ACS EARTH AND SPACE CHEMISTRY



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Article

# Production and Reactions of Organic Molecules in Clouds of Venus

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Cite This: https://doi.org/10.1021/acsearthspacechem.3c00261



ABSTRACT: For half a century, the possibility of organic molecules in sulfuric acid droplets in the clouds above Venus has been largely discounted. Here, we report the first results from an experimental exploration of this possibility, of primary interest to astronomers but also uncovering reactions that are remarkable to organic chemistry. This work provides a detailed mechanism of how small organic molecules might be generated in the sulfuric acid ($H_2SO_4$) aerosol droplets that form the clouds above Venus, starting from formaldehyde (HCHO), a simple one carbon species produced photochemically in the gas phase. Laboratory $^{13}C$ and $^{1}H$ nuclear magnetic resonance studies detail processes by which dissolved HCHO reacts with dissolved carbon monoxide (CO) to produce a two-carbon organic species, glycolic acid ($HOCH_2COOH$). They show that glycolic acid is surprisingly stable, for days or longer, depending on temperature, in concentrated $H_2SO_4$. However, glycolic acid slowly reacts further to give higher molecular weight organic materials, including colored and fluorescent species. These may contribute to the UV and visible light astronomy of Venus, and are guiding the design of an autofluorescence nephelometer scheduled to fly on a Rocket Lab mission to Venus in 2025.


KEYWORDS: *aerosols, formaldehyde, sulfuric acid, unknown absorber, Venus*



## 1. INTRODUCTION

The clouds and atmosphere above Venus have attracted renewed interest in part due to recent reports that these may hold phosphine ($PH_3$).[1,2] This, in turn, has revived discussions about the possibility of life above Venus, perhaps in droplets of concentrated sulfuric acid ($H_2SO_4$) that constitute the Venusian clouds[3−5] at altitudes where temperatures range between 270 and 370 K.[6−9] These discussions[10] reflect uncertainties associated with interpretations of observations of the Venusian clouds, and highlight the inadequacy of many models for the atmospheric chemistry of Venus.[11,12]

This is especially true with respect to organic molecules. Only "reduced" organic molecules are believed to provide sufficient complexity to support Darwinian evolution, the archetypal attribute of "life". Here, "reduced" means compounds with carbon−carbon and/or carbon-hydrogen bonds; these have oxidation states below that of carbon dioxide ($CO_2$), the principal gas in the Venusian atmosphere. Although not usually classified as "organic", carbon monoxide (CO) is reduced relative to $CO_2$, with carbon in the same oxidation state as in formic acid (HCOOH), which is a *bona fide* organic. HCOOH is known to dehydrate in concentrated (>85%) $H_2SO_4$ to give CO.[13,14]

Literature over the past 50 years has, with a few exceptions,[15] discounted organics as relevant to Venus as a target for observation, under the view that these would be destroyed by concentrated sulfuric acid. For example, Dayhoff and Sagan wrote that "[t]here can be no free carbon, hydrocarbons, formaldehyde, or any other organic molecule present in more than trace amounts" above Venus.[16] Such views have influenced models for the Venusian atmosphere, which "do not account for existence of reduced carbon compounds".[3,17] Large organics are seen as incompatible with the high acidities of the Venusian clouds.[18]

These remarks are not unreasonable, given the thermodynamic and kinetic instability of many organic species in laboratory studies in concentrated $H_2SO_4$.[19,20] However, very simple organics such as formaldehyde (HCHO) can be produced photochemically in $CO_2$-rich planetary atmospheres.[21] This work is the first to model the production of formaldehyde in the atmosphere of Venus, a molecule that might be a precursor for larger organics.

Early spectrometric estimates put a 1 ppm upper limit for HCHO. However, remote spectroscopic estimates for the amounts of HCHO must be unreliable. HCHO easily dissolves in concentrated $H_2SO_4$ droplets, where it becomes spectroscopically invisible.[22,23] Further, HCHO reacts reversibly with many nucleophiles to form products that are also largely invisible. For example, above Earth, HCHO with $H_2O$ is largely converted to its hydrate ($H_2C(OH)_2$).[24] With $SO_2$, HCHO forms hydroxymethanesulfonic acid ($HOCH_2-SO_3H$).[25]

Received: September 11, 2023
Revised: December 6, 2023
Accepted: December 7, 2023

