



Intermediates derived from *p*-terphenyl in the methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ionic liquid saturated with carbon dioxide: Pulse radiolysis study

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Abstract. Radiation-induced processes in ionic liquid (IL) methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ([MeBu₃N][NTf₂]) solutions containing *p*-terphenyl (TP) and saturated with carbon dioxide (CO₂) were studied using nanosecond pulse radiolysis technique with UV-vis detection. The transient absorption spectra generated in these solutions were assigned to TP radical anions (TP^{•-}) and triplet excited states (³TP*). Saturation of [MeBu₃N][NTf₂] solutions with carbon dioxide efficiently takes out presolvated electrons (e_{presolv}⁻) and solvated electrons (e_{solv}⁻). On the other hand CO₂ is not a scavenger of excited states of TP (¹TP*, ³TP*), which in the reaction with triethylamine (TEA) leads to the formation of TP^{•-}.

Keywords: Carbon dioxide • Ionic liquid • Methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide • *p*-Terphenyl • Pulse radiolysis • Radical ions

Introduction

Ionic liquids (ILs) represent a unique class of solvents. The growing interest in this class of solvents is connected with their interesting physical and chemical properties (e.g., non- or low volatility, thermal stability, and combustion resistance) [1–12]. They were proposed as good media for the absorption and reduction of carbon dioxide (CO₂) [13–18], which are related to the good solubility of CO₂ gas in ILs [19–28].

Given the backdrop of the increasing energy consumption leading to increased CO₂ emissions around the world, there is immense interest in, as well as keen demand for, new materials and technology for CO₂ capture. The negative impact of changes in the atmospheric concentration of carbon dioxide on the environment is a matter raised many times while debating the sources of, and sustainable consumption strategies for, energy. Reducing greenhouse gas emissions (carbon dioxide, methane, tropospheric ozone, chlorofluorocarbons, and nitrogen oxides), especially CO₂, is key to the future of global energy policy.

Millions of tons of CO₂ emissions annually are a direct result of the burning of fossil fuels used in electricity production.

The atmospheric concentration of CO₂ has increased by 31% since the beginning of the industrial age in the mid-18th century. This level has been higher than ever in the last 650 000 years (the period for which reliable data from the ice cores were obtained) [29]. It has been estimated that about

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75% of the increase in CO₂ concentration over the past 20 years is due to the burning of fossil fuels. The remaining 25% is largely due to land use, in particular deforestation [14]. In 2010, a total of 30.6 GT of CO₂ were released into the atmosphere [30]. The International Energy Agency reported that with regard to fuels, in 2010, 44% of the estimated CO₂ emissions came from coal, 36% from oil, and 20% from natural gas. A further increase in CO₂ concentration is expected due to the increased demand for fossil fuels, and thus their greater combustion and to a lesser extent change in land utilization.

Special Report on Emissions Scenarios states that the range of future CO₂ emissions will increase the concentration from 541 ppm to 970 ppm by 2100 [14]. Producing clean energy from sources of fossil fuels such as coal requires not only huge infrastructure but also efficient technologies for the capture and reduction of CO₂ emissions.

The high efficiency of catalysis involving metal complexes in ILs is a good application prospect of this factor to the radiation and the photochemical conversion of carbon dioxide (CO₂) in chemically useful energy products, and the CO₂ may then be an additional source of renewable energy. The advantage is the ability to synthesize ILs, and increased solubility of CO₂, dedicated for this purpose. ILs provide new perspectives for the development of this direction. They turn out to be an excellent environment for carrying out many chemical syntheses [1, 2]. Systems with high CO₂ solubility can be selected. Studies have appeared in which ILs serve a medium enabling the conversion of CO₂ into complex organic compounds [31, 32].

Not without significance is the value of ILs as alternative and more environmentally safe solvents of great importance for modern applications involving clean technologies. In particular, recycling ILs allows their repeated use, while enhancing the selectivity and efficiency of the products obtained.

The favorability for applications of ILs in the nuclear industry [4, 33] gave rise to the problem of their radiation chemistry.

There are many investigations that have used the pulse radiolysis technique, to investigate elementary processes in ILs, including the reactions of presolvated (e_{presolv}^-) and solvated (e_{solv}^-) electrons, and charge and H transfer reactions [34–50]. The stability of ILs under ionizing radiation [51–53] has also been examined.

