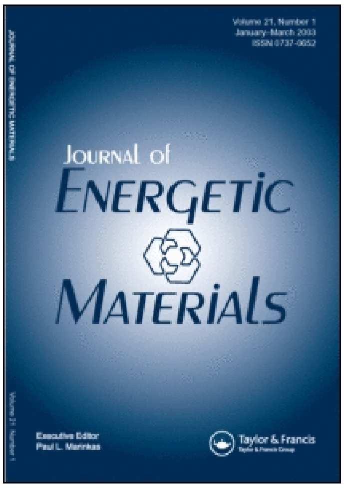

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# Thermal decomposition of energetic materials 32. on the instantaneous molecular nature of aqueous liquid gun propellants at high temperature and pressure before thermal decomposition

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# THERMAL DECOMPOSITION OF ENERGETIC MATERIALS 32. ON THE INSTANTANEOUS MOLECULAR NATURE OF AQUEOUS LIQUID GUN PROPELLANTS AT HIGH TEMPERATURE AND PRESSURE BEFORE THERMAL DECOMPOSITION

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## ABSTRACT

By analogy with recent studies on the molecular behavior of concentrated aqueous nitrate salt solutions at high pressure and temperature, hydroxylammonium nitrate-based liquid propellants would be expected to contain relatively covalent, contact ion pairs the instant before chemical decomposition ensues at high temperature and pressure. This may accentuate the first step of the decomposition process which appears to be proton transfer.

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# INTRODUCTION

The early reaction schemes that might occur in aqueous nitrate salt solutions are of in interest for gaining a complete phenomenological description of ignition/combustion in hydroxylammonium nitrate(HAN)-based liquid gun propellants (i.e. LGP1845, LGP1846, NOS305).[1] In practice, the propellant is pressurized and ignited as a dense spray of liquid droplets. Hence, many of these droplets experience a very rapid temperature and pressure rise before complete gasification ensues. For this reason, the behavior of concentrated aqueous solutions of nitrate salts above the critical point of pure water (374°C, 3200 psi) is of interest. The results might be projected to describe the behavior of thermally less stable solutions of HAN and alkylammonium nitrates. HAN solutions decompose above 140°C under slow heating conditions so that the ionic properties during an instantaneous surge to much higher temperature and pressure would be difficult to investigate experimentally. Unfortunately, few studies give a molecular description of aqueous nitrate salt solutions in the high pressure and temperature regime.[2]

Recently, the first broad-based study of the Raman spectra of concentrated aqueous nitrate salt solutions containing mono and divalent cations was completed.[3] By drawing on these and other data, a simple molecular description based on experiment can be put forth for how the salt components of liquid gun propellants might be expected to behave when they are subjected to a high pressure and temperature transient before the onset of massive decomposition.

## DO LGP DROPLETS EXPERIENCE A HIGH TEMPERATURE?

The endotherm synchronous with the loss of $H_2O$ from LGP1845 is strongly dependent on the applied pressure.[4] Figure 1 shows that significant loss of water (endotherm) occurs in the 180-220°C range when 500 psi Ar is applied.[4] This temperature range is lower than, but similiar to, the boiling temperature of pure water subjected to about the same applied pressure. A complicating feature in LGP1845 is the fact that $HNO_3(g)$ is formed from the decomposition of HAN. $HNO_3$ forms by an endothermic reaction which occurs approximately simultaneously with the water evolution. Therefore, for the purpose of illustrating that LGP1845 requires a high temperature to drive off water when under high pressure, $dT_b/dP$ for pure water up to the critical point (Figure 2)[5] is a useful qualitative analogy. Note that the boiling point of water reaches a quite high value under pressures that are an order of magnitude smaller than those that occur in a liquid propellant gun chamber. The critical point for aqueous salt solutions would be expected to be above that of pure water. Therefore, by inference, liquid LGP droplets in the thermal wave could experience a high instantaneous temperature while subjected to a high instantaneous pressure.

