

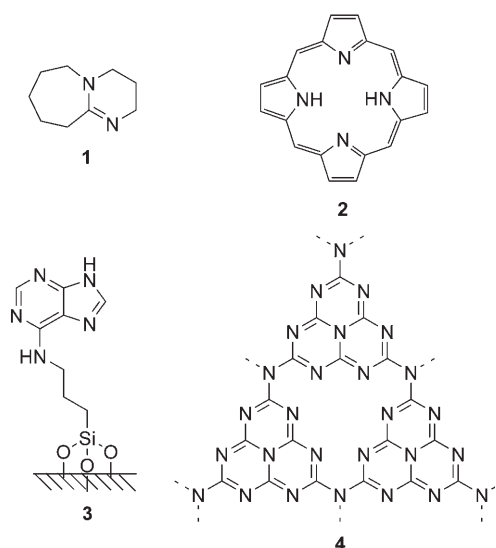
CO₂ ActivationMetal-Free Activation of CO₂ by Mesoporous Graphitic Carbon Nitride**

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The chemical activation of CO₂, that is, the splitting of its structure in a chemical reaction, is a major challenge in synthetic chemistry because of the very high thermodynamic stability of CO₂, which requires an efficient energy source for its activation. However, the fact that biogenic carbon (i.e., biomass) originates from the fixation of CO₂ implies that CO₂ activation must be one of the oldest reactions in biological systems and have already occurred in prebiotic times.^[1,2] Interestingly, in current photosynthetic systems, this process relies on the formation of a carbamate as the first step of the cycle,^[3] which may also have been the case in prebiotic systems, as a number of cyanide-based, nitrogen-rich, conjugated organic molecules, such as nucleic acids, porphyrins, and phthalocyanines, existed before life began.^[4]

In synthetic chemistry, numerous transition-metal catalysts for the activation of CO₂ have been explored.^[5,6] Previous metal-free attempts concentrated on the use of alkylated amidines and guanidines,^[7–10] such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **1**, Scheme 1). The structure of the DBU/CO₂ adduct involved was a matter of debate, but detailed analysis has shown it to be a hydrogencarbonate salt only.^[11] However, the use of more-nitrogen-rich molecules, such as adenine bound to mesoporous oxides (**3**, Scheme 1), was recently shown to promote CO₂ fixation through a “true” carbamate species, finally leading to organic carbonates.^[12] This finding led us to suspect that other heterogeneous surface structures containing a N=C=N binding motif would enable efficient CO₂ fixation and activation.

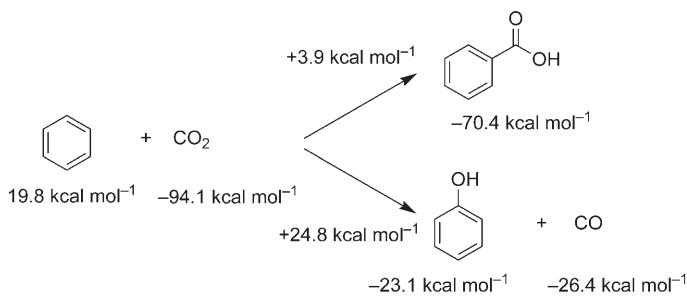
Recently, we introduced the mesoporous graphitic carbon nitride mpg-C₃N₄ (**4**, Scheme 1), which forms a new class of heterogeneous metal-free catalysts for Friedel–Crafts reactions.^[13,14] The catalyst mpg-C₃N₄ can be conveniently synthesized by polymerization of cyanamide in the presence of a silica template.^[15] The pore walls consist of tri-s-triazine units connected by planar amino groups. The solid-state material has many defects, but it is relatively chemically inert and is stable up to 600 °C. Our previous work gave evidence that this class of catalysts can activate aromatic systems by electron



Scheme 1. Nitrogen-rich molecules investigated for metal-free catalysis: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **1**); porphin (**2**); adenine grafted onto silica (**3**); idealized repeating motif of graphitic C₃N₄ (**4**).

transfer; these systems thus involve metal-free coordination chemistry.^[16]

Two possible reaction pathways can be envisaged for the reaction of benzene with CO₂ activated by mpg-C₃N₄: 1) a Friedel–Crafts-type condensation of benzene with CO₂ to yield benzoic acid, and 2) a (previously unknown) oxidation of benzene by CO₂ to yield phenol with evolution of CO (Scheme 2). The formation of benzoic acid is very weakly endothermic (calculated on the basis of the standard formation enthalpies in the gas phase)^[17] and disfavored entropically. The second reaction is moderately endothermic and entropically neutral. It is shown below that the energy needed for this reaction can indeed be provided by secondary energy



Scheme 2. Two possible reaction paths for the reaction of benzene and CO₂.

