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Radiation chemistry of solid acetone in the interstellar medium – a new dimension to an old problem

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A laboratory investigation of acetone, an interstellar and cometary molecule, has produced new results concerning its decomposition in a radiation environment. Mid-infrared spectroscopy has been used to follow amorphous acetone's destruction by ionizing radiation (1 MeV protons) at 20 K. Radiation products identified are the CH₄, CO, and CO₂ usually made in such experiments, along with ketene, allene, and the acetyl radical, all identified here for the first time in irradiated solid acetone. Evidence for the reduction product 2-propanol was suggestive, but a firm identification could not be made either for it or for the C₂ hydrocarbons (*i.e.*, C₂H₆, C₂H₄, C₂H₂). The acetyl radical was not observed as a radiation product. Isotopically labeled reagents were used to demonstrate ketene formation and to emphasize that multiple approaches are needed for robust assignments of infrared spectral features of irradiated icy solids. Results from a supporting radiation experiment with isotopically labeled acetic acid are described. Comparisons are made to a previous study of acetone's stability in extraterrestrial radiation environments, and caution is urged in measuring and interpreting CO abundances in irradiated icy solids.

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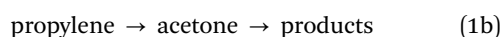
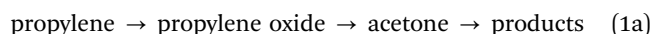
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1. Introduction

Just over a century ago, a predecessor to this journal published a brief paper by W. T. M. Wilsmore of University College London about his discovery of ketene, H₂CCO, through the decomposition of acetone and other carbonyl-containing molecules.¹ However, it is doubtful that the author anticipated that both acetone and ketene eventually would be identified in the interstellar medium (ISM). The paths by which interstellar acetone is produced and destroyed are uncertain, and little laboratory work has been reported to clarify them. In this paper we examine the radiation chemistry of acetone ices and report that ketene is among the reaction products.

Our interest in a solid-phase acetone-to-ketene conversion originated in the discovery² and our recent study³ of propylene oxide, an interstellar molecule. We showed that this epoxide was a radiation product of propylene (C₃H₆) and either O₂ or CO₂ as an O-atom source, and that acetone seemed to be made from either radiation-induced isomerization of propylene oxide (1a) or produced directly from the O + C₃H₆ reaction (1b).



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These sequences are suggestive, but we have found few publications on solid acetone's formation and destruction for support. In the absence of such information, one can argue from the behavior of isoelectronic molecules, such as acetic acid, shown in Fig. 1 along with acetone. Matrix-isolation studies have shown that elimination of CH₄ or H₂O from solid acetic acid gives CO₂ or ketene (H₂CCO), respectively, two 16-electron cumulated molecules.⁴ This led us to expect that the more-symmetrical acetone molecule might indeed decompose in the solid state to give ketene as the only cumulated product. Both acetone and acetic acid also are expected to yield CO by elimination, either in one step or several. As interstellar and cometary ices are much more reactive than rare-gas matrices, we were particularly interested in determining if either solid acetone or solid acetic acid would form ketene when exposed to ionizing radiation.

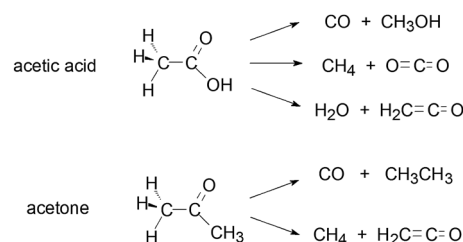


Fig. 1 Some decomposition products of two isoelectronic molecules.

Table 1 Positions of some acetone vibrations

Mode ν	Approximate motion	Amorphous, reflection 20 K, IR ^a	Amorphous, transmission 10 K, IR ^a	Solid 13 K IR ^b	Solid 77 K Raman ^c
13	CH ₃ asymm stretch	3002.0	3002.0	3001.8	3004.0
1	CH ₃ asymm stretch	3002.0	3002.0	3001.8	3004.0
9	CH ₃ asymm stretch	2966.5	2967.4	2967.0	2972.0
20	CH ₃ asymm stretch	2966.5	2967.4	2967.9	2972.0
2	CH ₃ symm stretch	2919.6	2920.5	2919.7	2920.0
14	CH ₃ symm stretch	2919.6	2920.5	2919.7	2920.0
3	C=O stretch	1704.0	1711.4	1711.0	1697.0
21	CH ₃ asymm def	1440.8	1441.6	1441.9	1444.0
10	CH ₃ asymm def	—	—	—	1431.0
4	CH ₃ asymm def	1418.0	1418.9	1419.1	1426.0
15	CH ₃ asymm def	—	—	—	1408.0
16	CH ₃ symm def	1362.0	1364.4	1364.0	1366.0
5	CH ₃ symm def	1351.1	1350.8	1351.8	1351.0
17	CCC asymm stretch	1226.2	1228.9	1229.5	1229.0
22	CH ₃ rock	1095.3	1095.6	1096.0	1098.0
6	CH ₃ rock	1068.9	1071.4	1070.0	1072.0
18	CH ₃ rock	897.0	897.3	897.9	905.0
11	CH ₃ rock	—	871.0	872.3	872.0
7	CCC symm stretch	—	791.2	791.1	796.0
19	CO in-plane def	—	533.6	—	533.0
8	CCC scissoring	—	—	—	497.0
23	CO out-of-plane def	—	—	—	402.0
24	Torsional	—	—	—	130.0
12	Torsional	—	—	—	112.0

^a This work; assignments at 1500–1400 cm⁻¹ are somewhat uncertain. ^b Values from Andrade *et al.*⁴ arranged to correspond to modes (ν) in the first column, but with the authors' peak near 1035 cm⁻¹ omitted. ^c Values from Harris and Levin.¹¹