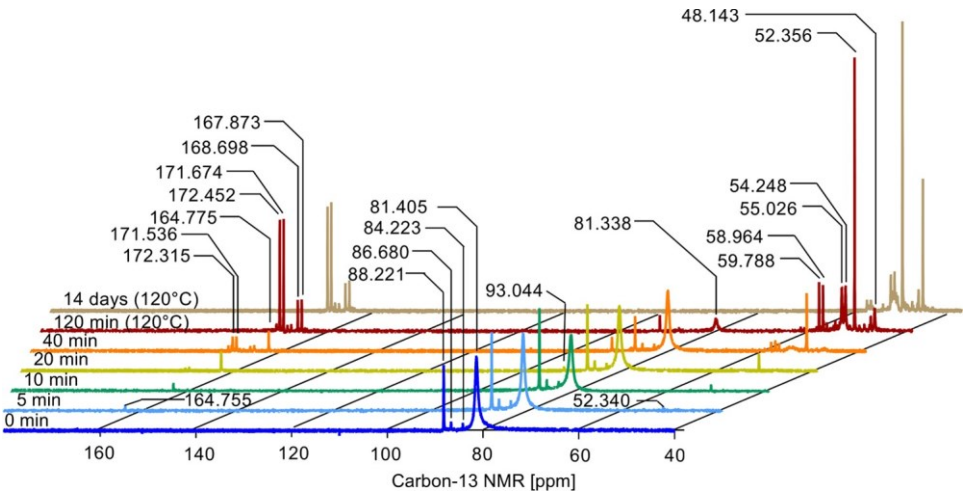


Figure 1. $^{13}C$ NMR spectra showing the movement of $^{13}C$ label from $H^{13}CHO$ (added as $^{13}C$-paraformaldehyde, broad signal at 81 ppm; $H^{13}CHO$ signals are at 88 ppm) from 0 to 40 min at 60 °C, followed by additional 2 h heating at 120 °C. The signal at 164.755 ppm appearing after 5 min is assigned as a derivative of "$H^{13}COOH$". The signal at 52.340 ppm is assigned to methanol and its derivative $^{13}CH_3OSO_3H$ (methyl hydrogen sulfate). Methanol is added to paraformaldehyde, and $^{13}CH_3OSO_3H$ accumulates over time. However, the first signal (at 164.755 ppm) reaches maximum at 20 min, then declines and, after heating at 120 °C, is lost to give additional signals at 167−173 ppm range. Coupling experiments (SI 1.3) show that the $^{13}C$ atoms giving these signals are not bonded to any H atoms. However, they are bonded to second $^{13}C$ atoms that give signals at 55−60 ppm; these are assigned to $R-O^{13}CH_2$- carbons (SI 1.2). Thus, the product is $R-O^{13}CH_2-^{13}COOH$, glycolic acid (R□H) or a derivative. (The NMR spectra are offset as indicated by diagonal lines for clarity.)

For these reasons, in a recent theoretical draft,[26] Spacek considered the possibility that organics may be observationally significant for Venus. His model for the diagenesis of organics in Venusian $H_2SO_4$ relied on studies from the petrochemical industry, which has long been interested in the reactivity of organic molecules in $H_2SO_4$.[27] Here, multicarbon organics are transformed to give mixtures of larger molecules that are called acid-soluble oils (ASO) or, prosaically, "red oil".[28]

Above Venus, this process would eventually form black carbon particles.[29,30] These would be resistant to evaporation or a cracking reaction. After falling from the clouds in a form of microscopic carbon solids, they would react in the Boudouard reaction with $CO_2$ to give CO at altitudes below ~40 km,[31] completing the proposed carbon cycle.[26] We address this process experimentally and its implications for the observational astronomy of Venus in a separate paper.

Here, we address steps missing in that proposed carbon cycle, specifically processes that form the *first* C−C bonds from one-carbon (C-1) species. We report here that the Venusian clouds likely hold a manifold of organics that proceed via reaction of CO, more reduced species, and higher molecular weight species that may yield spectroscopically observable products. These include a previously unsuspected reservoir of reactive species poised to capture HCHO and other transiently available reduced organics. These together make predictions that are today guiding Morning Star missions to Venus in 2025.[32,33]

## 2. RESULTS

We present in some detail the experiments that support these conclusions to bridge the gap between astronomy, planetary science, and mechanistic organic chemistry. Supporting Information provides more detail about the mechanistic studies, especially their use of isotopes and nuclear magnetic resonance (NMR) spectrometry to define reaction paths and assign product structures.

**2.1. HCHO Disproportionates to HCOOH and $CH_3OH$ in Concentrated $H_2SO_4$.** We first studied the reactivity of formaldehyde (HCHO) to understand how it might behave in concentrated $H_2SO_4$, a simulation of the Venusian cloud. Here, isotopically labeled formaldehyde ($H^{13}CHO$) was added (as its polymer, paraformaldehyde, $HO-(^{13}CH_2O)_n-H$) to 85% $HDSO_4$ at 60 °C. The fate of its single carbon atom was followed by $^{13}C$-nuclear magnetic resonance spectroscopy ($^{13}C$ NMR).

Unexpectedly, the signals due to formaldehyde and paraformaldehyde disappeared in minutes to give two new $^{13}C$ NMR signals. The new products have two kinds of carbon atoms, with chemical shifts of 164.8 and 52.3 ppm (Figure 1, see SI 1.1−1.2). The 164.8 ppm shift was consistent with a $^{13}C$ atom in $H^{13}COOH$ or a related molecule. The $^{13}C$ spin was coupled to a $^1H$ spin ($^1H-^{13}C$ coupling constant $J$ = 228.36 Hz) indicating that this product had a $^1H-^{13}C$ single bond (Figures S1 and S2). The upfield signals at 52.356 and 48.097 ppm came from $^{13}C$ atoms bonded to three hydrogen atoms and one oxygen atom, and were assigned to $^{13}CH_3OH$ (methanol, 48.967 ppm) and $^{13}CH_3OSO_3H$ (methyl hydrogen sulfate, 52.737 ppm), in rapid equilibrium (Figures S2 and S3). Both assignments were confirmed by adding authentic materials to the sample. Thus, addition of authentic $H^{13}COOH$ directly to a solution of $H^{13}CHO$ kept for 20 min in 85% $H_2SO_4$ at 60 °C gave the same 164.8 ppm signal (Figure S2, blue line, see SI 1.4). Bubbles of CO gas were observed to emerge in this experiment, indicating that HCOOH too can react (discussed in SI 1.4).[34] Addition of authentic $^{13}CH_3OH$ gave $^{13}CH_3OH$ and methyl hydrogen sulfate ($^{13}CH_3OSO_3H$) in a ratio depending on the concentration of $H_2SO_4$, consistent with literature (Figure S3).[35,36]

These results showed that HCHO in concentrated $H_2SO_4$ undergoes redox disproportionation"


https://doi.org/10.1021/acsearthspacechem.3c00261
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

$$H^{13}CHO + H^{13}CHO \rightarrow \text{“}H_3{}^{13}COH\text{”} \text{ (in some form)} + \text{“}H^{13}COOH\text{”} \text{ (in some form)}$$

This disproportionation is analogous to the Cannizzaro reaction of HCHO in alkaline water, where it is well studied by prebiotic chemists.[37] An analogous acid-catalyzed disproportionation reaction was observed by Prins in acetic acid-sulfuric acid mixtures.[38]

For chemists, this is an unexpected “redox disproportionation” reaction where molecules of HCHO, both at the oxidation level of elemental carbon, react to give one molecule of a more oxidized species (“$H^{13}COOH$”) and one molecule of a more reduced species ($^{13}CH_3OH$). Further, the more oxidized species reacts with $H^{13}CHO$ in another unexpected reaction to form a new carbon-carbon bond. The $^{13}C-^{13}C$ coupling constants allow the correlation of signals at 165−170 ppm to signals at 55−60 ppm. The two-carbon species glycolic acid is metastable.

