Heterogeneous NH_4ClO_4 Decomposition Using Isothermal and Pulsed Laser Mass Spectrometry

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A pulsed ruby laser-mass spectrometry technique was developed and applied, wherein granular mixtures of ammonium perchlorate (AP) and light-absorbing substrate materials were rapidly flash pyrolyzed (0.8 ms) within the low-pressure ion source chamber of a Bendix TOF Mass spectrometer. Gaseous products from AP mixed with carbon black, copper chromite, Fe_2O_3, and MnO_2 indicated a predominance of high-temperature heterogeneous reactions. The first step appeared to be proton transfer dissociation of AP into NH_3 and $HClO_4$. Adsorbed $HClO_4$ underwent rapid heterogeneous decomposition on the substrate material; ClO_2 and HCl were evolved as major products, but ClO_3, ClO, and Cl_2 were only minor products. Chemisorbed oxygen and oxygen carriers such as OH and ClO were likely formed on the substrate simultaneously, however. These could react with adsorbed NH_3 and its dehydrogenated fragments to form H_2O, NO, and HOCl as major gaseous products; N_2, N_2O, and NO_2 were minor products. Low-pressure isothermal decompositions of AP and AP/substrate mixtures in a glass capillary were utilized to compare product distributions. The site of $HClO_4$ decomposition (crystal vs substrate surface) was concluded to be at least as important as temperature and effective residence time in determining the predominant chemical pathways.

Introduction

DESPITE several hundred investigations on the decomposition and deflagration of ammonium perchlorate[1] and other solid-propellant ingredients over the past 15 years, there has been a notable scarcity of high-temperature pyrolysis studies that provide significant chemical information on the rapid gasification of deflagrating solids. The laser pyrolysis–mass spectrometry (LP) approach was developed in an attempt to satisfy certain aspects of this need. In particular, the present use of a pulsed ruby laser permitted selective study of heterogeneous reactions that occur when hot substrates (light-absorbing) contact NH_4ClO_4 (AP) and rapidly surface-heat the oxidizer by conduction.

The high-vacuum environment of the mass spectrometer ion source chamber, under which AP/substrate mixtures and other AP-based ingredients were pyrolyzed, was obviously not a practical condition for deflagration. The arrangement did, however, serve to eliminate several gas sampling problems and thus permit direct analyses of primary gaseous products, evolved from solid-phase and interfacial condensed-phase reactions, in the absence of complicating gas-phase diffusion and reaction effects.

The application of a pulsed laser as an intense heating source is especially suited to mass spectrometer pyrolyses at temperatures where the rate of volatilization is high. Slower methods of heating can produce large quantities of gaseous products during heat-up which "flood" a mass spectrometer before the desired temperature is attained. An important advantage of the laser application is the possibility of optimizing sample geometry and avoiding physical contact between the sample and reactive boundaries, as in heated capillaries, hot stages, or resistance-heated filaments. The monochromatic character of the laser often precludes a number of undesirable photochemical reactions.

The ruby laser used in the present LP studies exerted two main constraints on the experimental conditions, however. First, the relatively fixed pulse shape of 0.8 msec duration prevented an experimental study of time and total-energy effects at constant heating rate. Secondly, different optical absorbances of mixture components at 6943 Å (AP absorbs weakly) resulted in differential heating and variable light absorption in-depth. Although the absorbance differences were utilized advantageously to favor heterogeneous reaction pathways in the present AP system, both of the above "constraints" have been circumvented recently by using a CO_2 gas laser,[2] which emits at 10.6 μm (where AP absorbs strongly) and has a widely variable square-pulse duration and power output.

Experimental

Materials and Characterization

The ammonium perchlorate (AP) was a finely ground commercial grade, with particle size averaging about 30 μm. Initial exploratory LP were also carried out with Matheson-Coleman-Bell reagent grade material, finely ground; no differences in product distributions were noted. The carbon black was Fisher reagent grade, of particle size 1 μm or smaller. LP of this material yielded relatively small peaks due to H_2O, CO, and CO_2, and a somewhat smaller peak at mass 26. The copper chromite was Harshaw-Chemical Cu 0202, having a nominal composition of 82% CuO, 17% Cr_2O_3, and 1% impurities, and an average particle size of about 2 μm. The Fe_2O_3 and MnO_2 were reagent grade, having average particle sizes of about 1.5 μm and 80 μm, respectively.

To assure uniformity and satisfactory mixing, mixtures were lightly ground in a mortar just before use. Samples were lightly packed in a small aluminum dish and degassed in the mass spectrometer for at least $\frac{1}{2}$ hr. LP of the metal oxides yielded mainly O_2 and smaller amounts of H_2O. The O_2 evolved was sufficiently large to preclude reporting of accurate product O_2 values from LP of AP/metal oxide mixtures. Corrections for the excess H_2O evolved (estimated to be 10-20%) were not made in reporting product H_2O.

Presented as Paper 68-149 at the AIAA Sixth Aerospace Sciences Meeting, New York, January 22–24, 1968; submitted February 14, 1968; revision received February 16, 1970. The author gratefully acknowledges stimulating discussions with A. R. Saunders, the skillful experimental assistance of W. R. Cofer, III and G. C. Purgold, and the manuscript and figure preparation by J. LaNeave and N. Kemper.

