



# CO<sub>2</sub>: A Small Ubiquitous Molecule With a Lot of Astrochemical Debate Attached

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### Specialty section:

This article was submitted to  
Astrobiology,  
a section of the journal  
Frontiers in Astronomy and Space  
Sciences

**Received:** 19 February 2020

**Accepted:** 25 May 2020

**Published:** 24 June 2020

### Citation:

Bredehöft JH (2020) CO<sub>2</sub>: A Small Ubiquitous Molecule With a Lot of Astrochemical Debate Attached. *Front. Astron. Space Sci.* 7:33. doi: 10.3389/fspas.2020.00033

Water, carbon monoxide and carbon dioxide are the most abundant molecules in the condensed phase of interstellar dust grains. Water is formed by hydrogenation of oxygen species adsorbed on the surface of dust grains, while carbon monoxide is formed by reactions between ionized carbon and hydroxyl species in the gas phase. It is the second most abundant molecule in the gas phase after molecular hydrogen. The formation of carbon dioxide, however, cannot proceed in the gas phase as the addition of an oxygen to carbon monoxide is so exothermic that the new-formed molecule quickly breaks a C-O bond without a third body to transfer the excess energy to. It is commonly accepted that carbon dioxide is formed by energetic processing of carbon monoxide and water on grain surfaces. The exact mechanism of the oxidation of carbon monoxide and the intermediates formed in the process, however, are under some dispute. The role of the HOCO<sup>•</sup> radical in the oxidation of carbon monoxide is especially contested, as theory predicts it should not be able to dissociate the H-O bond to yield carbon dioxide, but it is experimentally observed in some studies of the reaction. The author presents here a short overview of established and recent experimental results in an attempt to reconcile seemingly contradictory results and give a comprehensive and consistent picture of the radiation induced reactions between carbon monoxide and water on grain surfaces.

**Keywords:** astrochemistry, comets, ISM, icy grains, secondary electrons

## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is found everywhere in the Universe. It has been determined the second or third most abundant condensable<sup>1</sup> molecule after water (H<sub>2</sub>O) and carbon monoxide (CO) (Hama and Watanabe, 2013). It has been identified in dense clouds, young stellar objects (Ehrenfreund and Charnley, 2000), comet Hale-Bopp (Irvine et al., 2000), and its abundance has even been measured *in situ* on the nucleus of comet 67P/Churyumov-Gerasimenko (Goesmann et al., 2015). The only exception to this is the high-mass protostellar object W33A, in which the abundance of methanol (CH<sub>3</sub>OH) exceeds that of both CO and CO<sub>2</sub> (Gibb et al., 2000). It is generally understood that CO<sub>2</sub> forms by oxidation of CO in the ice mantles surrounding interstellar dust grains. This is in agreement with the very low observed gas phase abundances of CO<sub>2</sub> (about a factor of 100

<sup>1</sup>Note that the two non-condensable substances hydrogen (H<sub>2</sub>) and Helium are disregarded throughout this entire review, because they can by their nature not contribute to condensed-phase chemistry.

less than in condensed phase) (Boonman et al., 2003) and the fact that gas-phase synthesis of CO<sub>2</sub> from CO and O atoms is very inefficient without a third body to transfer excess energy to. In fact, the electronically excited O(<sup>1</sup>D) is very efficiently quenched to the O(<sup>3</sup>P) ground state by interaction with CO. The intermediate CO<sub>2</sub> rapidly decays to vibrationally excited CO and ground state O(<sup>3</sup>P) (Shortridge and Lin, 1976). The exact mechanism by which oxidation of CO occurs, however, is less well agreed upon. While it is conceivable that CO undergoes radiolysis to C<sup>•</sup> and O<sup>•</sup> atoms, the latter of which can react with CO, the most abundant molecule in interstellar ices is water, which would hinder this reaction by dilution of CO and by rapid reaction with O atoms. It is thus reasonable to expect H<sub>2</sub>O to play the role as oxygen donor in the net reaction  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ . But since condensed phase chemistry rarely ever proceeds by such simple routes, the question of the exact mechanism of the oxidation of CO by H<sub>2</sub>O needs to be answered by experiment.