For planetary scientists, this means that to the extent that Venus can access HCHO, it gains access to (a) one-carbon molecules with both a higher and a lower redox state and (b) more complex compounds with a new carbon-carbon bonds that might accumulate under the right conditions.

**2.2. Nature of “HCOOH” in Venusian-Level (85%) $H_2SO_4$.** As discussed in SI 1.4, authentic species added to assign structure to a product may react further. Indeed, when formic acid is added directly to concentrated $H_2SO_4$, it loses $H_2O$ to generate bubbles of CO.[13] The rate of decomposition depends on the concentration of $H_2SO_4$ (Figure S4), and is small below 80% $H_2SO_4$ at 25 °C. The loss of CO displays an oscillatory behavior, attributed to the need for substantial amounts of dissolved CO to nucleate the formation of bubbles that then escape.[39] However, this might be less relevant in Venus’s clouds aerosols, where the dissolved gas equilibrates with the gas phase faster compared to bulk liquids.

We also observed CO effervescence when large amounts of HCOOH were added directly to >85% $H_2SO_4$ at 25 °C. However, we did not observe effervescence when “$H^{13}COOH$” was formed by acid-catalyzed disproportionation. Rather, the total $^{13}C$ was lost only gradually. This lack of visible effervescence is consistent with the view that when gradually formed as isolated molecules, CO is not present in amounts sufficient to nucleate bubble formation.

This motivated the question: Is the “$H^{13}COOH$” formed by acid-catalyzed disproportionation, giving a $^{13}C$ NMR signal at ∼164.775 ppm, canonical formic acid? To answer this question, we observed the $^{13}C$ NMR (Figure 2) and $^{1}H$ NMR (Figure S1) spectra of $H^{13}COOH$ over a range of $H_2SO_4$ concentrations, starting in deuterated water. Here, $^{1}H^{13}COOH$ has its canonical structure, with a $^{1}H$ NMR resonance of 8.032 ppm, with a $^{1}H-^{13}C$ coupling $J$ = 218.4 Hz (Figure S1).

The chemical shift changed as the amount of $HDSO_4$ increased, as did the $^{13}C$-$^{1}H$ coupling constant, which increased from 218.4 to 228.4 Hz (Figure S1C). This indicates that the C−H bond in whatever molecule is present in 90% $HDSO_4$ is stronger (has more “s character”, a change in the hybridization of the carbon forming the C−H bond, from $sp^2$ toward sp) than in canonical HCOOH. Based on these data, we assigned the structure of “formic acid” in concentrated $H_2SO_4$ as C-protonated carbon monoxide.[40,41] Here the, C-O bond has triple bond character; the molecule (C-protonated CO) can be represented as two resonance forms [H−$^{13}C^{+}$O] ↔ [H−$^{13}C\equiv O^{+}$] (see SI 1.6).

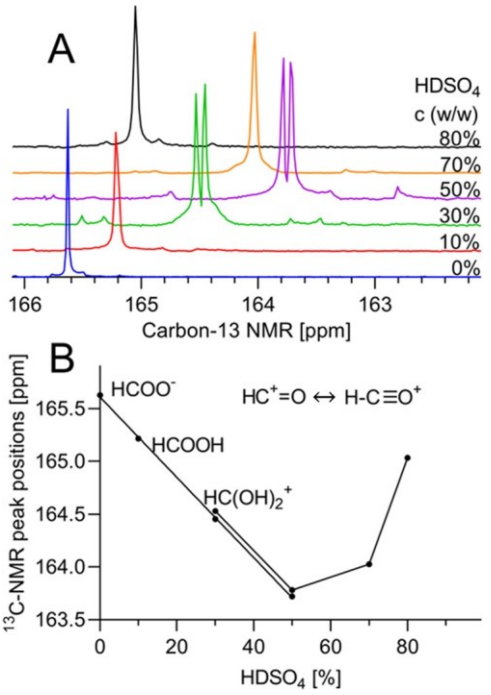


Figure 2. (A) Carbon NMR spectra of $^{13}C$ formic acid added to 0 to 80% $HDSO_4$. (B) Plot of peak positions from panel A with suggested predominant structures arising from the $H^{13}COOH$. The two peaks at intermediate sulfuric acid concentration are HCOOH (likely protonated) in slow (on the NMR time scale) equilibrium with {H−$C^{+}$O ↔ H−C≡$O^{+}$}.

**2.3. Reactivity of Protonated Carbon Monoxide in Concentrated $H_2SO_4$.** This section shows that CO is readily protonated in $H_2SO_4$ and that this is a mechanism for cloud aerosols to extract and concentrate CO from the gas phase.

Our experiments showed that protonated carbon monoxide indeed had Venus-relevant reactivity. In hours to days, even at room temperature at concentrations of >78% $HDSO_4$, $[H^{13}CO]^{+}$ is converted to $[D^{13}CO]^{+}$ (C-deuterated CO, Figure 3, and for kinetics of the H/D exchange Figures S5−S9. For H/D ratios in $HDSO_4$, see Table S2). Both the structure of $[D^{13}CO]^{+}$ and the rate of formation of its new C−D bond are clear from the 1:1:1 splitting of the $^{13}C$ signal at 164.5 ppm by carbon-deuterium coupling (deuterium has a nuclear spin of 1). The C−D coupling constant (33.43 Hz) was also consistent with a C−D bond with a strong *s* character. The deuterium perturbation of the chemical shift of carbon, approximately 0.206 ppm, was also consistent with a C−D bond with strong s character.

