This article is dedicated in memoriam to Professor José Barluenga Mur.

Abstract: The photolysis of iodide anion promotes the reaction of carbon dioxide with hydrogen sulfide or thiols to give quantitatively formic acid and sulfur or disulfides. The reaction takes place in acetonitrile and aqueous solutions, at atmospheric pressure and room temperature, by irradiation with a low pressure mercury lamp. This transition metal-free photocatalytic process for CO₂-capture coupled to H₂S-removal may have been relevant as a prebiotic carbon dioxide fixation.

Carbon dioxide (E°(CO₂/CO₂⁻) = -1.9 V versus the standard hydrogen electrode (SHE) reacts with hydrated electrons with a rate constant of 7.7 · 10⁹ L mol⁻¹ s⁻¹, which provide interesting opportunities for carbon dioxide reduction. Notwithstanding, the one-electron reduction of carbon dioxide requires, in order to be productive, of efficient hydrogen and proton transfer steps which prevent the carbon dioxide radical anion, a strong reductant itself, to deactivate by reaction with other species in solution, and of efficient scavengers for the oxidized species formed in the generation of hydrated electrons, which would otherwise compete with carbon dioxide as an electron sink. The redox potentials and reaction rates of the different intermediates involved in this complex system must then be finely tuned to conduct the reaction toward the desired transformation.

Thiols 1 seemed to us promising reagents for carbon dioxide reduction when coupled to the photolysis of the iodide anion as a source of hydrated electrons and iodine atoms. Indeed, thiols 1 are known to behave as hydrogen atom donors toward the radical anion of carbon dioxide in the gas phase to give formate anion and thiol radicals, and as reductants toward iodine to give disulfides 2 and hydrogen iodide through sulfenyl iodide intermediates 3 which undergo S₂I₂ at the sulfur atom by a second molecule of thiol. The assembly of these reactions outlines the photocatalytic cycle for the reduction of carbon dioxide to formic acid shown in Scheme 1. The present concern about the increasing anthropogenic emissions of carbon dioxide to the atmosphere, and the interest of the reductive transformations of carbon dioxide prompted us to explore this possibility by using 2-mercaptoethanol (1a) as a model substrate, and in acetonitrile-d₃ and water as solvents.

The reactions were performed by placing 5 mL of degassed acetonitrile-d₃ or aqueous solutions of 2-mercaptoethanol (1a) and lithium or potassium iodide, respectively, in a quartz test tube purged with carbon dioxide, and cooling the system in an ice-water bath under carbon dioxide (ca. 20 psi) for 20 min with magnetic stirring. The tube was then fixed to the motor unit of a rotary evaporator, and irradiated with a 36 W low pressure mercury lamp (λ = 254 nm) placed in parallel 2 cm above the test tube, under rotation and with magnetic stirring at room temperature. The reaction mixtures were suspensions of variable amounts of a pale yellow solid, smelled of hydrogen sulphide, and showed no overpressure. Aliquots of the decanted solutions were diluted with stock solutions of thiols 1, and analyzed by liquid chromatography.

Scheme 1. Reaction scheme devised for the iodide photocatalyzed reduction of carbon dioxide with thiols 1.

Supporting information for this article is given via a link at the end of the document.
The reaction led to the quantitative conversion of thiol 1a into the corresponding 2,2′-disulfanediylbis(ethan-1-ol) (2a), to give 64 % yield of formic acid in relation to the converted thiol 1a (Run 1, Table 1). This result suggested that thiol 1a partially undergoes unproductive disproportion under our reaction conditions.[17,18] In order to improve the competitiveness of carbon dioxide we performed the experiment with a 0.068 M solution of thiol 1a (molar ratio carbon dioxide:1a 3:5:1) under the same conditions. The reaction led to the quantitative conversion of thiol 1a to give formic acid (100 %) and disulfide 2a (72 %) (Run 2, Table 1).

The reaction was complete after 1 h, giving in this case 95 % of formic acid (Run 3, Table 1). No reduction of carbon dioxide was observed in the absence of either iodide salt or 2-mercaptoethanol (1a). Oxalic acid, formaldehyde and methanol were not detected as products in the reaction mixtures.

Once we proved that the photolysis of the iodide anion efficiently promoted the reduction of carbon dioxide to formic acid by thiol 1a in an acetonitrile-d3 solution, we explored the reaction in aqueous medium. The irradiation of a 0.034 M aqueous solution of 2-mercaptoethanol (1a) with 10 mol % of potassium iodide and saturated with carbon dioxide (molar ratio carbon dioxide:1a 2:2:1) led to a 92 % conversion of thiol 1a to give formic acid (90 %), 1,2-dihydroxyethanol (3) (42 %), disulfide 2a (26 %), ethanol (15 %), and unquantified amounts of hydrogen sulfide and sulfur (Run 6, Table 1). 1,2-Dihydroxyethanol (3) was identified from the 1H NMR signals at δ 64.98 and 6.40 ppm, correlated to signals at δ 64.98 and 6.20 ppm in the 13C NMR spectrum, and was confirmed by comparison with an authentic sample. This result shows that the reduction of carbon dioxide to formic acid by thiol 1a proceeds efficiently in aqueous medium as well, yet reveals significant changes in the reaction course.

