MATERIALS SCIENCE | SHORT COMMUNICATION

A novel synthesis of polymeric CO via useful hard X-ray photochemistry

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Abstract: We report on the synchrotron hard X-ray-induced decomposition of strontium oxalate (\(\text{SrC}_2\text{O}_4\)) pressurized to 7 GPa inside a diamond anvil cell (DAC). After some 4 h of irradiation in a white X-ray synchrotron beam, a dark reddish/brown region formed in the area of irradiation which was surrounded by a yellowish brown remainder in the rest of the sample. Upon depressurization of the sample to ambient conditions, the reacted/decomposed sample was recoverable as a dark brown/red and yellow waxy solid. Synchrotron infrared spectroscopy confirmed the strong presence of \(\text{CO}_2\) even under ambient conditions with the sample exposed to air and other strongly absorbing regions, suggesting that the sample may likely be polymerized CO (in part) with dispersed \(\text{CO}_2\) and SrO trapped within the polymer. These results will have significant implications in the ability to readily produce and trap \(\text{CO}_2\) in situ via irradiation of a simple powder for useful hard X-ray photochemistry and in the ability to easily manufacture polymeric CO (via loading of powders in a DAC or high volume press) without the need for the dangerous and complex loading of toxic CO. A novel means of X-ray-induced polymerization under extreme conditions has also been demonstrated.

Subjects: Chemical Physics; Chemistry; Condensed Matter Physics; Experimental Physics; Materials Chemistry; Matter & Solid State Physics; Physical Chemistry

Keywords: x-ray and pressure induced polymerization; useful hard X-ray photochemistry; polymeric carbon monoxide

1. Introduction
Our recent efforts to develop useful hard X-ray photochemistry (Pravica, Bai, & Bhattacharya, 2012; Pravica et al., 2011, 2012; Pravica, Sneed, Bai, & Park, 2013; Pravica, Hulsey, et al., 2014; Pravica, Liu, & Bai, 2013; Pravica, Popov, et al., 2013; Pravica, Sneed, Smith, & Bai, 2013; Pravica, Sneed, White, &
Wang, 2014a, 2014b; Pravica, Yulga, Tkachev, & Liu, 2009; Pravica, White, & Wang, 2015) have thus far enabled us to produce simple diatomic molecules (O₂ (Pravica et al., 2011; Pravica, Bai, & Bhattacharya, 2012; Pravica et al., 2012; Pravica, Bai, et al., 2013; Pravica, Hulsey, et al., 2014; Pravica, Popov, et al., 2013; Pravica, Sneed, White, et al., 2014b), Cl₂ (Pravica, Sneed, et al., 2013), N₂ (Pravica, Liu, et al., 2013), and F₂ (Pravica, Sneed, White, et al., 2014a; Pravica et al., 2015)) in situ inside a sealed and pressurized diamond anvil cell (DAC) by harnessing the highly penetrating, highly energetic, and highly focused properties of hard X-rays (>7 keV) to initiate decomposition reactions (e.g. KClO₄ + hν → KCl + 2O₂ (Pravica, Hulsey, et al., 2014). We have also initiated synthetic reactions of some of these newly generated species to form simple polyatomic products (H₂O and OF₂) via 2H₂ + O₂ → 2H₂O (Pravica, Sneed, White, et al., 2014b) and 2F₂ + O₂ → 2OF₂ (Pravica et al., 2015), respectively. We thus have an interest of developing novel routes of chemical synthesis of more complex and challenging-to-synthesize molecules via our available techniques. We also seek to produce detonation products (CO₂, H₂O, N₂, N₂O, etc.) in a highly controllable way utilizing useful hard X-ray photochemistry as a means to examine the effect of mixing (Pravica, Sneed, White, et al., 2014b; Pravica et al., 2015) on intermolecular potentials via Raman and infrared (IR) spectroscopy to aid in developing better codes to predict detonation behavior of explosives (https://www-pls.llnl.gov/?url=science_and_technology-chemistry-cheetah).

In that spirit, we sought to produce polyatomic CO₂ inside a DAC in situ using hard X-rays. Prior efforts to produce this important greenhouse atmospheric constituent molecule via X-ray irradiation of BaCO₃ failed (Pravica, Bai, et al., 2013). We thus sought to examine the oxalate ion (C₂O₂⁴⁻) as a potential source of CO₂ and/or CO. As there is one study of SrC₂O₄ under ambient conditions which evolved CO and CO₂ upon γ-irradiation at elevated temperatures (Bose, Bhatta, & Bhatta, 1998), we chose this compound as the candidate for hard X-ray irradiation.