The observed H/D exchange is important to planetary scientists because it shows that the Venus clouds harbor a reservoir of carbon monoxide in the liquid phase in equilibrium with protonated carbon monoxide that is spectroscopically obscure. This may influence Venus-relevant reactivity and observations (see Section 3).

The resonance at ∼ 178 ppm is assigned to dissolved $^{13}CO$. A similar resonance was observed when oxalic acid ($HOO^{13}C$-$^{13}COOH$) was placed in $H_2SO_4$ (Figure S10). Oxalic acid is known to decompose to CO and $CO_2$ in heated $H_2SO_4$.[43]


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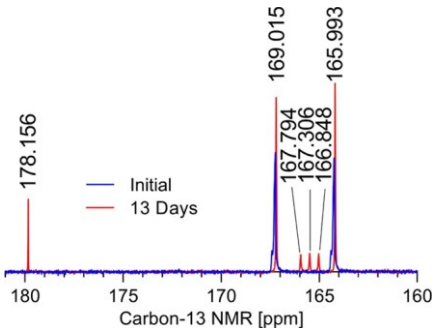


Figure 3. Downfield region of proton coupled $^{13}C$ NMR of products arising from dissolution of added $H^{13}COOH$ in 80% $HDSO_4$ the initial spectrum (blue) and after 13 days at room temperature (red). The initial spectrum shows only the resonances due to $H-^{13}C\Xi O^+$ (doublet at 166.347 and 163.356, H−C $J$ = 225.71 Hz). The shoulder peaks in the blue spectrum are tentatively assigned to canonical HCOOH before dehydration to $H-^{13}C\Xi O^+$. The triplet due to $D-^{13}C\Xi O^+$ (165.096, 164.653, 164.195, $J$ = 33.43 Hz) and resonance due to CO (178.908 ppm) appear after prolonged incubation (13 days in this case). To organic chemists, this is a new reaction. To planetary scientists, this means that gaseous CO present in the Venus atmosphere,[42] can dissolve in sulfuric acid aerosols in equilibrium with its protonated form, making a "CO equivalent" reservoir.

These data show that in more concentrated $H_2SO_4$, HCOOH protonated on the departing oxygen (at a rate dependent on acid activity) loses water (1) to give equilibrium (2)

$$HCOOH + H^+ \rightarrow [HCO]^+ + H_2O \quad (1)$$

$$[HCO]^+ + D \text{ } \forall \text{ } CO + H^+ + D \text{ } \forall \text{ } [DCO]^+ + H^+ \quad (2)$$

The reaction rate and equilibrium both depend strongly on the acid concentration. At high concentrations, faster CO generation (Figures S6 and S8), faster H/D exchange (Figures S7 and S9), and faster loss of the total $^{13}C$ signal (to outgassing; Figure S4) were all observed. This is consistent with literature.[44] At concentrations below ~80% $HDSO_4$, CO is neither accumulated or significantly lost, indicating that the rate of CO protonation (or deuteration) is faster than the rate of $[HCO]^+$ deprotonation or dedeuteration (Figures S6 and S7).

In 78% $HDSO_4$, only a small loss of $^{13}C$ signal is observed over 13 days (Figure S4), even though free CO is observed in the proton-deuteron exchange reaction (Figure S6). Here again, the local amounts of CO at any moment are not sufficient to nucleate bubble formation, and CO is gradually lost only via the liquid−gas interface.

These interpretations contradict previous proposals,[45] and have implications for Venus. They suggest that one-carbon species at the oxidation level of HCOOH (CO, $[HCO]^+$, and HCOOH) can accumulate as reservoirs in Venusian cloud aerosols in amounts far above that expected from a simple analysis of the CO gas ⇌ dissolved in the CO equilibrium.

From the results shown in Figure S8B, we estimate that 70% $H_2SO_4$ aerosols contain > 100× more carbon in a form of dissolved $[HCO]^+$ than as dissolved CO, while 80% $H_2SO_4$ aerosols contain >10× more carbon in a form of dissolved $[HCO]^+$ than as dissolved CO (Figure S8B). This reservoir is further shifted in favor of protonated and organic species if other organic carbon (such as formaldehyde) is present in the aerosol as HCHO reacts with CO and $H_2O$ (see below), efficiently absorbing CO from the atmosphere. A significant stabilization of $[HCO]^+$ is also observed when glycolic acid is present (Figure S15).

In the Venusian atmosphere, the concentration of $H_2SO_4$ is believed to (very broadly) increase with decreasing altitude, as temperature increases with decreasing altitude. Gases have in general lower solubility in hot solvents than in cold solvents, and CO is lost faster from more concentrated sulfuric acid (Figure S4). Thus, higher cloud droplets likely have more dissolved CO than lower cloud droplets.

**2.4. Fate of $[HCO]^+$ and HCHO in Concentrated $H_2SO_4$.** In the aqueous alkaline Cannizzaro reaction on Earth, HCOOH is a dead-end product, not progressing to form larger organic species. This is not the case in $H_2SO_4$. When generated from HCHO, the compound giving the $^{13}C$ NMR signal at 164.775 ppm increased over 20 min to a plateau. Upon further incubation, its concentration decreased as the molecule reacted further. The signal was ~50% consumed at 40 min and was gone at 2 h at 120 °C (Figure 1). Two new products emerged with new downfield $^{13}C$ signals. These products were assigned to "$HO^{13}CH_2{}^{13}COOH$" (glycolic acid), appearing from this reaction sequence

$$2H^{13}CHO \rightarrow \text{“}H^{13}COOH\text{”} + \text{“}H^{13}CH_3OH\text{”}$$

$$\text{“}H^{13}COOH\text{”} + \text{“}H^{13}CHO\text{”} \rightarrow \text{“}HO^{13}CH_2{}^{13}COOH\text{”}\ \text{(glycolic acid)}$$

