Electronic Supplementary Information

On the chemical reactions of carbon dioxide isoelectronic molecules CS_2 and OCS with 1-butyl-3-methylimidazolium acetate

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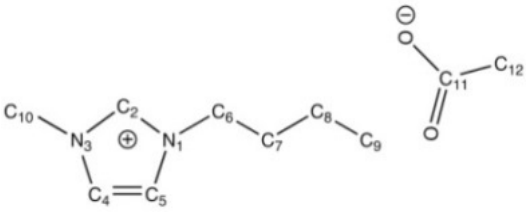
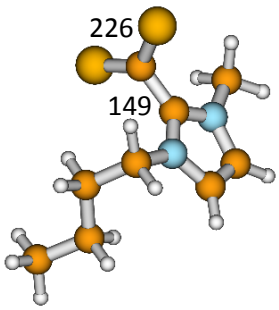
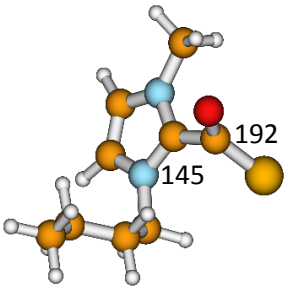
Schematic representation of the adducts formed in the CS_2 − [C_4mim] [Ac] and OCS − [C_4mim] [Ac] mixtures

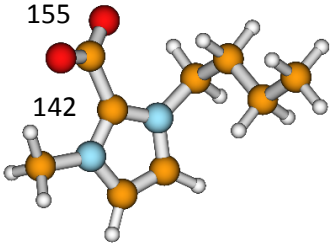




1-butyl-3-methyl-imidazolium-2-dithiocarboxylate [C_4mim] CS_2 (**1**)

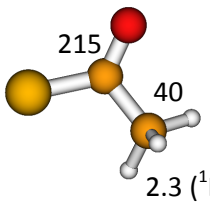


1-butyl-3-methyl-imidazolium-2-thiocarboxylate [C_4mim] COS (**2**)



1-butyl-3-methyl-imidazolium-2-carboxylate [C_4mim] CO_2 (**3**)

The ^{13}C NMR shifts of the carbon atom 2 and of the carbon atom of CS_2 [1], COS and CO_2 groups are displayed.



Thioacetate anion CH_3COS^- (**4**)

The ^{13}C and ^{1}H NMR shifts of the thioacetate anion are displayed.

Experimental conditions

The ionic liquid originated from Solvionic (purity greater than 98%), the CS_2 from Aldrich (purity greater than 99.9%), the ^{13}C labelled CS_2 from Aldrich (99 atom %), the OCS (purity greater than 97%) from Air Liquide and the ^{13}C labelled OCS (99 atom %, and enriched in ^{18}O at about 12%) from Isotec. The IL was dried at 353 K under a primary vacuum during more than 48 hours under a continuous stirring. The water content measured by Karl-Fisher titration was 530 ppm.

Carbon disulfide was added to the ionic liquid and as soon as the first drops fell down in the ionic liquid a red blood colour was observed accompanied by some degassing which was more and more evident with increasing CS_2 concentration. Several solutions with CS_2 concentration varying from 0.02 up to 0.3 mole fraction were prepared. The solutions were stirred and at least a waiting time of 15 minutes was observed.

Carbonyl sulfide was introduced under a 0.1 MPa pressure in the ionic liquid in a vacuum line and the solution was stirred more than 40 hours. Only a light yellowish coloration was observed. After isolating the container with the mixture under its vapor pressure, Raman spectra of the vapour phase were taken. Three mixtures have been prepared: two with $O^{13}CS$ (one, after 40 hours in the vacuum line, mixture IIA and other after 72 hours, mixture IIB) and one with OCS prepared one after 72 hours (mixture IIC).

The transfer of the solutions into NMR glass tubes (5 mm inner diameter) and into UV-visible quartz cells (1mm thickness) was done under argon atmosphere in a glove bag to avoid any contact with the atmosphere.

The Raman spectra were measured with a resolution of 1.6 cm^{-1} on a Jobin-Yvon HR8000 spectrometer with a Spectra Physics krypton-ion laser source operating at a wavelength of 752.5 nm with a power of 6 mW using a back-scattering geometry. Typical spectra have been collected during 600 seconds and accumulated 6 times to improve the signal to noise ratio. In order to take accurate line positions the spectrometer has been calibrated by recording different emission lines of a neon bulb.