2. Experimental
We used a symmetric-type DAC to perform the irradiation experiment. A 250-μm-thick stainless steel gasket was preindented to ~20 μm thickness, and a sample-containing hole of diameter ~130 μm was drilled via electric discharge machining. The diamonds each had a culet diameter of ~500 μm and were low fluorescence, type Ia quality. Fresh powdered SrC₂O₄ (Alfa Aesar > 95% purity) was manually loaded into the gasket hole using a needle along with one ruby for pressure measurement. The assembly was then sealed and pressurized to 7 GPa. No pressure-transmitting medium was used in this experiment which was conducted at room temperature.

The pressurized sample was irradiated at the 16 BM-B beamline in the Advanced Photon Source (APS) with white X-rays for approximately 4 h. Raman spectroscopy was attempted on the irradiated sample unsuccessfully due to very high sample fluorescence.

The sample was then transported (still at high pressure) to the Canadian Light Source (CLS) for post-irradiation IR studies some days later. We note in passing that in prior IR studies, the exciting IR beam does not excite fluorescence in samples and is a far-superior method to acquiring vibrational mode behavior in organic and stressed/damaged samples at high pressure (Pravica, Yulga, Tkachev, & Liu, 2009).

Mid-IR spectra were acquired at the 01B1-1 beamline using a Bruker Vertex 77v/S, Hyperion 3000 IR microscope. A liquid nitrogen-cooled MCT detector was used. The mid-IR microscope system typically focuses the IR beam which is then spatially filtered using a 100-μm-diameter circular aperture. The investigated spectral range was from 700 to 4,000 wavenumbers with a resolution of 1 cm⁻¹. An improvised jacket that surrounded the DAC and fit snugly between the objective and sample stage of the microscope with constantly flowing argon gas was used to reduce water vapor contamination.

Far-IR studies were also performed on the irradiated samples at the 02B1-1 beamline at the CLS. The collection optics and DAC were housed in front of the FT-IR system with a plexiglass enclosure.
The system was continuously purged from water vapor (as measured with a humidity sensor) using positive pressure nitrogen blowoff gas from a nearby liquid N₂ dewar. Far-IR spectra were collected using a Horizontal Microscope system on the Far-Infrared Beamline at the CLS. Far-IR synchrotron radiation was redirected from the sample compartment of a Bruker IFS 125 HR spectrometer® to a long working distance Schwarzhild objective focusing the light on the sample. A similar objective behind the sample collected the transmitted light and directed it to an off-axis parabolic mirror which refocused the light into an Infrared Laboratories® Ge:Cu detector. The spectrometer was equipped with a 6-micron mylar beamsplitter, and the data were collected using a scanner velocity of 40 kHz, 12.5-mm entrance aperture, and a resolution of 1 cm⁻¹. The Ge:Cu detector was set for 16× gain. The interferograms were transformed using a zero filling factor of 8 and a 3-term Blackman-Harris apodization function.

To obtain a background mid-IR reference spectrum, an IR-transmitting CaF slide was prepared with virgin, unirradiated SrC₂O₄ powder (~3-μm thick) for comparison purposes.

An IR transmitting diamond was used to hold a thin film (~3-μm thick) of virgin SrC₂O₄ for a far-IR standard measurement, also for comparison purposes. This fresh sample had been prepared by manually compressing fresh SrC₂O₄ between two diamonds in a symmetric-style DAC (without a gasket) and removing one of the diamonds. All measurements were performed in transmission and at room temperature. All presented spectra constituted the average of 512 scans with 2 s/scan.

3. Results

We present images of the virgin, unirradiated sample loaded at the APS in Figure 1 (left) and the same sample after a 4-h irradiation (right). As in prior irradiation studies (e.g. Pravica et al., 2011, 2012), there is no evidence that the sample temperature altered beyond ambient temperature. It is immediately evident that a very dark cross pattern has been formed after irradiation which was in the shadow of the incident X-ray beam (including a small amount of damage caused during the alignment of the sample into the beam). Outside of the irradiated region, the sample yellowed and darkened significantly. Raman spectroscopy was attempted to compare with the unirradiated spectrum taken before irradiation, but the irradiated sample was far too fluorescent in the presence of 532-nm laser light to collect any useful spectra. The Raman spectrum of the sample collected just before it was irradiated agreed well with http://webbook.nist.gov/cgi/cbook.cgi?ID=B6000066&Mask=80 suggesting that our sample commenced as highly pure SrC₂O₄.