To confirm this reaction, authentic $^{13}C$-glycolic acid was added to the mixture. Its signals superimposed on those of the glycolic acid formed from $H^{13}CHO$ (Figure S11). Further, the $^{13}C-^{13}C$ coupling constants for glycolic acid in neutral water ($J_{cc}$ = 58.70 Hz) was identical to the $^{13}C-^{13}C$ coupling constants for the major resonances in $H_2SO_4$. Accordingly, the major resonances in $H_2SO_4$ are assigned to canonical glycolic acid. The minor resonances were assigned to the glycolic acid sulfate ester. Upon dilution of glycolic acid in 90% $HDSO_4$ with $D_2O$ to give 85, 80, and 70% $HDSO_4$ these signals collapse to glycolic acid, with signals corresponding to those from glycolic acid without $H_2SO_4$ (Figure S12), analogically to methyl hydrogen sulfate − methanol equilibrium (Figure S3).[36]

**2.5. Mechanism of the Formation of Glycolic Acid ($HOCH_2COOH$).** To establish the mechanism of glycolic acid formation, we reproduced the process by incubating $H^{13}CHO$ in $HDSO_4$ overnight under $^{12}C$ (unlabeled) CO gas at ambient pressure at 60 °C. Signals corresponding to two derivatives of glycolic acid were observed (60.337 and 55.393 ppm; Figure 4); the $H^{13}CHO$ signal (81.488 ppm; Figure 4) was completely lost. The labeling pattern shows that carbon-2 of glycolic acid and glycolic acid sulfate ester comes from HCHO. This experiment also shows that gaseous CO is a source of organic carbon under Venus' cloudlike conditions, if HCHO is present.

The pattern of labeling shows that the −COOH carbon in glycolic acid comes from CO, and not HCHO. This is consistent with the mechanistic path in Figure 5 ("Koch mechanism") proceeding through carbonylation of protonated formaldehyde. A "carbenoid mechanism" involving insertion of hypothetical hydroxyethyl carbene onto not dehydrated formic acid is a less likely path.


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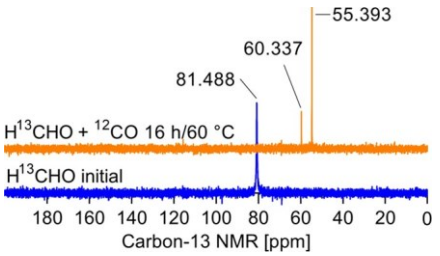


Figure 4. $H^{13}CHO$ (as paraformaldehyde; 81.5 ppm) dissolved in 85% sulfuric acid was exposed to CO at 60 °C overnight, yielding $^{13}C1/^{12}C2$ glycolic acid (55.4 ppm) and sulfate of $^{13}C1/^{12}C2$ glycolic acid (60.3 ppm) with no remaining $H^{13}CHO$. The 75% $H_2SO_4$ yielded after 16 h identical products, but with residual $H^{13}CHO$, indicating slower reaction. We expect the same reaction to take place in the Venusian cloud aerosols, converting the stored HCHO and dissolved CO to glycolic acid.

**2.6. Fate of Glycolic Acid.** These results establish that *controlled* small molecule organic chemistry can occur in the Venusian clouds: Carbon monoxide reacts with HCHO to form a glycolic acid. Glycolic acid (in its various forms) is remarkably stable in 85% $H_2SO_4$, even at elevated temperatures. $^{13}C$ signals from glycolic acid were still observable after incubation in 85% $H_2SO_4$ at 120 °C for 3 weeks, and for months at room temperature (Figure S13).

However, after prolonged incubation, glycolic acid reacts further to give colored, ultraviolet/visible (UV/vis) absorbent, and fluorescent species. The reaction rates were strongly dependent on the temperature and sulfuric acid concentration (Figures 6 and S14). Coloration and fluorescence were observed even as $^{13}C$ signals were still observable by NMR, indicating that only a small fraction of glycolic acid was converted to spectroscopically active species.

In general, organic compounds, including glycolic acid at higher concentrations, evolve through yellow and brown toward black mixtures. Thus, glycolic acid at >100 mM gave light brown, then darker, and eventually "black" solutions. We tentatively propose that the shorter wavelength absorption correspond to smaller, yet unidentified conjugated species, while the longer wavelength and broad-spectrum absorption is due to large compounds that we have previously described as "red oils".[26,28] Thus, lower temperatures and smaller reactant and $H_2SO_4$ concentrations lead to spectra with negligible absorption in the visible region. Prolonged reaction of concentrated mixtures at high temperature result in absorption over most of the visible range (Figure S14A−F).

From a chemical perspective, this is not unexpected. However, from a planetary science perspective, the concentration dependence is important. If the amounts of reduced compounds able to react with the dissolved CO were large, then the true color of the bulk liquid forming Venusian aerosols would be brown or black.

The fact that Venus clouds are pale-yellow[46] does not contradict this possibility. Reflection from microscopic aerosols is dominated by light scattering on the particles and not light absorption within the particles. Therefore, the pale-yellow coloration of the Venus's clouds may be entirely consistent with a very dark bulk liquid forming the aerosols. This is analogous to the foam above a beer having a lighter color than that of the beer in bulk. Victoria waterfalls turning dark brown river to white mist might provide an even better analogy. While the optical properties of the Venus's clouds are of interest to astronomers,[47,48] chemists are interested in the optical properties of the bulk liquid forming the aerosols. The important relation between the observed spectrum of the Venus aerosol versus the color of the bulk liquid from which the aerosol is derived will be, for the first time, quantitatively explored in a subsequent paper.