The NMR measurements were performed on a Bruker AVANCE III spectrometer operating at 600 MHz Larmor frequency for ^{1}H, 150 MHz for ^{13}C and 60 MHz for ^{15}N (France). The ^{1}H spectra were collected after a 30^{o} pulse with a 90^{o} pulse (t_{90}) of 8 μs. The number of scans was ranging from 512 to 1024 with a relaxation delay (d1) of 1 s. The ^{13}C spectra was acquired after a t_{90} =15 μs and d1=3 s. The ^{13}C proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. Finally these measurements have been completed by performing 2D NMR measurements using the standard ^{13}C -^{13}C - INADEQUATE sequence on the AVANCE II 400 MHz with a BBO probe at 400 MHz and 100 MHz for ^{1}H and ^{13}C. The samples were contained in standard 5 mm tubes filled with an external lock solvent of D_2O and calibrated with the H_2O signal at 4.8 ppm. Measurements were also performed in a Bruker AVANCE II spectrometer at 300 MHz Larmor frequency for ^{1}H, 75 MHz for ^{13}C (Portugal). The ^{1}H spectra were recorded

after a single pulse, t_{90}=14 μs and d1=5 s. The number of scans has been ranging from 512 to 1024. The ^{13}C spectra have been acquired after a single pulse with t_{90}=11 μs and d1=3 s. The ^{13}C proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. The temperature of the samples was regulated and stabilized to within ±0.5 K using gas flow.

UV-Visible spectra were performed in a double-beam spectrometer (Hewlett-Packard 8452A)

Experimental results

UV-Visible spectra

The signature of the chemical reactions in the two systems is confirmed by UV-Visible spectroscopy (Figure 1). In CS_2- IL (system I) two new transitions are observed at about 514 nm and 430 nm assigned to the signature of the $n \rightarrow \pi^*$ transition corresponding to the formation of sulfur containing adducts and non-existent in the spectra of the pure compounds and tentatively assigned to the presence of 1-butyl-3-methyl-imidazolium-2-dithiocarboxylate (**1**) [2]. A strong intensity enhancement of the $\pi \rightarrow \pi^*$ transitions (in the UV domain) characteristics of the imidazolium based compounds is observed. In OCS-IL (system II) the strongly enhanced intensity due to increased contributions of the $\pi \rightarrow \pi^*$ transitions in the UV domain is ascribed to the presence of [C_4mim] COS (**2**).

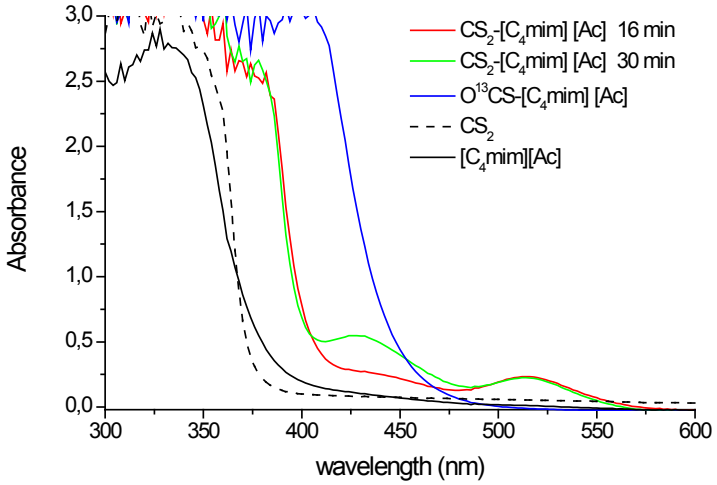


Figure 1 UV-Visible spectra of the CS_2 − [C_4mim] [Ac] mixture (x_{CS2}=0.03) and $O^{13}CS$ − [C_4mim] [Ac] (mixture IIA, blue) compared with those of pure CS_2 (dash) and [C_4mim] [Ac] (black solid line).

Additional Experiments I

Mixtures of [C_4mim] [TFA], [C_4mim] [BF4] and [C_4mim] [NTf2] with CS_2 have been prepared. No colour modification and degassing were observed. The ^{13}C NMR spectra show the resonance lines of the components of the mixture and do not display further lines originating from a reaction (see Figure 2 for the two first mixtures).

