Advantages in Using Inexpensive CO₂ To Favor Photocatalytic Oxidation of Benzylamines

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ABSTRACT: In this work, we investigate using carbon dioxide (CO₂) as an inexpensive reaction medium during the photocatalytic oxidative coupling of primary amines to the corresponding imines. As a model system, we study the reaction of benzylamines in acetonitrile over a potassium poly(heptazine imide) photocatalyst (K-PHI). We use CO₂ or argon (Ar) to saturate the reaction solution and the reactor headspace, and blue light (461 nm) to drive the reaction. When compared to the more expensive Ar, CO₂ boosts the conversion rate by creating a reaction intermediate with better electron donor properties. We also validate the influence of water content on the imine formation efficiency, and we observe higher catalytic activity of K-PHI, compared to a standard mesoporous graphitic carbon nitride (mpg-CN).

KEYWORDS: K-PHI, carbon nitride, photocatalysis, visible light, CO₂, benzylamine, oxidative coupling, cheap

INTRODUCTION

From the beginning of the 21st century, an extended branch of organic chemistry moved to the investigation of photocatalysis. This is a vast field of research covering a multitude of applications in organic synthesis, often characterized by reactions operated under mild conditions, in terms of temperature, pressure, and media. Moreover, photocatalysts show a great versatility as they can promote both oxidation and reduction reactions on their surface and the same material is often able to favor diverse chemical reactions.

Oxidative coupling of primary amines is a convenient model reaction as such compounds act as efficient electron donors during photocatalysis, as also previously discussed by our group. Furthermore, the products of the amine coupling, i.e., imines, have value as precursors in the synthesis of oxaziridines, or they can be photocatalytically converted to imidazoles, or used in C–C reductive coupling, etc. Imines are also used in the synthesis of various heterocycles (e.g. piperidin-2-ones, having physiologic activity) and in titrimetric determination of organolithium compounds. Therefore, we opted for investigating the conversion of a preliminary scope of benzylamines to the corresponding substituted N-benzylidene benzylamines.

Surveying some of the reaction conditions applied to the photocatalytic coupling of amines, Su and colleagues used a mesoporous graphitic carbon nitride (mpg-CN) photocatalyst, in combination with O₂ as a terminal oxidant to couple benzylamines. In a similar reaction, Raza and co-workers used WS₂ nanosheets as a photocatalyst. Similar reaction schemes are also included in the works of Yang et al. and of Kumar et al., who used Au/TiO₂ and CuO₂/carbon quantum dots (CQD), respectively. Furukawa et al. employed a Nb₂O₅ photocatalyst and O₂ as an electron acceptor. Liu et al. applied Pt nanoparticles in combination with metal–organic framework (MOF) PCN-777 to produce the imine, ammonia, and hydrogen from benzylamine.

In this work, we chose as photocatalyst a carbon nitride (CN) material developed and deeply investigated earlier: potassium poly(heptazine imide) (K-PHI). In general terms, CN materials are catalysts of great interest, because of three factors:

1. Their synthetic procedures are cost-efficient, thanks to the modest synthesis temperature and low price of the precursors. In fact, CNs are expected to cost only a few euros per kilogram in scaled-up production scenarios.
The materials feature high chemical stability and thermal stability up to 600 °C.

Their structure can be modified and tuned by inserting various functional groups. Carbon nitrides such as K-PHI, in the presence of electron donors, are photoreduced to long-lived tinted radicals, which are useful intermediates to trigger reduction reactions, even in darkness, hours after the photochemical formation of the radical.