**2.7. Quantitative Model of Photochemical HCHO Production in the Gas Phase.** We then used a photochemical model,[49] to predict the amount of formaldehyde (HCHO) and HCO radicals in the atmosphere of Venus. The details of the model are given in SI (SI 1.7). The model predicts that HCHO in the gas phase at an altitude of 60 - 70

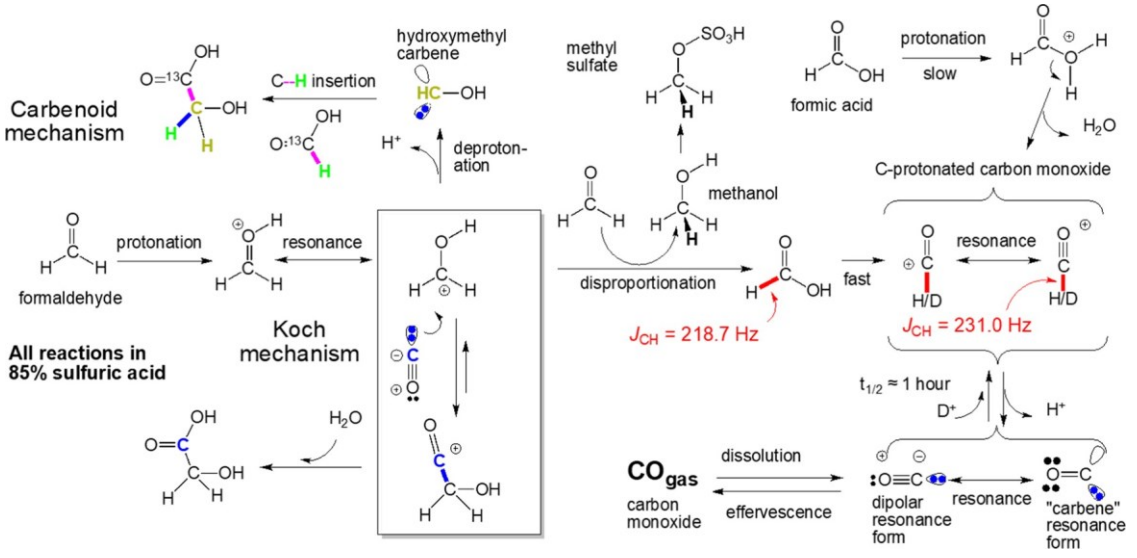


Figure 5. This scheme illustrates atom-by-atom how gaseous CO present in the Venus atmosphere, can move from the atmosphere to sulfuric acid aerosols, accumulate as $[HCO]^+$ and later react either as CO and $H_2O$ or HCOOH with reduced carbon, here HCHO. The production of glycolic acid from formaldehyde can be fed by gaseous CO or indirectly from HCOOH. Selective $^{13}C$ isotopic labeling proves that C1 of glycolic acid arises from the oxidized carbon species (CO or HCOOH), while C2 arises from the reduced carbon species (HCHO).


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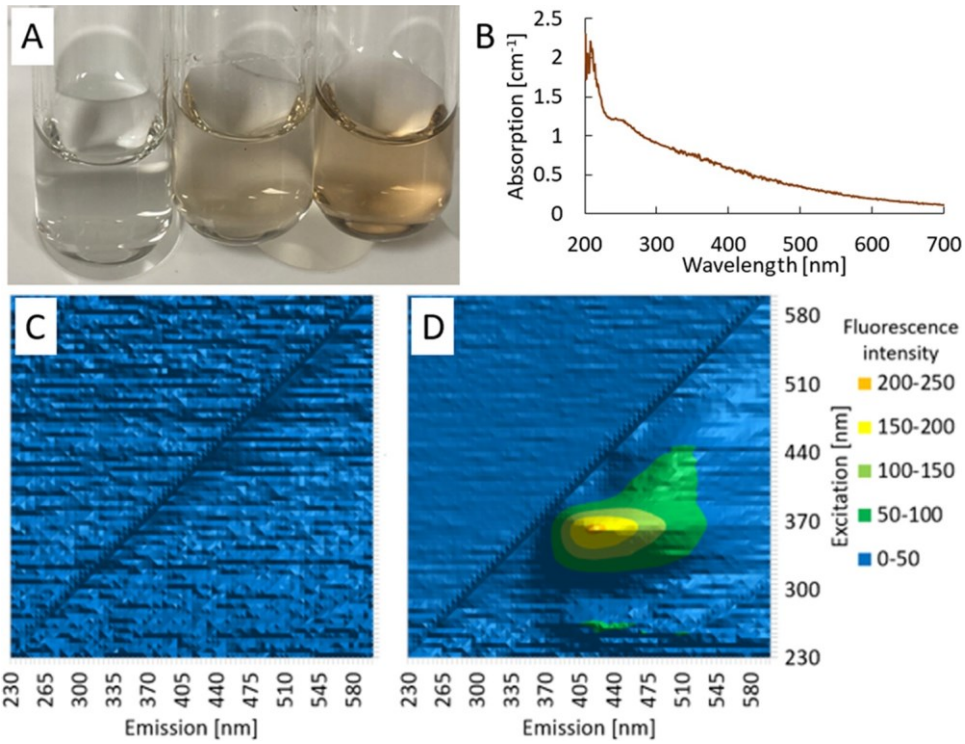


Figure 6. (A) Photograph of samples heated for 7 days at 100 °C, from left to right: 85% $H_2SO_4$ control (no glycolic acid), 100 mM glycolic acid in 70% $H_2SO_4$, and 100 mM glycolic acid in 85% $H_2SO_4$. After prolonged heating the solutions turn to dark brown or black. (B) Absorption spectrum of 10 mM glycolic acid in 85% $H_2SO_4$ heated at 100 °C for 7 days (see Figure S14 for more data). No fluorescence was detected immediately after addition of 10 mM glycolic acid to 85% $H_2SO_4$ (C), strong fluorescence emerged after heating the sample at 100 °C for 7 days (D).

km will be between 1 and 50 ppt, depending on the background chemistry.