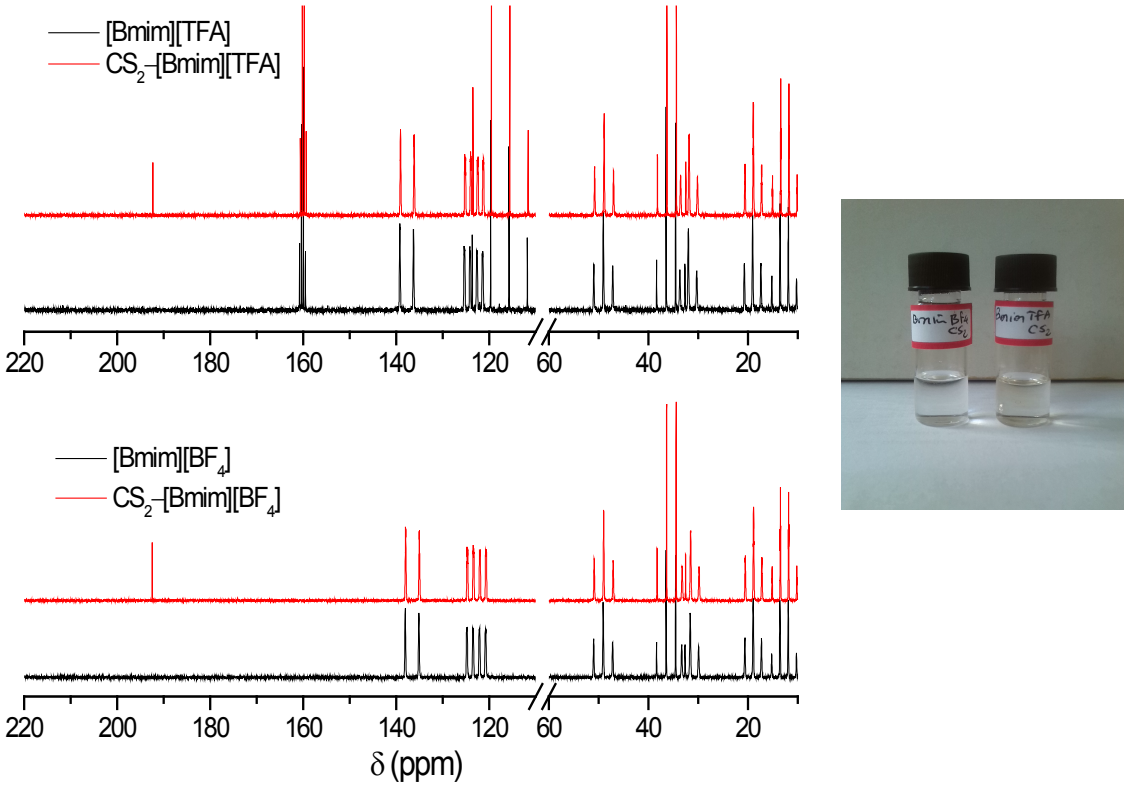


Figure 2 Comparison of the ^{13}C NMR spectra of the mixtures (red) with that of pure ionic liquid (black): CS_2 − [C_4mim] [TFA] mixture (x_{CS2}=0.05) (top); CS_2 − [C_4mim] [BF4] mixture (bottom). The resonance line observed at about 193 ppm is the spectral signature of CS_2. No colour modification was observed in these mixtures for more than 24 hours.

In contrast, imidazolium based ILs with carboxylate type anions (lactate, malonate and hexanoate) reacted with CS_2 and present a red-coloration similar to that observed for [C_4mim] [Ac] (Figure 3).