In looking into solid acetone's radiolytic decomposition we were led to the work of Andrade *et al.* on the irradiation of acetone at 16 K.⁵ However, the more closely we examined their paper, the more questions and concerns appeared. As an example, twice on the first page the experiment of Ruitkamp *et al.*⁶ is described incorrectly. The authors' infrared (IR) spectrum of amorphous acetone at 16 K is compared to earlier work, but it is not stated that the earlier study employed Raman spectroscopy and that the sample was at 77 K and described as polycrystalline. Three vibrations in the authors' Table 1 are described incorrectly or ambiguously, and the IR band strengths listed are based on a single reference value from a density-functional calculation for gas-phase acetone published by others and not checked against laboratory results. The acetone spectrum in the paper's Fig. 1 has an unmentioned peak near 1035 cm⁻¹ not reported by others. Formaldehyde was reported as a radiation product based on a band near 1180 cm⁻¹, but a stronger H₂CO feature was missing. The product abundances ($N_{k,f}$ values) of Table 3 in ref. 5 disagree with those in the text, and each of the band strengths used for radiation products has a problem. Those for CO and CO₂ were misattributed, the values for C₂H₄ and C₂H₆ could not be traced to their original sources from the references provided, and the value for H₂CO was based on an unverified calculation. The CH₄ band strength used is not in the sources cited.

The aim of the paper of Andrade *et al.*,⁵ determining the stability of a particular organic compound in an extraterrestrial environment, is one that we share. However, faced with the just-mentioned problems and uncertainties, we decided to start afresh and carry out new measurements. Here we present the IR spectrum of amorphous acetone along with a newly measured

refractive index, from which an acetone ice's density, thickness, and molecular abundance can be determined. We describe new experiments (a) to assess acetone's stability against exposure to ionizing radiation and (b) to identify some of this molecule's decomposition products. Supporting this work is a new radiation experiment on solid acetic acid. All of the new results reported will be useful in studying acetone's survival in low-temperature interstellar and solar-system environments. Just as important, this work is another example of how laboratory astrochemistry can establish connections among the many molecular types in low-temperature icy environments.

2. Experimental

Although essentially all relevant experimental details are provided in our earlier papers, it is convenient to mention some particulars here.^{3,7}

Ices were prepared by vapor-phase deposition of reagent-grade compounds onto a substrate (area \approx 5 cm²) held at 10–20 K, except in a few cases as noted, and always within a high-vacuum chamber (\sim 10⁻⁸ torr or lower). The acetone deposition rate when making ices gave an increase in the sample's thickness of about 3 μ m h⁻¹ as determined by interference fringes. For radiation experiments, the substrate was polished aluminum and measurements were made by reflection from it using a Thermo Nicolet Nexus 670 spectrometer. For non-radiation measurements, the substrate was a KBr window and transmission spectra were recorded with a Thermo iS50 spectrometer. The IR beam was unpolarized and aligned perpendicular to the sample's surface for transmission measurements and about 5° from

perpendicular for transmission–reflection–transmission work. Spectra typically were recorded from 3700 to 500 cm^{-1} as 200 scans (accumulations) at a resolution of 1 cm^{-1} unless otherwise noted.

Irradiations were done with a 1.0 MeV p^+ beam from a Van de Graaff accelerator operating at a current of about 1.0×10^{-7} A, as measured in the metal substrate underlying the ice sample. Using Ziegler's SRIM-2013.00 program,⁸ the range of a 1.0 MeV p^+ in solid acetone was calculated to be ~ 32 μm , with a stopping power of 260.3 $\text{MeV cm}^2 \text{g}^{-1}$ at the density we determined (see below). This corresponds to an incident fluence of 1×10^{14} $\text{p}^+ \text{cm}^{-2}$ being equivalent to a dose of 4.17 $\text{MGy} = 417 \text{ Mrad} = 2.51 \text{ eV molecule}^{-1}$.

All reagents were purchased from Sigma Aldrich. The gases used were CO , ^{13}CO , CO_2 , $^{13}\text{CO}_2$, CH_4 , $^{13}\text{CH}_4$, CD_4 , C_2H_4 , C_2H_6 , and C_3H_4 (allene). The liquid reagents used were acetone, 1-propanol, 2-propanol, acetaldehyde, acetone-2- ^{13}C (carbonyl position labeled), acetone- d_6 , and acetic acid-1- ^{13}C . Liquids were degassed with liquid nitrogen and freeze–pump–thaw cycles. Although deuterated acetone was available for a few experiments, we used ^{13}C -enriched acetone more often as the IR spectra tended to be cleaner, with less overlap among IR peaks.

3. Results

3.1 Refractive indices

Refractive indices at 670 nm (n_{670}) were measured with two-laser interferometry.⁹ This appears to be the first time that this approach has been used to determine n for solid acetone. Triplicate measurements gave $n_{670} = 1.345 \pm 0.005$ for amorphous acetone prepared at 16 K. Using the Lorentz–Lorenz equation and a specific refraction,¹⁰ of 0.2784 $\text{cm}^3 \text{g}^{-1}$, this n_{670} gave a density of $\rho = 0.763 \text{ g cm}^{-3}$ for amorphous acetone, agreeing with expectations from liquid acetone ($n_{\text{D}} = 0.784$, 25 $^\circ\text{C}$).¹¹

3.2 Irradiated acetone – destruction

To ensure that our IR spectra of acetone ices were not resolution limited, an initial set of spectra were measured at resolutions up to 0.5 cm^{-1} . Little-to-no change was seen beyond 1 cm^{-1} , so that was the resolution selected for subsequent work.

Fig. 2 and 3, trace (a) in each case, show the IR spectrum of amorphous acetone prepared by vapor-phase deposition at 20 K. Table 1 lists positions of selected IR peaks along with some literature results for comparison.^{5,12} Although the acetone sample of Andrade *et al.* was not stated explicitly to be amorphous, and its IR spectrum was compared to a Raman spectrum for a polycrystalline ice, a comparison with our results in Table 1 suggest that it indeed was an amorphous ice. Since spectra recorded in reflection can sometimes show small shifts in peak positions from transmission spectra, Table 1 includes our data from both types of measurements. A point of disagreement with the results of Andrade *et al.* is their spectrum's peak near 1035 cm^{-1} , which we did not find either in our spectra or in earlier publications. It is not known if that peak was from a contaminant, an instrumental artifact, or something else, or if it influenced the authors' results.

