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(U)KINETICS OF DECOMPOSITION OF AMMONIUM PERCHLORATE*+

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

KINETICS OF DECOMPOSITION OF AMMONIUM PERCHLORATE

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ABSTRACT

The decomposition of NH_4ClO_4 and of NH_4ClO_4-copper chromite mixtures has been studied by isothermal and adiabatic methods. Isothermal experiments resulted in identification of the reaction products and provided kinetic details. Adiabatic experiments provided a description of the rate of decomposition in a mathematical form adaptable to the analysis of combustion phenomena involving NH_4ClO_4. Reaction mechanisms for both uncatalyzed and catalyzed decomposition are proposed.

I. INTRODUCTION

Ammonium perchlorate (AP), a widely used oxidizer in composite propellants, is stable at room temperature but decomposes at a measurable rate at temperatures greater than about 150°C. The decomposition, an exothermic process, probably influences the combustion behavior of composite propellants based on AP. Determination of the nature and strength of that influence requires detailed kinetic knowledge of the reaction. Past studies[1-4] have revealed the principal kinetic features of the decomposition of pure AP. Up to a temperature of about 325°C, the region of low-temperature decomposition, reaction is autocatalytic but does not proceed to completion; only about 30 percent of the sample decomposes. At temperatures greater than about 375°C, the region of high temperature decomposition, the reaction ceases to be autocatalytic and decomposition proceeds to completion. The high temperature reaction probably involves the gaseous dissociation products NH_3 and $HClO_4$.

Kinetic studies of AP decomposition have been usually limited to analysis of the rate data in terms of nucleus formation, nucleus growth, and nucleus overlap. Quantitative chemical examination of the products of decomposition has been incomplete.[1,5] In the absence of a mass balance, the results obtained by Bircumshaw and Newman[1] indicated that the major products of the low temperature reaction are: N_2, O_2, ClO_2, N_2O, Cl_2, HCl, and $HClO_4$. However, the identity of $HClO_4$ was assumed and identification of ClO_2 as a product was based on analysis by an iodometric method that is subject to serious error if the products include acidic components with volatility comparable to that of Cl_2.

The reaction mechanism usually proposed for the decomposition involves electron transfer from ClO_4^- to NH_4^+ with the formation of either a molecular complex[6] NH_4ClO_4 or the radicals[2] $NH_4\cdot$ and $ClO_4\cdot$ and subsequent reactions to the final products. The observed activation energy is assumed to reflect primarily the energy requirement associated with the electron-transfer step. Various additives promote or catalyze the decomposition, including CuO[7], Cr_2O_3[8,9], MnO_2[9,10], and Fe_2O_3[11]. Catalysis is attributed to an increase in the rate of electron transfer at points of contact between catalyst and AP particles. This view of the reaction kinetics, while plausible, is highly speculative and cannot be regarded as established.

The above considerations indicate that the available information is inadequate for the analysis of combustion phenomena involving NH_4ClO_4. Consequently, the present study of the decomposition of NH_4ClO_4 was carried out with three major aims: (1) to obtain reaction rate data for analysis of combustion phenomena involving NH_4ClO_4; (2) to establish the product spectrum; and (3) to deduce, if possible, the reaction mechanisms for both the uncatalyzed decomposition and the catalyzed decomposition. The catalyst of particular interest is copper chromite, a burning rate promoter used in composite propellents based on AP. Because combustion phenomena involve high reaction temperatures, the study was limited to temperatures greater than 240°C, the temperature at which NH_4ClO_4 undergoes a crystal transition from the orthorhombic to the cubic form.

In this study two types of experiments were performed: The decomposition of loose powders of AP with and without catalysts at approximately constant temperature was examined in order to obtain data on the chemical product distribution; and the rates of decomposition of pressed powders of AP and additives under adiabatic conditions were measured. These data provide valuable information on the heat release rates as a function of temperature in a form suitable for the analysis of combustion phenomena.

