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Scope of chemical fixation of carbon dioxide catalyzed by a bifunctional monomeric tungstate

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ABSTRACT

The tungsten-oxo moiety in a simple monomeric tungstate, $TBA_2[WO_4]$ (**I**, TBA = tetra-*n*-butylammonium), showed bifunctional activation of both CO_2 and 1,2-phenylenediamine (**1a**). It was confirmed by ^1H, ^{13}C, and ^{183}W NMR spectroscopies that adducts **I–1a** and **I–(CO$_2$)$_n$** (n = 1 and 2) were formed by the reactions of **I** with **1a** and CO_2, respectively. These adducts played important roles in formation of the corresponding carbamic acid intermediates. The present bifunctionality could be applied to chemical fixation of CO_2 even at atmospheric pressure with various kinds of structurally diverse aryl diamines, primary monoamines, propargylic alcohols, and propargylic amines into cyclic urea derivatives, 1,3-disubstituted urea derivatives, cyclic carbonates, and cyclic carbamates, respectively.

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1. Introduction

Carbon dioxide (CO_2) is regarded as the primary anthropogenic greenhouse gas leading to global warming [1–7]. CO_2 is attractive as an abundant, non-flammable, easily available, and renewable carbon source in contrast with carbon monooxide (CO) and phosgene ($COCl_2$), and its transformation into useful and valuable chemicals is one of the most important technologies to construct a sustainable low-carbon society [1–7]. 1,3-Disubstituted urea derivatives are useful chemical intermediates in the synthesis of pharmaceuticals, agricultural chemicals, and in dye chemistry [8–11], and they are conventionally synthesized by reactions of amines with $COCl_2$, CO, isocyanates, ureas, and carbonates. In contrast with these synthetic methods, processes with CO_2 in the presence of base catalysts offer economical and environmental advantages due to the high atom efficiency and co-production of only water [9–11]. However, large energy inputs such as high CO_2 pressures, high reaction temperatures, and use of large amounts of bases and/or dehydrating agents are required due to its low reactivity. In these contexts, developments of catalytic CO_2 fixation with amines into urea derivatives at low CO_2 pressure (ideally at an atmospheric pressure (1 atm)) are still challenging and desirable tasks.

Polyoxometalates (POMs) are discrete anionic metal–oxygen clusters consisting of early transition metals (W, Mo, V, Nb, Ta, etc.) and have widely been used in diverse areas such as catalysis, material science, and medicine, because their chemical and physical properties can finely be controlled by choosing constituent elements and counter cations [12–16]. While POM-catalyzed CO_2 transformations such as photocatalytic reduction of CO_2 [17,18], cycloaddition of CO_2 to epoxides [19,20], and synthesis of dimethyl carbonate from methanol and CO_2 [21] have been reported, there are no examples of POM-catalyzed synthesis of 1,3-disubstituted urea derivatives from amines and CO_2. During the course of our investigation on developments of a series of POM catalysts efficient for various functional-group transformations [16], we have recently found unique basic properties of a simple monomeric tungstate, $TBA_2[WO_4]$ (**I**, TBA = tetra-*n*-butylammonium, Fig. 1(a)) [22–24], rare-earth-metal-containing POMs [25,26], and highly negatively charged lacunary POMs [27]. Especially, **I** can act as an efficient homogeneous catalyst for chemical fixation of CO_2 with aryl diamines and 2-aminobenzonitriles into cyclic urea derivatives and quinazoline-2,4(1*H*,3*H*)-diones, respectively [22,23].

In this paper, we investigate effects of catalysts on various chemical fixations of CO_2 and scope and limitation of the **I**-catalyzed system by adding the following new data: (i) effects of POMs and bases on reactions of 1,2-phenylenediamine, hexylamine, and 2-methyl-3-butyn-2-ol with CO_2 (7 new examples), (ii) reactions of aromatic (3 new examples), aliphatic (5 new examples), and propargylic amines (2 new examples), and (iii) attempts to synthesize asymmetric urea derivative and carbamate from primary/secondary amines and amine/alcohol, respectively (2 new examples). In addition, the interactions of various catalysts with **1a** and CO_2 and the role of **I** in chemical fixation of **1a** into **2a** are examined in more detail by means of ^1H, ^{13}C, and ^{183}W NMR spectroscopies and density functional theory (DFT) calculations.

