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THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE DURING GAMMA-RAY IRRADIATION*

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To assess radiation damage effects in propellants, pyrotechnics and similar materials, thermal decomposition measurements have been made, apparently for the first time, on ammonium perchlorate powders and crystals during gamma-ray irradiation.

In the past, almost all radiation damage studies on explosives, propellants, pyrotechnics and other pseudo-stable materials have been made by first irradiating samples and then, at a later time, performing some physical or chemical measurement to ascertain the extent of radiation damage. There are a number of well known reasons for performing radiation damage measurements during irradiation. One or more radiation induced effects may decay rapidly and entirely disappear by the time measurements are made. Radiation may trigger or catalyze a reaction which appears undesirable at a later time but might not be serious during the irradiation. Most importantly, radiation together with some functioning process, such as propellant burning, may produce large synergistic effects.

Ammonium perchlorate is the oxidizer used in most solid propellants and in many pyrotechnic devices such as explosive actuated switches. Also, it has been the subject of a large number of radiation damage investigations.[1-5] In particular, there have been a number of studies of radiation induced changes in the thermal decomposition kinetics. However, all of these studies were made by first irradiating samples and then making thermal decomposition studies at a later time. When ammonium perchlorate is decomposed at a fixed temperature, e.g. 227C, a sigmoid gas pressure vs. time curve is obtained. The curves normally contain induction, accelleratory and decay periods. The acceleratory and decay periods are described by Avrami-Erofeyev kinetics. After exposure to Co-60 irradiation prior to decomposition, the induction period decreases, the acceleratory period rate constant increases and the decay period constant either increases or remains constant. The radiation induced shortening of the induction period is accurately described by the equation:

$$\text{Induction period} = \text{Const}_1 - \text{Const}_2 \log (\text{dose}). \qquad (1)$$

Microscopic examination of crystals after exposure to 10^6 or 10^7 R shows pitting, voids, and microfracturing.

The decomposition measurements, described below, were made in a constant volume chamber equipped with a capacitance manometer to determine total gas pressure. This chamber is enclosed in a furnace that can be maintained at carefully controlled temperatures up to 700C. In addition, the sample chamber and furnace have optical quality fused silica windows to facilitate making optical absorption, luminescence, and other measurements during irradiation. This apparatus is installed in the facility at BNL for making optical and other measurements during gamma ray irradiation. It consists of a large concrete shield enclosing a remotely operated kilo curie Co-60 source and is equipped with a 14-meter-long dual beam

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spectrometer and optical relay system. All sensitive equipment is outside of the radiation field. Absorption, luminescence, gas evolution, and numerous other measurements can be made, usually simultaneously, during irradiation.

Gas evolution studies have been made on single crystals and powders of ammonium perchlorate, both at room temperature and at 227°C. Figure 1 shows a gas pressure vs. time curve for commercial powder being exposed at approximately 100R/s. This sample had not been irradiated previously. The curve increases in a smooth monotonic fashion. In marked contrast, the single crystal curve, Fig. 2, shows abrupt burst-like spikes superimposed on a continuous background. The spikes appear to occur at random times. Most likely they are caused by the abrupt release of gas, and the subsequent partial readsorption, accompanying micro fracture. The appearance of these spikes at these doses is not entirely unexpected. The previous microscope studies indicated they should occur when the exposure reached 10^6 or 10^7 R.

The gas pressure vs. time curve obtained by decomposing at 227C without radiation, Fig. 3, closely resembles similar curves obtained in the past, and with other apparatus. The other curves in Fig. 3, and the enlarged initial part, Fig. 4, were obtained by "turning-on" the source 1, 10 and 20 minutes after the thermal decomposition process had been started. In this case the exposure rate is 4.5 R/sec. In other words, these curves were obtained by simultaneously irradiating and heating. First, there is a marked decrease in the induction period. The observed periods are 23.5, 26.2, and 30.0 minutes for the 1, 10 and 20 minute delays between heating and irradiation.

The importance of this induction period data is demonstrated by comparison with data, summarized by Eq. 1, from samples exposed at room temperature prior to heating. When the irradiation is started one minute after heating the sample has accumulated approximately 6,000 R in the 23.5 minutes required to reach the end of the induction period. To achieve the same reduction by first irradiating and then heating the sample would have to accumulate an exposure of 2×10^5 R. The corresponding exposures for the 10 and 20 delays are 1×10^5 and 5×10^4. Thus, simultaneous heat and irradiation has produced a large synergistic effect.

Figures 3 and 4 indicate that irradiation has not effected the acceleratory and decay periods. Also, the numerous spikes shown in Fig. 1 are not observed.

Lastly, preliminary measurements, in which the exposure rates are as low as 1R/s, show similar large effects.

These observations lead to a number of conclusions. To begin, since these are, as far as we can determine, the first thermal decomposition measurements made during irradiation, and since they show large effects, they should be confirmed and expanded upon. In particular, they should be repeated using electron, x-ray, fission and 14 MeV neutron irradiations, etc. They point to the possibility that reactive systems, particularly propellants and pyrotechnic devices may be particularly susceptible to radiation during use. Finally, to evaluate radiation hazards in these systems it is essential to obtain improved understanding of the radiation related mechanisms involved.