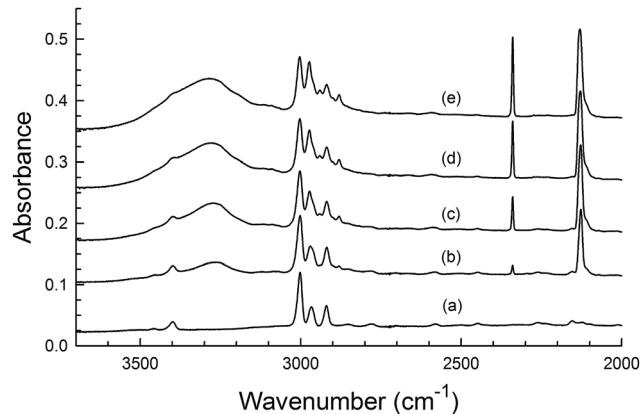


Fig. 2 Infrared spectra of amorphous acetone deposited at 20 K (a) before and after irradiations at 20 K of (b) 2×10^{14} , (c) 5×10^{14} , (d) 7.5×10^{14} , and (e) 1×10^{15} $\text{p}^+ \text{cm}^{-2}$. The ice's original thickness was about 0.75 μm . Spectra have been offset for clarity.

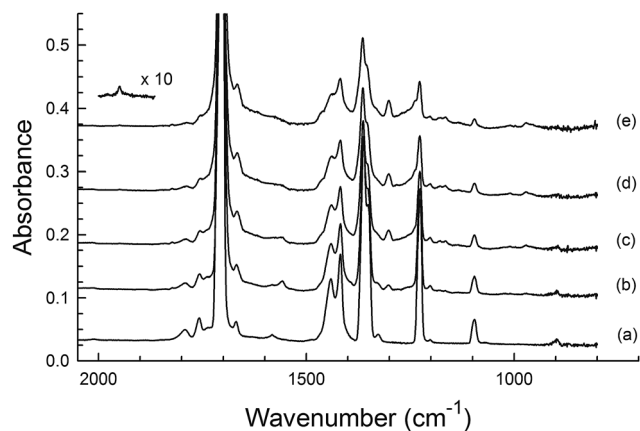


Fig. 3 Infrared spectra of amorphous acetone deposited at 20 K (a) before and after irradiations at 20 K of (b) 2×10^{14} , (c) 5×10^{14} , (d) 7.5×10^{14} , and (e) 1×10^{15} $\text{p}^+ \text{cm}^{-2}$. The ice's original thickness was about 0.75 μm . Spectra have been offset for clarity.

With our radiation experiments we were not especially concerned with measuring product abundances, but rather with determining the radiolytic half-life for the destruction of amorphous acetone and with making firm identifications of products, particularly any unreported ones. Traces (b)–(e) of Fig. 2 and 3 show the effect of increasing dose on the ice's spectrum. The C=O band is distorted and off-scale due to the sample's thickness and the band's intrinsic strength, but other IR bands smoothly decrease with increasing dose. This is particularly clear for the 1095 cm^{-1} peak. A first-order kinetics analysis (exponential decay) using the IR bands at 1226 and 1095 cm^{-1} gave an average slope of $1.3 \times 10^{-15} \text{ cm}^2 \text{p}^+ \text{cm}^{-2}$ (standard error $\approx 6\%$) for a half-life fluence of 5.3×10^{14} $\text{p}^+ \text{cm}^{-2}$ for acetone destruction, based on four measurements. In all cases, band areas, not peak heights, were used to follow the reaction. At radiation doses greater than in Fig. 2 and 3, band integrations were increasingly corrupted by the IR bands of products formed.

One of our interests in this work is comparing acetone's radiolytic destruction rate with that of other molecules. A common radiation-chemical measure of destruction is the number of molecules decomposed per 100 eV of energy absorbed, denoted $G(-M)$ with the minus sign indicating sample loss through a reaction. We found that for amorphous acetone at 20 K, $G(-\text{acetone}) \approx 5$. For comparison, our published¹³ values for glycine, alanine, and phenylalanine are 5.8, 7.2, and 3.0, respectively, so our acetone value seems reasonable. We plan to continue measurements of this type to assess the radiolytic stability of other organic molecules.

3.3 Background to spectral assignments

Fig. 2 and 3 with their broad overlapping IR features show the challenges met in assigning IR peaks and identifying products in irradiated solid acetone and many other astrochemical ice analogs. In general, the only IR assignments in which we have confidence are those with multiple lines of support, as opposed to assignments based only on a single IR peak and a reference to the literature. Among the supporting pieces of evidence sought, aside from simply a peak's position, were the following:

- Reference spectra are needed to assign IR peaks of reaction products in ices. However, variables such as ice composition, ice temperature, deposition temperature, deposition rate, radiolytic or photolytic dose, spectral resolution, modes of recording spectra (transmission vs. variety of reflection methods), and others all conspire to make spectral assignments suspect when they are based solely on a single IR peak and a reference to a published spectrum. For this reason, in studying reactions in ices we prefer to record reference spectra with the same methods and equipment used to follow the reactions themselves, instead of appealing solely to literature results.

- A leading practitioner of low-temperature spectroscopy has called isotopic shifts the "gold standard" for spectral identifications.¹⁴ A shift that is not observed when it should be can immediately rule out possible assignments and suggest new ones.

- The thermal behavior of a spectral band also can be useful in judging IR assignments. For example, on warming an ice to the point of sublimation all bands of a suspected product must change together. Also, assignments of IR peaks to simple free radicals should show that they are lost on warming before more-stable products.