Previous reports highlighted that CO₂ reacts with primary amines to form alkylcarbamic acids. We indeed observed that benzylamine reacts with CO₂ and produces benzylcarbamic acid. This interaction facilitates dehydrogenation of benzylamine to phenylmethanimine at first, and ultimately gives N-benzylidene benzylamine. Das et al. recently demonstrated that CO₂ indeed plays a significant role in the activation of amines to form new products under metal-free, visible-light-driven photocatalysis. CO₂ could then be used as an abundant and inexpensive gas environment in this class of photocatalytic oxidative coupling, substituting, for example, the inert nitrogen, which does not activate the amine substrate, or the much more expensive argon, often used as inert environment in chemistry. Even though photocatalytic oxidative benzylamine coupling has been proved using O₂ (pure streams or even air) as an electron acceptor, CO₂ could also represent an inexpensive and relatively inert alternative for photocatalytic applications that require an O₂-free reaction environment. Moreover, besides permanent gases, the most common byproduct in CO₂ flue streams (e.g., from the cement industry) is moisture. Water was actually demonstrated to act as an electron acceptor in the oxidative coupling of amines, thus favoring the conversion rate. As a result, we propose a photocatalytic method that uses long-living radicals of K-PHI and “wet but cheap” CO₂ as a weak Lewis acid reaction medium in order to activate benzylamines forillumination-driven electron accumulation in semiconductors (IDEAS) and for efficient conversion to imines.

## RESULTS AND DISCUSSION

In order to verify the possibility of using primary amines for capturing CO₂ and to verify their photocatalytic coupling using K-PHI, we performed a series of preliminary tests in acetonitrile solvent under various conditions (Table 1).

Benzylamine was chosen as a representative substrate. The yield of the corresponding imine, N-benzylidene benzylamine, was 88% when the reaction mixture was degassed and subsequently purged with CO₂ followed by irradiation with blue light (Table 1, entry 1). When a different carbon nitride was used, i.e., mpg-CN, the conversion decreased to 38% (Table 1, entry 2). On the other hand, substituting CO₂ for Ar resulted in an imine yield of 34% (Table 1, entry 3). No conversion was expected, as no electron acceptor was added to the reaction mixture. However, the small degree of conversion can be explained by trace amounts of moisture. In fact, we estimated the water content in the reaction mixture to be 147–1528 ppm (Table S1 in the Supporting Information). The experiments performed in wet acetonitrile with variable amount of explicitly added water (Table 1, entries 4–6) suggested that indeed H₂O enhances the yield of the imine (see later discussion related to the proposed mechanism). To further prove the catalytic role of H₂O, CO₂ was passed through a column filled with P₂O₅ desiccant before being bubbled in MeCN. The imine yield decreased from 88% to 74%, revealing that H₂O indeed coparticipates in the photocatalytic oxidative coupling of benzylamines (Table 1, entry 7). Without light, almost no imine was produced (Table 1, entry 8). Without catalyst, benzylamine is stable under light irradiation, both in the presence of CO₂ and under Ar (Table 1, entries 9 and 10). Furthermore, in the presence of K-PHI, already after 4 h of irradiation, the yield of the imine was 65%, whereas in the presence of mpg-CN, only a 22% yield was observed (Table 1, entries 11 and 12). Using these data, apparent quantum yield (AQY) of the imine was calculated to be 0.21% for K-PHI and 0.072% for mpg-CN (Table S2 in the Supporting Information). Higher yield of the imine in the case of K-PHI is explained by faster benzylamine oxidation via IDEAS (explained below), i.e., by better capacity of the photocatalyst of storing unpaired electrons and readily donating them to an electron acceptor. Using a more concentrated reaction mixture in CD₃CN (a reduced volume of solvent was used due to higher cost of the latter) gave the imine with slightly lower yield, but it also allowed for quasi-in situ characterization of the reaction mixture by H NMR (Table 1, entry 13).

Under similar conditions, mpg-CN produced the imine in 52% yield (Table 1, entry 14). When the reaction was performed under Ar, the yield of imine was 13% (Table 1, entry 15). Finally, experiments were conducted using ¹³C-labeled CO₂ to prove that CO₂, despite having a key role in mediating these photocatalytic reactions, is not photocatalytically reduced by K-PHI (Table 1, entry 16; see also discussion in the Supporting Information).