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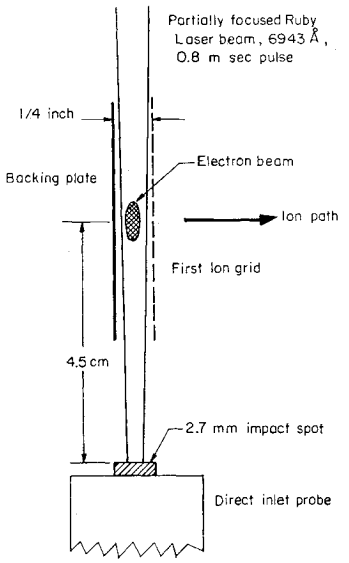

Fig. 1 Sampling configuration within low-pressure ion source chamber of Bendix TOF.

Apparatus

The sampling configuration is shown in Fig. 1. The partially focused pulsed laser beam entered the Model 14 Bendix TOF mass spectrometer ion source chamber vertically to impact samples about 45 mm below the electron beam. The basic optical system employed a 76-cm laser-to-sample distance, a moderately divergent 9.5 × 102 mm ruby rod (about 7 millirad) with reflective dielectric coatings on both ends, partial focusing with a 20-cm focal length lens, and defining apertures positioned before and after the lens.

A fixed 4-joule output pulse of 0.8 msec duration was used from the 20-joule ruby laser (Korad K-1) in order to maintain the same relative pulse shape and minimize long-term output degradation. Calibrated transmission filters (at 6943 Å) were used to vary the delivered impact energy, which generally ranged from about 2 to 10 cal/cm², depending on the sample.

Qualitative estimates of the surface distribution of impact energy were made by examining impacts on unexposed Polaroid film. A reproducible central spot of about 2.7 mm diam received a reasonably uniform distribution of energy (probably within ±15%); it was surrounded by an annular region in which the energy decreased radially to a sharp cut-off at about 3.5 mm.

The development of excessive pressures in the ion source region was alleviated by removing the standard pumping baffle, which opened up the entire cross section of the flight tube between the ion source and liquid N_2 trap/Hg diffusion pump system. Initial pressures were $<10^{-6}$ torr.

Discussion of Laser Pyrolysis Technique

The LP technique represents a new approach to the study of heterogeneous reactions between AP and various binder matrix constituents. The predominance of heterogeneous reaction pathways was determined primarily by the effective transparency of AP to 6943 Å light, and the relatively short heating pulse.† Impact energies in excess of 60 cal/cm² were required to produce a minimal mass spectrum with AP only. Thus when AP was flashed at much lower energies while in contact with light-absorbing carbon black or metal oxide catalysts, the substrate became preferentially heated and the dissociation/decomposition initially ensued at the hot substrate—AP interface. Subsequently, evolved gases caused particle separation effects to occur, new contact interfaces were established, and some of the product gases reacted with hot substrate particles.

It will be indicated later that, with the exception of $HClO_4$ and NH_3, the HCl-normalized gaseous product ratios were relatively insensitive to laser impact energy over threefold ranges. The reasons for this are unclear presently, although it seems plausible to consider temperature regulatory mechanisms such as a quasi-equilibrium vaporization and/or an effective particle contact time that decreases with increasing substrate temperature.

A few continuous time histories of product evolution rates from LP were measured by displaying the single-peak output of a Bendix 3012 analog. The smoothed results of ten laser impacts on a 5% Fe_2O_3/AP mixture are shown in Fig. 2, where the ion current intensities (proportional to evolution rate) were normalized to 100 and the laser peak power to 40. The laser pulse began at about 0.5 ms after triggering. With the exception of HOCl, all the product ion intensities began to rise at about 1.0 ms and peaked at about 2.4 ms. The respective half-peak time durations were 2.2, 4.0, and 19 ms for $HClO_4$, NH_3, and H_2O. HCl, ClO_2 (corrected for electron-impact fragmentation of $HClO_4$) and NO exhibited time histories similar to H_2O. HOCl did not begin its rise until about 3 msec.

The usual method of data recording consisted of photographing the entire mass spectrum (30 khz repetition rate) as it was displayed on a short-persistency phosphor oscilloscope from time zero up to a preselected time. Good photographic spectra were easily obtained in 2 msec or longer, which provided a check on product evolution histories. With 40 msec spectra, used most frequently to assure a complete time-averaged record, the measured mass peak heights corresponded to values of the maximum ion intensities attained; e.g., those seen in Fig. 2 at 2.4 msec. Under the present sampling conditions these reported ion intensities were considered to be approximately proportional to the respective maximum rates of product evolution.

Throughout the LP work each sample mixture was impacted sequentially up to 20 times, at varying energies, with each laser flash progressively deepening the impact crater. The lower limit of impact energy was generally that required for a readable mass spectrum; the upper limit corresponded to a condition where "flood out" and possible damage to the mass spectrometer were imminent. It was generally possible to explore a threefold energy range with each sample.

Treatment of Data

When the major pyrolysis products from sequences of up to 20 impacts were normalized with respect to HCl, the resulting product ratios were generally quite independent of impact number and also of laser impact energy, within the single-impact ratio error limit of about ±15%. Two exceptions,

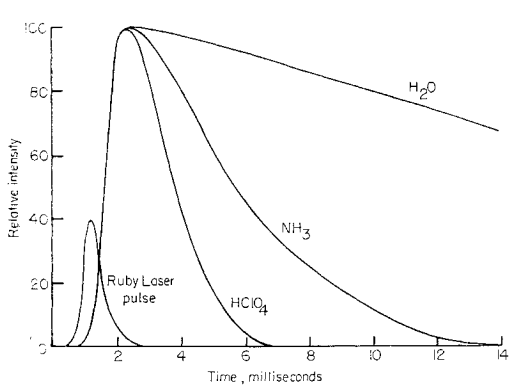

Fig. 2 Time dependence of product evolution in laser pyrolysis of a 5% Fe_2O_3/NH_4ClO_4 mixture.