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2. Experimental

Solvents and substrates were obtained from Kanto, TCI, or Aldrich (Reagent grade) and purified prior to the use [30]. Products were isolated and identified by comparison of their ^{1}H and ^{13}C NMR signals with the literature data. Deuterated solvents (D_2O, $CDCl_3$, DMSO-d_6, and DMF-d_7) were purchased from ACROS, C/D/N Isotopes, or Aldrich and used as received. TBA salts of tungstates (**I**, $TBA_2[W_6O_{19}]$, $TBA_4[W_{10}O_{32}]$, $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$, $TBA_8[H_2(\gamma\text{-}SiYW_{10}O_{36})_2]$, and $TBA_6[\gamma\text{-}H_2GeW_{10}O_{36}]$, Fig. 1(a)) were synthesized according to the literature procedures [25,27,31,32] and characterized by IR, NMR (^{1}H, ^{29}Si and ^{183}W), and elemental analysis.

A typical procedure for the **I**-catalyzed reaction of aryl diamines with 1 atm CO_2 was as follows: diamine (1 mmol), **I** (0.15 mmol), and *N*-methylpyrrolidone (NMP) (1 mL) were charged in a Schlenk tube with a magnetic stir bar. CO_2 (1 atm) was introduced by a balloon, and the reaction mixture was stirred at 140 °C for 24 h. The reaction solution was periodically analyzed by GC, LC, GC–MS, or NMR. A Teflon vessel placed in a stainless steel autoclave was used for reactions with CO_2 at 20 atm.

Quantum chemical calculations were carried out at the B3LYP level theory [33] with 6-31++G* basis sets for H, C, N, and O atoms, 6-31G* basis set for Si atom, and the double-ζ quality basis sets with effective core potentials proposed by Hay and Wadt [34] for W atom using Gaussian09 programs [35].

3. Results and discussion

3.1. Scope and limitation of the I-catalyzed chemical fixation

The **I**-catalyzed chemical fixation of 1 atm CO_2 with 1,2-phenylenediamine (**1a**) efficiently proceeded to give 2-benzimidazolone (**2a**), of which the ring structure is of particular interest in the fields of medicinal and biological chemistry [28,29], in 91% yield (Table 1). On the other hand, reactions did not efficiently proceed (<1–30% yields of **2a**) in the presence of typical inorganic and organic strong bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,1,3,3-tetramethylguanidine (TMG), Cs_2CO_3, *t*-BuOK, Et_3N, and TBAOH (Fig. 1(a)). Reactions also hardly proceeded even in the presence of other POMs including $TBA_8[H_2(\gamma\text{-}SiYW_{10}O_{36})_2]$ and $TBA_6[\gamma\text{-}H_2GeW_{10}O_{36}]$, which are active for cyanosilylation of carbonyl compounds with trimethyl cyanide and Knoevenagel condensation of carbonyl compounds with active methylene compounds, respectively [25,27] (Eq. (1)). Imidazolidone derivatives are obtained from alkyl diamines and CO_2 in the absence of catalysts [36]. On the other hand, **2a** has not yet been obtained in the absence of catalysts even under the harsh reaction conditions (60 atm of CO_2 pressure at 150 °C) [36] because reactivities of less nucleophilic arylamines with CO_2 are much lower than those of alkylamines [37]. To the best of our knowledge, stoichiometric as well as catalytic synthesis of benzimidazolones from aryl diamines and CO_2 has never been reported, while the synthesis of benzimidazoles by cyclization of **1a** with CO_2 and H_2 in the presence of a ruthenium catalyst has recently been reported [38].

