Studies in useful hard x-ray photochemistry: decomposition of potassium halates

Michael Pravica*, Brent Hulsey, Ligang Bai, and Daniel Sneed, Quinn Smith and Griffin Guardala

High Pressure Science and Engineering Center (HiPSEC) and Department of Physics, University of Nevada Las Vegas (UNLV), Las Vegas, Nevada USA, 89154-4002

*Corresponding author e-mail: pravica@physics.unlv.edu

Abstract. We performed a systematic study of radiation-induced decomposition rates of KClO₃, KClO₄, KBrO₃ and KIO₃ in glass capillaries using the monochromatic x-ray. We also performed a complementary white beam x-ray study to verify the presence of molecular oxygen released from the acatalytic, isothermal chemical reactions initiated by hard x-rays using a diamond anvil cell to seal the samples. The aim of these studies entailed better-understanding the effect of oxygen-oxygen distance and oxygen multiplicity in determining the x-ray induced decomposition rate of potassium halates to aid useful hard x-ray induced chemistry. The observed decomposition rate appears to strongly and inversely correlate with O-O distance which suggests that ionization events of oxygen atoms from the halate groups occur nearly simultaneously and irreversible chemical reaction of two ionized oxygen radicals occurs with a higher probability when they are closer to one another.

1. Introduction

By utilizing the highly ionizing, highly focused, and highly penetrating properties of hard x-rays (>5 keV), novel chemistry can be enabled – particularly in sealed or isolated chambers such as the diamond anvil cell (DAC), which will greatly aid science at extreme conditions by, e.g., enabling the loading of challenging [1-3] and even toxic gases (e.g. Cl₂ [4]) into DACs or other chambers (e.g. nuclear reactors). These novel methods of initiating chemistry will also afford significant chemical reaction control via high pressure [5-7], selection of irradiation energy [8], localized irradiation (with little heat input) [5,6], and the ease of introducing segregated and mixed reactants into sealed chambers [1] to perform x-ray photochemistry in situ. Initially, we observed the rapid decomposition of potassium chlorate (KClO₃) into molecular oxygen and potassium chloride using white x-rays [1,2] and monochromatic x-rays [4] from the Advanced Photon Source (APS) via the following acatalytic chemical reaction:

\[ 2\text{KClO}_3 + \text{hv} \rightarrow 2\text{KCl} + 3\text{O}_2. \]

Subsequently, it was observed that other simple molecular gases (e.g. O₂, H₂, N₂ and Cl₂) could be released in situ inside sealed chambers (such as a DAC) via penetrating hard x-rays and even at high pressure [1-4]. During the course of our studies, pressure was found to be an important variable
controlling the decomposition rate [5-7] and that there is a phase dependence of the decomposition rate of potassium chlorate [7,8]. We have also observed an apparent resonance of the x-ray induced decomposition rate of KClO₃ near 15 keV, which we attribute to a bondlength/x-ray wavelength coupling [9]. This observed effect, along with a prior-observed orientational dependence of x-ray induced decomposition of PETN [10] offers the hope of selectively irradiating certain bonds to initiate chemical reactions with yet more means of chemical control.

In the following report, we sought to expand our understanding of the reaction process by investigating the effect of cation size upon the radiation-induced decomposition rate. Preliminary evidence showed that the radiation-induced rate of KIO₃ was much slower than that of KClO₃ [9], suggesting that the oxygen-oxygen distance is an important factor in determining the decomposition rate. The greater this O-O distance (or the larger the anion), the less probability that freed or ionized oxygen radicals would irreversibly link up/react to form molecular oxygen. We thus sought to further this study by investigating the decomposition rates of KClO₃, KClO₄, KBrO₃, and KIO₃ to verify this under similar experimental conditions. We also sought to verify that oxygen was indeed released from all compounds by confining them in a sealed DAC and observing formation/release of O₂ via Raman spectroscopy [1,11].