In previous studies, the formation of the triplet and singlet excited states of *p*-terphenyl, TP, and ($^3\text{TP}^*$ and $^1\text{TP}^*$) in [MeBu₃N][NTf₂] IL was observed in the presence and absence of scavenger of electrons (e_{presolv}^- , e_{solv}^-) and excited states of the IL components, i.e., ([MeBu₃N]⁺)^{*} and ([NTf₂]⁻)^{*}, benzophenone (BP). It was found that the energy transfer from the excited states of [MeBu₃N][NTf₂] IL is of negligible significance [54].

Radiolysis of pure [MeBu₃N][NTf₂] IL results in not only excitation but also ionization of its components. As has already been reported elsewhere [36–42, 44], the basic products of pulse irradiation of [MeBu₃N][NTf₂] IL are presolvated electrons

(e_{presolv}^-), solvated electrons (e_{solv}^-), electron-deficient centers (IL[⊕]), radical anions (IL[⊖]), and excited states (IL^{*}) located on both the anions and cations of IL. Of late, some of the primary intermediates, i.e., e_{presolv}^- , e_{solv}^- and IL[⊕] resulting from the radiolysis of a pure [MeBu₃N][NTf₂] IL, were also studied using TP [55–56]. An initial broad optical absorption spectrum observed in the pulse-irradiated deoxygenated IL [MeBu₃N][NTf₂] was dominated by the absorption band allocated to e_{solv}^- , as was shown previously [41]. Direct observation of the remaining primary products originated from [MeBu₃N][NTf₂] was not possible. TP was chosen as a probe since the transients originated from TP (radical anions [TP⁻], radical cations [TP⁺], singlet excited states [$^1\text{TP}^*$], and triplet excited states [$^3\text{TP}^*$]) absorb in the available spectral region and are convenient for time-resolved measurements using UV-vis spectrophotometry [54–62]. Moreover, TEA was used as an electron donor and an effective scavenger of IL[⊕], $^3\text{TP}^*$, and TP⁺.

In this work, pulse radiolysis investigations of several reactions bringing about the formation of intermediates originated from TP were carried out in carbon dioxide solutions of [MeBu₃N][NTf₂] IL. Such an approach should help to defeat, in part, a domination of the e_{solv}^- absorption band and additionally the overlapping of the absorption bands resulting from the presence of TP⁻ and $^3\text{TP}^*$ in deoxygenated [MeBu₃N][NTf₂] IL with that resulting from the presence of TP⁺, at short times [56].

Experimental

Pulse radiolysis coupled with the time-resolved UV-vis spectrophotometry was performed using the INCT LAE 10 linear accelerator with typical electron pulses lengths of 7–10 ns. A detailed description of the computer controlled experimental setup has been given elsewhere [44]. The system consists of the 150 W “quiet” xenon lamp (Hamamatsu E7536) with a suitable housing and a power supply, the ORIEL MSH 301 monochromator with two switchable outputs (one for a R955 photomultiplier and the second one for the ANDOR intensified charge coupled device [ICCD] camera), and the LeCroy WaveRunner 6051A oscilloscope with an internal memory of 16 Mb.

The samples placed in quartz cells (with optical path 1 cm) were purged with CO₂ and exposed to a pulse irradiation. All experiments were conducted at room temperature 20 ± 2°C. The data were normalized to a dose of 15 Gy per pulse, which was measured using the dinitrogen monoxide-saturated thiocyanate (KSCN) dosimeter (with $G \times \epsilon = 4.8 \times 10^{-4} \text{ m}^2 \cdot \text{J}^{-1}$ for (SCN)₂⁻ at 472 nm) [63]. The dose absorbed by [MeBu₃N][NTf₂] was reckoned using a correction factor that considers the difference between the electron densities of the IL investigated and the value, conforming to the dose of 18 Gy absorbed by [MeBu₃N][NTf₂], ascertained using the KSCN dosimeter [36, 42].

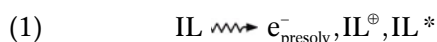
The concentration of [MeBu₃N][NTf₂] is ~2.6 M [55], and those of TP and TEA in [MeBu₃N][NTf₂] are 14 mM and 0.22 mM, respectively.