Unfortunately, as the diamonds were not of sufficient IR-transmitting quality, no useful IR signal could be obtained in either the far- or mid-IR range with the sample squeezed in between the diamonds. The DAC was then depressurized and the gasket was removed. It was immediately noted that the colored sample remained in the gasket so that IR spectra of the depressurized and reacted sample were successfully recorded without diamond interference. The far-IR patterns of the irradiated sample (still inside the depressurized gasket but with one diamond removed) and an unirradiated virgin sample (placed on the same IR-transmitting diamond) are displayed in Figure 2. Both spectra are background subtracted.
Figure 3 displays the background-subtracted mid-IR spectra of the ambient, unirradiated SrC$_2$O$_4$ sample along with that of the irradiated/decompressed sample. The virgin, unirradiated mid- and far-IR spectra agree generally well with the spectrum in Ito and Bernstein (1956). The far-IR unirradiated spectrum possesses two main modes near 515 and 775 cm$^{-1}$ which are assigned to COO out-of-plane rocking ($\delta$(CO$_2$)) and C$_2$O$_2^-$ anion deformation modes, respectively (Ito & Bernstein, 1956; D'Antonio, Torres, Palacios, González-Baró, & Baran, 2015). Progressing toward higher frequencies (Figures 2 and 3), two main modes are observed near 1,300 and 1,660 cm$^{-1}$ which are associated with $\nu$(CO$_2$) and $\nu$(CO) stretching modes, respectively (D’Antonio et al., 2015).

Examining the irradiated/decompressed far- and mid-IR spectra, dramatic changes are apparent. In the case of the far-IR irradiated/decompressed spectrum, moving from left to right in
wavenumber, a strong peak near 654 cm\(^{-1}\) and a lesser one near 680 cm\(^{-1}\) are likely associated with the O=C=O bending mode (\(\nu_2\)) (Isokoski, Poteet, & Linnartz, 2013). Progressing toward higher vibrational energies, there is a very sharp peak near 725 cm\(^{-1}\) which was also observed in Evans et al. (2006), Lipp, Evans, Baer, and Yoo (2005), except at a lower frequency of 704 cm\(^{-1}\). We suspect that this peak may be associated with CO\(_2\) (\(\nu_3\)) (Gunzler & Gremlich, 2002)). \(^1\) The relatively narrow peak near 880 cm\(^{-1}\) and the broad line near 1,020 cm\(^{-1}\) are likely SrO multiphonon bands (Jacobson & Nixon, 1968). Finally, the small peak near 1,130 cm\(^{-1}\) was also observed in the recovered poly-CO samples from Evans et al. (2006) and Lipp et al. (2005). Beyond this, there is strong absorption and mixing of bands complicating interpretation of the spectra above 1,130 cm\(^{-1}\).

In the case of the irradiated mid-IR spectrum, the two primary peaks near 1,275 and 1,650 cm\(^{-1}\) appear severely diminished (1,275 cm\(^{-1}\) line) or largely disappear (1,650 cm\(^{-1}\) line) again suggesting a significant reaction/transformation/polymerization of the sample. In their place, a number of new modes appear. At least three of these new lines are associated with CO\(_2\): The vibration near 2,349 cm\(^{-1}\) is the \(\nu_3\) antisymmetric \(^{12}\)C=O stretch (Isokoski et al., 2013). The peak near 1,850 cm\(^{-1}\) may possibly be associated with the CO\(_2\) bending mode with an overtone observed near 3,700 cm\(^{-1}\) (Evans et al., 2006) or the \(\nu_3 + \nu_1\) mode (Hansen, 1997; Isokoski et al., 2013).

Two other new peaks near 880 and 1,030 cm\(^{-1}\) are from SrO (Jacobson & Nixon, 1968). Finally, other newly appearing peaks may be attributed to polymeric-CO near 1,120 and 1,270 cm\(^{-1}\) (Evans et al., 2006; Bernard, Chiarotti, Scandolo, & Tosatti, 1998; Santoro et al., 2015).

4. Discussion

When pressure was released, the recovered sample appeared to be quite intact and stable—even sticking completely to the gasket when removed from the DAC with no residue left behind on the diamonds. We attempted Raman spectroscopy but found, as did other researchers (Evans et al., 2006; Lipp et al., 2005) that the sample appeared to rapidly decompose/burn where the laser light was incident upon the material and the region where the laser was incident transformed into a shiny/metallic-looking material which we suspect to be graphitic carbon.

