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Photocatalytic Reverse Semi-Combustion Driven by Ionic Liquids

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Abstract: The simple photolysis of CO_2 in aqueous solutions to generate CO and/or hydrocarbons and derivatives in the presence of a catalyst is considered a clean and efficient approach for the use of this gas as a C1 building block. Despite the huge efforts dedicated to this transformation, either using semiconductors or homogeneous catalysts, only small improvements on the catalytic activity have been achieved so far. We report that simple aqueous solutions of organic salts – denominated ionic liquids – can efficiently photo-reduce the CO_2 to CO without the use of photosensitizers or sacrificial agents. The system relies on the formation of the $[CO_2]^{\bullet-}$ intermediate; via homolytic C-C bond cleavage in a cation-CO_2 adduct of imidazolium-based ionic liquids (ILs). The system continued producing CO up to 2.88 mmol.g^{-1} IL after 40 h of irradiation and represented apparent quantum yield of 3.9%, when an aqueous solution of 1-*n*-butyl-3-methylimidazolium-2-carboxylate ($BMIm.CO_2$) ionic liquid was used. The organo-photocatalytic principles of our system may help to develop more simple and efficient organic materials to produce solar fuels from CO_2 under mild conditions which represents a real alternative to those based on semi-conductors and homogeneous metal based catalysts.

Introduction

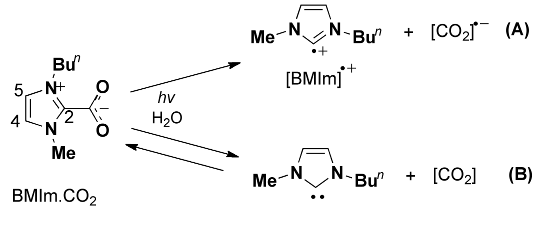
Despite a growing number of climate change mitigation policies, increasing investments associated with the capture and storage technologies for CO_2, the anthropogenic emissions of this gas are inexorable growing.[1] Hence, there is a growing interest in finding large-scale commercially viable end-use opportunities for the CO_2 utilization. In the last decade, carbon dioxide photo-reduction to CO and/or hydrocarbon derivatives (artificial photosynthesis) has grown into a blooming field of research.[2, 3] A simple combination of sun light, aqueous solutions saturated with carbon dioxide and an appropriate photocatalysts may yield CO (reverse semi-combustion) and/or hydrocarbon derivatives (reverse combustion).[4, 5] The photocatalytic CO_2 conversion over semiconductors employs photo-excited electrons/holes to drive the simultaneous processes of water oxidation at the valence band and CO_2 reduction at the conduction band.[5] However, the high-energy barrier for CO_2 activation, side reactions such as hydrogen evolution, and high rates of electron-hole pair recombination of the employed photocatalysts, mainly based on semi-conductors and hybrids materials, still remain unsolved challenges to be faced.[6, 7] Although promising advances have been achieved to enhance the CO_2 conversion, the catalytic activity and/or selectivity is still very low.[3, 8-10] The photocatalytic reduction of CO_2 can also be performed with homogenous based metal catalysts employing appropriate sensitizers and sacrificial electron donors. However, much remains to be done to generate more durable, simple, recyclable, and efficient photocatalytic systems.[9, 11-13] Moreover, the photo-generated CO can be used for the catalytic functionalization of various substrates.[14]

Ionic liquids (ILs, Figure S1) are known to solubilize and, in some cases, to activate carbon dioxide by stabilizing radical/anionic species[15, 16] and hence, may constitute an attractive material for CO_2 photoreduction.[17] Most important, theoretically, excess of charge localization/holes (generated electrochemically or by radiation) may be formed in ILs.[18]