II. EXPERIMENTAL

A. Studies at Constant Temperature

Powder samples for kinetic study were usually prepared from hand ground crystalline NH_4ClO_4 (Matheson-Coleman-Bell, Reagent Grade) that has been recrystallized from water.* Sample mass was between 1 and 2 grams in order to obtain adequate quantities of reaction products for chemical analysis. Three powdered catalysts were used: (1) copper chromite (CC), nominal composition $CuO \cdot Cr_2O_3$ (Harshaw Cu 0202), (2) cobalt oxide (J. T. Baker Co., Reagent Grade, 71.2 wt% Co $\sim Co_2O_3$), and (3) Fe_3O_4 (Fisher Scientific Co., purified).

The experiments were carried out in a flow system (Fig. 1) which allowed continuous measurement of the rate of decomposition and permitted control of the composition of the gas in contact with the sample. The components of the apparatus included a rotameter for measuring the flow rate of the carrier gas (helium), a reaction cell and sample, a cold trap cooled by liquid N_2, a chemical trap filled with NaOH pellets, a thermal conductivity detector to monitor the over-all rate of reaction, and a gas chromatography system to determine the O_2 and N_2 concentrations in the effluent from the monitoring detector. Accessory devices included a vaporizer for introducing H_2O into the carrier gas, and flow controls for introducing NH_3 into the carrier gas.

Reaction cells, fabricated from Pyrex sealing tubes (25 mm o.d.), were provided with glass rupture discs to prevent explosion in the event of sample ignition. The gas chromatography apparatus comprised a sampling

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* Recrystallization was eventually discontinued when it became apparent that material not visibly tinged with yellow behaved kinetically like recrystallized material.

valve, an eight-foot column of 5 Å molecular sieve to separate O_2 from N_2, and a thermal conductivity detector.

Most experiments were carried out in the following way. A reaction cell of known weight containing a weighed sample was inserted into the flow line. The desired flow rate of helium, 150 cc/min was established and the system flushed with helium before insertion of the reaction cell into a salt bath heated to the desired reaction temperature. About five minutes were required to heat the sample and cell to the bath temperature. During reaction the output of the thermal conductivity detector used to monitor the over-all rate reaction was recorded on a strip chart. Periodically, a sample of the effluent was withdrawn and the O_2 and N_2 content measured by means of the gas chromatography apparatus. The output of the gas chromatography detector was also recorded on a strip chart. On completion of an experiment, the cell and contents were reweighed to determine weight loss and the extent of decomposition.

In the case of pure NH_4ClO_4, experiments of the kind described were done at bath temperatures between 250 and 325°C. Experiments with AP/catalyst mixtures were limited to temperatures less than 300°C to avoid sample ignition. At 250°C, experiments were terminated prior to completion of reaction. At higher temperatures the reaction was permitted to proceed essentially to completion.

The primary experimental results derived from our measurements were: total weight loss and rates of formation of O_2 (r_{O_2}) and N_2 (r_{N_2}). The mass loss of the sample due to decomposition was obtained from the total weight loss. A correction based on equilibrium vapor pressure data[12] was applied for mass loss owing to sublimation. The chart record of the gas chromatography detector output yields rates of production of O_2 (r_{O_2}) and of N_2 (r_{N_2}) at intervals during reaction. Because only a few data points could be obtained prior to the time of maximum reaction rate, the output of the monitoring detector, $\sim (r_{O_2} + r_{N_2})$, was used when necessary as an interpolation guide.