2. Experimental

Our first experiment was performed at the 16 ID-B beamline of the High Pressure Collaborative Access Team (HP-CAT) at the Advanced Photon Source. “White” x-ray radiation was filtered using a tunable monochromator to supply 20 keV x-rays. KClO₃ (Alfa Aesar 99+%), KClO₄, KBrO₃, and KIO₃ powders (Sigma Aldrich®, 99+%, >99.8%, and >99.5%, respectively) were separately and individually ground with a mortar and pestle and each placed in one of four 1 mm capillaries (i.e. one for each compound). Each capillary was separately aligned into the x-ray beam using a Si photodiode and then irradiated with monochromatic x-rays. Diffraction patterns were collected via a Pilatus ® detector. Selected diffraction peaks (usually the largest present) were then followed as a function of time to obtain decay constants [5-7, 9].

In the second study, a symmetric-style DAC with 250 μm thick stainless steel gaskets was employed to pressurize KClO₄, KBrO₃, and KIO₃ for our experiments; we have already demonstrated that O₂ is produced in KClO₃ [1]. The diamonds used each had a culet ~300 μm in diameter. The sample-confining gasket was preindented to ~ 50 μm thickness and a sample hole of diameter 140 μm was drilled via electric discharge machining (EDM). Sample powder was loaded into the gasket hole along with one ruby ball (for pressure measurement purposes) and then the assembly was closed to seal the sample. No pressure transmitting medium was used in our experiments. The sample was confined and pressurized as a means of control, isolation, and to slow the decomposition process for easier study [1,7]. We chose to pressurize our samples at 1 GPa based on our earlier studies of the decomposition rate of KClO₃ [7]. We used the same gasket for each sample, ultrasonically cleaning the DAC and gasket and introducing fresh powder for each new sample. The advantage of using a DAC for this study is that any released oxygen will remain inside the DAC and can be easily verified via Raman spectroscopy [1]. Each sample was irradiated with white beam x-rays for approximately 3 hours which was based upon the beamtime available to us for the experiment. The x-ray beam was 5 μm in horizontal and 15 μm in vertical in its full width at half maximum (FWHM). The primary goals of these efforts entailed the verification of the presence of molecular oxygen after irradiation as has been observed in KClO₃[1]. All of our studies were conducted at room temperature.

3. Results

During our experiments, there was no evidence of sample temperature change during irradiation, which agrees with our prior studies [2,5,6]. However, color change did occur in each of the capillaries. We present representative x-ray diffraction patterns of KIO₃ and KClO₃ in figure 1. Each pattern was acquired over 1 - 60 sec depending on how fast the material would decompose. After acquiring a series
of patterns for each compound, the integrated intensities were plotted versus integrated irradiation time and decay constants were obtained by taking the log of the background-subtracted spectra.

Figure 1. Representative diffraction patterns of KIO₃ (left) and KClO₄ (right), each confined in a capillary, using 20 keV x-rays.

Figure 2 displays the results of the first-order decomposition rates as a function of oxygen-oxygen distances within each species [8,12-14]. There is an obvious trend of an increasing decomposition rate with decreasing anion size (IO₃⁻ -> BrO₃⁻ -> ClO₃⁻), with the exception of ClO₄⁻, which is not in the same family of anions. Our goal of studying KClO₄ involved investigation of the effect that adding more oxygen atoms within the unit cell would have on altering the decomposition rate. It is apparent that the rate considerably increases.

Figure 2. Measured decay constants of the studied halates versus oxygen-oxygen distance.

For the second experiment, O₂ was produced in all of the irradiated samples confined in a DAC with the exception of the KIO₃ sample. As the decomposition was considerably slower (based on an earlier study [9]), we did not irradiate the sample sufficiently long enough to release measurable oxygen. One other possibility is that the pressure was not high enough (1 GPa) to confine the oxygen in sample with considerable open space (due to the large iodine atoms within the unit cell) so that the
oxygen leaked out or diffused throughout the sample. We have observed rapid diffusion of molecular oxygen in irradiated KClO₄ [15]. The other samples (KClO₄ and KBrO₃) showed the strong presence of the oxygen vibron near 1550 cm⁻¹ [11] after irradiation. It should also be noted that the flux at the 16 BM-B beamline is far less than the flux at 16 ID-B beamline. We display our evidence for the presence of molecular oxygen after irradiation of KClO₄ and KBrO₃ in figure 3.