The major hurdle to making HCHO in the atmosphere is the availability of atomic hydrogen. The dominant source of hydrogen is from the photodissociation of $H_2S$. We modeled the amount of $H_2S$ that would be expected if the atmosphere were at equilibrium near the surface. Our predicted concentration of $H_2S$ in the clouds is consistent with the remote nondetection of $H_2S$ above the clouds.[50] Although $H_2S$ has been detected by various atmospheric probes,[51,52] the probe detections exceed equilibrium. Largely for this reason, the accuracy of these measurements does not enjoy a consensus.

For these reasons, our prediction seems to offer a reasonable lower limit for the formation of HCO. The abundances of HCO and HCHO both depend critically on the amount of nitric oxide (NO) in the atmosphere. Concentrations of NO of 5.5 ppb result in 50× lower HCHO and 10× lower HCO.

NO has been proposed in the atmosphere of Venus,[53] with estimated abundance ~5.5 ppb at 50 km.[53] If these abundances are representative of average Venus atmospheric NO abundances, then NO chemistry will provide the most stringent limit on the concentration of gas phase HCHO produced at the top of the clouds. However, it was suggested that lightning, the only known source of NO in the clouds of Venus,[53] might be absent.[54] The details of the atmospheric chemistry can be found in the SI (SI 1.7).

We also used the gas-phase abundance to estimate the steady-state concentration in the aerosol particles, accounting for dissolution and rainout. Our model predicts concentrations of HCHO monomers, polymers and immediate reaction products with $H_2SO_4$ in the liquid phase of the cloud aerosols to be approximately $1.4 \times 10^{-4}$ M at 60 km, where HCHO in gas phase is at peak abundance.

## 3. DISCUSSION

This work has implications for our understanding of the potential of organic chemistry in sulfuric acid aerosol droplets above Venus. Thus, contrary to literature, the Venusian cloud aerosols almost certainly hold significant amount of reduced carbon, as dissolved CO, $[HCO]^+$, and (some) HCOOH. These species are primed to react with organic material with a lower redox state, starting with photochemically produced HCHO, but including organics arriving from meteoritic infall, and potentially via other pathways beyond the scope of our model (Figures 7 and S16).

Venusian chemistry contrasts with that of standard chemistry above Earth. For example, the acid Cannizzaro disproportionation process of HCHO differs from analogous processes in alkaline aqueous environments often mentioned in Terran prebiotic chemistry. Thus, the formose process,[55] often invoked as a source of prebiotic sugars,[56] converts HCHO by C−C bond formation to carbohydrates in alkaline water. However, the initial C−C bond formation is very slow. This gives a bimolecular Cannizzaro reaction an opportunity to convert HCHO to $CH_3OH$ and HCOOH. Neither of these species reacts further in alkaline environments. Further, absent minerals,[57−59] the resulting 2-carbon species (glycolaldehyde) is not metastable. Rather, it rapidly enolizes, with further reactions giving unproductive "organic tar".[60]

The opposite was the case in the strongly acidic Venusian reactions. Here, glycolic acid is surprisingly metastable, producing colored compounds at very slow rates, even at elevated temperatures (120 °C). Thus, in this one unexpected


https://doi.org/10.1021/acsearthspacechem.3c00261
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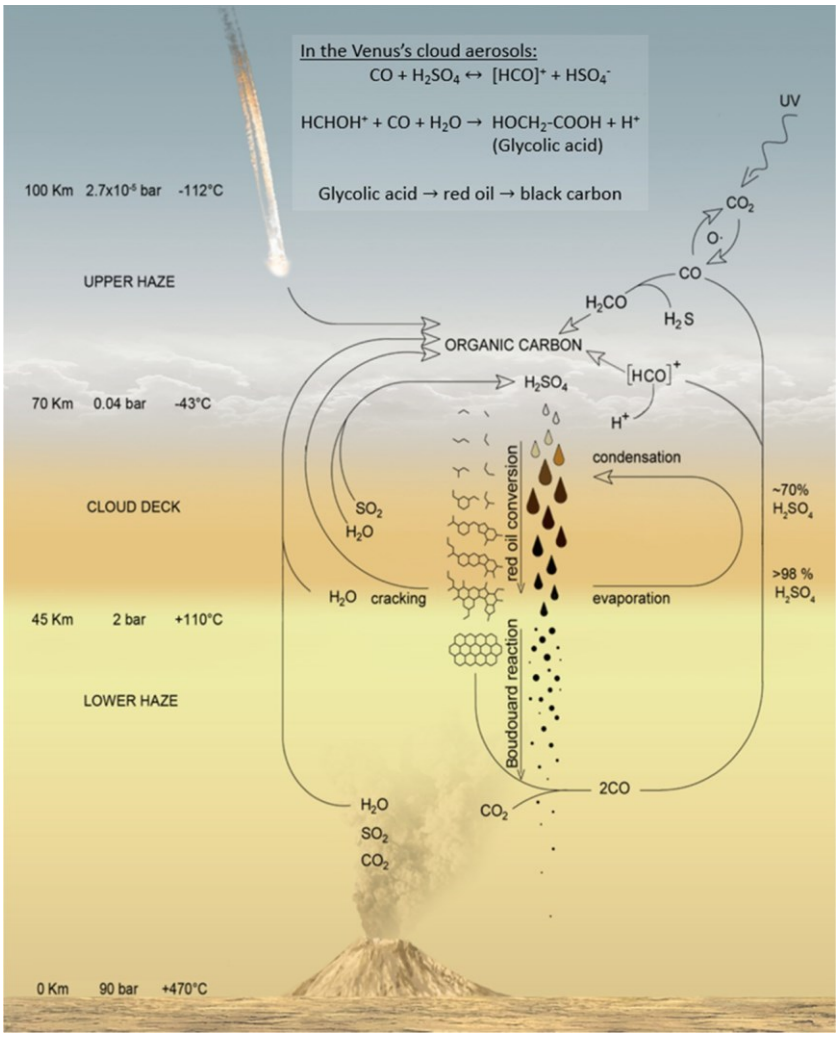


Figure 7. Proposed organic carbon cycle in the atmosphere of Venus. Compare ref 26.

way, hot strongly acidic nonaqueous Venusian clouds are better environments to generate complex organic chemistry than the cold slightly alkaline water often invoked as environments where life may have arisen on Earth.