## A MODEL FOR LGP BEHAVIOR AT HIGH TEMPERATURE

Because concentrated HAN solutions in water decompose above 140°C, extremely fast diagnostics and temperature jump methods would be needed to ascertain the molecular behavior at high temperature and pressure. A more tractable experiment is to use a stable nitrate salt of a monovalent ion, such as $NaNO_3$, in place of HAN. $NaNO_3$ is thermally stable in aqueous solution to at least 450°C.

Concentrated $NO_3^-$ salt solutions contain solvent separated ion pairs and contact ion pairs at room temperature.[6] As the temperature is increased to 450°C under 30 MPa, lineshape analysis, Fourier transformation, and curve resolution of the symmetric $NO_3^-$ stretch permits the change in the concentration of the contact ion pairs and the solvent separated ion pairs to be resolved. Figure 3 shows the concentration of the contact ion pairs in 6.82m $NaNO_3$ as a function of temperature. Note that as the temperature is increased the tendency is to form contact ion pairs. In fact, this behavior is general to all nitrate salts studied to date ($Li^+$, $Na^+$, $Zn^{2+}$, $Ca^{2+}$, $Cd^{2+}$)[2,3] and largely originates from the decrease in the dielectric constant of $H_2O$ (and, hence its ion solvating power) with increasing temperature.[7] Thus, ionic salts in solution become increasingly molecular and have increasingly more covalent interaction between the anion and cation as the temperature increases. This same phenomenon can be expected to occur with the ions comprising a liquid gun propellant. HAN and the alkylammonium nitrate fuel will become more covalent, molecular-like ion pairs at higher temperatures.

How the hydroxylammonium and nitrate ions instantaneously come together in solution is a matter of conjecture. No doubt these is a strong statistical component. However, there is no question as to how they prefer to associate because the crystal structure of HAN is known.[8] As shown in Figure 4 the association is dominated by discrete hydrogen bonds. As the $NO_3^-$ and $NH_3OH^+$ ions relax toward one another at high temperature with less of the competition of mediating hydrogen bonding with $H_2O$, it would be expected that proton transfer between the anion and cation, and between the cation and $H_2O$ would be enhanced. It then follows that proton transfer between the anion and cation leading to $HNO_3$ should be (and is)[4] the first detected chemical reaction in the decomposition of HAN-based liquid gun propellants.

## ACKNOWLEDGMENT

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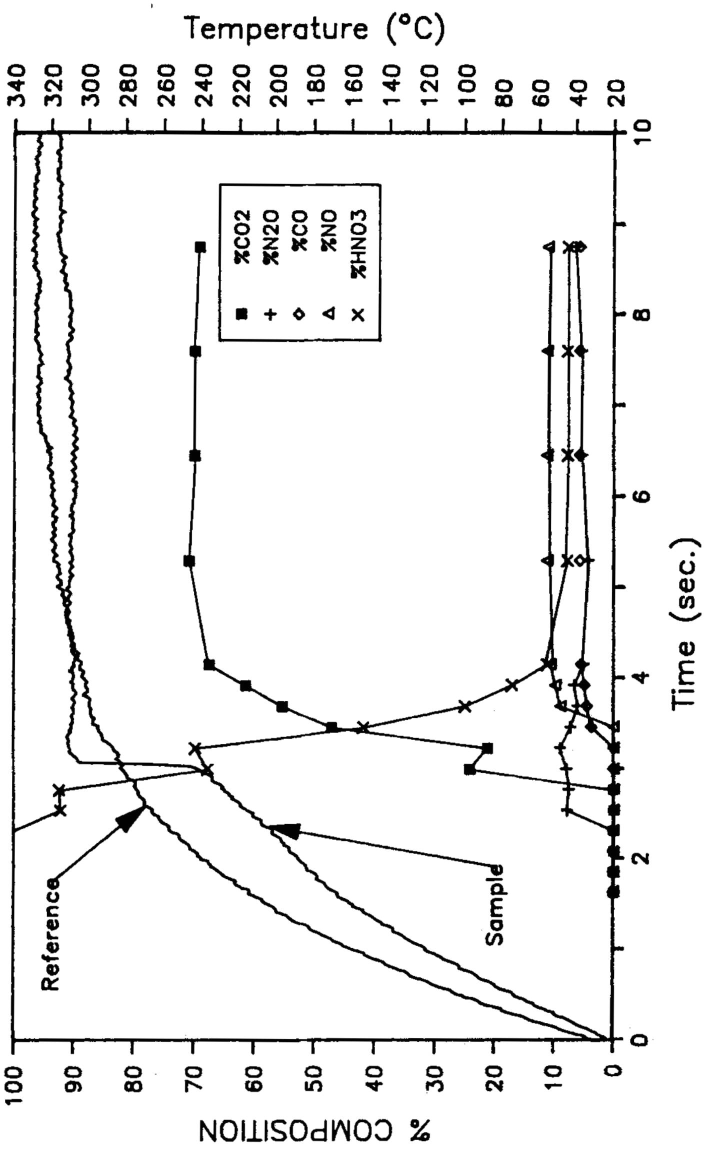