[1] P.J. Herley and P.W. Levy, "Effects of X- and Gamma-ray Radiation on the Thermal Decomposition of Solid Orthorhombic Ammonium Perchlorate. Part I. Experimental and Results", J. Chem. Phys. 49, 1493 (1968)

[2] P.J. Herley and P.W. Levy, "Effects of X- and Gamma-ray Radiation on the Thermal Decomposition of Solid Orthorhombic Ammonium Perchlorate. Part II. Kinetics and Discussion", J. Chem. Phys. 49, 1500 (1968)

[3] P.W. Levy and P.J. Herley, "Effects of Radiation on the Thermal Decomposition Induction Period in Ammonium Perchlorate and Other Pseudo-stable Materials", J. Physical Chem. 75, 191 (1971)

[4] P.J. Herley and P.W. Levy, "Microscopic Observation of X-ray and Gamma-ray Induced Decomposition of Ammonium Perchlorate Crystals", Proc. of American Nuclear Soc. A.I.A.A. Conf. on Natural and Man-Made Radiation in Space. NASA Tech. Memorandum X-2440 (1972), p. 584

[5] P.J. Herley, C.S. Wang, G. Varsi and P.W. Levy, "Effects of Fast Neutron, Gamma-ray, and Combined Radiations on the Thermal Decomposition of Ammonium Perchlorate Single Crystals", J. Chem. Phys. 60, 2430 (1974)

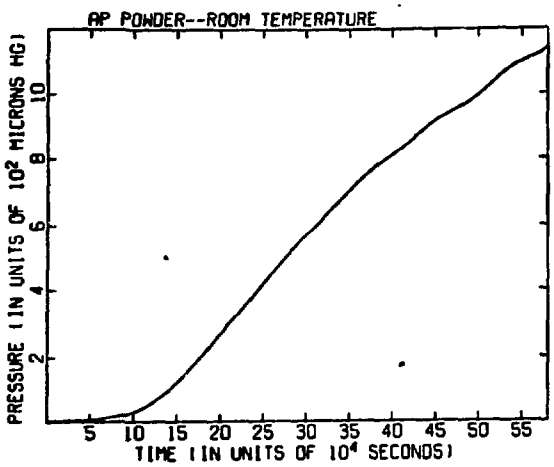

Fig. 1. Gas evolution from commercial AP powder exposed to Co-60 irradiation at 100 R/s and at room temperature.

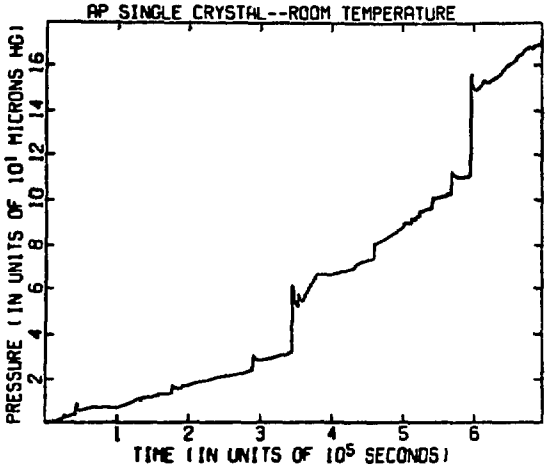

Fig. 2. Gas evolution from purified AP single crystal exposed to Co-60 irradiation at 100 R/s and at room temperature.

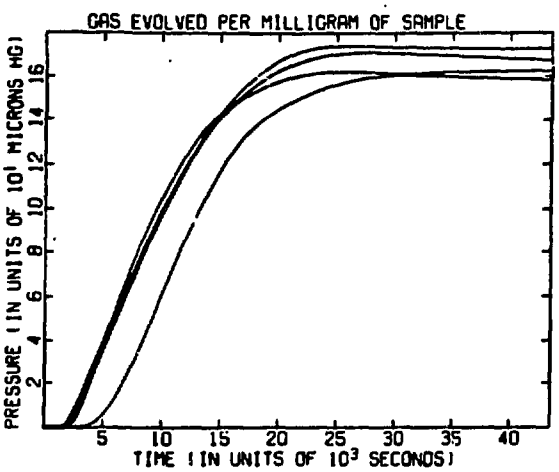

Fig. 3. Gas evolution from purified AP single crystals at 227C. Sample with longest induction period was not irradiated. Others were exposed at 4.5 R/s beginning at 1, 10, and 20 minutes after heating.

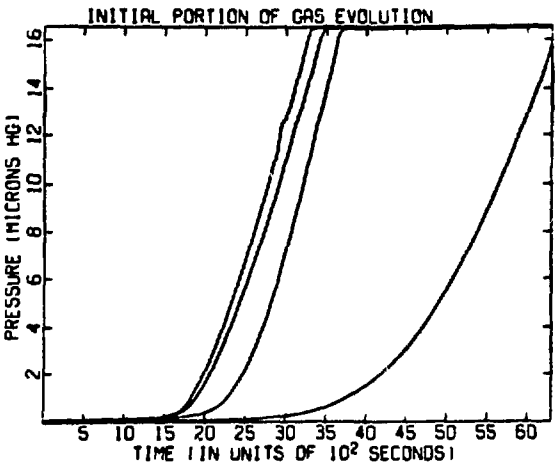

Fig. 4. Initial portions of the curves shown in Fig. 3, showing the marked reduction in induction period.