We sought to prove that the observed polymeric synthesis was largely X-ray induced by conducting a separate far-IR high-pressure study of SrC\(_2\)O\(_4\) up to 19 GPa using petroleum jelly as a pressure-transmitting medium which will be reported in more detail in a subsequent paper. We present the preliminary results in Figure 4. The far-IR pattern found no evidence of pressure-induced
polymerization or decomposition as the acquired IR spectrum after pressure release returned to that obtained under ambient conditions. Examining Figure 1 (left), there is also no visual evidence of chemical reaction when pressurized to 7 GPa until irradiation (right photo) at the same pressure.

By irradiating the pressurized sample, we produced molecular CO$_2$ and an energetic polymer which largely appears to be polymeric carbon monoxide that is recoverable—similar to experiments that studied pure CO under high pressure (Evans et al., 2006; Katz, Schiferl, & Mills, 1984; Lipp et al., 2005). We also produced SrO which, considering just the stoichiometry of C and O, would support the idea that we formed polymerized carbon suboxide (p-C$_3$O$_2$) (Katz et al., 1984; Snow, Haubenstock, & Yang, 1978). However, given the observation that CO$_2$ remained in the reacted sample/polymer (even after over one month after the sample was opened to ambient conditions) and the similar varying colored appearance of the sample observed in earlier studies of CO (Evans et al., 2006; Lipp et al., 2005), we suspect that the synthesized polymer is poly-CO. We also did not observe a maximum in transmission near 2,200 cm$^{-1}$ (Katz et al., 1984; Snow et al., 1978)—rather, a broad window of transmission in that region which suggests that p-C$_3$O$_2$ was not present. Therefore, we propose the following reaction sequence:

$$\text{SrC}_2\text{O}_4 + h\nu \rightarrow \text{SrO} + \text{CO}_2 + \text{CO}.$$  
$$n(\text{CO}) \rightarrow \text{poly-CO}$$

The CO would be highly reactive especially under the highly ionizing conditions wrought by highly penetrating and highly energetic hard X-rays and would then polymerize into poly-CO with further irradiation and within the matrix of inert CO$_2$ and SrO, explaining the absence of CO in the mid-IR spectra (Ewing, 1962). At a pressure of 7 GPa and 300 K, the newly produced CO would react to form poly-CO based on the phase diagram in Ceppatelli, Serdyukov, Bini, and Jodl (2009).

5. Conclusion
We have observed that hard X-ray irradiation of strontium oxalate (pressurized inside a diamond anvil cell to 7 GPa) has initiated a powerful chemical reaction(s) which polymerized the sample and produced CO$_2$ and SrO in situ within the poly-CO matrix. The CO$_2$ appears to be trapped within the polymer even when the gasket was depressurized to ambient pressure and removed from the DAC. The Sr atoms appear to have bonded with oxygen to form SrO. Future experiments will ascertain if the SrO segregates or is merely dispersed throughout the sample. The polymer is a highly colored substance with waxlike, even “gooey (Evans et al., 2006)” consistency after exposure to air that appears to be very similar to recovered polymeric CO that has been produced by pressurizing CO above 5 GPa in earlier studies (Evans et al., 2006; Lipp et al., 2005). We found no evidence that pressure by itself has any significant role in the polymerization of SrC$_2$O$_4$ as it does in the case of pure CO. However, pressure in combination with X-ray irradiation is likely vital to this process. This enables far more control in the synthesis.

We have thus discovered a novel and easy route of chemical synthesis for a form of polymeric CO. We have also, for the first time, produced CO$_2$ via useful hard X-ray photochemistry which expands our repertoire for future chemical decomposition reactions (and synthesis) and which will aid us in our efforts to study the effects of diffusion, mixing, and segregation on detonation products (and other chemical species) under extreme conditions. It also enables the synthesis of an interesting polymer interspersed with an inert oxide which may have future electronic and/or optical applications.

To the best of our knowledge, this study represents the first polymerization of any compound via a combination of hard X-ray irradiation and pressure.

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**Note**

1. We note in passing that have routinely observed vibrational shifts from our X-ray photochemical products that differ slightly due to differing chemical environments (Pravica, Sneed, White, et al., 2014b) and our method of producing this polymer is very different from prior syntheses of poly-CO (Evans et al., 2006; Lipp et al., 2005).

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