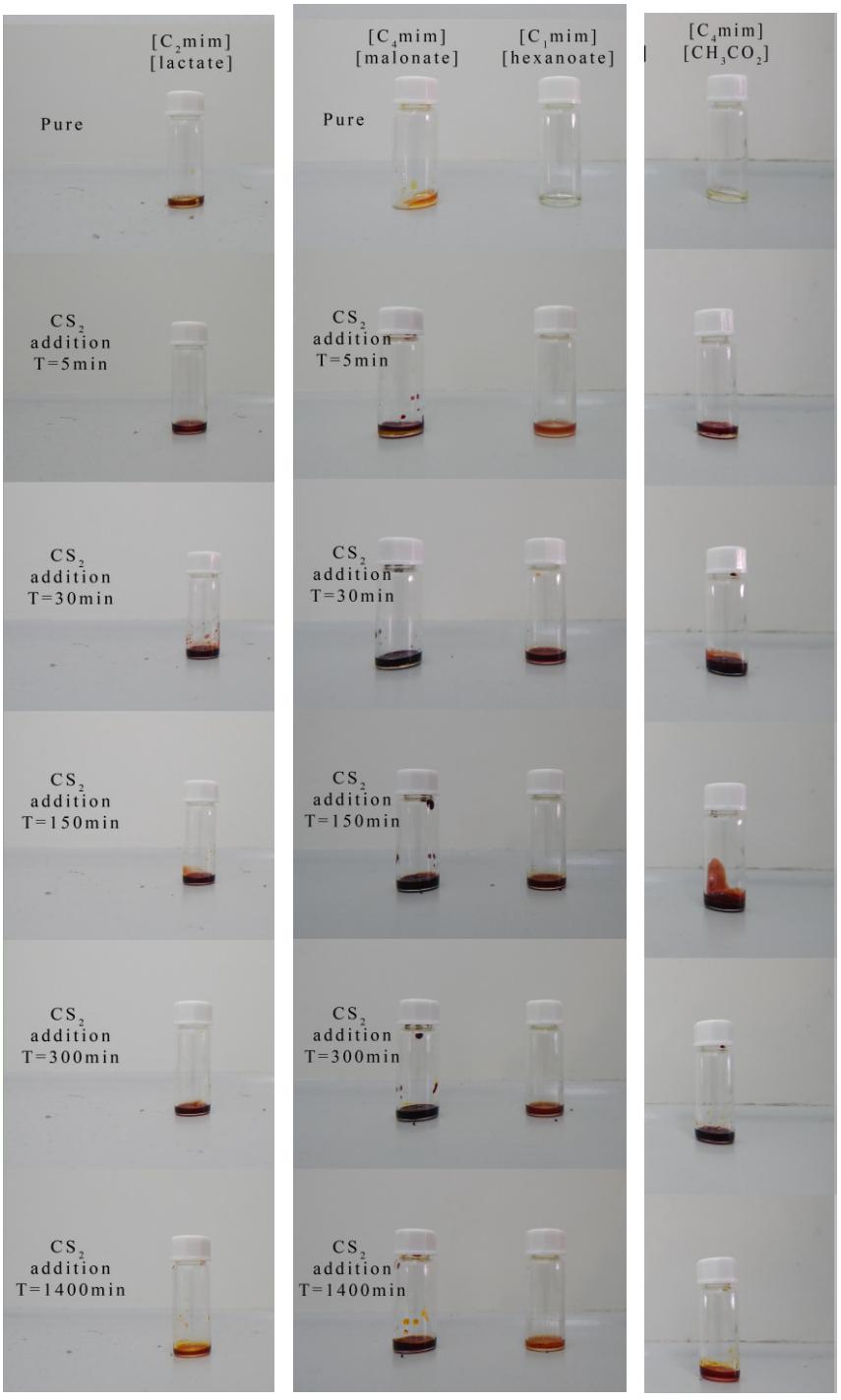


Figure 3 Evolution with time of the reaction of CS_2 with [C_2mim] lactate, [C_4mim] malonate and [C_1mim] hexanoate compared with to that of [C_4mim] [Ac].The lactate has a brownish-coloration and changes to dark-red after CS_2 addition.

NMR spectra

The 2D HMBC ^{1}H-^{15}N NMR sequence in the $O^{13}CS$ − $[C_4mim]$ [Ac] mixture (IIB) shows correlation between the secondary lines of the protons 4 and 5 and the ^{15}N secondary lines observed at 160 and 172 ppm (Figure 4).