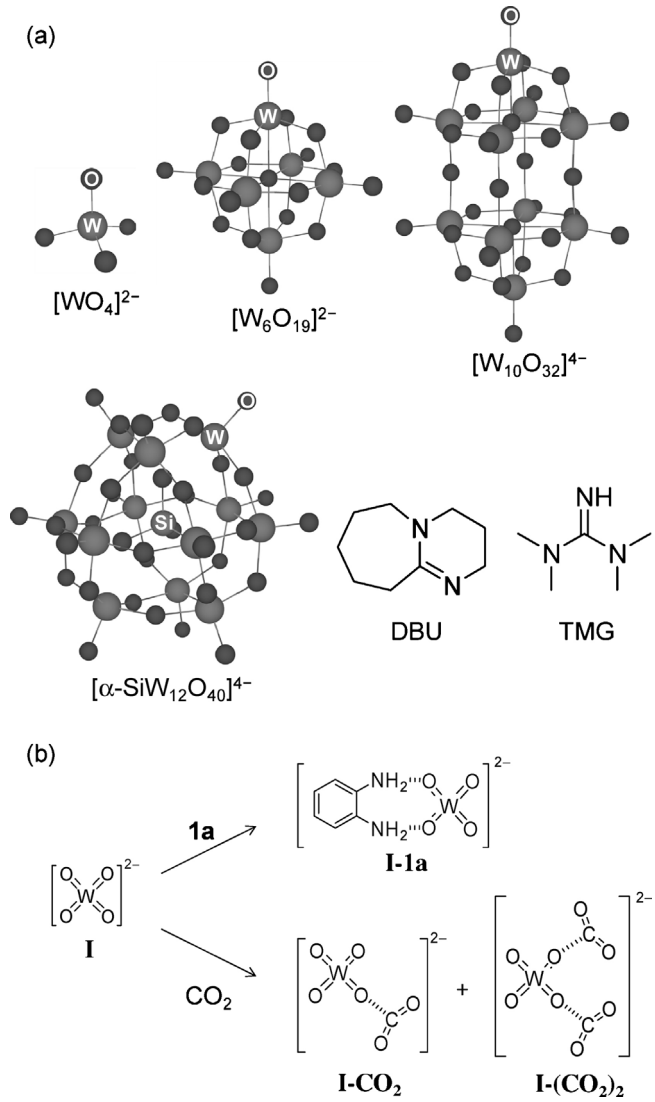
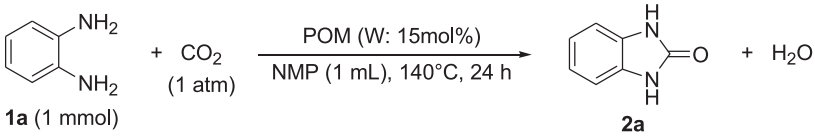


Fig. 1. (a) Molecular structures of POMs and organic bases and (b) proposed activation of **1a** and CO_2 by **I**.

The **I**-catalyzed system could be applied to chemical fixation of CO_2 with various kinds of structurally diverse aryl diamines (Table 1). 1,2-Phenylenediamines with electron-donating as well as electron-withdrawing substituents (**1a**–**1d**) and 1,8-diaminonaphthalene (**1e**) were converted into the corresponding cyclic urea derivatives (**2a**–**2e**) in moderate to high yields at 1 atm of CO_2. At 20 atm of CO_2, high to excellent yields of the corresponding cyclic urea derivatives could be obtained even with low catalyst loadings. The turnover number (TON) reached up to 186 for the 4 mmol scale-reaction of **1b** and the value was much higher than those (0–52) reported for base-catalyzed reactions of amines to urea derivatives [8–11]. The present system could not be



I: 91% yield
$TBA_6[\gamma\text{-}H_2GeW_{10}O_{36}]$: 10% yield
$TBA_8[H_2(\gamma\text{-}SiYW_{10}O_{36})_2]$: 3% yield
$TBA_2[W_6O_{19}]$, $TBA_4[W_{10}O_{32}]$, $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$: <1% yield (1)

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