† Results from our CO_2 laser pyrolysis technique[2] fully support the aforementioned dominance of heterogeneous reaction pathways.

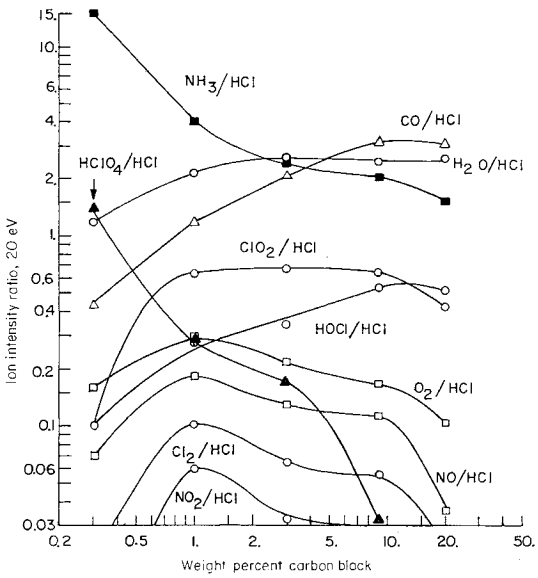

Fig. 3 Ruby laser pyrolyses of NH_4ClO_4/carbon black mixtures.

however, were normalized $HClO_4$ and NH_3, which increased sometimes with impact number and decreased with increasing impact energy.

In cases where $HClO_4$ was evolved in relatively large quantities, ClO_2 ion due to electron impact of $HClO_4$ had a relatively short appearance time compared to product ClO_2. The latter could be read directly by excluding the less-intense transient peak contribution from $HClO_4$ fragmentation. In other cases where $HClO_4$ was evolved in small quantities, the product ClO_2 peak was as intense and well defined as other stable product peaks. In some instances ClO_2/HCl exhibited a slight tendency to decrease with increasing impact energy, but to a much lesser extent than $HClO_4$.

After several hunderd LP results were compared over a wide range of sample compositions, it appeared justifiable to report only numerical averages of HCl-normalized product ratios obtained from 10 to 20 successive LP on a sample at different energies. Note that the special characteristics of $HClO_4$ and NH_3 evolution (short-lived and energy-sensitive) preclude absolute comparisons with other specie measurements.

Results

LP of AP/Carbon Black System

The AP/carbon black system was studied to serve as one type of reference. It was thought that purely thermal decomposition pathways should compete favorably with reactions otherwise catalyzed by direct oxygen exchanges and/or electron transfer processes characteristic of transition metal oxides.

Averaged gaseous product distributions from LP of different weight percent carbon black/AP mixtures are shown in Fig. 3. Note that the products of dissociative evaporation, NH_3 and $HClO_4$, decreased in relative abundance with increasing carbon black. In a sense these may be considered primary reactants. Since a 3.1 $NH_3/HClO_4$ ion intensity ratio (20 eV) corresponded to a unity mole ratio (in low-pressure heated-capillary pyrolyses of AP decomposition residues), there was also a large stoichiometric deficiency of evolved $HClO_4$, compared to NH_3, throughout. Similar deficiencies were seen in the AP/metal oxide systems (presented later). Although some preferential desorption of NH_3 (over adsorbed $HClO_4$) is attributable to the transient heating behavior of AP under vacuum conditions (see Ref. 2), these results obviously reflect the lower thermal stability characteristic of adsorbed $HClO_4$.

Inspection of the product distributions in Fig. 3 indicates that the extent of $HClO_4$ decomposition and NH_3 oxidation increased strongly with added carbon black. Note especially that ClO_2 and HOCl emerged as characteristic heterogeneous decomposition products. CO became increasingly abundant, indicating substrate oxidation, and the CO_2/HCl product curve (not shown) coincided closely with ClO_2/HCl. It was surprising that O_2, Cl_2, and NO_2 were not very abundant. These results contrast sharply with isothermal decompositions of AP, where all three were major products of condensed-phase decomposition (presented later). LP of AP crystals spread on a graphite substrate yielded product distributions much the same as those shown for the 1–9% carbon black systems, thus further supporting the concept of heterogeneous interfacial reactions initiated at hot substrate/AP interfaces.

Results were also obtained from LP of a 30% (estimated) carbon black/$^{15}NH_4ClO_4$ mixture, where N_2 and N_2O were mass separated from CO and CO_2, respectively. The 20 eV ion intensity ratios, normalized to HCl = 1.00, were $N_2 \cong 0.1$, CO = 2.9, $N_2O \cong 0.05$, $CO_2 = 0.76$, NO < 0.1, $NO_2 < 0.01$, $ClO_2 = 0.31$, HOCl = 0.44, and $O_2 < 0.1$. From this, and also some LP of $^{15}NH_4ClO_4$ on graphite, it appeared that neither N_2 nor N_2O were major decomposition products in the AP/carbon black system.

Ion intensities of the m/e = 14, 15 peaks were always negligibly small in comparison to NH_3 (~1%), so that N and NH can be ruled out as significant gaseous products in the carbon black and also metal oxide/AP systems. The average NH_2/NH_3 ion intensity ratio (20 eV) in the carbon black/AP system was 0.27, compared to nearly constant values of 0.31 and 0.30 in isothermal pyrolyses of AP decomposition residues at 260 and 380°C. Thus most of the NH_2 ion observed was probably due to electron-impact of NH_3.