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Table 1: Reaction of benzene, anisole, or chlorobenzene with various CO₂ sources in the presence of mpg-C₃N₄ as catalyst.^[a]

	CO ₂ source	Solvent	Coreactant	<i>t</i> [h]	Conversion [%] ^[b]	Product ^[c]
1	–	benzene	triethylamine (200 mg)	20	0	–
2	NaHCO ₃ (200 mg)	benzene	–	20	46 ^[d]	phenol (100%)
3	NaHCO ₃ (100 mg)	benzene	–	20	100 ^[d]	phenol (100%)
4	NaHCO ₃ (400 mg)	heptane	benzene (100 mg)	20	100 ^[e]	phenol (100%)
5	NaHCO ₃ (200 mg)	anisole	–	20	0	–
6	NaHCO ₃ (200 mg)	chlorobenzene	–	20	0	–
7	CO ₂ (10 bar)	benzene	–	24	0	–
8	CO ₂ (10 bar)	benzene	triethylamine (200 mg)	12	20 ^[f]	phenol (65 %), biphenyl (35 %)
9	CO ₂ (3 bar)	benzene	triethylamine (200 mg)	24	13 ^[f]	phenol (29 %), biphenyl (71 %)
10	CO ₂ (10 bar)	benzene	pyridine (200 mg)	48	0	–
11	–	benzene	triethylamine (200 mg), phenol (1 g)	48	5	biphenyl (100%)
12 ^[g]	CO ₂ (10 bar)	benzene	triethylamine (200 mg)	24	0	–

[a] In a typical reaction mpg-C₃N₄ (100 mg) was added to the desired solvent (either heptane or the pure aromatic compound; 10 mL) in a 100-mL stainless steel autoclave. The CO₂ source was added and the closed autoclave was heated to 150 °C. [b] Conversion rates were determined by GC–MS with an internal standard (toluene) as the ratio between the formed products and the initial amount of limiting reactant. [c] The percentage in parentheses is the amount of the specified product in the reaction mixture, as determined by GC–MS with an internal standard. [d] Conversion calculated with respect to the initial amount of NaHCO₃. [e] Conversion calculated with respect to the amount of benzene. [f] Conversion calculated with respect to the amount of base. [g] Reference experiment without catalyst.

sources, such as the neutralization enthalpy of the phenol, the hydration of CO, or other subsequent reactions. In this reaction pathway, the very stable component CO₂ would be converted into a more reactive species, which would then be available for further chemical reactions. As previously described metal-free activation of CO₂ resulted only in the formation of organic carbonates, this pathway would then lead to new, previously unknown CO₂ chemistry. Incidentally, such a reaction could also provide an alternative to the usual cumene process for phenol production or even to more advanced syntheses relying on the direct oxidation of benzene with oxygen or nitrous oxide.^[18]

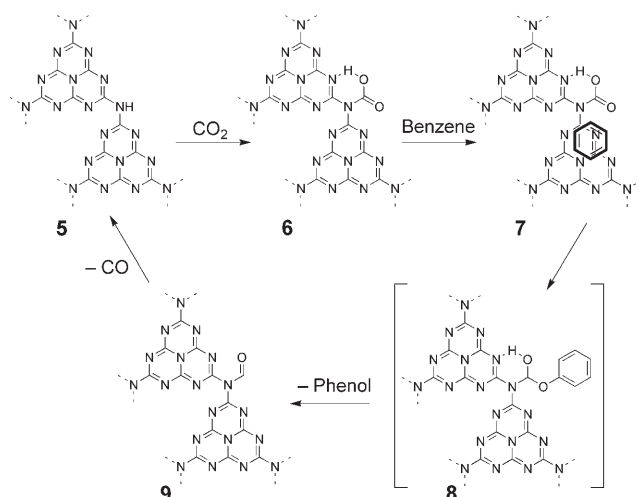
We thus undertook to test these reactions with various CO₂ sources and various aromatic compounds (benzene, anisole, and chlorobenzene) with mpg-C₃N₄ as catalyst. The reactions were performed at 150 °C in a 100-mL stainless steel autoclave fitted with a teflon mantle with 100 mg of mpg-C₃N₄.^[15] NaHCO₃ or gaseous CO₂ (3–10 bar) was used as the carbon dioxide source. Either heptane or the aromatic substrate itself (10 mL) was used as the solvent. After the reaction was complete, the reaction mixture was neutralized and then analyzed by GC–MS. To identify and quantify the products, they were isolated and analyzed by ¹H and ¹³C NMR spectroscopy (Table 1). The extents of conversion were calculated on the basis of the limiting reactant (benzene, the CO₂ source, or the base).