The objective of the work described herein is to develop IL photocatalysts that would promote the formation of the activated CO_2 intermediates, which then react with water photoproducts to produce CO akin to those pathways induced electrochemically.[19] We have chosen the zwitterionic IL 1-*n*-butyl-3- methylimidazolium-2-carboxylate ($BMIm.CO_2$) to test whether such a route was feasible. The photoactivation of this zwitterion may provide reactive species such as the imidazolium radical cation, which has already been detected under radiolytic degradation conditions from imidazolium cations.[20] In addition, CO_2 radical anion ($[CO_2]^{\bullet-}$) could be evoked by the photolysis of this zwitterion in the presence of photosensitizers.[21]

Results and Discussion

We firstly tested the photoreduction of aqueous $BMIm.CO_2$ (Scheme 1) under argon atmosphere employing a Xe lamp (300 W). The gaseous products were analyzed and quantified by GC (Figure 1a), and the aqueous phase by ^1H and ^{13}C NMR (see Figures S8-9).



Scheme 1. Possible pathways involved in the photolysis of $BMIm.CO_2$ adduct during CO_2 photo-reduction.

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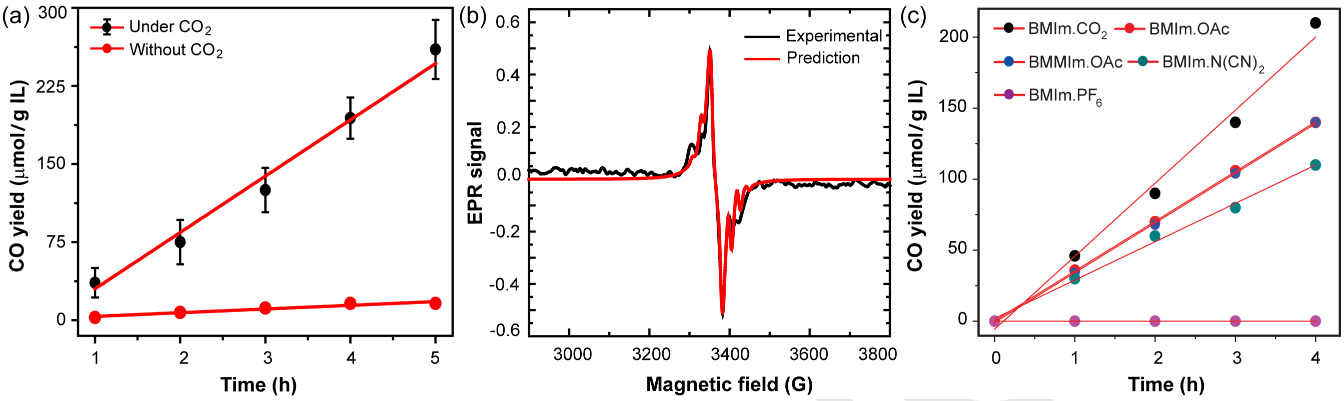

Figure 1. (a) Reaction conditions: BMIm.CO_2 IL (5 mg, 0.027 mmol), CO_2 (atmospheric pressure), H_2O (3 mL), temp. (25 ˚C), Xe lamp (300 W) and BMIm.CO_2 IL (126 mg, 0.69 mmol under argon), the error bars have been obtained from at least three experiments, (b) Experimental and simulated ESR spectra of 1-*n*-butyl-3-methylimidazolium radical obtained from the photolysis of BMIm.CO_2 aqueous solution and (c) Photo-catalytic reduction of CO_2 by different ILs. Reaction conditions: IL (5 mg), CO_2 (atmospheric pressure), H_2O (3 mL), temp. (25 ˚C), and Xe lamp (300 W).