The IL was synthesized according to the procedure described earlier [41]. All other chemicals and gases, being of the highest and purest grade available, were used as supplied.

Results and discussion

Pulse radiolysis of [MeBu₃N][NTf₂] solution saturated with carbon dioxide containing TP

As a result of ionization of the IL, presolvated electrons (e_{presolv}^-), electron-deficient centers (IL^{\oplus}), and excited states of ionic liquids (IL^*) are formed (see reaction 1). Presolvated electrons (e_{presolv}^-) are converted eventually to solvated electrons (e_{solv}^-) (see reaction 2). In CO₂-saturated [MeBu₃N][NTf₂] containing TP, e_{presolv}^- and e_{solv}^- react with CO₂, leading to the formation of carbon dioxide radical anions (CO₂^{•-}) (see reactions 3 and 4).



Thus, reactions 3 and 4 eliminate the direct reaction of TP with the e_{presolv}^- and e_{solv}^- , and the formation of TP^{•-}. The CO₂^{•-} is characterized by a wide absorption band with low intensity in the UV range with a maximum at $\lambda = 235 \text{ nm}$ ($\epsilon = 3000 \text{ M}^{-1} \cdot \text{cm}^{-1}$) [63], which does not have the absorption spectrum within the experimentally available wavelength range.

The second-order rate constant of the reaction of carbon dioxide with hydrated electrons in aqueous solutions was found to be $k = 7.7 \times 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [63, 64]. CO₂^{•-} has strong reducing properties and the redox pairs CO₂/CO₂^{•-} is $E = -2.21 \text{ V}$ vs. saturated calomel electrode (SCE) [65, 66]. The estimated solubility of carbon dioxide in the IL [MeBu₃N][NTf₂] is $\sim 60 \text{ mM}$.

Irradiation of a 14 mM TP solution that is CO₂-saturated results in an absorption band with an intensity at a maximum of $\lambda = 450 \text{ nm}$ immediately after a pulse clearly smaller (Fig. 1A) than in an analog saturated argon solution (Fig. 1B) [55] and oxygen solution (Fig. 1C) [56]. The resulting initial broad absorption band with a maximum for $\lambda = 450 \text{ nm}$ is the result of the overlap of the absorption derived from the ³TP* and to a lesser extent the TP^{•+}. TP^{•+} is formed in a reaction of the electron-deficient centers originated from ionic liquid (IL[⊕]) with TP (see reaction 5) and its absorption bands, as recorded by Liu *et al.* [59]. Also, the reaction of CO₂ with TP^{•+} cannot be excluded (see reaction 6). This is due to the concurrent presence of ³TP* and TP^{•+}, which absorb in this region as well (vide Table 1 in Kocia's study [56]). CO₂ reacts with a presolvated and solvated electron, thus eliminating the direct reaction of TP with the electron and thus the formation of TP^{•-}. TP excited states (¹TP* and

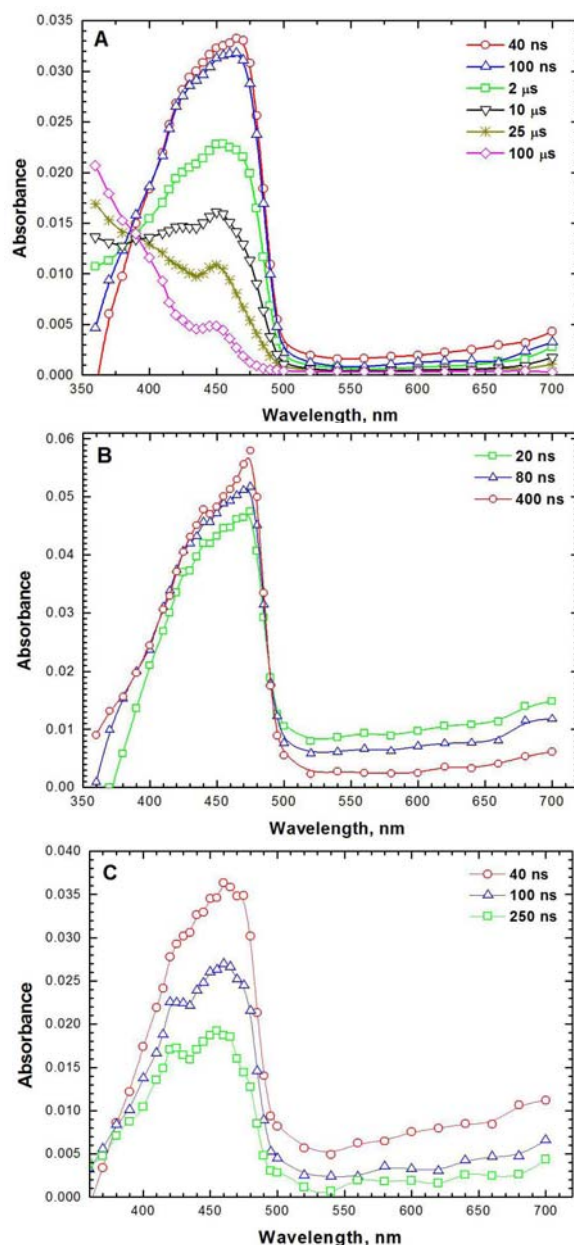
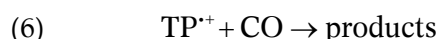
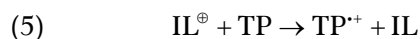


