

COMMENT

on article entitled “CO₂ Chemisorption Behavior in Conjugated Carbanion-Derived Ionic Liquids via Carboxylic Acid Formation”

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The paper in the title proposed an interesting chemical sorbent for CO₂, exemplifying unusual chemistry, and reported promising chemisorption capacities. The carboxyl moiety formation was highlighted as the only CO₂ chemisorption product. We would hereby like to question the chemical identity of the CO₂ chemisorption product reported in this publication. Below, the considerations in favor of a different product are provided based on general chemical wisdom and ab initio calculations.

Understanding the specific identity of the chemisorption product is of paramount importance.¹⁻² Indeed, a carboxylated ionic liquid can further capture CO₂ through the electrostatic attraction between the polar group(s) and the quadruple moment of the CO₂ molecule. The protonation state directly influences the thermodynamics of such additional physisorption and more accurately rationalizes the experimentally observed yields.

The authors suggest that the most likely product of CO₂ chemisorption involving the malononitrile anion is (NC)₂-C⁻-OOH (Figure 1). This conclusion was derived based on experimental FTIR and NMR spectroscopic measurements and computationally unraveled

negative reaction enthalpies. While the signals supporting the proposed structure are, indeed, present in the reported spectra, the provided evidence does not seem to be exhaustive. Particularly, in the presented FTIR spectrum, the frequency of 1626 cm^{-1} was indicated by the authors to be characteristic of the protonated carboxyl group. De facto, this signal only confirms the presence of the carboxyl anion.³ To confirm the formation of -COOH , additional peaks should have been recorded. For instance, the detection of the O-H vibrations represents the cornerstone. Note that the chemisorption product remains to be negatively charged and, therefore, its hydrogen bonding with other such anions is not likely. This feature must be accounted for upon assigning the signals. In $^1\text{H NMR}$, the carboxyl group signal appears between 10-13 ppm. Yet, we did not find this region among the provided experimental NMR spectra. Some signals overlap with others. They must be interpreted with great caution, particularly in the case of such a peculiar methanide anion. The commented paper states that the C-H signal in $^1\text{H NMR}$ is seen before CO_2 capture but disappears after CO_2 capture. The complete disappearance of this signal looks rather unusual, assuming that proton transfer always involves a non-negligible activation barrier. It is unlikely that all protons leave the negatively charged carbon atom of the carboxylated malononitrile anion, *vide infra*. Lastly, it is unclear why the sorbent can be smoothly regenerated when keeping CO_2 in the form of the -COOH group, as the experimental study claims. We cover this issue below as well, in light of additional simulations.

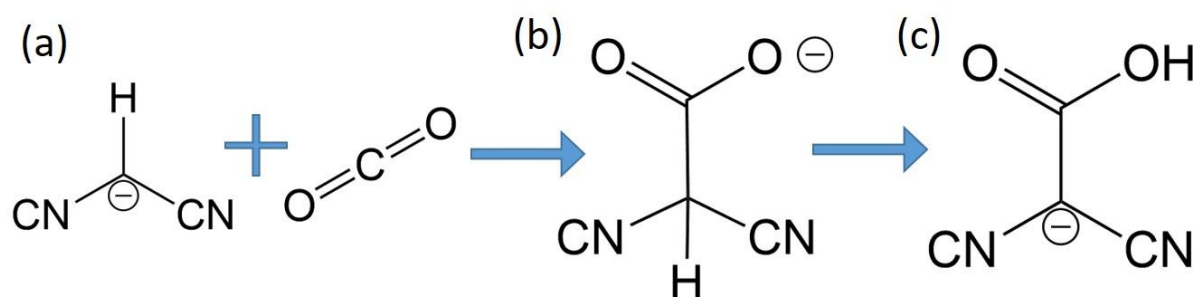


Figure 1. The stages of CO_2 chemisorption at the malononitrile anion: (a) sorbent and sorbate; (b) $(\text{NC})_2\text{CH-COO}^-$ anion, (c) $(\text{NC})_2\text{C}^--\text{COOH}$ anion. The tetramethylphosphonium cation is present in the system but omitted in the figure for clarity.

The previously published assignment of the CO₂ chemisorption product did not involve a consideration of activation barrier(s) associated with the hydrogen transfer (Figure 1). Herein, we unravel the corresponding transition state, show that its shape and height contradict the reported chemisorption product, and thereby suggest an alternative product, which is free from the posed concerns.

The commented paper reports only selected energetic effects related to CO₂ capture. To give an idea of the entire set of the physisorption and chemisorption events and total energy alteration, we computed the full energy reaction profile for the CO₂ chemisorption by the malononitrile anion of the corresponding tetraalkylphosphonium ionic liquid (approximated by tetramethylphosphonium cation and malononitrile anion in our simulations). Initial CO₂ dissolution in the ionic liquid (physisorption) proceeds without a barrier. Its energy effect amounts to -25 kJ/mol. The subsequent grafting of CO₂ to the methanide carbon of the malononitrile anion proceeds with a tiny positive free energy change, +10 kJ/mol. The activation barrier of this chemisorption reaction equals 29 kJ/mol. Herewith, the (NC)₂CH-COO⁻ anion emerges (Figure 1b).