We detected CO (3.9 µmol.g^{-1}.h^{-1}) and CO_2 as the only gaseous products together with traces of H_2 (Figure 1a) after 5 h of reaction, and the BMIm cation associated with the carbonate anion (CO_3^{2-}) was identified by NMR experiments of the aqueous phase (Figures S2 and S3). Performing the same reaction under CO_2 atmosphere, the same products (gaseous and aqueous) were observed, but with an increase production rate of CO up to 56 µmol.g^{-1}.h^{-1} as shown in Figure 1a. The presence of these compounds in both, the gaseous and the aqueous phase (Figure S2 and S3), suggests that the photolysis proceeds through the formation of the BMI radical cation ($[BMIm]^{\bullet+}$) and the CO_2 radical anion ($[CO_2]^{\bullet-}$), formed by homolytic cleavage of the C2—CO_2 bond in the BMIm.CO_2 IL. The origin of CO from the CO_2 photoreduction was verified by performing the reaction with $^{13}CO_2$ and the aqueous solution of BMIm.$^{13}CO_2$ IL that produces ^{13}CO detected by the appearance of a signal at *m/z*=29 in the GC-MS (Figure S4).

The reaction may proceed via two distinct pathways (Scheme 1): (i) the homolytic cleavage of BMIm.CO_2 to generate the radical cation and anion ($[CO_2]^{\bullet-}$) (Scheme 1(A), photo pathway) or (ii) the heterolytic cleavage leading to the unproductive path Scheme 1(B) (thermal pathway) with the formation of the N-heterocyclic carbene (NHC) and CO_2.

By Electron Spin Resonance (ESR), the possible involvement of radical species during the photolysis of BMIm.CO_2 (Figure 1b) was verified and the predicted ESR signal at 3365 G of the imidazolium radical cation $[BMIm]^{\bullet+}$ [20] was observed after 15 minutes of irradiation at 254 nm (-196 °C). The simulated and detected ESR signals present excellent agreement (Figure 1b and S4). Afterward, the frozen $[BMIm]^{\bullet+}$ was thawed to room temperature and the aqueous solution was then submitted to a CO_2 flux for a period of 1 minute followed by another freezing (-196 °C, Figure S5) in the attempt to observe the reverse reaction, that is, the CO_2 incorporation restoring the zwitterion BMIm.CO_2. The signal corresponding to the radical cation presented a noteworthy drop in its amplitude due to its consumption.

When the frozen solution was once more irradiated (254 nm) for 5 minutes, an increase in the amplitude of the signal related to the radical cation was observed again (Figure S5). The formation of the $[CO_2]^{\bullet-}$ (estimated half-life time of 10 ns)[22] as well as the imidazolium cation radical could not be evidenced by Raman spectroscopy in BMIm-CO_2 aqueous solution submitted to the same irradiation conditions applied to the ESR experiments, indicating that this radical anion is rapidly consumed via paths suggested in Scheme 2.[23] NHCs (N-heterocyclic carbenes) have been already evoked to explain laser flash photolysis results of a zwitterionic carboxylate derivative, in which $[CO_2]^{\bullet-}$ is formed and, in the presence of water, affords formate $[HCO_2]^-$ without mentioning the corresponding radical cation.[21].

Therefore, the possible reaction pathways involved in the CO_2 photoreduction occurs via the formation of $[CO_2]^{\bullet-}$ that reacts with CO_2 to generate the CO_2 dimer radical anion $[C_2O_4]^{\bullet-}$ that, by addition of another $[CO_2]^{\bullet-}$, produces the CO and carbonate as observed in electrochemical reductions (Scheme 2).[19]

The imidazolium cation is likely to be regenerated by the reaction of $[BMIm]^{\bullet+}$ with a bicarbonate radical anion that was observed by ESR from the 1-*n*-butyl-3-methylimidazolium hydrogen carbonate (BMIm.HCO_3) salt (Figure S6). The produced basic carbonate/bicarbonate can then deprotonate the imidazolium cation forming the NHC-carbene that by interaction with CO_2 regenerates the zwitterion BMIm.CO_2 (Scheme 2). The activation energy for the equilibrium between BMIm.CO_2 and BMIm.HCO_3 has been estimated as only 19.6 kcal.mol^{-1} in water, the formation of BMIm.HCO_3 by the reaction of BMIm.CO_2 and H_2O is relatively fast (20 min). [24]

The ^1H and ^{13}C NMR spectra of the aqueous phase of the BMIm.CO_2 IL confirms the generation of CO_3^{2-} when the reaction was performed under argon (Figures S2 and S3). The HCO_3^-

