ELECTRON AND PHOTON INTERACTIONS WITH $KClO_4$

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ABSTRACT

The interaction of $KClO_4$ with electron beam and x-ray photons was examined. From the Auger data, it was found the electrons rapidly decompose $KClO_4$. High resolution XPS showed $KClO_4$ to be unstable to non-monochromatic Mg and Ti photon sources and stable to monochromatized AlK_α x-ray radiation. These data are discussed in terms of degradation mechanisms involving: (1) sample heating and (2) electronic excitations or charge accumulation.

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I. INTRODUCTION

The basic mechanism involved in the "firing" of pyrotechnic materials is not known. A series of examinations leading to an understanding of this firing mechanism is presently under way at the Mound Facility. In 1975, studies of the surface structure of high energy (HE) materials and the interaction of these materials with various metal containers were initated. The HE materials that have been studied include: the pyrotechnic $TiH_x/KClO_4$ [1-3], the Al/Cu_2O machinable thermite [4-7], the PETN, HMX, and RDX explosives [8], and the PBX-7407 and LX-16 plastic-bonded explosives [8]. It has been concluded from these early studies that the titanium subhydride particles are coated with thin oxides, suboxides, and/or hydroxides of titanium [1]. The oxidation state of titanium was determined to be primarily a +4, although other states were characterized. In more recent studies, it was shown that these suboxides of titanium (or subhydrides) become oxidized to a +4 state by simple mixing with the $KClO_4$ oxidizer and that dissolution of the oxides upon heating in vacuo proceeds through an intermediate suboxide. The oxides on titanium metal were shown to begin dissolving at $\sim$300°C [2,3].

In the thermite studies [4-7], it has been established that: 1) aluminum powders from the manufacturer have a layer of oxide on the particle surface, 2) the surface oxide increased after room temperature mixing with Cu_2O oxidizer, 3) the aluminum oxide thickness doubled after hot pressing of the stoichiometric Al/Cu_2O mixture, and 4) the interfacial region formed between the aluminum metal and cuprous oxide during hot-pressing was at least 100Å in thickness.

In studies on the two PBX's, PBX-9407 and LX-16, it was concluded that the Exon coating on 9407 was complete and $\geq$100Å; whereas in LX-16, the coating was <100Å or even incomplete. In other studies Auger analysis has been used to characterize the surface composition and oxide thickness for an iron-nickel alloy and showed the thicker oxides to have the least propensity for atmospheric hydrocarbon adsorption. In this paper,

the surface characterization of the $KClO_4$ oxidizer used in $TiH_x/KClO_4$ Mound pyrotechnic mix is discussed. The two techniques used were Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL

A. Auger Electron Spectroscopy (AES)

Anhydrous $KClO_4$ was pressed into a pellet at a pressure of 10^4 psi and mounted in the UHV chamber of the Auger instrument. AES spectra were obtained with a Varian scanning Auger spectrometer. The electron beam energy used was 5 kV and the spot size was <20 micrometers. During each analysis the electron beam was rastered over a 10^4 micrometer squared area ($\sim 10^{-4} cm^2$). The electron beam current was 0.01 microamperes. The base pressure was $\sim 1 \times 10^{-6}$ Pa.

B. Electron Spectroscopy of Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS)

Anhydrous $KClO_4$ was lightly sprinkled on one side of doubled-sided 3M sticky tape, which had already been affixed to a copper sample holder. The XPS analyses were performed on three different spectrometers: (1) a Kratos ES300 with Mg, Ti and Al anodes, (2) a Vacuum Generators (VG) ESCALAB 5 with Mg and Al anodes and (3) a Leybold-Heraeus LH-10 with Mg and Al anodes. The first two instruments (Kratos and VG) have Al x-ray monochromators. The data were taken in all cases with a base pressure of $<1 \times 10^{-6}$ Pa. The wattage in each case conforms to the following table:

Instrument	Mg	Al	Al Monochromator	Ti
Kratos	240W	-	360W + 900W	300W
VG	300W	-	-	-
LH	300W	-	-	-

The Cl 2p, O 1s and K 2p photo peaks were monitored as a function of time. With the L-H instrument, a quadrupole mass analyzer connected directly to the source chamber was used to monitor changes in the residual atmosphere. The pressures were in all

cases measured with an ionization gauge. Chemical shifts were measured relative to the kinetic energy positions of K 2p and C 1s. A duPont model 310 curve resolver was used to deconvolute the spectra.