FIGURE 1

The thermal profile of 1.5 µL of LGP1845 superposed on the quantified gas products when the sample is heated at 110°C/sec under 500 psi Ar. Note the endotherm corresponding, in part, to evolution of $H_2O$ in the 180-220°C range.

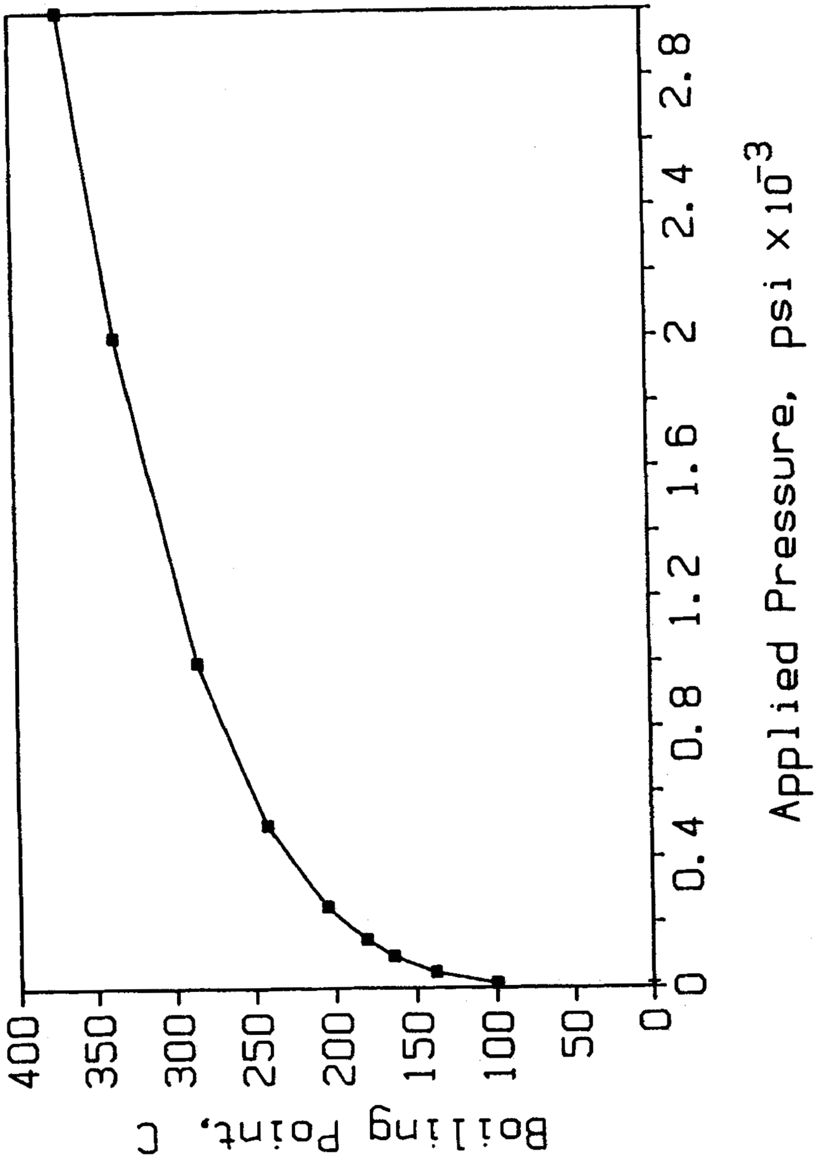

FIGURE 2

The boiling temperature of pure $H_2O$ as a function of the applied pressure.