In order to track the formation of the different products in aqueous medium, we performed a series of experiments with variable reaction times (Runs 5-7, Table 1), by using 30 mol % of potassium iodide to minimize the direct photolysis of thiol 1a (the absorbances at 254 nm for iodide and thiol 1a under these reaction conditions were 0.3334 and 0.0319, respectively). The reaction performed for 30 min (Run 5, Table 1) showed a 75 % conversion of thiol 1a to give disulfide 2a (74 %), formic acid...
(48 %), and 1,2-dihydroxyethanol (3) (14 %). By extending the irradiation time to 90 and 180 min (Runs 6 and 7, Table 1), we observed increasing yields of formic acid and 1,2-dihydroxyethanol (3), which reached 152 % and 53 %, respectively, associated to the progressive depletion of disulfide 2a and increasing conversion of thiol 1a.

These results show that thiol 1a converts into disulfide 2a at the early stages of the reaction and, thereby, that disulfide 2a is able to reduce carbon dioxide to formic acid under our reaction conditions. This fact was ascertained by irradiating a 0.034 M aqueous solution of disulfide 2a with 50 mol% of potassium iodide saturated with carbon dioxide (Run 8, Table 1), which gave formic acid (69 %), 1,2-dihydroxyethanol (3) (57 %),[19] thiol 1a (17 %), ethanol (6 %), and unquantified amounts of sulfur and hydrogen sulfide, with a 51 % conversion of the starting disulfide 2a (Run 8, Table 1).

The formation of thiol 1a and 1,2-dihydroxyethanol (3) in this reaction[19] evidenced that the actual reductants of carbon dioxide under our reaction conditions are intermediate S-H functionalities formed from disulfide 2a at the expense of the side-chain hydrogen atoms. This process proved to be very sensitive to the solvent. Indeed, the reaction of disulfide 2a with carbon dioxide in acetonitrile-d3 under our standard conditions converted only 9 % of disulfide 2a to give formic acid in 43 % yield as the only product (Run 9, Table 1).

Finally, we performed the reaction with hydrogen sulfide as a hydrogen donor.[20] The reduction of carbon dioxide by hydrogen sulfide has been frequently hypothesized as a prebiotic process[21] yet the actual reaction conditions to perform this transformation have not been described up to now. The irradiation of a 0.023 M aqueous solution of hydrogen sulfide saturated with carbon dioxide (molar ratio carbon dioxide:hydrogen sulfide 3:2:1) in the presence of 10 mol% of potassium iodide under our standard reaction conditions led to a suspension of elemental sulfur. The 1H and 13C NMR analyses of the decanted solution showed the formation of formic acid in quantitative yields relative to the starting hydrogen sulfide (Equation 1). The reaction in the absence of potassium iodide did not lead to formic acid.

The basic chemical steps devised in Scheme 1[8-12] rationalize the experimental results shown in Table 1 and Equation 1, yet further research is required to ascertain the actual reaction paths, intermediates, and competing processes under the different reaction conditions. For instance, the involvement of solvated electrons versus inner-sphere electron transfer, the role of protons as competitive electron sinks,[22] the possible intermediacy of species like the radical anions of thiol 1 and iodine, the radical adducts [RSH·I·] and [RSH·SR ·], or the [I3-·] anion, as well as the possible alternative reaction paths of carbon dioxide, are significant mechanistic issues requiring detailed investigation.

The impact of the solvent on the formation of S-H functionalities at the expense of side-chain hydrogen atoms of disulfide 2a is an interesting feature of the results shown in Table 1. The reaction probably proceeds through electron capture by 2a followed by dissociation of the C-S or S-S σ-bonds of disulfide 2a radical anion,[23] hydrogen abstraction from the methylene group α to the sulfur atom by the radical intermediate, collapse of the C-centered radical with the iodine atom, and hydrolysis of the resulting α-iodoalcohol to give 1,2-dihydroxyethanol (3) and restore the iodine anion into the solution. The hydrolysis step and the solvation of the anionic intermediates involved in this sequence would account for the better performance of this reaction in water compared to acetonitrile. Hydrogen abstraction by thyl radicals from aminoacid side-chains has been recently shown to occur in the photo-degradation of peptides and aminocids.[24]

In summary, we have described a transition metal-free photocatalytic process for reducing carbon dioxide to formic acid with thiols 1 and hydrogen sulfide, in which iodine atoms mediate the transfer of electrons from the sulfur atom to carbon dioxide. This primary photosynthetic reaction involving iodide salts, carbon dioxide, and hydrogen sulfide may have been relevant as a prebiotic process for carbon dioxide fixation.[21] This novel CO2-capture /H2S-removal process may be further improved by using electron and hydrogen donors photoactivated in the visible region.[25] Indeed, the reactions described herein may be involved nowadays in the chemistry of anoxic natural waters, in which dissolves organic matter would be the source of hydrated electrons.[26]

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Connecting the dots: the electron photodetachment from iodide anion, the hydrogen transfer from thiols to carbon dioxide radical anion, and the oxidation of thiols by iodine, define a robust and transition metal-free photocatalytic method for the reduction of carbon dioxide to formic acid by thiols and hydrogen sulfide at atmospheric pressure in aqueous and acetonitrile solution.