## EXPERIMENTAL DATA ON CO + H<sub>2</sub>O

There have been numerous studies of the radiation-induced chemistry of CO and H<sub>2</sub>O, as should be expected for the two most abundant molecules in the Universe (disregarding H<sub>2</sub>). The means of irradiation span UV light (Milligan and Jacox, 1971; Allamandola et al., 1988; Watanabe and Kouchi, 2002; Watanabe et al., 2007), slow electrons (Yamamoto et al., 2004; Schmidt et al., 2019), fast electrons (Bennett et al., 2011; Petrik et al., 2014a,b), X-ray (Laffon et al., 2010) as well as wide range of ion beams. Since ion beams introduce another potential reaction partner, complicating the reaction routes further, they will not be discussed here in depth. The proton beam experiments alone would warrant a full review paper for their extremely rich and interesting chemistry.

In all of the above studies, CO and H<sub>2</sub>O are condensed at cryogenic temperatures (10–35 K) and are then be subjected to irradiation. Along with CO<sub>2</sub>, formaldehyde (H<sub>2</sub>CO), formic acid (HCOOH), and CH<sub>3</sub>OH were all identified as products of energetic processing. In all but the Schmidt et al. study, reaction progress was monitored by infrared (IR) spectroscopy (and sometimes complementary techniques as well). This allowed the authors to monitor stable products as well as reactive intermediates, as long as their abundance was high enough. The downside of IR spectroscopy in condensed phase is that bands tend to be very broad and overlap due to the manifold chemical surroundings experienced by individual molecules. This makes definite band assignment difficult or downright impossible. Further complicating the issue is the fact that IR spectra of intermediate species are often not well-known, or intermediates are species that are not IR active at all, such as atomic O. The two key intermediate radical species HCO<sup>•</sup> and HOCO<sup>•</sup> were, however, observed.

In experiments with isotopic labeling, Yamamoto could show that the formation of CO<sub>2</sub> predominantly proceeds by a reaction between CO and H<sub>2</sub>O rather than from CO alone. Experiments by Petrik et al. showed that CO<sub>2</sub> yields are highest, when CO and H<sub>2</sub>O are well-mixed, while in diffusion-limited scenarios

the hydrogenation products H<sub>2</sub>CO and CH<sub>3</sub>OH are favored because of the high mobility of H<sup>•</sup> radicals even at cryogenic temperatures. These observations led to the rationalization that the reaction is triggered by radiolysis of H<sub>2</sub>O, forming H<sup>•</sup> and OH<sup>•</sup> radicals. These react with CO to form HCO<sup>•</sup> or HOCO<sup>•</sup>, respectively. Subsequent additions of further H<sup>•</sup> and OH<sup>•</sup> radicals then yield H<sub>2</sub>CO, CH<sub>3</sub>OH, and HCOOH. CO<sub>2</sub> formation was explained by the loss of an H<sup>•</sup> from the HOCO<sup>•</sup> intermediate.

The problem with this interpretation is that for every cleavage of H<sub>2</sub>O, equal numbers of H<sup>•</sup> and OH<sup>•</sup> radicals are formed. This means that the ratios between the different products should be predictable and, above all, fixed. Which they weren't. In their 1988 study, Allamandola et al. found a much higher abundance of CO<sub>2</sub> than Milligan and Jacox did in 1971. Moreover, while Milligan and Jacox saw a significant IR signal, which was later assigned to HOCO<sup>•</sup>, the later study couldn't find a trace of the same intermediate. Watanabe and Kouchi did observe that the rate of decrease in CO was faster than the rate of increase in CO<sub>2</sub> abundance, which hinted at some intermediate, but could not identify it in their IR measurements. In their later 2007 study Watanabe et al. did observe some small traces of HCO<sup>•</sup> but no HOCO<sup>•</sup> which led them to propose a reaction scheme based solely around the HCO<sup>•</sup> intermediate. And all this was just for the UV irradiation.

In the 2011 electron irradiation experiments by Bennett et al. HOCO<sup>•</sup> was unambiguously identified as an intermediate. By that time, however, quantum-chemical calculations had shown that the HOCO<sup>•</sup> radical should be stabilized in a water matrix, quickly losing all its excess energy and making the reaction to CO<sub>2</sub> impossible (Goumans et al., 2008), a concept that would later also be shown by molecular-dynamics simulations (Arasa et al., 2013). One huge benefit that the Bennett study had over the previous studies was, however, that it looked at more than one product. The authors monitored CO<sub>2</sub>, H<sub>2</sub>CO, and HCOOH at the same time. The difficulties in identifying all products and intermediates from an IR spectrum, led most authors to focus on one product of the reaction and observing its formation with increasing dose of radiation. Bennet et al. circumvented this in part by also looking at the stable reaction products by mass spectrometry. By simultaneously looking at several products, some additional insight into the messy situation around the HOCO<sup>•</sup> radical could be gained. The authors proposed for the first time that HOCO<sup>•</sup> was the precursor to HCOOH. But ultimately, they also couldn't explain the formation of CO<sub>2</sub> comprehensively.

