup>13</sup>C NMR (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 163.91.

### 2.4. Quantum mechanical calculations

The carboxylation reactions of methylamine by CO<sub>2</sub> in the presence of K<sub>3</sub>PO<sub>4</sub>, KHCO<sub>3</sub>, or KHCO<sub>3</sub>-KH<sub>2</sub>PO<sub>4</sub> were theoretically investigated using a Gaussian 03 program [32]. Methylamine was

**Table 1**

Catalytic activities of various catalysts for the carboxylation of BuNH<sub>2</sub>.<sup>a</sup>

Entry	Catalyst	C (%) <sup>b</sup>	Y (%) <sup>c</sup>
1	–	5.6	5.5
2	K <sub>3</sub> PO <sub>4</sub>	79.0	79.0
3	Na <sub>3</sub> PO <sub>4</sub>	63.5	63.4
4	Li <sub>3</sub> PO <sub>4</sub>	24.8	24.6
5	K <sub>2</sub> HPO <sub>4</sub>	24.5	24.4
6	KH <sub>2</sub> PO <sub>4</sub>	23.0	22.9
7	KHCO <sub>3</sub>	64.8	64.7
8 <sup>d</sup>	KHCO <sub>3</sub>	75.5	75.5
9 <sup>e</sup>	KHCO <sub>3</sub> /KH <sub>2</sub> PO <sub>4</sub>	80.8	80.7
10	CsOH/[BMIm]Cl	74.3	74.3
11 <sup>f</sup>	[BMIm]OH	40.3	40.2
12	[BMIm]Cl	43.9	43.8
13	<i>n</i> -Bu <sub>4</sub> PBr	48.9	48.8
14	Cs <sub>2</sub> CO <sub>3</sub>	69.8	69.6
15	CaO	14.6	13.7

<sup>a</sup> Reaction condition: BuNH<sub>2</sub> (50 mmol), catalyst (0.5 mmol), NMP (20 mL), T = 170 °C, P = 5 MPa (CO<sub>2</sub>), t = 4 h.

<sup>b</sup> C: conversion of BuNH<sub>2</sub>.

<sup>c</sup> Y: yield of 1,3-dibutylurea.

<sup>d</sup> KHCO<sub>3</sub>: 1.5 mmol.

<sup>e</sup> Molar ratio of KHCO<sub>3</sub>/KH<sub>2</sub>PO<sub>4</sub> = 2.

<sup>f</sup> [BMIm]OH: 1-butyl-3-methylimidazolium hydroxide.

chosen as the model amine since it is the simplest system that can be used to resemble our catalytic reactions. The geometry optimizations and thermodynamic corrections were performed using hybrid Becke 3–Lee–Yang–Parr (B3LYP) exchange–correlation functional with the 6–31+G\* basis sets for C, H, N, O, and P. In order to obtain the most stable geometries, all kinds of possible interaction patterns were optimized. No restrictions on symmetries were imposed on the initial structures. All stationary points were verified as minima by full calculation of the Hessian and harmonic frequency analysis.

## 3. Results and discussion

### 3.1. Carboxylation of BuNH<sub>2</sub> with CO<sub>2</sub>

During the course of our study to develop high performance catalysts for the carboxylation of amines by CO<sub>2</sub>, we have found that K<sub>3</sub>PO<sub>4</sub> exhibits much higher activity than other alkali metal phosphates for the carboxylation of BuNH<sub>2</sub> to produce 1,3-dibutylurea. As listed in Table 1, all the alkali metal phosphates produced 1,3-dibutylurea in moderate to excellent yields when the carboxylation of BuNH<sub>2</sub> was conducted at 170 °C for 4 h. As a whole, the activity of the alkali metal phosphate increased with increasing basicity of the alkali metal phosphate [33–36]. This is reasonable because the activation of CO<sub>2</sub> and amines would be much easier in the presence of a more basic catalyst.

However, the significantly lower activity of K<sub>2</sub>HPO<sub>4</sub> than that of KHCO<sub>3</sub>, which has a similar basicity, is hard to explain by the basicity alone. It is assumed that HCO<sub>3</sub><sup>–</sup> is more effective than KHPO<sub>4</sub><sup>–</sup> in the rate-determining dehydration step of the carboxylation of BuNH<sub>2</sub> (vide infra).

The outstanding catalytic performance of K<sub>3</sub>PO<sub>4</sub> was further demonstrated via a comparison of its activity with those of other active catalysts so far reported, including *n*-Bu<sub>4</sub>PBr, [BMIm]Cl [28], 1-butyl-3-methylimidazolium hydroxide ([BMIm]OH) [30], CsOH/[BMIm]Cl [31], and Cs<sub>2</sub>CO<sub>3</sub> [37]. As can be seen in Table 1, K<sub>3</sub>PO<sub>4</sub> exhibited approximately 5–40% higher 1,3-dibutylurea yields when the carboxylation reactions of BuNH<sub>2</sub> were conducted under the same condition. For comparison, the activity of CaO (*pK<sub>b</sub>* = 1.2) with similar basicity to K<sub>3</sub>PO<sub>4</sub> (*pK<sub>b</sub>* = 1.6) was also evaluated, but the yield of 1,3-dibutylurea was only 13.7%, suggesting that the basicity of a catalyst is not a sole factor in determining its carboxylation activity.

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