### Table 1. Screening of the Reaction Conditions

| entry | photocatalyst | time (h) | environment | H₂O addition (μmol) | yield (%) |
|-------|---------------|----------|-------------|---------------------|-----------|
| 1     | K-PHI         | 24       | CO₂         |                     | 88        |
| 2     | mpg-CN        | 24       | CO₂         |                     | 38        |
| 3     | K-PHI         | 24       | Ar          |                     | 34        |
| 4     | K-PHI         | 24       | Ar          |                     | 42        |
| 5     | K-PHI         | 24       | Ar          |                     | 50        |
| 6     | K-PHI         | 24       | Ar          |                     | 73        |
| 7     | K-PHI         | 24       | CO₂ (dry)   |                     | 74        |
| 8     | K-PHI         | 24       | CO₂         |                     | 1         |
| 9     | –             | 24       | CO₂         |                     | 7         |
| 10    | –             | 24       | Ar          |                     | 7         |
| 11    | K-PHI         | 4        | CO₂         |                     | 65        |
| 12    | mpg-CN        | 4        | CO₂         |                     | 22        |
| 13    | K-PHI         | 24       | CO₂         |                     | 74        |
| 14    | mpg-CN        | 24       | CO₂         |                     | 52        |
| 15    | K-PHI         | 24       | Ar          |                     | 13        |
| 16    | K-PHI         | 24       | ¹³C–CO₂      |                     | 65        |

*Reaction conditions: 0.05 mmol of benzylamine; 5 mg of photocatalyst; 3 mL of MeCN; 1 bar of pressure; T = 35 °C; light intensity, 52 mW cm⁻² (blue LED, λmax = 461 nm); relative standard deviation of the method is 5%. H NMR yields (see NMR results section in the Supporting Information). Conditions as in entry 1, but CO₂ was passed through a column filled with P₂O₅, before entering the reaction tube, in order to remove moisture. Conditions as in entry 1, except that the reaction was performed in darkness. Conditions as in entries 1–3, but using 1 mL CD₃CN instead of 3 mL MeCN. Conditions as in entry 1, but using ¹³C-labeled CO₂. A different setup was used (see the Supporting Information).
The suggested method was further extended to other benzylamines. The corresponding imines were obtained with yields of 72%−96% (Scheme 1). Electron-donating m-CH$_3$ and o-CH$_3$ groups gave the products in higher yields, while p-CH$_3$ and p-OCH$_3$ in lower yield. Similarly, electron-withdrawing o-F group decreased the yield, while p-F slightly increased the yield. Analysis of the data on Scheme 1 reveals that no distinct correlation between the nature of substituents and the yield of the imine exists. Apparently, this is a result of quite similar oxidation potentials of substituted benzylamines.

**Scheme 1. Scope of Substituted Benzylamines Investigated in This Work**

| Substituent | Yield (%) | Conversion (%) |
|-------------|-----------|----------------|
| m-CH$_3$    | 90 (100)  |                |
| o-CH$_3$    | 95 (100)  |                |
| p-CH$_3$    | 87 (100)  |                |
| m-F         | 98 (100)  |                |
| o-F         | 92 (100)  |                |
| p-F         | 90 (100)  |                |

*Here, $^1$H NMR yields are given as percentages. Conversion of benzylamines is given in parentheses. Reaction conditions: 0.05 mmol of amine substrate; 5 mg of K-PHI; 3 mL of MeCN; 1 bar CO$_2$; $T_{bath} = 35$ °C; light intensity = 52 mW cm$^{-2}$ (blue LED, $\lambda_{max} = 461$ nm).*
Scheme 2. Proposed Mechanism for Photocatalytic Oxidative Coupling of Benzylamines to N-Benzylidene Benzylamine in the Presence of CO₂ and H₂O

![Diagram of the proposed mechanism]

“Imine formation mediated by CO₂ is drawn with gray arrows. NMR, EPR, and elemental analysis refer to a previous work." The mechanism mediated by H₂O is drawn in light blue and is based on known scientific literature. "

i.e., 1.203–1.242 V vs Ag/AgCl (sat. KCl). 26 Because of a much more positive potential of the valence band (VB) in K-PHI, +2.2 V vs NHE, 19 this CN catalyst does not “distinguish” between different benzylamines and oxidizes them equally well. (R)- and (S)-1-phenylethan-1-amines gave the imines in slightly lower yields, apparently because of the steric effect of the methyl groups next to the reactive N-center. Furan-based amines gave products in much lower yields, presumably because of a side reaction of furan ring oxidation (see Figure S6 in the Supporting Information).