Isothermal Decompositions (ID) of Pure AP

Results from LP of AP/carbon black mixtures were notably different from previous low external pressure (10^{-6} torr) ID of AP in a Bendix TOF mass spectrometer. In the ID studies, loosely packed samples of reagent grade AP were pyrolyzed in a 9 × 1 mm filament-heated glass capillary, positioned 25 mm below the ionizing electron beam.‡ Fragmentation patterns, and with the exception of H_2O, relative sensitivities were determined experimentally from pure gases to calculate ID mole ratios from 70 eV ion intensities. The time-independent condensed-phase decomposition product ratios are plotted vs temperature in Fig. 4. At 200°C the results were well accounted for by

$$3\ NH_4ClO_4 \rightarrow HCl + Cl_2 + N_2O + NO_2 + (\tfrac{7}{4})O_2 + (\tfrac{22}{4})H_2O$$

Minor products (<0.1 Cl_2) in these cases were N_2, NO, and ClO_2.

Figure 4 also shows more recent low-pressure ID results calculated from 20 eV data by using empirically determined (matched in overlap region) sensitivity factors. Relatively small but increasing quantities of NO and N_2 (not shown) were formed at temperatures above 300°C. Note that the above results were obtained at much lower pressures than used previously,[3–5] so that desorption and primary condensed-phase reactions were favored over secondary reaction effects.

Of the six major products of condensed-phase decomposition, from ID of AP, only H_2O and HCl were major products in LP of carbon black and metal oxide/AP mixtures; the same conclusion holds for high-temperature CO_2 laser pyrolyses of pure AP.[2] This fact by itself suggests that significant

‡ The effective absence of electron-impact decomposition of 1) the solid sample and 2) any AP sublimate formed in the ion source, was demonstrated. The strong appearance of NH_3 and $HClO_4$ only in late ID stages (from postdecomposition AP residue), ruled out 2, and also eliminated thermal cracking of $HClO_4$ by the ion source hot filament as a significant "source of decomposition products."

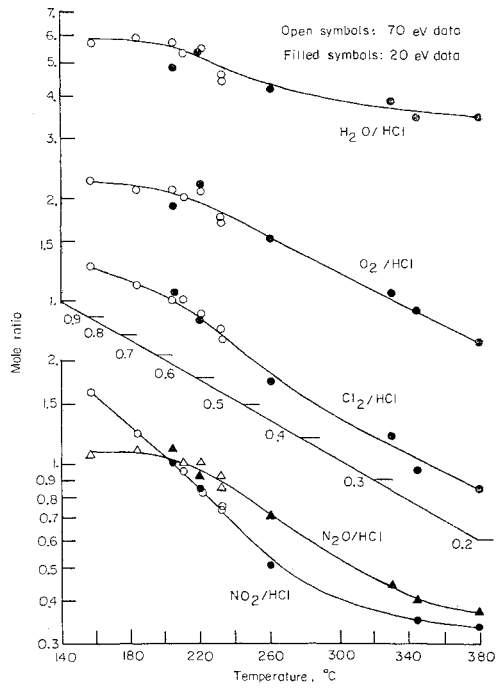

Fig. 4 Condensed-phase decomposition products of NH_4ClO_4 heated in a glass capillary at low pressure within ion source chamber of Bendix TOF.

basic differences existed in the respective decomposition mechanisms.

A dominant feature of the ID results for AP was the systematic increase in HCl mole fraction with temperature. Some of the increase at higher temperatures (say, >260°C) was likely due to heterogeneous $HClO_4$ decomposition on the glass capillary wall. However, comparisons of sequential results at 380°C indicated that Cl_2/HCl decreased only from 0.30 to 0.26 while $HClO_4$/HCl ion ratio increased from 0.1 to 3 before pyrolysis of the decomposition residue (AP) was complete. Although the application of equilibrium considerations to heated-capillary AP decompositions is of questionable validity, it is notable that the Deacon equilibrium, $H_2O + Cl_2 \rightleftharpoons 2HCl + \frac{1}{2}O_2$, strongly favors the observed decrease in Cl_2/HCl with increasing temperature, at constant pressure. Pressure effects are considered next.

A comparison of AP products in Fig. 4 with others obtained at pressures of several torr[4-5] indicates a two-to-fourfold increase in Cl_2/HCl mole ratio with increased pressure, at 225° to 300°C. Although the reported values[4-5] are somewhat uncertain, due to incomplete product separation and secondary reactions during isolation and wet-analysis of the "nonvolatile (at −78°C) residue," our comparatively lower Cl_2/HCl suggests that much of the present "excess" HCl would probably undergo condensed-phase oxidation to Cl_2 at higher pressures; i.e., where desorption is effectively slower, and the Deacon equilibrium favors an increase in Cl_2/HCl.

The absence of significant quantities of ClO_2 (and HOCl) during ID of AP up to 380°C, and also during high-temperature CO_2 laser pyrolyses of AP,[2] is considered relevant, especially since $HClO_4$ was also evolved in significant quantities; i.e., the decomposition of adsorbed $HClO_4$ on preferred AP crystal sites apparently favors Cl_2 formation and evolution over ClO_2 evolution. Note that desorption of ClO_2 from the AP should not have been a limiting factor since both Cl_2 and ClO_2 were significant products during ID of $KMnO_4$-doped AP (presented later).

The LP of AP/metal oxide mixtures are now presented, followed by a summary of characteristic features and interpretations that were found applicable to all the AP-mixture systems.