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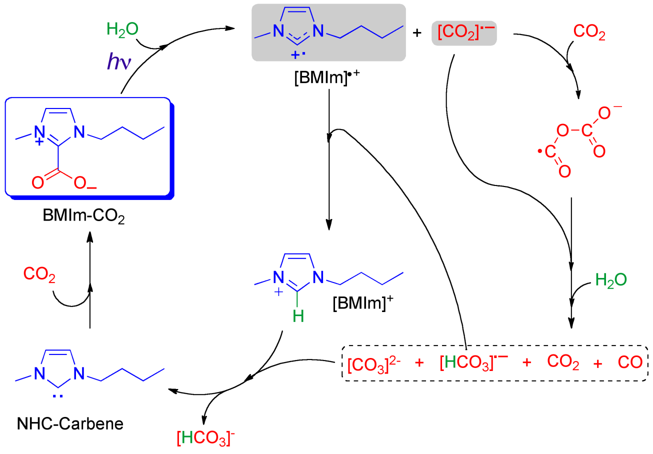

Scheme 2. Possible species involved in the CO_2 photo-reduction driven by ILs (for details see text).

and CO_3^{2-} species were detected at the end of the photo-reduction (Figure S2-c). Only HCO_3^- was observed within the first 30 min of irradiation under CO_2 atmosphere (Figure S7) with the production of CO indicating that the bicarbonate is consumed during the reaction, close to estimated time necessary to attain the equilibrium for the formation of BMIm.CO_2 from the reaction of BMIm.HCO_3 and water.[24] Note that by ESI-MS and NMR analysis of the aqueous solution after the reaction no other species have been observed.

Moreover, the IL containing the basic acetate anion (BMIm.OAc) also exhibits significant activity toward the photo-reduction of CO_2 to CO (134 μmol.g^{-1} IL, Figure 1c) and the typical ESR signal of the imidazolium radical cation was observed (Figure S8 and Tables S1 and S2). In general, ILs containing basic anions may generate the imidazolium zwitterion (BMIm.CO_2) when interacting with CO_2, and possibly photo-induce the reduction of CO_2 toward CO. Only CO_3^{2-} was detected by ^{13}C NMR analysis in aqueous solution of BMIm.OAc IL after irradiation under CO_2 (Figure S9), which corroborates that bicarbonate (HCO_3^-) is generated and consumed during the reaction. The origin of CO from CO_2 was confirmed by the photo-reduction of $^{13}CO_2$ by an aqueous solution of the BMIm.OAc IL that yields ^{13}CO (Figure S10). Of note that no CO was observed when aqueous solution of BMIm.OAC IL was irradiated under argon atmosphere.

When the imidazolium cation has the C2 position blocked as is the case in 1-*n*-butyl-2,3-dimethyl imidazolium acetate (BMMIm.OAc), the production of CO was slightly less than the BMIm.OAc IL during the first 3 h of reaction yielding 132 μmol.g^{-1} IL (Figure 1c). In this case, the formation of the zwitterion can occur only at the less favorable C-4 and C-5 positions of the imidazolium ring.[25] However, even in this case, the radical cation was observed by ESR analysis. The radical is localized closer to one of the N-imidazolium positions (Figure S11-a), and the expected multiplicity of the observed signal confirms the formation of the radical cation at C-4 (or C-5).

Other ILs that are less prone to the formation of the zwitterion BMIm.CO_2 are less active as CO_2 photo-reduction catalysts (Figure 1c). For example, 1-*n*-butyl-3-methylimidazolium diacyanimide (BMIm.N(CN)$_2$) IL photo-reduces the CO_2 to 110 μmol.g^{-1} of CO (the ESR signal still observable albeit the low intensity as shown in Figure S11-b) whereas in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMIm.PF$_6$) IL no production of CO has been detected. This phenomenon may be correlated with the basicity of the anions, which may play an important role in the CO_2 sorption, and subsequently formation of the BMIm.CO_2 zwitterion that drives the generation of CO during the photo-reduction process. Therefore, it is plausible to assume that the most probable limiting step is the formation of the imidazolium-CO_2 adduct[26] that is related to anion basicity.