The most recent study of the problem is by Schmidt et al. (2019). The authors build on the Bennett experiments in the sense that they too used mass spectrometry and they too looked at all known products of the reaction. To overcome the limitation of the previous study, however, they also implemented another experimental technique that Yamamoto et al. tried in 2004: Looking at product yields not in dependence of irradiation time, but in dependence of electron energy  $E_0$ . Yamamoto et al. looked at the CO<sub>2</sub> yield after 10 min of electron irradiation at 5, 10, 15, 20, 25, 30, 40, and 50 eV of  $E_0$ . The energy-dependence of the process yields some interesting information about the primary interaction of radiation with H<sub>2</sub>O molecules. In order to understand why product yields at different electron energies  $E_0$

are useful in understanding the underlying chemistry, a very brief explanation of some basic concepts of electron-driven chemistry might be needed.

## A BRIEF INTRODUCTION TO ELECTRON-MOLECULE INTERACTIONS

The reason why UV light, electron beams and X-rays should produce the same chemical products from condensed H<sub>2</sub>O:CO mixtures might at first be surprising. The modes of primary interaction between the different types of radiation and a molecule are quite different. UV light typically has energies (3–10 eV) that can excite valence shell electrons of a molecule  $M \rightarrow M^*$ , where the asterisk denotes an (electronically) excited state, while X-rays with their energies in the 100s of eV have enough energy to knock a core electron out of a molecule  $M \rightarrow M^+$ . Electrons on the other hand can have energies from near 0 eV all the way up to GeV, as seen in cosmic rays. Therefore, they can trigger a huge range of different processes. This is why the study of condensed phase astrochemistry is so often conducted using electron beams. They can trigger a huge variety of processes and at the same time are much easier to operate, tune and quantify than sources for X-Ray or extreme UV radiation.

But why do UV, electrons and X-ray cause the same types of chemical reactions to occur? This has to do with the processes that happen after the primary interaction. Any type of radiation that has an energy above the ionization threshold of a substance can knock an electron out of a molecule<sup>2</sup>. The electron that leaves the molecule, however, does not simply disappear. It can interact with surrounding molecules, of which there are many in the condensed phase, just as an electron from an electron beam would. These so-called “secondary electrons” typically have energies in the range between 2 and maybe 10–20 eV. The cross-section for electron-molecule interactions in this energy range is very large (Böhler et al., 2013), and they are produced in vast numbers (Boyer et al., 2016). This makes them responsible for the majority of chemical processes that are observed in energetic processing of ices. There are three principal ways of interaction of an electron  $e^-$  and a molecule  $M$ . The electron can excite the molecule, transferring some of its energy. This can happen when  $E_0$  is above the excitation threshold of the molecule, from which energy the cross section steadily rises:



The electron can knock an additional electron from the molecule, if its  $E_0$  is above the ionization threshold of the molecule, again with rising cross section for higher energies



<sup>2</sup>Hence the name “ionizing radiation.”

and finally the electron can attach to the molecule, which can happen in narrow, well-defined energy ranges of  $E_0$ , called resonances:



Any of these three forms of the molecule  $M^*$ ,  $M^+$ ,  $M^-$  can go on to dissociate by breaking a bond. In the case of neutral excitation, the dissociation of the molecule is called neutral dissociation (ND) and it typically yields two radicals



The case of the molecule losing an electron is called electron impact ionization (EI), in case the energy of the impinging electron is high enough, this will lead to dissociative ionization (DI),



and finally electron attachment can also lead to something called dissociative electron attachment (DEA):



In all of the cases, a radical species ( $B'$ ) is formed. These radicals are responsible for the formation of new bonds and thus chemical change. Since the energy dependence of these processes is different (resonant vs. steadily rising from different onsets), the processes can be distinguished by looking at the energy dependence of the formation of a product.