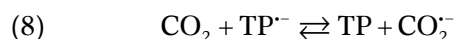
Fig. 1. Transient absorption spectra registered after pulse irradiation of carbon dioxide (A), argon (B), and oxygen (C) saturated solutions of [MeBu₃N][NTf₂] IL containing 14 mM TP after the following time delays on the spectra shown, respectively. The dose applied was 18 Gy.

³TP*) remain, but the ¹TP* is a short-lived state and was not observed on the available timescale of the pulse radiolysis system. The ³TP* lives longer (see reaction 7), and so it will be one of the individuals responsible for the shape of the absorption band with a maximum for $\lambda = 450 \text{ nm}$. The absorption recorded in Fig. 1 after electron pulse decreases and is characterized by absorption maximum located at $\lambda = 450 \text{ nm}$ with a slightly higher intensity. This spectrum can be assigned, with no doubt, mainly to ³TP*, keeping in mind its spectral properties (vide Table 1 in Kocia's study [56]).





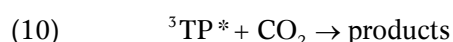
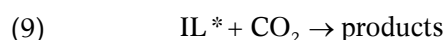
Direct reactions involving TP and CO₂ and their anion radicals in both directions are probably too slow for observation under the pulse radiolysis. Perhaps the equilibrium is established according to reaction 8. Since the redox pairs TP/TP^{•-} E = -2.45 V vs. SCE) [62] is more negative than the redox pairs CO₂/CO₂^{•-} and CO₂ concentration is several times higher than TP concentration, one can expect that the equilibrium (see reaction 8) will be shifted to the right.



CO₂ reduction by TP^{•-} has been observed only in the presence of intermediate catalysts, transition metal complexes, e.g., iron and cobalt porphyrins, cobalt and iron phthalocyanines, cobalt corrins, or cobalt and iron corroles [67–72]. The photochemical activity of TP was particularly investigated in connection with CO₂ reduction [71]. In such systems, the CO₂ bound in the form of an appropriate complex was more easily reduced.

The transient spectra acquired after pulse irradiation of the carbon dioxide (A), argon (B), and oxygen (C) saturated [MeBu₃N][NTf₂] IL containing 14 mM of TP at various time delays are presented in Fig. 1.

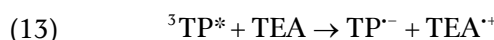
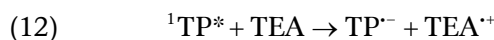
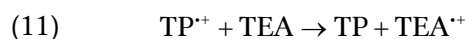
The presence of ³TP* at short time domains in the presence of 60 mM CO₂ clearly shows that energy transfer from the excited IL* to TP (reaction 7) can contend to some degree with the quenching of the excited IL* by CO₂ (reaction 9). On the other hand, the lack of ³TP* at longer time scales (which in Ar-saturated and O₂-saturated ³TP* was still present [55, 56]) proves its quenching by CO₂ (see reaction 10).



The respective absorbances presented at λ = 470 nm as a function of the logarithm of time are not single exponentials (Fig. 2). The decays happening within the time range <1 μs to <10 μs confirm in all probability the reactions of ³TP* (see reaction 10) and TP^{•+} (see reaction 6) with CO₂.