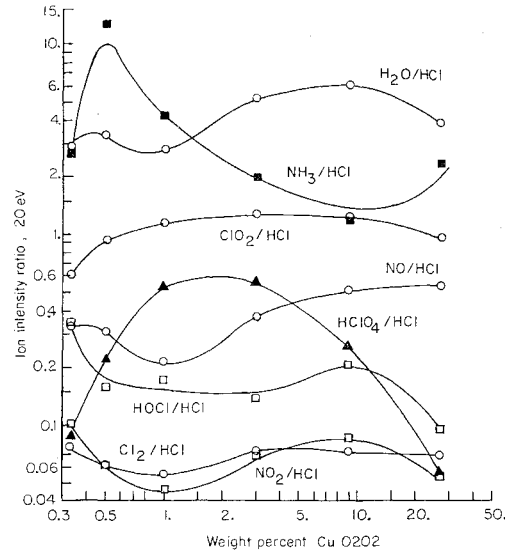

Fig. 5 Ruby laser pyrolyses of NH_4ClO_4/Copper chromite mixtures.

LP of AP/Metal Oxide Systems

Averaged gaseous product distributions from LP of AP/copper chromite (Cu 0202), Fe_2O_3, and MnO_2 mixtures are shown in Figs. 5–7, respectively. Other possible products in the *m/e* range 2–200 were either nonexistent or detected in very small quantities (N_2, N_2O, ClO, and ClO_3 are discussed later). Although the product ratios varied significantly with metal oxide type and percentage, the results had a number of features in common. Note in particular that 1) $HClO_4$ generally exhibited a large stoichiometric deficiency in the gas phase, compared to NH_3, 2) H_2O was the predominant reaction product, and its relative abundance tended to correlate with NO except at very high substrate additions, 3) the concentrations of ClO_2 and HCl usually exceeded Cl_2 by an order of magnitude, 4) NO predominated over NO_2 by a substantial margin (expected at high temperatures), and 5) HOCl was always significant and characteristic product of heterogeneous decomposition.

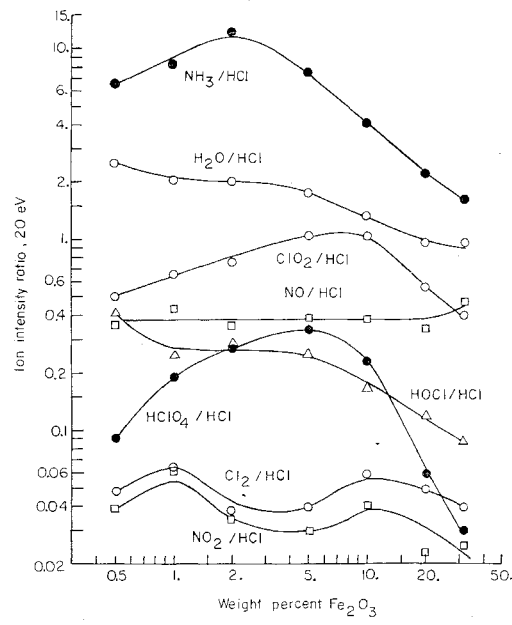

Fig. 6 Ruby laser pyrolyses of NH_4ClO_4/Fe_2O_3 mixtures.

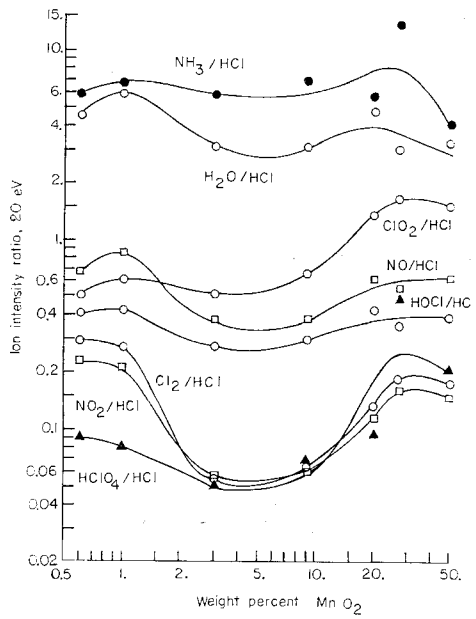

Fig. 7 Ruby laser pyrolyses of NH_4ClO_4/MnO_2 mixtures.

Although ClO ion was always observed and measured, the relative abundance of ClO radical appeared to be quite small. Corrected ClO/HCl ion ratios§ varied significantly (0–0.02 to 0.16) with mixture composition, but tended to correlate quite well with respective Cl_2/HCl data in the AP/metal oxide and carbon black systems. Corrected ClO/Cl_2 ion ratios averaged 1.15 ± 0.5, based on the 17 most reliable determinations out of a possible 25 in Figs. 3, 5–7.

Some early product distributions obtained from LP of ground $^{15}NH_4ClO_4$/metal oxide mixtures are shown in Table 1, in which N_2 and N_2O were mass-separated from CO and CO_2, respectively. Although the mixtures were somewhat high in metal oxide concentration, compared to those in Figs. 5–7, the results generally indicate that N_2 and N_2O were minor decomposition products.

Generalizations on LP of AP/Substrate Mixtures

The following generalizations and interpretations characterize some of the more important mechanistic features of the LP results from carbon black, Cu 0202, Fe_2O_3, and MnO_2/AP mixtures.