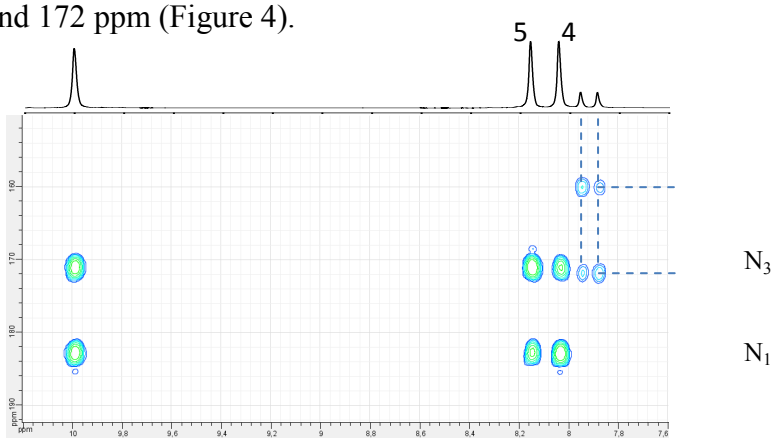


Figure 4 2D HMBC ^{1}H-^{15}N NMR sequence in the $O^{13}CS$ − $[C_4mim]$ [Ac] mixture (IIB).

The ^{1}H NMR spectra of the mixtures show an intense new line at about 2.3 ppm, secondary lines of the protons 10, 6, 4 and 5 (Figure 5). Moreover, formation of nascent acetic acid is detected at about 18 ppm for fresh solutions and changing with time to reach 12 ppm (one month later), suggesting that the acetic acid molecules tend to form cyclic dimers mostly existing in the pure acid[3]. This situation was previously observed for CO_2−$[C_4mim]$ [Ac][13].

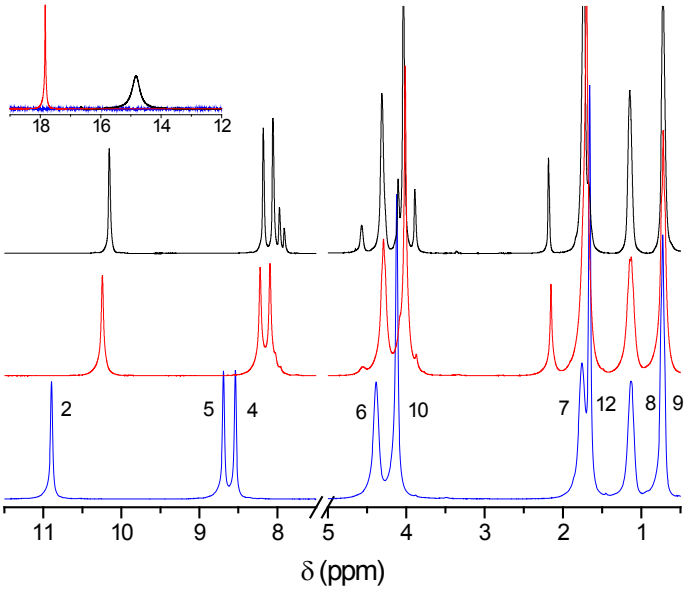


Figure 5 Comparison of the ^{1}H NMR spectra of OCS − $[C_4mim]$ [Ac] (mixture IIC after one week from the solution preparation, black) and CS_2 − $[C_4mim]$ [Ac] mixture (x_{CS2}=0.20, fresh

solution, red) with that of pure [C_4mim] [Ac] (blue). The spectral domain of the nascent acetic acid is displayed in the inset.

The 2D HSQC ^{1}H-^{13}C NMR sequence in the O^{13}CS − [C_4mim] [Ac] mixture (IIB) shows a direct correlation between the new lines situated at about 2.3 ppm (^{1}H) and at about 40 ppm (^{13}C) (Figure 6). This carbon new line is associated to a quartet as put in evidence from the comparison of the ^{13}C spectra with and without decoupling (Figure 7).

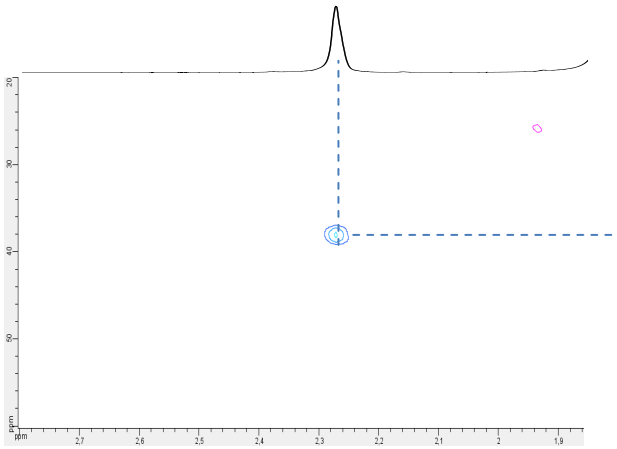


Figure 6 2D HSQC ^{1}H-^{13}C NMR sequence in the O^{13}CS − [C_4mim] [Ac] mixture (IIB).