III. RESULTS AND DISCUSSION

A. Surface Studies of $KClO_4$ with Electron Beams

In order to examine the interaction of a particle with another particle, it is necessary that the probing beam diameter be less than the particle dimension. Since the majority of pyrotechnic particles (oxidizers and fuels) are $\geq 1\mu$ in diameter, it is necessary that the probing beam be $<1\mu$. In Auger surface analysis, an electron beam of $<1\mu$ has been achieved routinely. However, at small electron beam diameters and at currents sufficient to generate Auger signals, sample heating and electronic excitations or charge accumulation on the sample will be the greatest. These effects can cause electron beam induced damage in the sample surface. $KClO_4$ being a nonmetallic material, it will be susceptible to such electron beam damaging effects. The results of analyzing powdered $KClO_4$ with AES is discussed in this section.

An electron beam having a current density ($\sim$0.1mA/cm^2) was impinged on $KClO_4$. Figure 1 illustrates the K(L-MM) and Cl(L-VV) Auger analog signals which were then observed from: (a) a freshly irradiated surface and (b) a surface that had been irradiated for 15 minutes. The K Auger was measured at 251 eV for both (a) and (b), and the Cl Auger was observed at 186.5 eV for (a) and 179 eV for (b), respectively. The Auger shift relative to the potassium Auger 251 eV peak is, therefore, 7.5 eV. The data show a distinct effect on the Cl Auger signal due to electron beam damage. This effect agrees in magnitude with the XPS work of Copperthwaite and Lloyd [9] which showed a 10 eV binding energy shift in the Cl 2p level between ClO_4^- and Cl^-, and agrees in direction with that predicted

from the molecular orbital diagram of Cl^- and ClO_4^-[10]. We have attempted to measure the deomposition rate of $KClO_4$ under electron beam irradiation. These data are plotted in Figure 2. If we assume that the 0 Auger is observed from $KClO_4$ and assume that the decomposition is first order, a rate constant of $\sim 3\ min^{-1}$ can be calculated. Also apparent from the data is a decrease in the Cl Auger signal and a corresponding rise in the 0 Auger signal as the time of electron beam irradiation increases. This is explainable in terms of electron stimulated desorption of the chlorine and either an electron stimulated adsorption of oxygen or a simple oxidation of the damaged surface. This has been observed on other halide salts[11-14].

As mentioned previously, electron beam alterations in the sample surface may result from (a) heating or (b) electronic excitations or charge accumulations. (Actually ther are several different processes involved. These are discussed in more detail by Pantano and Madey[15].) If heating is the cause of $KClO_4$ degradation, lowering the beam power, or increasing the electron beam diameter should decrease damage. This is due to the fact that the $KClO_4$ sample temperature rise is directly proportional to the beam power and inversely proportional to both the thermal conductivity of the sample and the electron beam diameter. Thus, the study of the electron beam induced decomposition of $KClO_4$ becomes increasingly possible with Auger spectrometers that use very low electron beam currents and pulse counting. Clearly, $KClO_4$ can be expected to be susceptible to beam heating. Likewise, localized beam heating may be especially prevalent if Auger microanalysis with high beam energies and an extremely small spot size is used. Perhaps even beam heating plays a major role in assisting in the other beam damage mechanisms.

Holloway[16] has shown that heating caused oxide diffusion in the Auger analysis of loose TiH_x powder, whereas no diffusion was detected in compacted powder. In the case of loose powder, the

irradiating electron beam heats the thermally insulated powder particles and causes diffusion of the oxide layers into the bulk. This does not occur with the compacted powder. Still, however, we might find it impossible to measure $KClO_4$ with Auger spectroscopy simply because the degradation effects are just too large. We predict that this will certainly be the case in Auger microanalysis.

B. Surface Studies of $KClO_4$ with Photons

Figure 3 compares the Cl 2p XPS $KClO_4$ spectra excited by: (a) non-monochromatic MgK_α photons, and (b) monochromatic AlK_α photons. These data clearly show the advantage of observing pyrotechnic reaction products of $KClO_4$ (i.e., lower oxidation products, such as ClO_3^- and Cl^-) with the AlK_α monochromatic excitation source. Since the x-ray satellites are removed, this monochromatic spectra allow for the direct detection of these lower oxidation states to <1%, in just a single five-minute scan. More importantly no detectable photodecomposition occurs with AlK_α photons from the x-ray monochromator; whereas immediate decomposition transpires with non-monochromatic x-radiation. In Figure 4 the photodecomosition rate from both types of radiation are compared. The non-monochromatic data were obtained on three different instruments (Kratos, □: Leybold-Heraeus, 0: and Vacuum Generators, ●) and the monochromatic data on one (Kratos, X).