Surprisingly, the second reaction, namely, the oxidation of benzene to phenol, takes place whenever a CO₂ source and a sufficiently strong base are present (Table 1, entries 2–4, 8, 9). The reaction products are free of benzoic acid, the product of direct carboxylation of benzene. The only side reaction observed is the formation of biphenyl in the presence of a large excess of benzene (Table 1, entries 6 and 7). This product probably results from the arylation of benzene with phenol, as indicated by the fact that under similar conditions with the same catalyst a mixture of benzene and phenol yielded 5% biphenyl (Table 1, entry 11). Unfortunately, reactions with other aromatic compounds such as anisole

(Table 1, entry 5) or chlorobenzene (Table 1, entry 6) failed to yield any detectable product even at higher temperatures (up to 180 °C for chlorobenzene and 220 °C for anisole). This result is consistent with previous observations that anisole is far less reactive than benzene in mpg-C₃N₄-catalyzed Friedel–Crafts reactions.^[14] The most straightforward explanation is that steric hindrance prevents effective adsorption of substituted arenes on the tri-s-triazine units.

A careful FTIR investigation of the catalysts after the reaction indicated the formation of a carbamate species, as a new IR bands appear at 1419 cm^{–1} in the spectrum of the powder. These observations are in good qualitative agreement with the formation of a carbamate on an adenine derivative reported by Ratnasamy and co-workers.^[12] We thus postulated that the first step of our catalytic process involves the formation of a carbamate species, presumably on surface primary or secondary amino groups of mpg-C₃N₄ (Scheme 3). The existence of such amino groups, which result from incomplete condensation of the tri-s-triazine units, was previously demonstrated by Lotsch and Schnick.^[19] The formed carbamate would then be well positioned to react with an aromatic molecule activated by the catalyst.^[14] The hypothetical [2+2] addition of an aromatic C–H bond of the benzene to the C=O double bond would result in the formation of a hemiacetal, which could easily eliminate phenol to yield a formamide. The latter can eliminate CO, as reported for the thermolysis of formamide.^[20]

DFT calculations were undertaken to support the first steps of the proposed reaction mechanism. The geometry of a model tri-s-triazine unit was optimized (see the Supporting Information for computational details) along with the geometries of the corresponding carbamate (**6**) and adduct with benzene (**7**, Scheme 3). The first step is slightly endothermic (8.9 kcal mol^{–1}), which is again consistent with the fact that CO₂ is stable and carbamates eliminate CO₂, except under alkaline conditions (the neutralization enthalpy is –13.34 kcal mol^{–1}). DFT calculations also reveal that the adsorption of benzene on the model tri-s-triazine unit is weakly exothermic



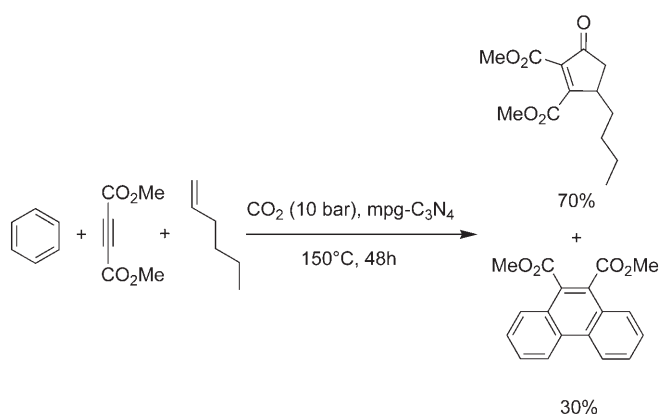
Scheme 3. Possible mechanism for the formation of phenol from benzene and CO_2 catalyzed by mpg- C_3N_4 .