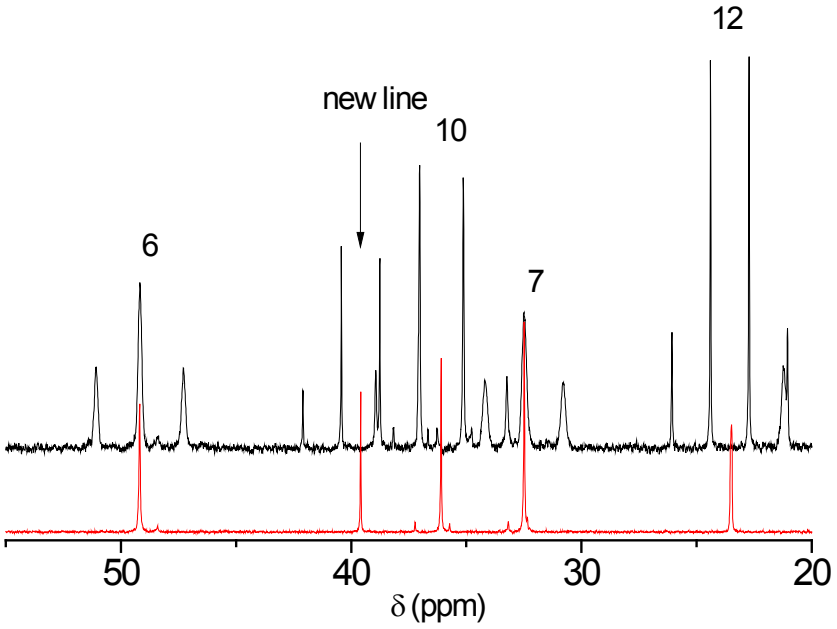


Figure 7 ^{13}C NMR spectra in the O^{13}CS − [C_4mim] [Ac] mixture (IIB) with (bottom) and without proton decoupling (top).

The 2D HMBC ^{1}H-^{13}C NMR sequence in the same mixture (IIB) shows a correlation between the new lines situated at about 2.3 ppm (^{1}H) and at about 215 ppm (^{13}C) (Figure 8).

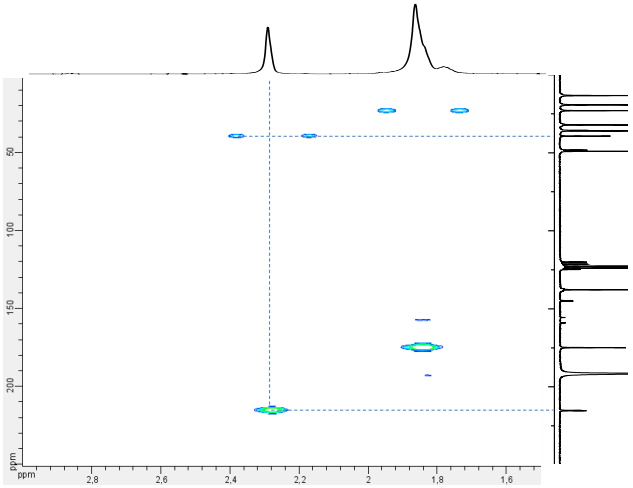
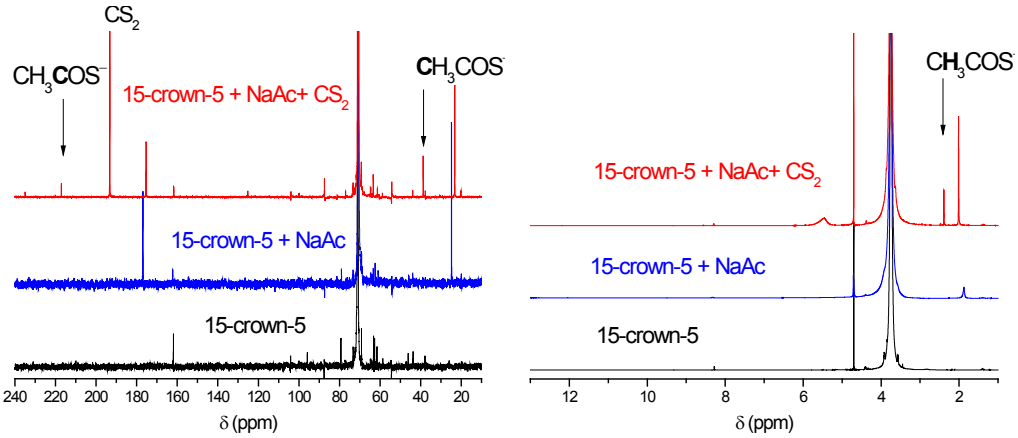