- A critical factor in any assignment is the underlying chemistry. An assignment of an IR peak to a particular reaction product is stronger if a similar reaction is observed for another member of the same homologous series or for an isoelectronic molecule or ion. Our assignment of an IR feature to ketenimine from CH_3CN led to a prediction of similar IR peaks for reactions of other aliphatic nitriles, which experiments confirmed.¹⁵

- As in classical synthetic chemistry, independent reaction paths giving the same spectral feature can be used to strengthen assignments. See our OCN^- work.¹⁶

- Competitive reactions can help elucidate the identities of certain species. For example, small amounts of electron scavengers (e.g., N_2O , SF_6) can block redox pathways, just as adding small

amounts of a base can alter H^+ transfers, with results that can change an IR spectrum. See Demyk *et al.* for a good example.¹⁷

- There also is the intangible factor of chemical expectations, sometimes referred to as chemical intuition. An IR assignment that seems at odds with the structure and reactions of a particular ice component is seldom correct. See, for example, our examination of the claim that irradiated methanol-containing ices might yield IR-detectable amounts of acetone.¹⁸ Considering the molecular structures of the starting material and the product, the claim was unattractive.

To this list of laboratory approaches to assigning IR peaks of astrochemical ices, one can add modern computational chemistry methods, such as density-functional and *ab initio* methods. Our primary use of these has been to compute isotopic shifts, which could then be compared to observed shifts to judge their acceptability.

3.4 Irradiated acetone – product formation

3.4.1 H_2O and alcohols. Fig. 2 and 3 also show that new IR features appear with increasing dose. Perhaps most prominent, on the left in Fig. 2 a pronounced increase in absorbance is seen near 3300 cm^{-1} . This could be from H_2O contamination, and so control experiments were carried out, such as allowing ices to sit a few hours or irradiating bare substrates, but none of these blanks produced the large 3300 cm^{-1} feature of Fig. 2. Irradiating acetone- $2\text{-}^{13}\text{C}$ produced this same broad band and at the same position, but irradiating acetone- d_6 caused it to shift to about 2440 cm^{-1} , the region of O–D vibrations. We concluded that this band is from either the radiolytic formation of H_2O from acetone or the synthesis of one or more alcohols, 2-propanol (isopropanol) being the expected reduction product of acetone. The latter also is consistent with the appearance of other new features in the $3000\text{--}2800\text{ cm}^{-1}$ region (*vide infra*). Actually, it could be difficult to distinguish between 1- and 2-propanol as reaction products using only IR spectra.

3.4.2 CO_2 and CH_4 . Continuing to the right in Fig. 2, the sharp peak rising with dose near 2340 cm^{-1} and the weaker one near 1300 cm^{-1} in Fig. 3 are from CO_2 and CH_4 , respectively, assignments supported by comparisons with spectra we measured for each compound. Irradiating ^{13}C - and deuterium-labeled acetone gave CH_4 isotopic shifts of about 1 and 31 cm^{-1} , respectively, as expected for $^{13}\text{CH}_4$ and CD_4 .^{19,20} The CO_2 peak did not change when acetone- d_6 was used, but shifted $\sim 65\text{ cm}^{-1}$ with the ^{13}C sample, as expected for $^{13}\text{CO}_2$.²¹ On warming the irradiated ice, CH_4 was lost before unreacted acetone, consistent with methane's higher volatility. Since CH_4 is a radiation product of many compounds with a methyl group, such as C_2H_6 , CH_3CN , and CH_3OH , and CO_2 is produced by irradiating most any compound with a CO bond, even those as diverse as alanine, H_2CO_3 , and C_3O_2 , the formation of CH_4 and CO_2 from acetone was not surprising. Comparisons with reference spectra, experiments with isotopologues, and observations on warming irradiated acetone all supported these two assignments.

3.4.3 H_2CO and C_2 -hydrocarbons. Andrade *et al.* reported four other radiation products of acetone besides CO_2 and CH_4 .⁵ An IR peak near 1165 cm^{-1} was assigned to formaldehyde

(H₂CO), but since a stronger band near 1500 cm⁻¹ was not seen in their spectra or ours, we have to reject that assignment. Assignments for C₂H₆ and C₂H₄ are unconvincing as they were based on just one peak position, taken from the literature in each case. Infrared bands for these hydrocarbons overlap substantially with bands from other molecules, such as alcohols, making unique assignments difficult. Small features growing into our spectra in Fig. 3 at 1200–1100 cm⁻¹ could be from one or more alcohols, but the evidence is weak, and warming our irradiated acetone ices did not provide clarity.

3.4.4 CO and ketene (H₂CCO). The remaining product reported by Andrade *et al.* was CO.⁵ In our experience, CO, like CO₂ and CH₄, is a radiation product of many organic compounds. Fig. 2 shows the growth of a band near CO's fundamental at 2140 cm⁻¹, but the position near 2126 cm⁻¹ in (b) and (c) is too low for carbon monoxide. With continued irradiation, the peak moved closer to 2130 cm⁻¹ with the final irradiation (e). With the reactions of Fig. 1 in mind, we speculated that these IR changes were due to ketene (H₂CCO) being produced, with its intense ν₂ fundamental overlapping CO's peak. We addressed this problem of spectral overlap by irradiating amorphous acetone-2-¹³C at 20 K. Fig. 4 shows the relevant IR region. The two peaks growing in are assigned to ¹³CO (2087.7 cm⁻¹) and H₂C¹³CO (2070.8 cm⁻¹) based on positions already measured in

our lab.²² The ketene feature initially grew with radiation dose, reached a maximum intensity for a fluence near 5 × 10¹⁴ p⁺ cm⁻², and then weakened on continued irradiation, while the ¹³CO feature continue to grow. Warming the irradiated ice resulted in the ¹³CO peak of Fig. 4 being lost before the H₂C¹³CO feature was, as expected.