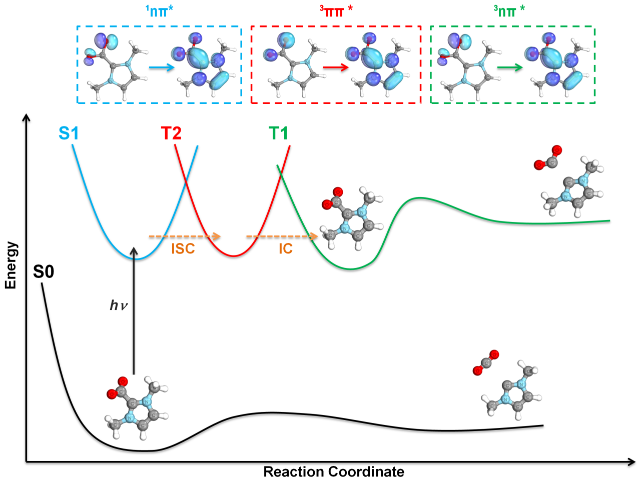

Figure 2. Schematic overview of the MMIm.CO_2 photo-dissociation. The lower barrier is the releases of CO_2 in the ground state (path B). In the excited state (path A), the first step is the excitation of the MMIm.CO_2 to S1 and subsequent ISC with T2 that achieve T1 by IC. In the T1 state occurs the release of $[CO_2]^{•-}$.

Quantum mechanical calculations were performed to elucidate the possible pathways involved in the photolysis of BMIm.CO_2. For an adequate description of excited states the multi-configurational methods CASSCF//CASPT2 were used. These calculations performed on the simpler 1,3-dimethylimidazolium-CO_2 adduct (MMIm.CO_2) corroborate that path B (Scheme 1) occurs in the ground state with energetic barriers around 10 kcal/mol, confirming that this path is the major (Figure S12 of Supporting Information) for CO_2 release. We also observed that the reaction coordinate for CO_2 release in the S1 excited state possesses a very high-energy barrier (See Figure S13 of Supporting Information). However, the excited S1, T1, and T2 states present very similar energies, and thus; we suppose that the release of $[CO_2]^{•-}$ occurs in the triplet state T1, presenting the energy barrier lower than for CO_2 release in the S1 state (See Figure S14 of Supporting Information). A schematic overview of the MMIm.CO_2 photo-dissociation is illustrated in Figure 2.

The S1 state has ^{1}nπ* character, whereas T1 is of ^{3}nπ* character. Hence, intersystem crossing (ISC) between these two states should be negligible according to the El-Sayed rules.

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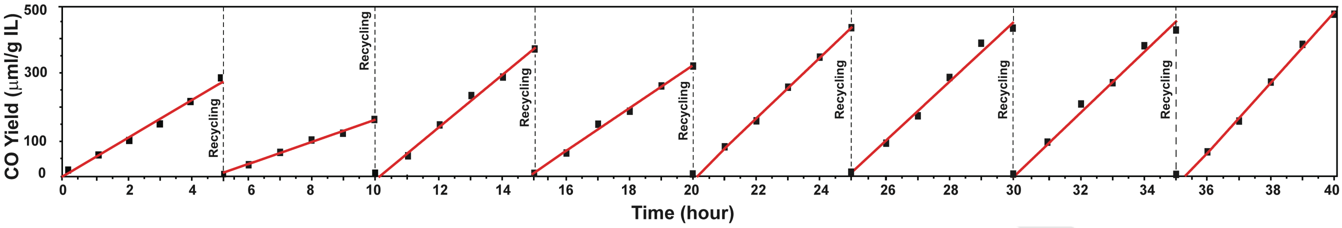

Figure 4. The recycling test of CO_2 photo-reduction by aqueous solution of $BMIm.CO_2$ IL. Reaction conditions: $BMIm.CO_2$ IL (5 mg, 0.027 mmol), CO_2 (1 bar), H_2O (3 mL), temp. (25 ˚C) and Xe lamp (300 W).