Figure 8 2D HMBC ^{1}H-^{13}C NMR sequence in the $O^{13}CS$ − [C_4mim] [Ac] mixture (IIB).

Additional Experiments II *

CS_2 –'Naked' Sodium Acetate

The dilution of dried sodium acetate in 15-crown-5 to obtain 'naked' acetate followed by mixing CS_2 (in excess to $NaCH_3COO$) gave a yellowish solution. The ^{13}C and ^{1}H NMR spectra obtained 20 hours after preparation of the ternary mixture allowed identifying the formation of thioacetate (arrowed in Figure 9).



* We acknowledge one of the referees for suggesting these additional experiments.

Figure 9 ^{13}C and ^{1}H NMR spectra of a 15-crown-5-$NaCH_3COO$-CS_2 mixture (20 h after preparation) compared with those of crown ether and of its mixture with $NaCH_3COO$ showing the formation of thioacetate.

CS_2 – N,N-dimethyl-N-ethylammonium acetate

The dilution of CS_2 in N,N-dimethyl-N-ethylammonium acetate (N0112 acetate) gave also a yellowish coloration. The ^{13}C NMR spectrum, obtained 72h after preparation, allowed identifying the formation of thioacetate (arrowed in Figure 10).

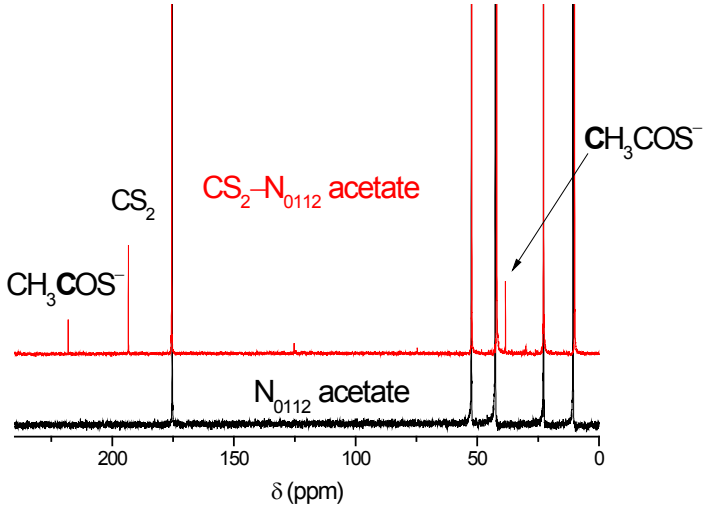
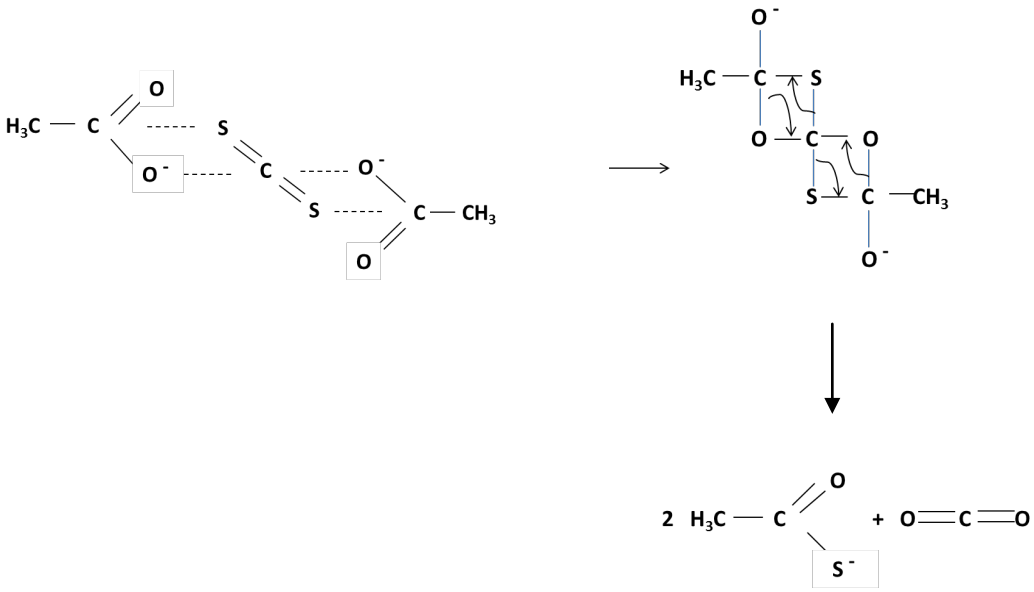