The mechanism of the benzylamine condensation was investigated using 15N-labeled benzylamine. By combining 15N, 1H, and 13C NMR spectra of a 15N-benzylamine solution saturated with CO₂, the quantitative conversion of the amine to 15N-benzylcarbamic acid was confirmed (Figure 1a). This also proves that benzylcarbamic acid participates in the photocatalytic reaction rather than benzylamine itself when CO₂-saturated MeCN is chosen as the reaction environment. When actually performing the photoreaction using 15N-benzylamine as a reagent, the formation of ammonia in the form of 15NH₃ or 15NH₄⁺ is observed as a peak at −1.4 ppm in the 15N NMR spectrum of the reaction mixture (Figure 1b). Figure 1c shows the yield of imine, depending on the load of K-PHI. The imine yield increased when a larger amount of K-PHI was employed. Indeed, as previously demonstrated, 4 K-PHI can store up to ~1000 μmol of unpaired electrons per gram of photocatalyst. This gives another piece of evidence that IDEAS plays a role in the benzylamine oxidation, as a higher load of K-PHI can host a larger number of electrons from the benzylamine electron donor. On the other hand, the yield of the imine under Ar was almost the same when 5 mg and 40 mg of K-PHI were used, suggesting that even though more catalytic sites were provided, the reaction proceeds slower in the absence of CO₂. This observation strengthens the hypothesis that the benzylcarbamic intermediate indeed boosts the photocatalytic reaction, thanks to its better electron donor properties, compared to benzylamine. As previously mentioned, the conversion in Ar, ~7%–34%, is explained by the presence of trace amounts of water, which could participate as an electron acceptor and also due to IDEAS 4 (Table 1, entries 4–6). The yield of the imine was higher when the reaction was performed at lower temperature (i.e., the oil bath temperature set at 35 °C, see Figure S4 in the Supporting Information). It might be explained by destabilization of the intermediates on the path of imine formation and lower solubility of CO₂ at elevated temperature (in our case, 80 °C). The CO₂ pressure had almost no effect on the yield of the imine (Figure S7 in the Supporting Information), which is fact that suggests that the molecule is regenerated during each photocatalytic cycle when the benzylcarbamic acid reacts to form the final imine product.

Graphitic carbon nitrides (g-CN) generally have particle sizes of few micrometers or larger, unless special conditions are employed to produce materials with a particular morphology, e.g., wires 27 or cubic mesoporous materials. 28 For comparison, K-PHI is always assembled in smaller particles ranging from 50 nm to 200 nm. 29 By cross-checking the data from the benzylamine conversion, the K-PHI crystal unit-cell parameter, 30 and particle size distribution (see Figure S8 in the Supporting Information), it is possible to provide a first-round estimation of the turnover frequency (TOF) for a single
nanophotoreactor with an average diameter of \(~94\) nm. These assumptions lead to a calculated TOF of \(~69(1)\) s\(^{-1}\).

Based on this evidence, we propose the mechanism shown in Scheme 2 (gray pathway), as well as Scheme S2a in the Supporting Information. CO\(_2\) initially reacts with benzylamine, forming benzylcarbamic acid. Upon light irradiation, K-PHI* is excited to K-PHI\(^{−}\). The carboxylic acid promptly acts as an electron donor and transfers 1 electron to the excited photocatalyst, which turns to the radical anionic K-PHI\(^{−}\) form, which is characterized by a color change from yellow-orange to blue-green (detected by electronparamagnetic resonance (EPR) in our previous work\(^8\)). The electron-poor benzylcarbamic acid, now in the form of radical cation, proceeds further in the reaction cycle by releasing CO\(_2\) and two protons and combining with a second carbamic acid molecule. We suggest that gaseous H\(_2\) is not produced here, based on elemental analysis data showing that K-PHI after reaction has an increased hydrogen content (in the form of H\(^{−}\))\(^8\) and based on experiments monitoring pressure changes in the reactor headspace (see Figure S9 in the Supporting Information). Pressure change data, product analysis, and experiments with \(^{13}\)C-labeled CO\(_2\) also allowed us to confirm that CO\(_2\) is regenerated during the photocatalytic cycle rather than being converted to other compounds (see discussion in the Supporting Information). This last reaction step leads to the formation of the imine product upon the release of another CO\(_2\) molecule and NH\(_3\) (detected via NMR in both its \(^{15}\)NH\(_3\) and \(^{15}\)NH\(_4\)\(^+\) forms; see Figure 1b, as well as Figure S16 in the Supporting Information).