The primary driving force for decomposition was conduction of heat to AP particles from laser-heated substrate particles. Gas-solid heterogeneous reactions probably predominated after the onset of AP gasification. The characteristic product evolution time histories (typified by Fig. 2) and distributions obtained in this work, and also Ref. 2, indicate that 1) $HClO_4$ and NH_3 can be considered "primary reactants" during ruby LP, 2) subsequent heterogeneous decomposition was very rapid, and presumably occurred at high temperatures, and 3) preferential adsorption/decomposition of $HClO_4$ on the substrate generally occurred, based on stoichiometric deficiencies of evolved $HClO_4$, compared to NH_3, and also relatively high Cl/N atom balance estimates (not shown) derived from evolved decomposition products.

Inconclusive evidence was found for $HOClO_3 \rightarrow HO\cdot + ClO_3\cdot$ proposed by Levy[6] as being rate determining in the homogeneous decomposition of $HClO_4$ above 330°C. In all four LP systems, conditions were found where 20 eV ClO_3/$HClO_4$ ion ratios significantly exceeded (30–100%) the values of 1.33 and 1.49 obtained from ID of AP at 260 and 380°C. However, since excess ClO_3 ion may arise from enhanced fragmentation of $HClO_4$ at higher vibrational temperatures, the presence of evolved ClO_3 was somewhat uncertain. Note that much stronger evidence was recently found for ClO_3 evolution associated with condensed-phase decomposition (rather than dissociative evaporation) in high-temperature CO_2 laser pyrolyses of pure AP; however, ClO_2 was not a major product in this system.[2]

Since ClO_2 was always a major gaseous product (except at 0.3% carbon black), and was evolved over a much longer duration than $HClO_4$ and the aforementioned "trace" of ClO_3, it must be considered a primary "quasi-stable" intermediate in the heterogeneous decomposition of $HClO_4$. Since Cl_2 and ClO were always evolved in much smaller quantities than ClO_2, and since the thermal decomposition of ClO_2 (which is rapid at 50°C and 200 mm Hg[7]) involves some production of ClO radicals and obeys the over-all stoichiometry $2\ ClO_2 \rightarrow Cl_2 + 2O_2$ under a variety of conditions,[8] ClO_2 decomposition as shown was largely incomplete under LP conditions.

A large portion of the observed HCl probably originated from heterogeneous decomposition of $HClO_4$. Indirect support for this is given by mass spectrometer results of Heath and Majer,[9] which indicate that HCl was the most abundant ion (70 eV) when $HClO_4$ was decomposed heterogeneously on a platinum filament at low pressures and temperatures ranging from "just visibly glowing" at 40 ma to "bright red" at 120 ma.

In the same $HClO_4$ decomposition experiments,[9] O_2 was the second most abundant ion, and ClO_2 was the third most abundant. Confirmation of the former result in LP of AP/metal oxide mixtures was not possible, since the O_2 evolved when metal oxides were flashed alone precluded accurate O_2-difference determinations. The latter ClO_2 finding, supported by a more recent detailed study of $HClO_4$ decompositions,[10] is felt to be an excellent indirect confirmation of the present LP results.

NO was always a major product in the AP/metal oxide systems, in contrast to its role as a minor product in ID of AP and also CO_2 laser pyrolyses of AP.[2] From the ion intensity standpoint the following inequality applied to the nitrogen-containing products in the AP/metal oxide systems: $NO \gg N_2 > N_2O > NO_2$. NO appeared to be comparatively less abundant in the AP/carbon black system than with the metal oxides, which are known to be effective NH_3 oxidation catalysts.

LP of AP Propellant System

A 15% aluminized PBAA/AP propellant was studied with the LP technique in an effort to observe products arising from heterogeneous reactions in a "real" composite system, as shown in Fig. 8. The sample was impacted repeatedly, with progressively increasing energy, using a sequence of transmission filters. Approximately 20 μm aluminum spheres were formed from the 7 μm aluminum powder, within this energy range. Thus the binder matrix attained at least 660°C. The normalized ClO_2 and NH_3 ion intensity ratios were relatively insensitive to impact energy over the range 4–10 cal/cm². The arrow (bottom left) indicates the range of 70 eV ClO_2/HCl ratios found in several LP of AP/carbon black mixtures and AP crystals resting on a solid graphite substrate. $HClO_4$ was seen in very small quantities in the PBAA series, as were O_2, Cl_2, and NO_2. From the ion intensity standpoint, the butadiene monomer appeared to be the major organic product.

LP vs ID in Various AP Systems

In order to provide a basic phenomenological comparison between LP and slower bulk decompositions of mixed AP

§ Calculated by subtracting the following 20 eV fragmentation contributions obtained under selected ID and LP conditions where the number of ClO-ion sources was minimized: $ClO/HClO_4 = 0.10$, $ClO/ClO_2 = 0.38$, and $ClO/HOCl = 0.15$.

systems at lower temperatures, additional heated-capillary ID of AP/metal oxide mixtures and AP doped with $KMnO_4$ and $CrO_4^=$ were run at low external pressure. Both ClO_2 and HOCl were observed as characteristic "heterogeneous products" in all cases.

Further considerations of a possible transition in the dominance of primary heterogeneous reactions led to the correlation in Fig. 9a. The ID of pure AP progressed downward along the arbitrarily drawn line with increasing temperatures, from 205 to 380°C, but LP of AP/carbon black was characterized by Cl_2/HCl ratios about an order of magnitude smaller.