3.4.5 Allene. An unexpected observation was that irradiating acetone slowly produced a weak but distinct IR feature near 1950 cm⁻¹, which we assigned to the strong ν₆ vibration of allene, H₂C=C=CH₂, based on a comparison to an allene spectrum we recorded. The ¹³C and deuterium isotopic shifts for this 1950 cm⁻¹ peak were 47 and 37 cm⁻¹, respectively, in good agreement with literature values of 47 and 36 cm⁻¹ for H₂C=¹³C=CH₂ and D₂C=C=CD₂, respectively.^{23,24}

3.4.6 Acetonyl radical (H₂C-C(=O)CH₃). Irradiation of amorphous acetone also gave rise to a small IR peak near 1558 cm⁻¹, which rose and then fell with increasing dose, as seen in Fig. 3. It decayed rapidly on warming the irradiated sample to ~50 K, and had ¹³C and deuterium shifts of about 31 and 6 cm⁻¹, respectively. Based on this peak's position, thermal behavior, isotopic shifts, electron spin resonance work,²⁵ and chemical expectations (see Discussion), it was assigned to the CO stretch of H₂C-C(=O)CH₃, the acetonyl radical. We saw no clear IR evidence for any other radicals, such as acetyl (see below) or methyl ([•]CH₃), or for the enol isomer of acetone, H₂C=C(OH)CH₃.^{26–28} We also saw no clear evidence for the formation of other carbonyl compounds, such as acetaldehyde.

3.4.7 Supporting work – acetaldehyde. Irradiation of acetaldehyde, H₃C-C(=O)-H, was used to generate the acetyl (H₃C-C=O) and formyl methyl (H₂C-C(=O)H) radicals for reference purposes. Irradiating acetaldehyde at 10 K produced an IR peak at 1840 cm⁻¹ that was removed from the spectrum either by warming to about 50 K or by exposing the irradiated ice to visible light for 30 min (60 watt tungsten bulb, 25 cm from sample), a change that was accompanied by a 15% growth in the CO band. This IR peak at 1840 cm⁻¹ was assigned to the acetyl radical based on the combination of peak position (literature²⁹ value = 1844 cm⁻¹), photosensitivity,³⁰ and CO growth, the reaction being H₃C-C=O → [•]CH₃ + CO as expected for acetyl destruction. This peak was never seen in our irradiated acetone ices. In the same experiments, irradiation of acetaldehyde also produced a peak at 1573 cm⁻¹. It was unaffected by visible light, but decayed rapidly at ~50 K. Its position and thermal behavior, and previous work,²⁶ all suggest an assignment to the C=O stretch of H₂C-C(=O)H.

3.4.8 Supporting work – acetic acid. To support our observation of ketene formation from acetone, we also irradiated amorphous acetic acid-1-¹³C, H₃C-¹³COOH. Fig. 5, traces (a) through (f), shows the spectral changes in the same region as Fig. 4, again with the growth of ¹³CO on the left and H₂C¹³CO on the right. The warming sequence shown in traces (g) through (m) demonstrates that ¹³CO was lost first as the temperature rose. The peak remaining at 140 K, for H₂C¹³CO, was slowly lost at that temperature. We also found that the CO yield was greater from acetic acid (Fig. 5) than from acetone (Fig. 4) for roughly the same ice thickness, the same

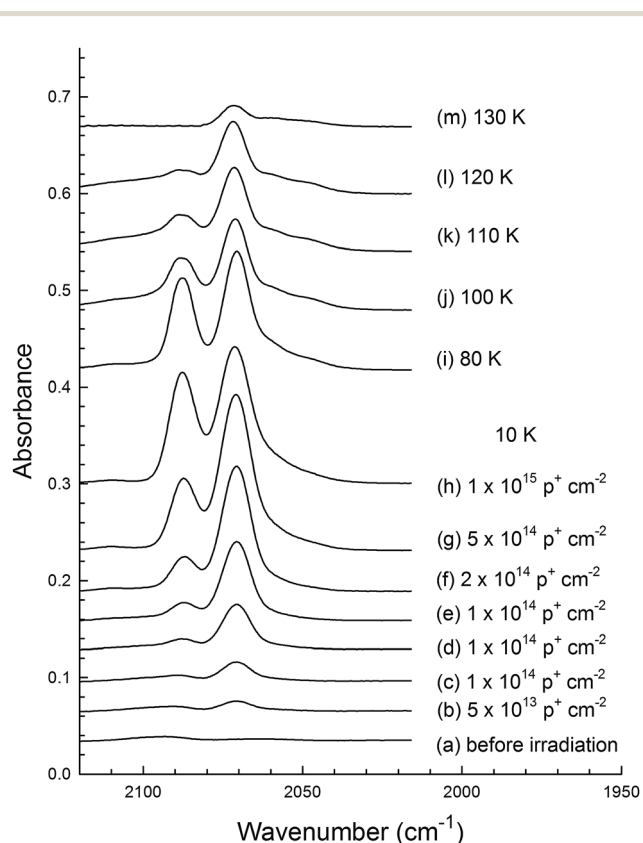


Fig. 4 Infrared spectra of acetone-2-¹³C, before and after irradiation at 20 K showing the growth of ¹³CO and H₂C¹³CO. The proton fluences were as given in the figure. Traces (i)–(m) show the effect of warming the irradiated ice. The ice's original thickness was about 1.0 μm. Spectra have been offset for clarity.

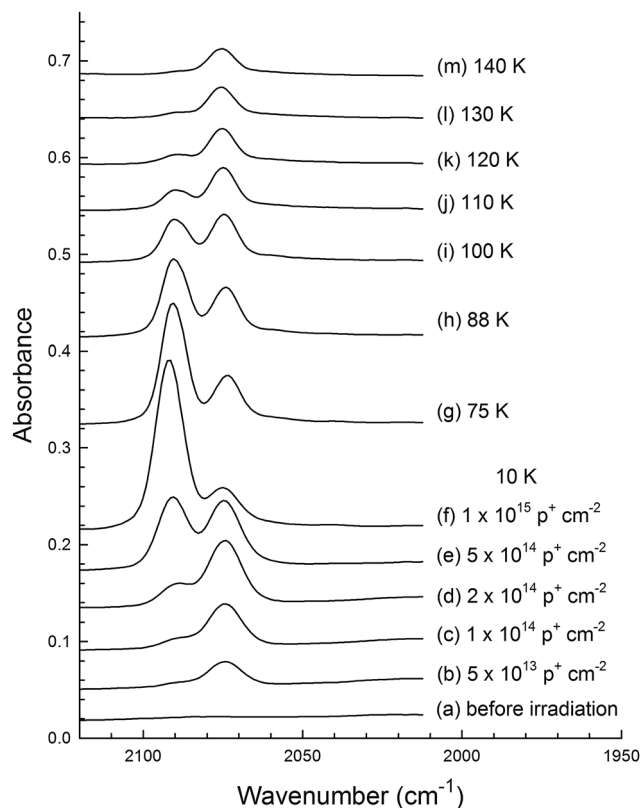


Fig. 5 Infrared spectra of acetic acid- $1-^{13}\text{C}$, before and after irradiation at 10 K, (a)–(f), showing the growth of ^{13}CO and $\text{H}_2\text{C}=\text{C}=\text{O}$. Traces (g)–(m) show the effect of warming the irradiated ice. The proton fluences were as given in the figure. The ice's original thickness was about $1.0\ \mu\text{m}$. Spectra have been offset for clarity.