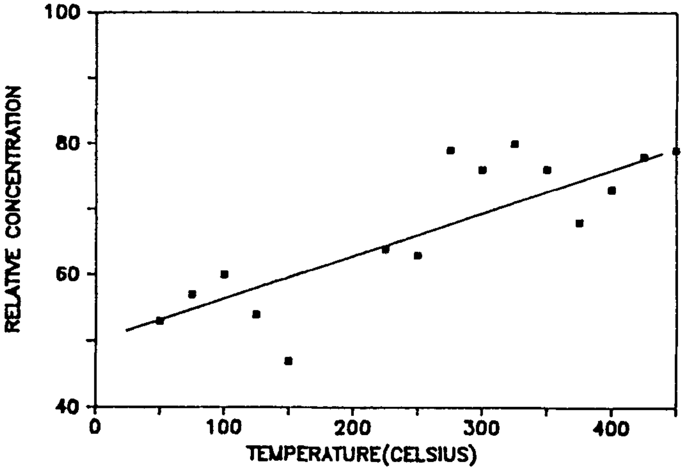

FIGURE 3

The relative concentration of the $Na^{+}\cdots NO_3^{-}$ contact ion pair as a function of temperature in 6.82m $NaNO_3$.

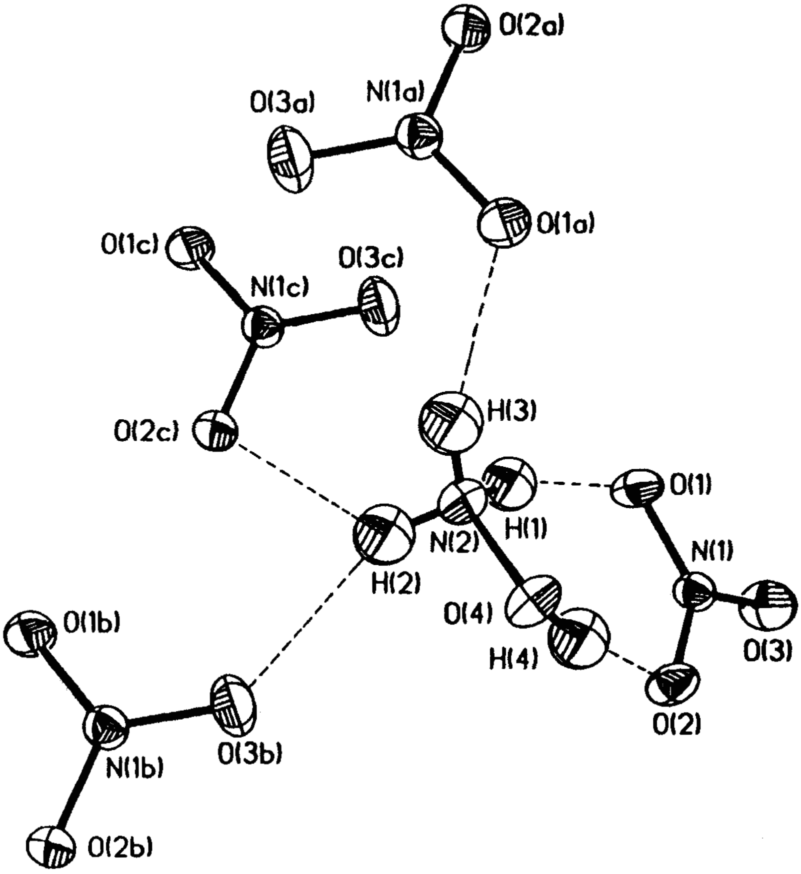

FIGURE 4

The packing of $NO_3^-$ ions about one $NH_3OH^+$ ion in solid $[NH_3OH]NO_3$.