Pulse radiolysis of [MeBu₃N][NTf₂] solution saturated with carbon dioxide containing TP and TEA

To further observe the absorption spectra of the corresponding intermediates originated from TP, triethylamine (TEA) was added (concentration up to 0.22 mM) to the [MeBu₃N][NTf₂] IL. TEA is a well-known scavenger of radical cations (see reaction 11) and excited states (see reactions 12 and 13). It is, however, unreactive toward solvated electrons and radical anions [55, 56, 60, 61].



The transient spectra acquired after pulse irradiation of the carbon dioxide-saturated [MeBu₃N][NTf₂] IL containing 14 mM of TP and 0.22 mM TEA at various time delays are presented in Fig. 3.

The transient absorption spectra registered from 40 ns to 2 μs after the pulses were characterized by a strong absorption band with λ_{max} = 470 nm and a weaker absorption band with λ_{max} = 440 nm indicating formation of TP^{•-} (Fig. 3) via reaction 13. As in the case of solutions without TEA, carbon dioxide efficiently eliminates presolvated electrons (see reaction 3) and solvated electrons (see reaction 4). Therefore, excited states of TP remain. This is possible because carbon dioxide, unlike oxygen [56], is not a scavenger of excited states. On the other hand, it is known that excited states react with TEA. ¹TP* reacts quickly in solutions, while ³TP* reacts more slowly. However, both give TP^{•-} in these reactions (see reactions 12 and 13). Thus, ³TP* is visible in the recorded spectra (increased absorption at λ = ~450 nm), and at the same time the disappear-

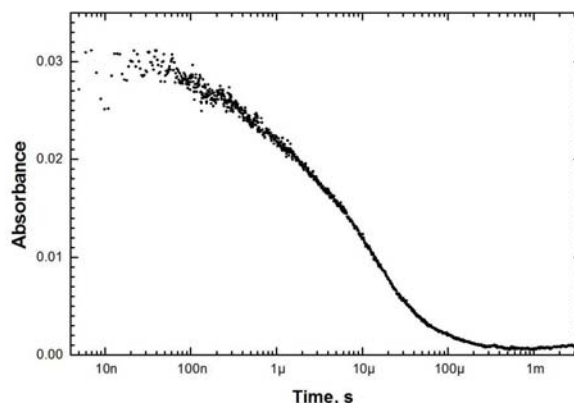


Fig. 2. The absorbance measured at λ = 470 nm as a function of the logarithm of time after pulse irradiation of carbon dioxide-saturated [MeBu₃N][NTf₂] IL solutions containing 14 mM TP.

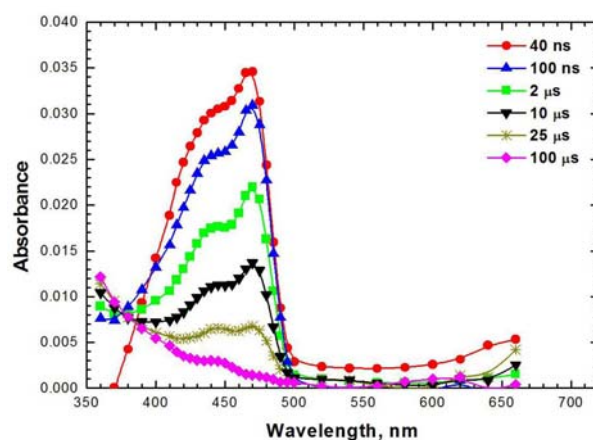


Fig. 3. Transient absorption spectra registered after pulse irradiation of carbon dioxide-saturated solutions of [MeBu₃N][NTf₂] IL containing 14 mM TP and 0.22 mM TEA after the following time delays: 40 ns (circles), 100 ns (up triangles), 2 μs (squares), 10 μs (down triangles), 25 μs (stars), and 100 μs (diamonds). The dose applied was 18 Gy.