In the commented paper, the formation of a protonated carboxyl group is assumed (Figure 1c). The formation of this chemisorption product anticipates a proton transfer from the carbon atom of the carboxylated anion to the carboxyl group of this same anion (Figure 2). While the product is valid (low-energy stationary point), we question whether it can form without substantial heating. The computed activation barrier exhibits a noteworthy height of 160 kJ/mol. In turn, the energy effect is -19 kJ/mol. The commented paper correctly designates it as the lowest-energy CO₂ chemisorption product. Overall, the free energy effect of CO₂ physisorption significantly exceeds the free energy effect of CO₂ chemisorption. We also report an overall CO₂ capture reaction energy gain of -35 kJ/mol, which is consistent with the previously published data.

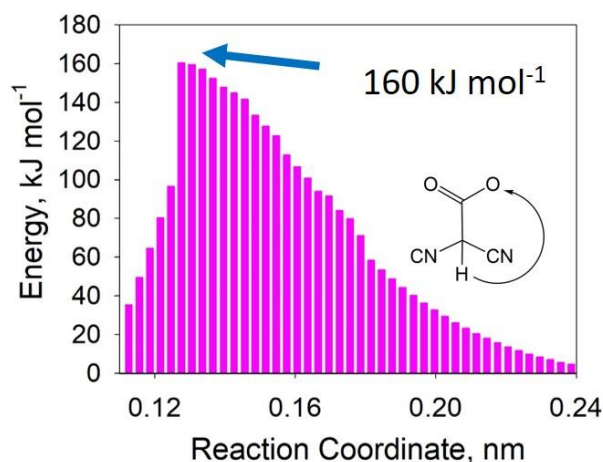


Figure 2. The search of the transition state along the reaction coordinate of the hydrogen atom transfer (see the inset). The reaction is characterized by an activation energy barrier of 160 kJ/mol. Note that the numerical value of the activation barrier was computed between the corresponding stationary points, accounting for zero-energy corrections.

The computed proton transfer activation barrier corresponds to about 64 standard kT products. While such reactions can proceed at a low rate, their equilibrium cannot be fully shifted rightward. In the experimental NMR spectrum, the C-H signal must persist both before and after the CO₂ capture. We hereby underscore that the reported reactions were carried out at standard conditions. Next, we attempted to unravel possible additional transition states that would possess essentially lower activation barriers and thereby support the original interpretation of the chemisorption results. Different reaction pathways were tested via relaxed potential energy scanning. Furthermore, the PM7-MD Born-Oppenheimer trajectories were recorded for an ion pair of the tetramethylphosphonium cation and malononitrile anion for 100 ps at 400 K to get an idea of possible non-intuitive proton transfer pathways. None of these measures provided a decreased proton transfer barrier.

In the cycling stability experiments, the ionic liquids were regenerated by bubbling nitrogen through the CO₂-saturated mixture for 30 min at 60 °C. The complete CO₂ desorption was observed, allowing for a smooth continuation of the CO₂ absorption, according to the established in-lab protocol. Such a successful and rather quick CO₂ desorption is deemed to be incompatible

with the persisting activation barrier of 160 kJ/mol for the reverse proton transfer reaction to restore the methanide geometry.

The proton transfer from the alpha-carbon atom to the adjacent electrophilic moiety has been characterized in the case of cations (tetraalkylphosphonium,⁴⁻⁵ trialkylsulfonium⁶). This is because cations fosters the electrophilicity of proton thanks to their aggregate charge. However, the analogous proton transfer in the case of an anion, such as malononitrile, is much less likely because an anion suppresses the proton's electrophilicity. The slope of the reported reaction energy profile suggests that the overcome of the activation barrier is rather hindered.

We believe that the formation of the $(\text{NC})_2\text{CH-COO}^-$ anion as a primary chemisorption product fits the available observation better than the $(\text{NC})_2\text{CH-COO}^-$ anion. Furthermore, the deprotonated carboxylate groups⁷ are known to strongly attract CO_2 molecules, e.g., in polyurethanes. The stationary points of the corresponding CO_2 physisorption products are exemplified in Figure 3. The multiple carbon...oxygen electrostatic interactions occurring at pairwise distances of roughly 300 pm bring a substantial enthalpic stabilization of the physisorbed CO_2 . This additional fraction of CO_2 sorption energy perfectly corroborates the experimentally reported capacities.

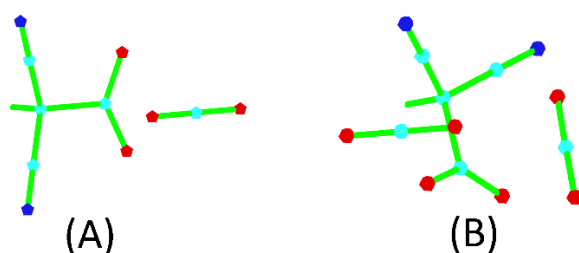


Figure 3. Carbon dioxide physisorption by the saturated MN chemisorbent: (a) stationary point for the sorbent and one sorbate molecule; (b) stationary point for the sorbent and two sorbate molecules.

To recapitulate, the determination of the primary chemisorption product is of paramount importance to correctly describe further CO₂ capture. For instance, the deprotonated carboxyl moiety electrostatically coordinates two additional CO₂ molecules.

References

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