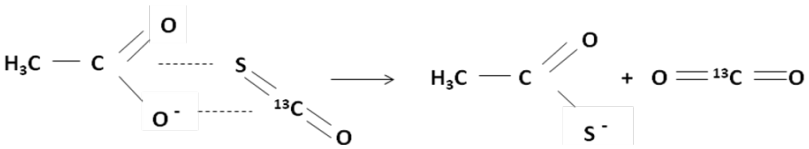
Figure 10 ^{13}C NMR spectrum of the CS_2−N,N-dimethyl-N-ethylammonium acetate mixture (almost equimolar) obtained 72h after preparation and showing the formation of thioacetate.

Elementary steps of the reactive scheme tentatively proposed for the formation[†] of:

- **Carbon Dioxide in system I**

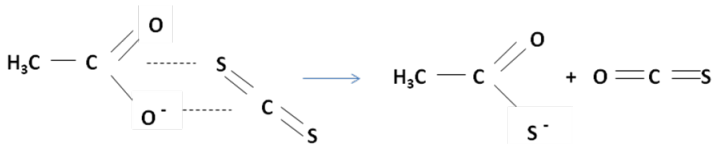


- **Carbon Dioxide in system II**

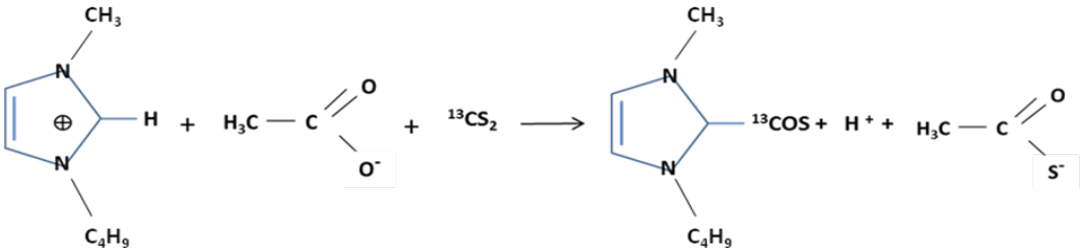


[†] The intermediate steps in which the carbene species is formed as referred in the introduction of the text [4-15] are not presented here.

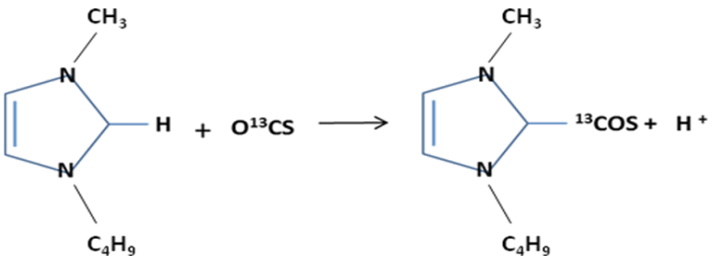
- **Carbonyl Sulfide in system I**



- **1-butyl-3-methyl-imidazolium-2-thiocarboxylate in system I**



- **1-butyl-3-methyl-imidazolium-2-thiocarboxylate in system II**



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