ID of Cu 0202, Fe_2O_3, and MnO_2/AP mixtures, at the one percent addition level, are also shown in Figure 9a. Sample temperatures generally ranged from 250-300°C, and the data are displaced considerably (up and right) from ID of pure AP at the same temperature. A simple explanation of this behavior (high Cl_2/HCl ratio) is that Cl_2 originated from two sources under these ID conditions, in which the packed capillary functioned somewhat analogous to a porous bed reactor. First, Cl_2 and HCl were evolved as normal condensed-phase decomposition products of AP. Secondly, Cl_2 was probably formed by relatively slow (compared to LP) heterogeneous oxidation of HCl and step-wise decomposition of $HClO_4$ on the metal oxide catalysts; i.e., since $HClO_4$ and the intermediate ClO_2 were always observed in significant quantities during ID, some "undetected" ClO_2 likely decomposed further to Cl_2 and O_2. A similar argument might be applied to the correspondingly high NO_2/HCl ratios, recognizing that additional NO_2 could result from heterogeneous oxidation of NH_3 on the metal oxide catalysts at 250-300°C. The ID Cu 0202 results are in substantial agreement with those of Rosser, Inami, and Wise[5] in that Cl_2 and O_2 were major products.

In contrast to the ID results for metal oxide catalyst/AP mixtures, the LP results for these catalysts are clustered in the lower left region of Fig. 9a. Here, both NO_2 and Cl_2 were minor products in comparison to the primary heterogeneously produced products HCl, ClO_2,H_2O, NO, and HOCl. Catalyst additions over the range of 0.3–50% did not appear to have a significant effect on the applicability of the correlation.

Figure 9a also shows results obtained from AP containing isomorphously substituted $KMnO_4$ in 1.06 and 1.68 mole %

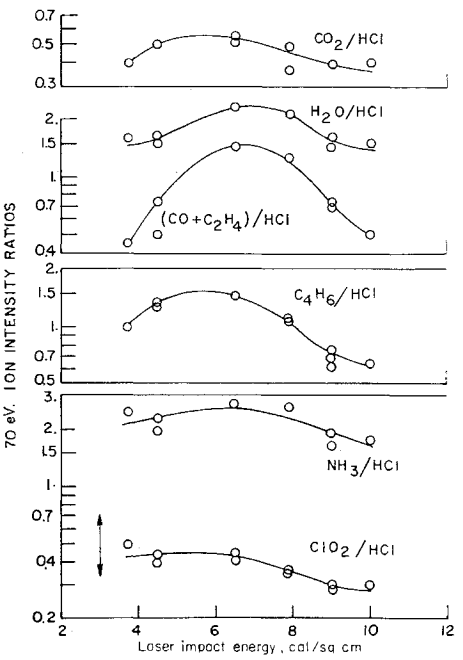

Fig. 8 Ruby laser pyrolyses of a 15 % aluminized PBAA/AP propellant.

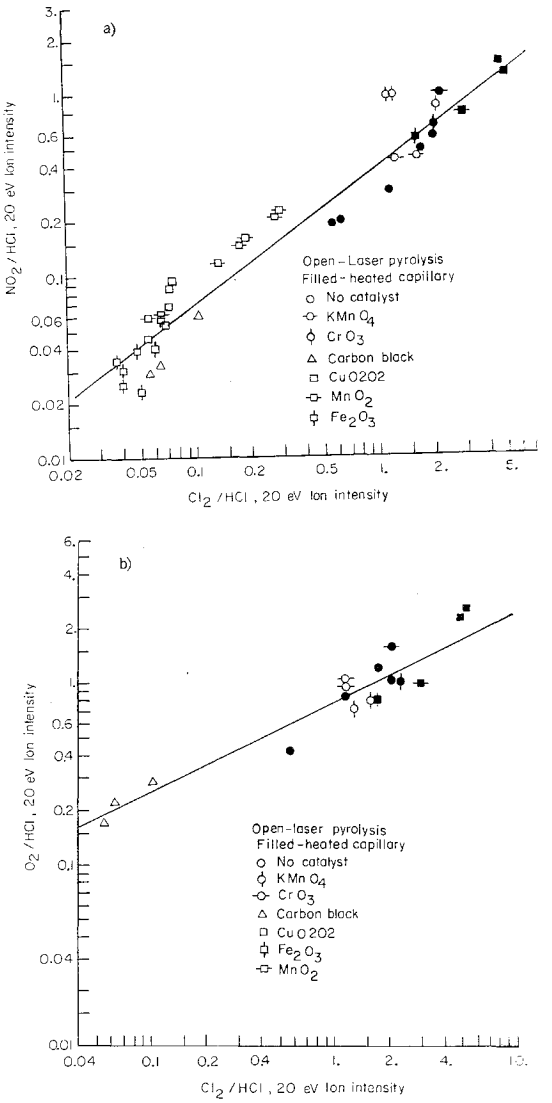

Fig. 9 Some product comparisons between ruby laser and isothermal pyrolyses of various NH_4ClO_4 systems which suggest a variable dominance of heterogeneous decomposition pathways, depending on reaction conditions.

quantities. The presumably high-temperature LP results (2–6 cal/cm²) are located in the same upper right region that characterized an ID result at 185°C. Similar findings are shown for $CrO_4^=$ (derived from solution of CrO_3) doped AP. ClO_2 was always evolved in the respective LP (and ID), but ClO_2/Cl_2 appeared to vary somewhat with impact energy and percent additive. Despite relatively high productions of Cl_2 and NO_2, the significant evolutions of ClO_2 and HOCl, and also abnormally high rates of ID were indicative of some "catalyzed behavior," which presumably involved valence changes in the Mn and Cr—containing ions.