Typical experimental results for the decomposition of pure AP at 275°C are shown in Fig. 2. Time is measured from the onset of detectable reaction. As observed by others, the decomposition is autocatalytic. Because of sample self-heating, mathematical analysis of the form of the rate curve was not attempted. While both r_{O_2} and r_{N_2} vary with time in a similar manner, the ratio r_{N_2}/r_{O_2} is not constant. The ratio falls precipitiously from an unknown initial value to a minimum at about the time of maximum reaction rate. The subsequent increase is much slower than the initial decrease. As shown in Fig. 3., the decomposition of an AP/CC powder mixture is apparently also autocatalytic. The maximum rate of reaction, however, is greater than that of the same amount of AP and the variation of r_{N_2}/r_{O_2} with time is more extreme. The presence of CC also results in an increased but still incomplete degree of decomposition.

Visual inspection of AP/CC samples during reaction revealed a change in catalyst color from black to brown early in the reaction. The ability of CC to catalyze decomposition appeared to be lost in the process, as evidenced by the limited degree of reaction and by the fact that a reacted sample of AP/CC can be raised to temperatures greater than 300°C without ignition. The brown form of CC, unlike the black form, is slightly soluble in H_2O, and very soluble in strong NH_3 water. The water extract, yellow in color, gives an orange precipitate with $AgNO_3$ and presumably contains $CrO_4^{=}$. The NH_3 extract, green in color, presumably contains Cr^{+3}. The black residue remaining after treatment with NH_3 water is presumably unaltered CC. In the one case in which the amount of unaltered CC was measured 71 wt% of the original material was recovered. These observations indicate that during reaction some of the catalyst chromium is oxidized by an unknown product of reaction to $CrO_4^{=}$ and that catalyst effectiveness decreases as a result of the oxidation.

The reaction responsible for the oxidation of the catalyst appears to involve a chemical species which is the product only of the catalyzed decomposition, as demonstrated by the following qualitative experiment. A porous alumina sphere coated with CC powder when suspended about 1 cm above a bed of decomposing AP did not change color. It may be concluded that the catalyzed, but not the uncatalyzed reaction, produces a strongly oxidizing product, such as a chlorine oxide, able to oxidize Cr^{III} to Cr^{VI}.

The sensitivity of the rate of decomposition of pure AP to water vapor and NH_3 at ~ 275°C was determined. It was found that a pressure of NH_3 of ~ 2 torr completely suppressed decomposition for the hour of observation. Water vapor also inhibited decomposition but to a lesser degree. A pressure of ~ 500 torr of H_2O reduced the maximum rate of decomposition by about a factor of three and also reduced the amount of decomposition to about 15 percent in a time that would otherwise have resulted in ~ 25 percent decomposition.

Ammonia (at a partial pressure of about 2 torr) does not inhibit the decomposition of AP/CC (5 wt%) at ~ 275°C as evidenced by the fact that reaction continues at a nearly constant rate. Visual inspection of the sample revealed that the CC retains its original color and that the reduction in catalytic activity associated with oxidation of the CC particles has been prevented. Moreover, the reactivity of an AP/oxidized CC sample at ~ 275°C can be restored by exposure of the bed to NH_3 ($p \sim$ 2 torr) and reduction of the oxidized Cr^{VI} to Cr^{III}. The oxidized form is easily reducible by NH_3 but in the absence of added NH_3 the pressure of NH_3 within the sample is insufficient to prevent oxidation of the CC. The equilibrium pressure of NH_3 at 275°C, for instance, is only 0.06 torr. Presumably, at higher temperatures, higher pressures of NH_3 from dissociation would prevent loss of catalytic activity or would restore activity previously lost.

The product yields of O_2 and N_2 can be determined by graphical integration of rate data. However, determination of other products requires analysis of the material condensed in the liquid-nitrogen cold trap immediately downstream of the reaction cell. These trapped products were separated into two fractions by vapor distillation into a helium carrier gas at the temperature of dry ice-acetone (-80°C). The volatile products were recondensed in a trap cooled by liquid N_2 and subsequently transferred to a conventional gas-handling system for analysis by reaction with Hg. The nonvolatile products were dissolved in water and analyzed by aqueous methods for Cl^-, NO_3^- (in some cases), and total acid. The degree of separation of the product fractions was acceptable but not complete.