However, the ISC may occur between S1 and T2, which possesses a $^3\pi\pi^*$ character. This transition is allowed according to the El Sayed rules. At least, the T1 state is achieved by internal conversion (CI) from the T2 state. In the T1 state, the dissociation of $[CO_2]^{\bullet-}$ is evolved, although a considerable energy barrier must be exceeded (around 28 kcal/mol). The spin density (Figure 3) in the T1 state is concentrated at the C2 of the imidazolium ring and the carbon of the CO_2 moiety, indicating homolytic cleavage of the C2-CO_2 bond. Therefore, path A (Scheme 2) is the minor one, but the generated $[CO_2]^{\bullet-}$ is rapidly consumed to yield CO. Finally, there are two major problems during the photo-reduction of CO_2, a) absorption of CO_2 and b) activation of CO_2. These problems can be solved by the introduction of imidazolium-based ILs. ILs make imidazolium-adduct ($BMI.CO_2$), these imidazolate-adduct not only facilitates CO_2 adsorption but also promotes CO_2 activation by reducing the potential for the formation of $CO_2^{-\bullet}$ and the overall barrier of the redox reaction, in this case the homolytic cleavage of the Im-CO_2 bond generating the reactive $[CO_2]^{\bullet-}$ that rapidly yields CO (Scheme 2).

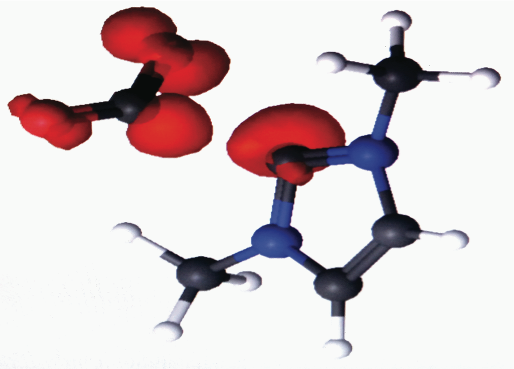

Figure 3. Spin density of the diradical ($[MMIm]^{\bullet+}$ + $[CO_2]^{\bullet-}$) formed in T1 state.

It was also evaluated the long-time stability of the $BMIm.CO_2$ IL for CO_2 photo-reduction through the cycling test. After each cycle of five hours, the reactor was degassed with argon (Figure 4). Then the reactor was filled with CO_2 and the IL solution was re-used for the next run. It can be observed that the $BMIm.CO_2$ maintains its activity, becoming eventually increased with time due to the augmentation of carbonate and bicarbonate in the aqueous solution corroborating the reaction paths suggested in Scheme 2. The CO productivity attained by the IL (2.88 $mmol.g^{-1}$ IL (72.0 $\mu mol.g^{-1}.h^{-1}$)) after 40 h is within the same range and often higher when compared with rather sophisticated semi-conductors decorated with noble metal nanoparticles that are usually not recyclable (for comparison see Table S3-4) or with homogenous metal based catalysts that operate in the presence of photo-sensitizers and sacrificial electron donors.[9] Note that the turnover number (TON) for the CO_2 conversion is larger than 1 after 40 h, indicating that this photo-reaction can be also catalytic in the IL. Moreover, the obtained quantum yield of 3.9% is the same range of those usually observed in photolysis by semi-conductors (for references see Table S3).