The gas phase photochemical production of HCHO, followed by its uptake into the aerosols and its further chemical transformations via glycolic acid presented here, is likely an incomplete description of the organic carbon cycle above Venus. For example, organics might be (photo)-chemically produced directly in the aerosols, for example, by single electron reduction of $[HCO]^+$. Alternatively, disproportionation of carbon at oxidation level of CO to carbon with oxidation level of $CO_2$ and HCHO is known to occur in the gas phase.[61] Perhaps analogical disproportionation can occur when CO in equilibrium with its protonated form is dissolved in sulfuric acid under conditions of the Venus's clouds.

The presented model also does not account for the possibility of preferential selection and accumulation of aerosols with higher contents of complex dark organic carbon in the upper cloud via means of negative gravitophotophoresis, proposed to uplift absorbing aerosols in the Earth atmosphere.[62−64] If a long-term accumulation of organics in the Venus's cloud aerosols is possible, our experimental results indicate that the aerosols contain more nonvolatile organics than predicted by our "rainout" model. Selection for aerosols resisting sedimentation and destruction below the cloud, if present over geologic times, should be of interest to astrobiologists.

Setting aside the issue of hypothetical Venusian life, these data have significance for the private in situ exploration of Venus. They are guiding the design of the autofluorescence nephelometer planned to fly to Venus as the first of the Morning Star Missions (supported by Rocket Lab, Breakthrough Initiatives, and MIT).[32,33] The probe is planned to launch to Venus aboard Rocket Lab's Electron Rocket in late 2024 or early 2025.

Further, it was predicted that concentrated sulfuric acid is more common than water as the major solvent in exoplanets.[65] Sulfuric acid oceans might form on exoplanets where the bedrock is fully converted to sulfate minerals. Therefore, missions to Venus guided by laboratory studies (such as these) may also influence remote observations of exoplanets in the appropriate regions surrounding their stars. The fact that concentrated sulfuric acid promotes the existence of complex organic chemistry has significant implications for exoplanet astrobiology.

## 4. EXPERIMENTAL SECTION

Fluorescence spectra were obtained on a Hitachi F-4500 fluorescence spectrometer in quartz cuvettes ($L$ = 1 cm).


https://doi.org/10.1021/acsearthspacechem.3c00261
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Absorption spectra were obtained on an Agilent Cary 3500 Multicell UV−vis Spectrophotometer in quartz cuvettes ($L$ = 1 cm).

Carbon-13 labeled materials and deuterated water were obtained from Cambridge Isotope Laboratories, Inc.

CO was 99.99% from a tank (Matheson Gas).

All NMR spectra were recorded on a Bruker 300 MHz spectrometer.

Sulfuric acid concentrations are indicated as the w/w concentration in water. To allow deuterium locking in NMR experiments, deuterated sulfuric acid ($HDSO_4$) was prepared by mixing fuming sulfuric acid (Alfa Aesar, analyzed to contain 15.34% (w/w) free sulfur trioxide, and 9.369 ppm iron. Product no. 45542 Lot number Y26F068) with amount of $D_2O$ (Cambridge Isotope Laboratories, Inc. D, 99.99%) corresponding to molar ratio of $H_2SO_4$ /$H_2O$ in indicated w/w percentages. The H/D molar ratios are summarized in Table S2.

Sulfuric acid for spectrophotometric studies was freshly distilled and mixed with water to remove trace contaminants. Work with concentrated and fuming sulfuric acid, especially when heated, was executed with extreme caution using appropriate protection. Carbon monoxide gas levels were continually monitored; a carbon monoxide tank was operated within a fume hood. All workers were familiarized with the risk management associated with all of the chemicals used during the experiments.

## ■ ASSOCIATED CONTENT

### * Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.3c00261.

Help with an interpretation of the presented NMR data (SI 1.1−1.6); description of the photochemical model (SI 1.7); proton NMR spectra of $H_{13}COOH$ in various concentrations of $H_2SO_4$ and their analysis (Figure S1); $^{13}C$ NMR spectra of $H_{13}CHO$ (added as paraformaldehyde) in $H_2SO_4$, compared to standard additions of $H_{13}COOH$, and $^{13}CH_3OH$ (Figure S2); $^{13}C$ NMR spectrum of $^{13}CH_3OH$ in various concentrations of $HDSO_4$ (Figure S3); $^{13}C$ NMR kinetic study of $H^{13}COOH$ in 78−91% $H_2SO_4$ (Figure S4−S9 and Table S1); $^{13}C$ NMR spectrum of heated $^{13}C$ oxalic acid in 85% $H_2SO_4$ (Figure S10); $^{13}C$ NMR analysis of $^{13}C$ glycolic acid in $H_2SO_4$ (Figures S11−S13); UV−vis absorption spectra of glycolic acid—progression toward absorbing species (Figure S14); $^{13}C$ NMR spectra of mixture of $^{13}C$ glycolic acid with $H_{13}COOH$ in 85% $H_2SO_4$ (Figure S15); optical properties of 85% $H_2SO_4$ incubated with Murchison meteorite (Figure S16) (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are indebted to support from Firebird Biomolecular Sciences, LLC, MIT, the Breakthrough Foundation, and Cavendish Laboratory at the University of Cambridge. We wish to acknowledge a helpful discussion with the team behind the Morning Star Missions.

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