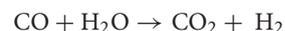
## RESOLVING THE ISSUE OF CO<sub>2</sub> FORMATION WITH SLOW ELECTRONS

The 2019 Schmidt et al. study made use of slow electrons with an energy resolution of 0.5 eV in the range between 2 and 20 eV, which is the energy range for secondary electrons. By looking at the energy dependence of the formation of the known products, CO<sub>2</sub>, H<sub>2</sub>CO, and HCOOH by post-irradiation mass spectrometry, they could finally untangle the reaction sequence and shed some light on the formation pathways not only for CO<sub>2</sub>, but also for H<sub>2</sub>CO and HCOOH. It was observed that all three products had a common energy dependence with a steady rise in product yield starting from around 6–7 eV. This clearly was an ND process, as it was not resonant and started at an energy far below the ionization threshold of either H<sub>2</sub>O or CO. This indicated that there must be one common or at least similar reaction pathway leading to either of the three products. Superimposed on the energy dependencies of H<sub>2</sub>CO and HCOOH, but not CO<sub>2</sub>, there were two resonant structures, one at around 4 eV in H<sub>2</sub>CO formation and one at around 10 eV for HCOOH formation. These resonances coincide with known electron attachment resonances. The lower energy channel at 4 eV leads to formation of CO<sup>•-</sup> which is very unstable and immediately detaches the electron in pure CO. In a water matrix, however, it can react to form OH<sup>-</sup> and HCO<sup>•</sup>. The higher

energy channel is an electron attachment to H<sub>2</sub>O, which decays into H<sup>-</sup> and OH<sup>·</sup>. The OH<sup>·</sup> radical then reacts with CO in a barrierless addition to form HOCO<sup>·</sup>. While the intermediates themselves could not be observed, their reaction products H<sub>2</sub>CO and HCOOH could. It would indeed seem that HOCO<sup>·</sup> is an important intermediate of the reaction between CO and H<sub>2</sub>O, it just is not an intermediate to CO<sub>2</sub> formation. This reconciles a lot of the previous work in which HOCO<sup>·</sup> was experimentally observed with the theoretical predictions that the reaction of HOCO<sup>·</sup> to CO<sub>2</sub> would be energetically infeasible.

But if neither HCO<sup>·</sup> nor HOCO<sup>·</sup> are intermediates on the route to CO<sub>2</sub>, what is? The energy dependence of CO<sub>2</sub> formation strongly suggests an ND process, but ND to water yielding H<sup>·</sup> or OH<sup>·</sup> is ruled out for significant CO<sub>2</sub> production, as there is no enhanced production of CO<sub>2</sub> at the resonance energies where HCO<sup>·</sup> and HOCO<sup>·</sup> are known to exist. There is another known ND process in CO yielding C<sup>·</sup> and O<sup>·</sup>, but since it was experimentally observed that most CO<sub>2</sub> is formed by involving H<sub>2</sub>O (Yamamoto et al., 2004; Laffon et al., 2010; Schmidt et al., 2019) this seems very unlikely. Also, the energy at which this process starts is much higher than the observed onset (McConkey et al., 2008). At the energies observed here, there is however, another ND process in H<sub>2</sub>O. Starting from around 7 eV, H<sub>2</sub>O can dissociate into H<sub>2</sub> and O(<sup>1</sup>D/<sup>3</sup>P). This would seem

counter-intuitive at first, since dissociation of both H-O bonds in H<sub>2</sub>O requires significantly more energy than 7 eV, but the energy yield from the recombination of 2 H<sup>·</sup> to H<sub>2</sub> is enough to offset the deficit. The authors thus present their finding that the formation of CO<sub>2</sub> is one of the extremely rare cases where a net reaction equation like



is indeed indicative of the actual reaction mechanism. By carefully looking at all products of the reaction between H<sub>2</sub>O and CO, and by doing so with an energy resolution that allowed the authors to distinguish different reaction channels, they could work out that, in the end, everybody was right: HOCO<sup>·</sup> is indeed an important intermediate, just not on the path to CO<sub>2</sub>, HOCO<sup>·</sup> is indeed stabilized by the matrix, which is why it could be observed in some cases, and the net stoichiometric equation for oxidation of CO is truly describing the reaction mechanism.

## AUTHOR CONTRIBUTIONS

JB confirms being the sole author of this work and has approved it for publication.

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**Conflict of Interest:** The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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