temperature, and the same radiation dose, but we did not investigate this difference.

4. Discussion

4.1 Irradiated solid acetone – spectral assignments

From the radiation-chemical literature we could predict some of the products likely to be seen in IR spectra of irradiated solid acetone. The safest predictions were CH_4 and CO , with C_2H_6 somewhat lower in abundance than either.^{25,31,32} Both CH_4 and CO were firmly identified in our work. Other products could be anticipated, but were either inherently difficult to observe (*e.g.*, H_2) or expected to have lower abundances (*e.g.*, C_2H_4). Roughly comparable in yield to C_2H_6 in previous work is acetone's reduction product, 2-propanol (isopropanol, $\text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3$).

The earlier paper of Andrade *et al.* had assignments for C_2H_6 and C_2H_4 , each based on a single IR peak, $2881\ \text{cm}^{-1}$ for C_2H_6 and $955\ \text{cm}^{-1}$ for C_2H_4 . Aside from our reluctance to make single-peak assignments, these two deserve comment. First, 2-propanol is an expected radiolysis product of acetone and it has IR peaks near both 2881 and $955\ \text{cm}^{-1}$. Also, our spectra show small changes near 2973 and $2941\ \text{cm}^{-1}$ that could be from C_2H_6 formation, but there too 2-propanol shows IR features. In short, 2-propanol might account for four different

IR peaks observed, plus the growth from an OH stretch in the $3500\text{--}3000\ \text{cm}^{-1}$ region. As for other possible products, the published spectrum⁵ of irradiated solid acetone also shows growth near 3230 and $760\ \text{cm}^{-1}$, regions where solid acetylene (C_2H_2) has its two strongest IR absorbances. – The purpose of these comments is simply to emphasize the difficulty of making firm assignments of broad overlapping features in IR spectra of irradiated ices without using approaches such as those described in Section 3.3. Further work, such as with reference mixtures of isopropanol and acetone, might reveal if either alcohols or hydrocarbons beyond CH_4 , or both (or neither), are produced in these experiments.

As for other reaction products, we already have presented evidence for the synthesis of ketene and allene. Our identification of acetyl, $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3$, is based on a thermal behavior that matches what we expect for a radical and on isotopic shifts that are as expected when compared to those of $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{H}$.²⁶ Also, the peak position for $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3$ at $1558\ \text{cm}^{-1}$ is somewhat lower than that for $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{H}$ at $1574\ \text{cm}^{-1}$, as expected for the molecule with the greater mass. The $1558\ \text{cm}^{-1}$ position is reasonable for a CO stretch as the resonance $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3 \leftrightarrow \text{H}_2\text{C}=\text{C}(\text{O}^\bullet)\text{CH}_3$ will drop the CO bond order from 2, with a concomitant decrease in the vibrational wavenumber from the usual $1700\ \text{cm}^{-1}$ region. That $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3$ is present agrees with expectations from essentially all, if not simply all, studies of acetone's photo- and radiation chemistry.

Although the present paper is more focused on product identifications than product abundances, a few comments about the latter are appropriate. Our reflection arrangement for recording IR spectra permits carefully maintained temperatures and the easy determination of radiation doses, particularly compared to some work on other substrates. However, accurate quantification of reaction yields can be difficult due to a non-adherence of spectral bands to Beer's law.³³ All we can say at present is that the maximum acetone-to-ketene yield in the present experiments is on the order of a few percent, based on work in our previous ketene paper.²²

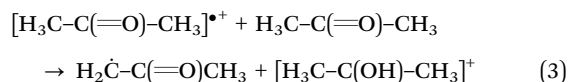
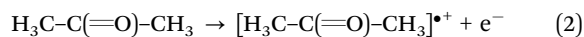
Our second comment on abundances is to emphasize that using IR spectra to determine product yields in irradiated ices requires accurate IR band strengths. Most ices examined by astrochemists are amorphous, but until recently no band strengths (A' values) for amorphous CO_2 , CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 , among other compounds, were available. Without accurate band strengths, there is little reason for high confidence in abundances calculated from IR spectra. Similar comments apply to the results of mass-balance calculations based on such abundances. Also, without accurate A' values for abundance calculations and a carefully established set of chemical reactions, analyses of reaction kinetics can become simply curve-fitting exercises.

4.2 Radiation chemistry

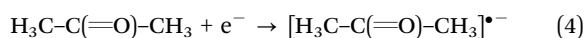
Studies of the radiation chemistry of acetone and other ketones go back at least 50 years,^{25,31,32} with a report of H_2 formation from irradiated acetone published even earlier.³⁴ Radiolysis products

arise from both ionization and excitation reactions initiated by the secondary electrons generated by the incident radiation, in our case 1 MeV p^+ . Unfortunately, many astrochemical papers, even those involving ionizing radiation, ignore the ionization processes but both types of reactions are important.

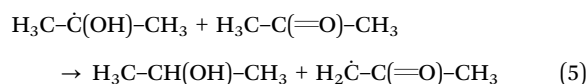
Ionization of acetone will generate a radical cation which can either act as an acid and transfer H^+ to a neighboring molecule or act as a radical and abstract H from a neighboring molecule, the products being the same in each case. See reactions (2) and (3) below.