![Figure 3.](image)

Figure 3. Representative Raman plots showing the release of molecular oxygen after irradiation with 20 keV x-rays for KBrO₃ (left) and KClO₄ (right). The top plots display the spectra from irradiated samples and the bottom plots are spectra before irradiation in the 1500-1600 cm⁻¹ region.

4. Discussion
These results confirm that the x-ray induced decomposition rate is not due to simple absorption of x-rays by the heaviest elements (I, Br, Cl) as the decomposition rates would then be in an opposite trend if the decomposition were solely to absorption of energy within the unit cell. Instead, the critical factor involves the oxygen-oxygen distance. When high energy x-rays or cascading electrons interact with atoms, oxygen atoms are ionized and radicals form. If, two oxygen radicals are created within the time frame required for the radicals to lose energy and relax by combining with the rest of the rump halate group, then the two radicals may react to form O₂ if they are close enough to one another. If not, the oxygen radical returns to the anion, and no permanent chemical reaction occurs. The closer oxygen radicals are to one another within a given time frame, the higher the probability of irreversible chemical reaction. Our observations appear to confirm this viewpoint.

5. Conclusion
We have performed a series of experiments that will further the new field of useful hard x-ray induced chemistry. The effect of anion size on the hard x-ray induced decomposition rate of potassium halates has been verified. Reduced anion size enables ionized oxygen radicals to link up with one another with a higher probability and that species with more oxygen atoms within the unit cell (i.e. KClO₄) release oxygen more readily with x-ray irradiation. We have also verified that O₂ is released as expected in each of the in situ x-ray initiated chemical reactions studied with the exception of KIO₃ which decomposed too slowly at pressure and/or in which O₂ quickly diffused away from the irradiated region more rapidly than the other samples. Via anion and cation selection, yet another useful mechanism of chemical reaction control can be realized under extreme or isolated conditions.

Acknowledgements
We thank Stanislav Sinogeikin for aid in the measurements. We acknowledge support from the DOE Cooperative Agreement No. DE-FC08-01NV14049 with the University of Nevada, Las Vegas. We also acknowledge partial support from the Department of Energy National Nuclear Security Administration under Award Number(s) DE-NA0000979. Use of the Advanced Photon Source is
supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. HPCAT is supported by DOE-BES, DOE-NNSA, NSF, and the W. M. Keck Foundation.

References
[1] Pravica M, Bai L, Park C, Liu Y, Galley M, Robinson J and Bhattacharya N 2011 Rev. Sci. Inst. 82 106102
[2] Pravica M, Bai L, Park C, Liu Y, Galley M, Robinson J and Hatchett D 2012 Rev. Sci. Inst. 83 036102
[3] Pravica M, Liu Y and Bai L 2013 Chem. Phys. Lett. 555 113-15
[4] Pravica M, Sneed D, Bai L and Smith Q 2013 Chem. Phys. Lett. 590 74-6
[5] Giefers H, Pravica M, Liermann P and Yang W 2006 Chem. Phys. Lett. 429 304-09
[6] Giefers H and Pravica M 2008 J. Phys. Chem. A 112 3352-59
[7] Pravica M, Bai L and Bhattacharya N 2012 J. Appl. Cryst. 45 1117-20
[8] Yedukondalu N, Ghule V and Vaitheeswaran G 2013 J. Chem. Phys. 138 174701
[9] Pravica M, Bai L, Sneed D and Park C 2013 J. Phys Chem. A 117 2302-06
[10] Pravica M, Quine Z, Romano E, Bajar S, Yulga B, Yang W and Hooks D 2007 AIP Conf. Proc. 955 1117-20
[11] Akahama Y and Kawamura Y. 1996 Phys. Rev. B 54 15602-05
[12] Marabello D, Bianchi, R, Gervasio, G and Cargnoni F 2004 Acta Crysta. A 60 494-501
[13] Telfer G, Gale J, Roberts K, Jackson R, Wilde P and Meenan P 1997 Acta Crysta. A 53 415-20
[14] Bayarjargal L, Wiehl L, Friedrich A, Winkler B, Juarez-Arellano E A, Morgenroth W and Haussühl E 2012 J. Phys.: Cond. Matt. 24 325401-11
[15] Pravica M, Popov D, Sinogeikin S, Sneed D, Guardala G and Smith Q 2013 Appl. Phys. Lett. 103 224103