The decomposition on all three instruments caused by radiation from the non-monochromatic source was found to occur at the same rate. This might not be surprising since all the XPS data were taken at approximately the same x-ray power (∿250 W). Again, it is important to note that there was no decomposition detectable with the x-ray monochromator after 15 hr of irradiation. However, after an additional 5 hr of radiation at 900W a detectable amount of ClO_3^- decomposition product was observable. The Cl 2p XPS spectrum following this dose of radiation is shown in Figure 5.

The decomposition of $KClO_4$ has been fitted to a first-order process ($-\frac{dc}{dt} = K[c]$). The rate constant, K, was determined to be 1.68×10^{-2} min for the initial decomposition, i.e., up to the first 30 min of irradiation. At longer exposures a significant deviation from first-order behavior is seen. A rate constant was also calculated from the O 1s XPS data and was found to be approximately one-fifth the rate of the perchlorate decomposition.

The major importance of this XPS data is that monochromatic AlK_α radiation does not cause decomposition. Thus, XPS can be used in studying the average surface chemistry of $KClO_4$ or pyrotechnic mixes (such as $TiH_x/KClO_4$) employing $KClO_4$ as the oxidizer. This conclusion is in contradiction to previously published work of Copperthwaite and Lloyd[9]. In their work on $NaClO_4$, they attributed the decomposition to the AlK_α x-rays; however, they showed no data with monochromatic AlK_α radiation.

Decomposition of $KClO_4$ by photons must be due to , as in the case of electron beam damage, either (1) sample heating or (2) electronic excitations caused by Bremsstrahlung radiation. We have previously increased the sample heating <u>via</u> x-ray tube heating. The result was an increase in the rate of $KClO_4$ decomposition[1]. Likewise, the sample heating was lowered by the use of a monochromator, where the x-ray tube is farther removed from the $KClO_4$ sample and decomposition was found to cease. Thus, the data presented suggest that sample heating in the x-ray tube is the cause of $KClO_4$ instability using non-monochromatic x-ray sources. This may not be the complete story, however, since high energy Bremsstrahlung is also reduced in a monochromatized x-ray source. Upon irradiating $KClO_4$ with TiK_α photons, the rate constant was determined to be 2.5×10^{-2} min. This rate constant was calculated from data taken with MgK_α photons, prior to and following a TiK_α irradiation for 14 hr. This rate constant was calculated with just four data points, two before and

two following TiK_α exposure, and assumes that the perchlorate decomposition under TiK_α is linear over 14 hr. If TiK_α excitation is similar to the data in Figure 4, the initial rate would be much faster. Since the photon energy for TiK_α is ~4500 kV, which would represent a high energy Bremsstrahlung source of radiation, electronic excitations or ionizations could also be the cause of $KClO_4$ decomposition under non-monochromatic radiation.

IV. CONCLUSIONS

In this paper, we have shown that electron beam irradiation of $KClO_4$ with beam current densities of 0.1 mA/cm^2 causes $KClO_4$ to rapidly decompose. The K, Cl, and O Auger signals were monitored during irradiation. A first-order rate constant of 3 min^{-1} was calculated from the O Auger data. The rate of $KClO_4$ decomposition was also observed during irradiation with photons. Non-monochromatic MgK_α and TiK_α anodes, operated at 240 to 300W, and monochromatized AlK_α sources, operated at 360 and 900W, were used. Again, as with electron beams, rapid decomposition of $KClO_4$ was noted within a few minutes upon exposure to non-monochromatic Mg or Ti x-rays; however, no detectable damage could be observed upon exposure to monochromatized AlK_α photons. First-order rate constants of $10^{-2}min^{-1}$ were calculated for $KClO_4$ decomposition when exposed to Mg and Ti x-ray. The data are presented in light of possible electron and photon degradation mechanisms. However, with the limited data taken to date, it is impossible to determine which mechanism(s) is involved in the electron or photon decomposition of $KClO_4$.

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