Electron capture by an acetone molecule through

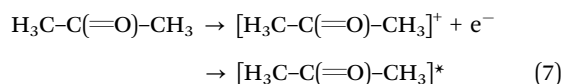
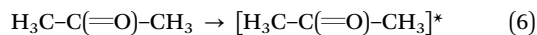


will give a ketyl radical anion. The neutral product $H_2\dot{C}-C(=O)CH_3$ in (3) is the acetyl radical we observed. Both neutralization of the cation product of (3) and protonation of the radical anion in (4) gives the isopropyl radical, $H_3C-\dot{C}(OH)-CH_3$, which can abstract a hydrogen atom from a nearby acetone molecule through

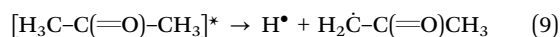
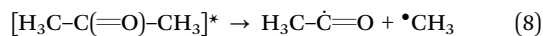


to make 2-propanol (isopropanol).

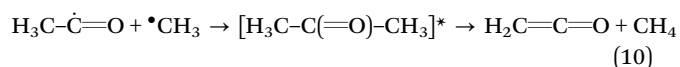
Electronic excitation of acetone molecules can be achieved either by an interaction with a secondary electron or by geminate recombination of a cation–electron pair:



The likely resulting bond breakages are of C–C and C–H single bonds as follows:

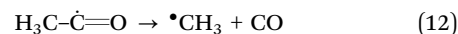
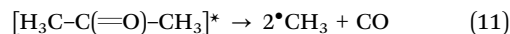


We did not detect either of the radicals produced in (8), perhaps because of the cage effect of the solid state enhancing recombination. Recombination of the radical pair in either (8) or (9) could produce ketene, perhaps through an excited state such as



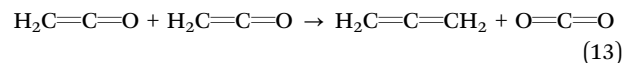
or simply through a radical–radical disproportionation. Some of the H atoms of (9) might remain trapped in the ice, but some are expected to be sufficiently mobile and energetic to abstract a hydrogen atom from a nearby acetone molecule to make $H_2\dot{C}-C(=O)CH_3$, again, and H_2 .

Subsequent radiolysis will bring about dissociation of the ketene made in (10), in agreement with our observation that ketene's abundance goes through a rise and fall. The resulting CH_2 fragments could couple to make C_2H_4 , although we have no firm evidence for it. The formation of CO is probably from either CO elimination by an excited state of acetone or dissociation of $H_3C-\dot{C}=O$, reactions (11) and (12),

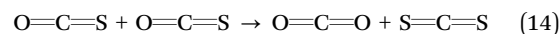


or simply by ketene dissociation. Coupling of two methyl radicals would generate C_2H_6 .

Having addressed CO, CH_4 , H_2CCO , and $H_2\dot{C}-C(=O)CH_3$, which we observed, and having considered $CH_3CH(OH)CH_3$, C_2H_6 , C_2H_4 , and H_2 , which one might suspect as solid-phase reaction products, we turn to allene and CO_2 . To our knowledge, allene has not been reported as a radiation product of acetone, although this might be due to the limitations of the instrumentation and protocols employed by earlier workers. Allene and CO_2 each has a cumulated bonding arrangement as does ketene: $H_2C=C=CH_2$, $O=C=O$, and $H_2C=C=O$, respectively. Therefore, we suggest that ketene dimers undergo a solid-phase rearrangement or exchange in irradiated acetone to make the allene and CO_2 we observed. The overall reaction is (13) below.

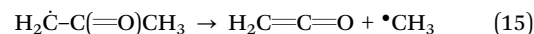


For support we point out that thermal decomposition of gas-phase ketene gives both of these products^{35,36} and that elegant matrix isolation studies³⁷ have shown that diketene can photodecompose both into two ketene molecules and a CO_2 + allene pair. A similar rearrangement was observed in our earlier study of the radiation chemistry of OCS.³⁸



It would be interesting to examine other cumulated systems, such as NNO + OCS or NNO + $^{18}OC^{18}O$, to see if similar exchange reactions occur.

Although most of the reactions just written are well-established in the radiation-chemical literature, others are possible. Another possibility for CO_2 formation is a reaction of excited CO molecules with ground-state CO.³⁹ An alternative synthesis of ketene is through the decomposition of $H_2\dot{C}-C(=O)CH_3$



as reported by Zeldes and Livingston⁴⁰ and used for acetone pyrolysis in the Rice-Herzfeld mechanism.⁴¹ The $\bullet CH_3$ formed could abstract an H atom from a neighboring acetone molecule to make CH_4 .

4.3 Acetone and astrochemical connections

The radiolytic half-life dose we measured for acetone can be calculated from the product of the mass of an acetone molecule,

the stopping power of a 1.0 MeV p^+ in acetone, and the fluence for destruction of half the initial acetone molecules. The result is a half-life dose of about 14 eV acetone molecule⁻¹ (23 MGy or 2300 Mrad). This can be compared to the estimated radiation dose to an ice mantle on a grain in a dense interstellar cloud, ~ 3 eV per H_2O molecule (18 amu), or about 10 eV per acetone molecule (58 amu), over a cloud lifetime of $\sim 10^7$ years.^{42,43} This interstellar dose is achieved in our experiments by a fluence of $\sim 4 \times 10^{14} p^+ cm^{-2}$, well within the range of Fig. 2–5. Put another way, our half-life dose would correspond to about 14 million years in the dense interstellar medium.

Another dose comparison is to the earlier work of Andrade *et al.* who used 40 MeV Ni^{11+} ions as their radiation source. The semi-log plots in their Fig. 5 are equivalent to a first-order kinetics analysis, such as we have used, and their paper gives an average slope, interpreted there as a destruction cross section, of $\sim 3.6 \times 10^{-13} cm^2 ion^{-1}$, equivalent to a half-life dose of about 0.92 eV molecule⁻¹ using a stopping power of 5010 MeV $cm^2 g^{-1}$ from Ziegler's SRIM program.