Conclusions

In summary, simple imidazolium salts associated with basic anions, such as acetate, furnishing cation-CO_2 adducts can be photoactivated to generate CO without the use of any photosensitizers and sacrificial agents. The ESR experiments clearly verify the involvement of the imidazolium cation radical indicating that the activation path occurs via homolytic cleavage of the imidazolium cation-CO_2 adduct to yield the CO_2 radical anion that undergoes reduction to CO by the reaction paths akin to those reported for electrocatalytic CO_2 reductions. Our results open a new avenue of opportunities for the development of simpler and more efficient organocatalysts for CO_2 photoreduction when compared to those based on homogeneous catalysts or semi-conductors. One of the key points is the formation of cation-CO_2 adducts that can be photoactivated to generate both, the cation radical and the CO_2 radical anion.

Experimental Section

General. The ionic liquids 1-*n*-butyl-3-methylimidazolium-2-carboxylate ($BMIm.CO_2$),[27] 1-*n*-butyl-3-methylimidazolium acetate (BMIm.OAc),[28] 1-*n*-butyl-2,3-methylimidazolium (BMMIm.OAc),[28] 1-*n*-butyl-3-methylimidazolium bicarbonate ($BMIm.HCO_3$) and 1-*n*-ehtyl-3-methylimidazolium hexafluorophosphate ($BMIm.PF_6$)[29] were prepared according to literature procedures. Whereas, 1-*n*-butyl-3-methylimidazolium dicyamide ($BMIm.N(CN)_2$) IL was purchased from

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Sigma-Aldrich. All the ILs were dried under vacuum and argon for 2 days prior to use. All ESR measurements were performed in a Bruker spectrometer (Bruker EMXplus, Germany), equipped with an X-band (9 GHz) high sensitivity cavity (Bruker ER 4119HS, Germany) using frozen samples inside a quartz finger Dewar filled with liquid nitrogen. 400 microliters of the aqueous ionic liquid solution (0.22 molar for each ionic liquid) were collected and transferred to a 1 mL de-capped syringe and frozen in liquid nitrogen. The frozen cylindrical samples were transferred to a quartz finger Dewar (Noxygen, Germany) filled with liquid nitrogen, placed inside the resonator and their ESR spectra were recorded at -196 °C. This procedure ensured identical volumes for all samples, allowing the quantitative comparison among the recorded ESR spectra. The instrumental settings were 2 mW microwave power, 10 G amplitude modulation, 100 kHz modulation frequency, 1000 G sweep width, 3365 G central field and 50s sweep time. The peak-to-peak amplitude, that is the difference between the lowest and the highest amplitudes in the first derivative spectrum, was used to detect signal quantification. NMR analyses were performed on a Bruker Avance 400 spectrometer, equipped with a BBO 5 mm probe with z- gradient operating at 400 MHz for ^{1}H, and 100 MHz for ^{13}C. The spectra were obtained at 298 K unless otherwise specified. Chemical shifts are reported in parts per million (ppm, δ) referenced to D_2O and DMSO-d_6 as an external reference (capillary). The UV-Vis spectra of the ILs are presented in Figure S15. The NMR spectra (^{1}H and ^{13}C) before and after photolysis using BMMIm.OAc and BMIm.N(CN)$_2$ are presented in Figures S16 and S17, respectively. The generated gases during the photocatalytic reaction were quantified by gas chromatography (GC) using an Agilent 6820 equipped with a Porapak Q 80-100 Mesh column and argon as carrier gas. The gaseous products were simultaneously analyzed with a thermal conductivity detector (TCD) and a flame ionization detector (FID, Figure S18). Aliquots of 100 µL from the gas phase were removed from the head of the photo-reactor reactor in desired time intervals and injected with a syringe containing a Hamilton sample lock valve. In order to detect the generated ^{13}CO, a mass spectrometer (QIC 20®-Hiden Analytical) configured with the ionization of 70 eV was used.