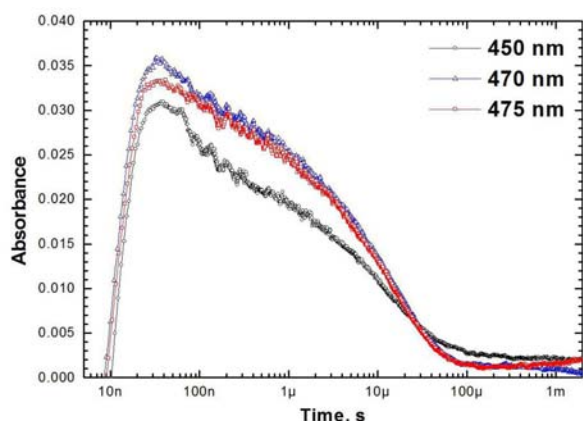


Fig. 4. The absorbance measured at $\lambda = 450$ nm (black circles), $\lambda = 470$ nm (red squares), and $\lambda = 475$ nm (blue up triangles) as a function of the logarithm of time after pulse irradiation of carbon dioxide-saturated [MeBu₃N][NTf₂] IL solutions containing 14 mM TP and 0.22 mM TEA.

ance of TP^{•-} will be slowed down by the formation of TP^{•-} in reaction 13, which is a slower reaction. On the other hand, ¹TP* present only during the impulse can give TP^{•-} in reaction 12, while absorption from TP^{•+} is substantially reduced due to the elimination of TP^{•+} and its precursors in the reaction with TEA (see reaction 11).

The absorbance measured at $\lambda = 450$ nm, $\lambda = 470$ nm, and $\lambda = 475$ nm (Fig. 4) as a function of the logarithm of time after pulse irradiation of carbon dioxide-saturated [MeBu₃N][NTf₂] IL solutions containing 14 mM TP and 0.22 mM TEA show several exponential decays in the observed time scale.

In measuring the absorption decay for $\lambda = 450$ nm, $\lambda = 470$ nm, or $\lambda = 475$ nm, the aim is to answer the question of whether ³TP*, as a result of its reaction with TEA, is converted to a TP^{•-} or to other products. If these three waveforms are compared, the share of the first stage of decay for $\lambda = 450$ nm (Fig. 4) is almost twice that of the second stage. For $\lambda = 470$ nm (Fig. 4) and $\lambda = 475$ nm (Fig. 4), the separation of the decay into individual stages is too complex. Complex absorption decay curves (Fig. 4) show that there are probably at least two individuals, ³TP* and TP^{•-}. The pseudo first-order rates constant for $\lambda = 450$ nm, $\lambda = 470$ nm, and $\lambda = 475$ nm absorption decay were calculated and are equal to $\sim 1.4 \times 10^5$ s⁻¹, $\sim 1.0 \times 10^5$ s⁻¹, and $\sim 5.6 \times 10^5$ s⁻¹, respectively. Decay for $\lambda = 450$ nm (Fig. 4) in the range up to 1 μ s is slightly faster than for $\lambda = 470$ nm (Fig. 4). A faster decay corresponding to $\lambda = 450$ nm (representing the maximum absorption of ³TP*) may also indicate that the reaction of ³TP* with TEA has a role in leading the formation of TP^{•-} (see reaction 13).

Summary

Measurements conducted of the [MeBu₃N][NTf₂] solutions containing TP and saturated with carbon dioxide, an electron acceptor, showed that the direct reaction of CO₂ with TP^{•-} is too slow for observation under pulse radiolysis. The wide absorption band obtained immediately after the pulse with a maxi-

mum for $\lambda = 450$ nm is the result of the overlap of the absorption originating from the triplet excited state of TP and the radical cation of TP.

No presence of TP^{•-} can be explained by the fact that CO₂ (which exhibits a good solubility in [MeBu₃N][NTf₂]) reacts effectively with presolvated and solvated electrons, thus eliminating the direct reaction of TP with the electrons and thereby forming TP^{•-}.

However, in the irradiated TP solution saturated with CO₂ with the addition of TEA, the share of TP^{•-} in the registered spectrum can be seen. It arises from the conversion of excited states of TP, primarily ¹TP*.

The obtained results confirm that ILs are a suitable medium for the recognition of reaction mechanisms related to CO₂ reduction. The high efficiency of CO₂ absorption makes ILs good candidates for environmental applications, and they could thus be successfully used, among other utilities, in membranes for capturing CO₂ from natural gas before combustion and flue gases after combustion.

The obtained results will contribute to the development of research on CO₂ capture and conversion, and in the future, perhaps to the creation of a CO₂ trading market, which will enable its capture and conversion into commercial products.

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