The above results lend further, albeit diverse, support for the concept that both the site of $HClO_4$ decomposition and the temperature-time history significantly affect the decomposition chemistry. The apparent favoring of Cl_2 formation when adsorbed $HClO_4$ (or possibly a NH_3—H—ClO_4 intermediate) decomposes on a "pure" AP crystal surface seems to be in sharp contrast to heterogeneous $HClO_4$ decomposition on "catalytic" surfaces, where ClO_2 is evolved as an intermediate when the effective residence time is short.

The apparent transition of pyrolysis behavior in Fig. 9a, based on the NO_2/HCl and Cl_2/HCl ratios, was also found to apply to O_2/HCl on a limited basis; i.e., LP of AP/metal oxide mixtures were excluded since some O_2 was evolved when pure metal oxides were flash heated. These results are shown

Table 1 Product distributions obtained from LP of $^{15}NH_4ClO_4$/metal oxide mixtures; 20 eV ion intensities

	Cu 0202	Fe_2O_3	MnO_2
Wt% (estimated)	50	50	70
HCl	1.00	1.00	1.00
N_2	0.20	0.14	0.31
CO	0.2	0.19	0.2
N_2O	0.11	0.04	0.13
CO_2	0.75	0.57	0.45
NO	0.88	0.67	0.40
NO_2	0.08	0.03	0.06
ClO_2	0.72	0.31	1.65
HOCl	0.30	0.09	0.38
$NH_3 + H_2O$	15	3.3	12.3

in Fig. 9b. Further evidence indicated that N_2O/HCl also exhibited the same general trend in behavior. This was seen in isothermal decompositions of pure AP in Fig. 4, in LP of $^{15}NH_4ClO_4$/metal oxide mixtures in Table 1, and in ID of metal oxide/AP mixtures as follows. The 20 eV (N_2O + CO_2)/HCl ratios were 2.38 and 2.47 for Cu 0202, 1.04 for Fe_2O_3, and 1.15 for MnO_2; all of these indicate substantial N_2O formation after a suitable correction for CO_2 is applied.

Summary and Conclusions

Consistent evidence has indicated that in pulsed ruby laser pyrolyses (LP) of AP mixed with finely divided carbon black or metal oxide substrates, the predominant decomposition pathways involved high-temperature heterogeneous reactions. Since open sample geometries and initial pressures below 10^{-6} torr were employed, desorption was favored and gas phase reactions probably had a negligible effect on the product distributions.

The first decomposition step appeared to be proton transfer dissociation of AP into NH_3 and $HClO_4$. Both were always observed initially, but there was generally a large stoichiometric deficiency of $HClO_4$ in the gas phase. Adsorbed $HClO_4$ appeared to have undergone a rapid heterogeneous decomposition on the substrate material, wherein ClO_2 and HCl were evolved in relatively large quantities. Small quantities of ClO_3 were also detected, suggesting some HO-ClO_3 cleavage, but not in the comparatively high abundance found in CO_2 laser pyrolyses of AP.[2] Relatively little decomposition of the ClO_2 appeared to occur under LP conditions, since ClO and Cl_2 were evolved in comparatively small quantities. Chemisorbed oxygen and/or other oxygen carriers such as OH and ClO were most probably formed on the substrate simultaneously, however. These could react with the substrate, as in the case of carbon, and also abstract hydrogen from adsorbed NH_3 and its dehydrogenated fragments to form H_2O and NO, which were observed as major decomposition products; N_2, N_2O, and NO_2 were found to be minor products. HOCl was a significant and characteristic product of heterogeneous decomposition, but was generally evolved a few milliseconds after the above products were detected.

Low-pressure isothermal decompositions (ID) of AP, doped AP and AP/substrate mixtures, heated in a glass capillary up to 380°C, were also presented. Comparisons of results obtained form the two pyrolysis techniques indicated significant differences in product distribution, and hence decomposition mechanism; e.g., ClO_2 and HOCl were not products of pure AP decomposition in the present ID, or in high-temperature CO_2 laser pyrolyses.[2] Further LP vs ID comparisons, in which the Cl_2/HCl ratio varied by two orders of magnitude, provided additional evidence for a transition in pyrolysis behavior relating to the extent of heterogeneous $HClO_4$ decomposition. The site of $HClO_4$ decomposition appeared to be at least as important as temperature and effective residence time in determining the predominant chemical pathways. CO_2-laser pyrolyses[2] of pure AP, $KMnO_4$-doped AP and AP/metal oxide mixtures at heating rates between 40 and 220 cal/cm²sec fully support this conclusion.

Results on the flash pyrolysis of AP on graphite substrates, and kinetic spectroscopy of the gaseous products,[11] support the present findings of ClO_2 and NO formation as major products (in the AP/carbon black and graphite systems). The ClO_2 attained maximum concentration soon after initiation of the xenon pyrolysis flash (<20μsec), and then underwent a rapid photochemical (UV) dissociation into ClO. The NO was formed more slowly, and required more than one msec to attain maximum concentration.

The roles that various chlorine oxides play in the decomposition and combustion of AP are pivotal to our understanding. Unfortunately these compounds are difficult to observe by less direct sampling means because of their high reactivity. Mechanisms based on the probable chlorine oxides have been tentatively formulated to explain the role of $HClO_4$ vapor in ignitions of uncatalyzed and catalyzed solid propellant fuels,[12–14] and, more generally, the fate of $HClO_4$ and NH_3 during AP decomposition and combustion under a variety of experimental and practical conditions.[1,15]

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