($-4.8 \text{ kcal mol}^{-1}$, step 3). The results of these calculations indicate that the first steps of the mechanism are favorable at least under alkaline conditions.

The need for a relatively strong base (NaHCO_3 with $\text{p}K_{\text{a}} = 10.3$ or triethylamine with $\text{p}K_{\text{a}} = 10.6$) for any conversion to be observed (the addition of weaker bases such as pyridine ($\text{p}K_{\text{a}} = 5.2$) is insufficient) may also be related to the acidic character of phenol ($\text{p}K_{\text{a}} = 10.0$), thus enabling the phenolate as an electron-rich molecule to be the leaving group from this overall very electron-rich structure. Another possible explanation lies in the fact that the equilibrium of this reaction can be displaced when one of the products is consumed by a second reaction. The deprotonation of phenol by the auxiliary base may play this role. Such a shift of the reaction equilibrium is certainly also the reason why, in the presence of triethylamine as a coreactant, the reaction only takes place with a large excess of benzene. The excess benzene reacts with the phenol to give biphenyl, thus shifting the equilibrium in the direction of the products.

The generated CO is a valuable reaction intermediate, as it is also coordinated to the catalyst and can undergo further reactions. To confirm that CO really is produced in the reaction and is available for further reaction, we quenched it in a Pauson–Khand (PK) reaction. This reaction, the cyclo-trimerization of CO, an alkene, and an alkyne to form a cyclopentenone, is a very useful synthetic tool and in our case serves as evidence for the formation of CO.^[21,22] We added 1-hexene and dimethylacetylene-1,2-dicarboxylate (DMAD) to the standard reaction mixture (Scheme 4). The production of dimethyl-4-butylcyclopent-2-en-1-one-2,3-dicarboxylate (the expected Pauson–Khand product) in rather high yield (70% at 100% conversion with respect to DMAD) indeed proved the presence of CO. Interestingly, no phenol was detected and all the formed biphenyl was consumed in a Diels–Alder reaction with DMAD to form dimethylphenanthrenedicarboxylate (30% yield).

In conclusion, we have shown that mpg- C_3N_4 can chemically activate CO_2 . Formally, CO_2 is split into a $\text{O}^\bullet$ diradical,



Scheme 4. Pauson–Khand reaction for the in situ detection of CO formation.

which is consumed by the oxidation of benzene to phenol, and CO, which is available for subsequent reactions involving the formation of C–C bonds for the synthesis of organic structures (exemplified herein with a Pauson–Khand reaction). In biological photosynthesis, the energy for CO_2 splitting is not provided by a substrate, but by photons. It is thus very tempting to ask whether our simple chemical model could be a first step towards artificial photosynthesis (i.e., the formation of organic compounds and oxygen from CO_2).

Experimental Section

All reactions were carried out in a 100-mL stainless steel autoclave fitted with a teflon mantel, internal thermoregulation, a 60-bar manometer, and a magnetic stirrer (Berghof, BR-100). When NaHCO_3 was used as the CO_2 source, the given amount of salt was placed directly in the autoclave with mpg- C_3N_4 (100 mg) and the solvent (either heptane or the aromatic compound; 10 mL), and then the reactor was closed and heated to 150°C. When the CO_2 source was gaseous CO_2 , mpg- C_3N_4 (100 mg) was placed in the reactor together with the solvent and the required amount of base (either triethylamine or pyridine), and the reactor was closed. The autoclave was then flushed three times with CO_2 , pressurized with CO_2 (3 or 10 bar), and then heated to 150°C.

The reaction mixture was neutralized with 1M HCl and injected directly into the GC–MS (Agilent Technologies, GC6890N, MS5975). The products were isolated by extraction with toluene and, after evaporation of the solvent in vacuo, analyzed by ^1H and ^{13}C NMR spectroscopy in CDCl_3 (Bruker DMX 400).

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