If water is present in the reaction medium, it can act as an electron acceptor, as reported in the scientific literature.\(^{3,11,25,31}\) Benzylamine acts as an electron donor instead of benzylcarbamic acid, despite the latter being a better one, and a different reaction path is followed (light blue pathway in Scheme 2, as well as Scheme S2b in the Supporting Information). Nevertheless, similarly to the photocatalytic reaction mediated by CO\(_2\), imine is produced together with NH\(_3\).

In summary, according to the mechanism we propose herein, the consecutive push–pull of electrons mediated by K-PHI allows for the successful coupling of two benzylamine molecules, stepping through benzylcarbamic acid intermediates. K-PHI works in a manner similar to a battery by charging (i.e., reduction of K-PHI* to K-PHI\(^{−}\)) and discharging (i.e., oxidation of K-PHI\(^{−}\) back to K-PHI). Showing a better ability to even out the input and output flow of electrons via IDEAS, this material outperforms the standard choice carbon nitride photocatalyst mpg-CN.

The feature of carbon nitride materials to store electrons has a clear influence on their performance in the oxidative coupling of benzylamines in the presence of CO\(_2\). Thus, higher conversion of benzylamine (e.g., see Figures 1c and 1d) correlates with higher electron capacity of the employed photocatalyst. The large capacity of K-PHI to store electrons is equal, in practical terms, to a few hundred micromoles of the electron donor molecules per gram of photocatalyst that are oxidized presumably instantly via IDEAS.\(^4\) The charged photocatalyst then acts as an “electron pump”, readily injecting unpaired electrons into an available electron acceptor (e.g., O\(_2\)). Therefore, matching a photocatalyst with large electron capacity with an efficient electron donor within the framework of illumination-driven electron accumulation in semiconduc-

**CONCLUSIONS**

IDEAS mediated by benzylamine and combined with CO\(_2\) as an amine activating agent was applied for preparation of a series of synthetically useful imines with yields of 72%–96%. The results of the photocatalytic tests agree with our earlier data\(^1\) on performance of K-PHI, in comparison with covalent carbon nitrides (for example, mpg-CN). Regardless of the reaction type and substrates structure, K-PHI always demonstrates higher activity. Having the comprehensive data on charge storage ability of carbon nitrides and their performance in coupling of benzylamines, we conclude that IDEAS is responsible for faster kinetics. Benzylamine captures CO\(_2\) and stores it in the form of benzylcarbamic acid, while IDEAS accelerates the photocatalytic reaction by rapid oxidation of the benzylcarbamic acid. The entire system operates under visible-light irradiation and ultimately yields imines from benzylamines.

CO\(_2\) was demonstrated to favor and accelerate the photocatalytic oxidative coupling of benzylamines by producing a more efficient electron donor: benzylcarbamic acid. Moreover, the moisture present in the solvent or in the gas stream was confirmed to also promote the imine formation by acting as an electron acceptor in the photocatalytic cycle. In the light of these two experimental observations, we conclude that wet streams of CO\(_2\), such as flue gas streams from cement industry after desulfurization/denitrification steps, are a convenient and inexpensive alternative as a reaction atmosphere to highly expensive and pure inert gases used in laboratory research, such as argon.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c02176.

Experimental section, synthesis procedure of the catalyst, description of the reaction setups, proposed mechanism of photocatalysis, and further products characterization (PDF)

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Notes

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