It is still somewhat rare to have two such determinations of radiolytic destruction for the same organic compound measured independently in different laboratories under similar conditions. A comparison can be made by using the postulated proportionality between the cross sections for destruction of acetone and the stopping powers (S) of the radiations employed. Taking from the work of Godard *et al.*,⁴⁴ the proportionality can be expressed as just (cross section) $\propto S^a$, with “ a ” thought to be between 1 and 2. Ratios can be formed between our results and those of Andrade *et al.* with the ratio of cross sections as $(3.6 \times 10^{-13})/(1.3 \times 10^{-15}) = 277$ and the ratio of stopping powers as $(5010/260) = 19.3$, so that $a \approx 1.9$, an acceptable result. Verifications and measurements with other ions and energies are needed to test and extend this result.

Concerning reaction products in astrochemical-ice analogues, the sets of final products formed in different radiation experiments are expected to be roughly the same, although differences in reaction mechanisms may exist. A standard interpretation for differences is that the larger the stopping power the greater will be the abundances of molecular products formed by the recombination of radicals and ions. For acetone radiolysis, this is consistent with the observed variation in C_2H_6 yield with radiation type.³² Also, if an irradiation involves a source with a large stopping power then too high a dose will make it easy to miss intermediate species like ketene or acetyl that show a rise and fall in abundance with increasing dose.

Another astrochemical consideration is the molecular-structural aspects of our work. We have shown that the presence of either acetone or acetic acid implies the presence of ketene in an icy extraterrestrial radiation environment. The same almost certainly will be true for other solid-phase molecules with the basic structure $-CH_2-C(=O)-X$, a suggestion that can be traced back to ketene's discovery.⁴⁵ Two attractive candidates for study are acetaldehyde ($X=H$) and acetamide ($X=NH_2$) ices. We suspect that each will produce ketene, so that an astronomical observation of either molecule can suggest that ketene also is present. A third candidate is methyl acetate ($X=OCH_3$), which in a recent paper was reported to produce CO_2 , CO , CH_3OH and $(CH_3)_2O$ on

irradiation with 2 keV electrons.⁴⁶ However, these identifications are unsatisfactory as CO_2 is a common laboratory contaminant, CO is one of its products, and both CH_3OH and $(CH_3)_2O$ were identified only by a change of a background slope. Inspection of the authors' IR spectrum of irradiated methyl acetate shows that the band assigned to CO has an asymmetric shape, which might be due to ketene formation. An irradiation of ^{13}C -labeled starting material could resolve the issue.

The lack of H_2O -ice in our samples means that they are imprecise analogues of interstellar, cometary, and other ices. However, some of the influence of H_2O -ice can be predicted. We expect most of the reactions we have written also will be operative in a H_2O -rich environment, (13) involving pairs of ketene molecules being an exception. The acetone radical anion will still be produced and converted into an isopropyl radical from which isopropanol will form, reaction (5). The acetone radical cation will transfer H^+ to a H_2O molecule, leaving the acetyl radical. To the extent that the acetone-to-ketene conversion is intramolecular, as we suspect, then it too will be operative in H_2O -rich extraterrestrial ices. Of course in a H_2O -rich ice mixture, indirect action of the radiation will compete with the direct action we have studied, but the final radiation-chemical products of acetone are expected to be similar to those identified here.

Another type of experiment desired is the irradiation of acetone trapped in a non-polar ice matrix, such as N_2 . The results might find application to the N_2 -rich ices of Pluto or to the non-polar components of interstellar ices.

Finally, we return to our original motivation, reaction sequences (1a) and (1b) in our Introduction. The interstellar paths to acetone remain unclear and so a sequence from a hydrocarbon (propylene) to acetone and then to ketene is of interest. A similar path for other alkenes will generate the larger ketones found both in radiation-chemical experiments and in meteorites.⁴⁷ In turn, these larger ketones can undergo Strecker chemistry to generate meteoritic amino acids.⁴⁸ Closer to the present paper are observations with the Atacama Large Millimeter/submillimeter Array (ALMA) that recently have found acetone near a low-mass solar-type protostar.⁴⁹ Our results suggest that a search for ketene could be successful. Another recent paper reported acetaldehyde and glycolaldehyde in a solar-type star-forming region.⁵⁰ Since both molecules possess the $-CH_2-C(=O)-X$ group, it is not surprising that the same paper reported a detection of ketene.

5. Summary, conclusions, future work

The variety and number of reaction paths in astronomical ices is so large that it is essential to establish trends involving prototypical molecules and structural types. Here that has been done for the simplest ketone, acetone, showing that it can be reduced to ketene and, we suspect, oxidized to one or more alcohols. Our new results with solid acetic acid support ketene's formation and lead one to suspect that many molecules having a $-CH_2-C(=O)-X$ group would yield the same. Along these lines,

the present work may have connections to cometary chemistry. The Rosetta mission's ROSINA mass spectrometer detected several molecules with the $-\text{CH}_2-\text{C}(=\text{O})-\text{X}$ group, including acetone and acetic acid, at the nucleus of comet 67P/Churyumov-Gerasimenko.⁵¹ A mass-spectral peak at $m/z = 42$, which might correspond to ketene, also was reported.

For laboratory astrochemists we caution that the IR spectral overlap between CO and ketene means that laboratory measurements of CO formation in ices can be corrupted by ketene's presence. Checks with isotopically labeled reactants are encouraged as way to circumvent this problem.

We also have demonstrated the formation of acetyl, $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3$, in an irradiated acetone ice. This substituted methyl radical is uv-sensitive and would only be stable in an astronomical setting if protected from light. We know of no quantitative IR measurements of either the photochemical or thermal stability of the acetyl radical. A related case to examine in ices would be the formation and stability of $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{H}$ from frozen acetaldehyde. Given recent studies of the obstacles to and intricacies of free-radical processes on interstellar ice grains, reactions involving radicals, such as $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{CH}_3$ and $\text{H}_2\dot{\text{C}}-\text{C}(=\text{O})\text{H}$, could be of interest.^{52,53}

Conflicts of interest

There are no conflicts to declare.

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