Co 2 : a small ubiquitous molecule with a lot of astrochemical debate attached

Health & Medicine

Introduction

Carbon dioxide (CO_2) is found everywhere in the Universe. It has been determined the second or third most abundant condensable 1 molecule after water (H_2O) 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_3OH) exceeds that of both CO and CO_2 (Gibb et al., 2000). It is generally understood that CO_2 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_2 (about a factor of 100 less than in condensed phase) (Boonman et al., 2003) and the fact that gas-phase synthesis of CO_2 from CO and O atoms is very inefficient without a third body to transfer excess energy to. In fact, the electronically excited O(^{1}D) is very efficiently quenched to the O(^{3}P) ground state by interaction with CO. The intermediate CO_2 rapidly decays to vibrationally excited CO and ground state O(^{3}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 $C^{\cdot}$ and $O^{\cdot}$ 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_2O to play the role as oxygen donor in the net reaction $CO + H_2O \rightarrow CO_2 + H_2$. 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_2O needs to be answered by experiment.

Experimental Data on $CO + H_2O$

There have been numerous studies of the radiation-induced chemistry of CO and H_2O, as should be expected for the two most abundant molecules in the Universe (disregarding H_2). 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_2O are condensed at cryogenic temperatures (10–35 K) and are then be subjected to irradiation. Along with CO_2, formaldehyde (H_2CO), formic acid (HCOOH), and CH_3OH 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 $HCO^{\cdot}$ and $HOCO^{\cdot}$ were, however, observed.

In experiments with isotopic labeling, Yamamoto could show that the formation of CO_2 predominantly proceeds by a reaction between CO and H_2O rather than from CO alone. Experiments by Petrik et al. showed that CO_2 yields are highest, when CO and H_2O are well-mixed, while in diffusion-limited scenarios the hydrogenation products H_2CO and CH_3OH are favored because of the high mobility of $H^{\cdot}$ radicals even at cryogenic temperatures. These observations led to the rationalization that the reaction is triggered by radiolysis of H_2O, forming $H^{\cdot}$ and $OH^{\cdot}$ radicals. These react with CO to form $HCO^{\cdot}$ or $HOCO^{\cdot}$, respectively. Subsequent additions of further $H^{\cdot}$ and $OH^{\cdot}$ radicals then yield H_2CO, CH_3OH, and HCOOH. CO_2 formation was explained by the loss of an $H^{\cdot}$ from the $HOCO^{\cdot}$ intermediate.

The problem with this interpretation is that for every cleavage of H_2O, equal numbers of $H^{\cdot}$ and $OH^{\cdot}$ 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_2 than Milligan and Jacox did in 1971. Moreover, while Milligan and Jacox saw a significant IR signal, which was later assigned to HOCO $^{\cdot}$, 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_2 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 $^{\cdot}$ but no HOCO $^{\cdot}$ which led them to propose a reaction scheme based solely around the HCO $^{\cdot}$ intermediate. And all this was just for the UV irradiation.

In the 2011 electron irradiation experiments by Bennett et al. HOCO $^{\cdot}$ was unambiguously identified as an intermediate. By that time, however, quantum-chemical calculations had shown that the HOCO $^{\cdot}$ radical should be stabilized in a water matrix, quickly losing all its excess energy and making the reaction to CO_2 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_2 , H_2CO, 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 $^{\cdot}$ radical could be gained. The authors proposed for the first time that $HOCO^{\cdot}$ was the precursor to HCOOH. But ultimately, they also couldn't explain the formation of CO_2 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_2 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_2O 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_2O: 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 → 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 2 . 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:

$M + e^- \rightarrow M^* + e^-$ (slower)

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

$M + e^- \rightarrow M^{+\cdot} + 2e^-$,

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

$M + e^- \rightarrow M^{-\cdot}$.

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

$M^* \rightarrow A^\cdot + B^\cdot$.

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),

$M^{+\cdot} \rightarrow A^+ + B^\cdot$,

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

$M^{-\cdot} \rightarrow A^- + B^\cdot$.

In all of the cases, a radical species ($B^{\cdot}$) 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_2 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_2, H_2CO, 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_2, but also for H_2CO 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_2O 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_2CO and HCOOH, but not CO_2, there were two resonant structures, one at around 4 eV in H_2CO 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 $CO^{\cdot-}$ which is very unstable and immediately detaches the electron in pure CO. In a water matrix, however, it can react to form OH^{-}

and $HCO^{\cdot}$. The higher energy channel is an electron attachment to H_2O, which decays into H^- and $OH^{\cdot}$. The $OH^{\cdot}$ radical then reacts with CO in a barrierless addition to form $HOCO^{\cdot}$. While the intermediates themselves could not be observed, their reaction products H_2CO and HCOOH could. It would indeed seem that $HOCO^{\cdot}$ is an important intermediate of the reaction between CO and H_2O, it just is not an intermediate to CO_2 formation. This reconciles a lot of the previous work in which $HOCO^{\cdot}$ was experimentally observed with the theoretical predictions that the reaction of $HOCO^{\cdot}$ to CO_2 would be energetically infeasible.

But if neither $HCO^{\cdot}$ nor $HOCO^{\cdot}$ are intermediates on the route to CO_2, what is? The energy dependence of CO_2 formation strongly suggests an ND process, but ND to water yielding $H^{\cdot}$ or $OH^{\cdot}$ is ruled out for significant CO_2 production, as there is no enhanced production of CO_2 at the resonance energies where $HCO^{\cdot}$ and $HOCO^{\cdot}$ are known to exist. There is another known ND process in CO yielding $C^{\cdot}$ and $O^{\cdot}$, but since it was experimentally observed that most CO_2 is formed by involving H_2O (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_2O. Starting from around 7 eV, H_2O can dissociate into H_2 and $O(^1D/^3P)$. This would seem counter-intuitive at first, since dissociation of both H-O bonds in H_2O requires significantly more energy than 7 eV, but the energy yield from the recombination of 2 $H^{\cdot}$

to H_2 is enough to offset the deficit. The authors thus present their finding that the formation of CO_2 is one of the extremely rare cases where a net reaction equation like

$$CO + H_2O \rightarrow CO_2 + H_2$$

is indeed indicative of the actual reaction mechanism. By carefully looking at all products of the reaction between H_2O 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: $HOCO^{\cdot}$ is indeed an important intermediate, just not on the path to CO_2, $HOCO^{\cdot}$ 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.

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.

Footnotes

1. ^ Note that the two non-condensable substances hydrogen (H_2) and Helium are disregarded throughout this entire review, because they can by their nature not contribute to condensed-phase chemistry.

2. ^ Hence the name “ ionizing radiation.”

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