Preparation of BMIm.$^{13}CO_2$ ionic liquid

BMIm.$^{13}CO_2$ IL was prepared according to the reported literature.[27] Typically, 1-n-butyl-3-methyl imidazolium chloride (6.32 g, 0.036 mol) was dissolved in dry DMF (25 mL). In a stainless-steel reactor (100 mL) containing glass (Parr Series 5000 Multiple Reactor System), 3.83 g (0.036 mol) of dry Na_2CO_3 was added under argon atmosphere. After closing, the reactor was filled with $^{13}CO_2$ (10 bar) and the reaction mixture was heated to 110 ° C for 36 h. The reactor was cooled and depressurized. The solution was filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile produced 4.7 g of a light-yellow solid, which was characterized by NMR (Figure S19) as a mixture of 1-n-butyl-3-methylimidazolium-2-carboxylate, 1-n-butyl-3-methylimidazolium-4-carboxylate and 1-n-butyl-3-methylimidazolium-5-carboxylate.

Photo-reduction of CO_2

A 100 mL Schlenk tube containing 40 mL of degassed distilled water was saturated with CO_2 (50 bar) at a rate of 2 mL min^{-1}. The photocatalysis was performed in a quartz reactor vessel equipped with a water-circulating jack to maintain the temperature at 25 ^{o}C and to protect of infrared radiation. 3 mL of CO_2-saturated water was mixed with the desired amount of freshly prepared IL and poured into the reactor under argon atmosphere. After degassing the argon, CO_2 was inserted into the reactor by a filled balloon. The reaction mixture was stirred at room temperature for 30 min. After removing the CO_2 balloon, the reactor was placed in front of 300 W Xe lamp. Gaseous products were withdrawn by gas-tight syringe from the reactor's headspace in desired time intervals and analyzed by GC. After the photocatalysis, the liquid phase was analyzed by NMR. For the evolutions of intermediates by NMR analyses all the reactions were performed with 120 mg of IL under our standard conditions.

Computational details

Quantum mechanical calculations have been carried out on a single 1,3-dimethyl-2-carboxyl-imidazolium zwitterion (MMIm.CO_2). The theoretical calculations were performed using the MS-CASPT2//CASSCF protocol.[30] The geometry optimizations of the excited states and ground states were carried out using the state-average complete active space self-consistent field level (SA-CASSCF), and for these geometries the energies were computed using the multi-state complete active space second-order perturbation theory (MS-CASPT2). The convergence criterion with respect to the energy change and the norm of the gradient was the Baker criteria (1.0 e^{-6} and 3.0 e^{-4} with respect to the energy change and the norm of the gradient, respectively).[31] The small ANO basis set (ANO-S-VDZP) was employed in all calculations[32] carried out with the OpenMolcas program.[33] Excited state geometries and configurations along the reaction path were optimized with an active space including 14 electrons and 10 orbitals and state-averaged over four states (SA4-CASSCF(14,10)). The active space has been spanned by seven occupied (six bonding π orbitals and a non-bonding orbital at the oxygens) and three virtual orbitals of π * type. This active space was maintained during the subsequent geometry optimizations. All the orbitals included in the active space are shown in Figure S20. For the correction of energy of the states, the CASPT2 was averaged over four states (MS4-CASPT2). Orbitals have been rendered by the IboView program.[34]

Acknowledgements

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Keywords: Carbon dioxide • Ionic liquids • photocatalysis • carbon monoxide • solar fuels

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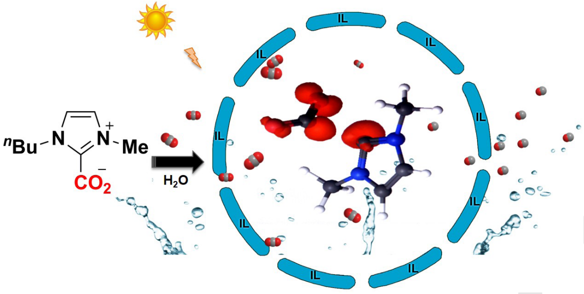
Simple aqueous solutions of ionic liquids can efficiently photo-reduce the CO_2 to CO without the use of photosensitizers or sacrificial agents. The system relies on the formation of the $[CO_2]^{\bullet-}$ intermediate; via homolytic C-C bond cleavage in a cation-CO_2 adduct of imidazolium-based ionic liquids (ILs).



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