Analysis of the volatile fraction by reaction with Hg[13] yields unambiguous results only if Cl_2, N_2O, and NOCl are present. Cl_2 is completely absorbed, N_2O is inert, and NOCl yields NO. The procedure [13] consisted essentially of measuring the quantity of gas before reaction with Hg, $Cl_2 + N_2O + NOCl$, the quantity of gas after reaction with Hg, $N_2O + NO$, and the quantity of gas volatile at -160°C,* NO. The yield of each of the components can then be readily deduced. It was found necessary to transfer the condensed volatile fraction into the gas handling system by vacuum distillation at dry ice-acetone temperature in order to prevent entry of small, but detectable quantities of H_2O and acid, presumably HCl, into the system.

The volatile product fraction usually consisted primarily of Cl_2 and N_2O. Some NOCl was present as indicated by detectable orange color in the condensed products when the NO yield exceeded about 0.03 mole percent. However, intermittent condensation of the volatile products during the course of reaction with Hg revealed a sequence of color changes from yellow (Cl_2) or orange (NOCl) through green to blue to white; the ultimate yield of NO must therefore reflect the presence of NOCl and either NO_2 or a material that reacts with Hg to give NO_2 as an intermediate, such as HNO_3 or NO_xCl ($x = 2,3$). Because the volatility of NO_2 and HNO_3 at the transpiration temperature (-80°C) is low ($p \sim 0.01$ torr), their presence in the volatile fraction in significant quantities is unlikely. Both NO_2Cl and NO_3Cl are substantially more volatile and would, if formed, appear in the volatile fraction. Consequently, the cited color changes are attributed to the presence of a small quantity of either NO_2Cl or NO_3Cl. These observations apply both to the decomposition of pure AP and to the catalyzed decomposition.

Major quantities of NO_2 and ClO_2 must not be present in the volatile fraction if unequivocal results are to be obtained. NO_2 reacts to form (1/2)NO, while ClO_2 is absorbed.[1] The separation by volatility insures the absence of NO_2 but not of ClO_2. However, solid ClO_2 is orange in

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* isopentane slush

color and its presence in significant amount in the trap would be detectable by eye. Orange color was only detectable when NOCl, also an orange solid, was a product. Because ClO_2 might be formed as an intermediate, an AP sample was decomposed under vacuum at ~ 275°C, a temperature at which ClO_2 is reported to be a major product.[1] The products were condensed on a nearby cold finger cooled by liquid N_2. The only visible color was that of solid Cl_2. Consequently, we concluded that ClO_2, if formed as an intermediate, decomposes with great rapidity, and is not an observable stable product.

Analysis of the nonvolatile residue remaining in the product trap after removal of the volatile products was done in a way similar to that used by Bircumshaw and Newman.[1] The residue was first dissolved in 100 cc H_2O. The resulting solution is known to contain substantial quantities of acid and Cl^-. The bulk of the HCl despite its high volatility at -80°C remains in the nonvolatile fraction, presumably in hydrated form. Small amounts of Cl_2 and ClO^- were also present but not in sufficient quantity to interfere seriously with our analytical procedures. Nitrite ion was not detectable by a procedure adapted from Ref. 14. The yield of acid was obtained by titration of a 25 cc aliquot with 0.1 M NaOH to a phenolphthalein endpoint, and the yield of Cl^- by titration of the neutralized solution with 0.1 M $AgNO_3$ to a Ag_2CrO_4 endpoint. The yield of unidentified acid is obtained by difference. Identification of the unknown acid, believed to be HNO_3, for samples of AP decomposed at 275°C in the presence of CC up to 2.7 wt% was made by means of an analytic procedure[15] for NO_3^- adapted to milligram quantities of NO_3^- (5 cc aliquot of original solution). The method involves the reduction of NO_3^- to NO by Fe^{++} in hot, strong H_2SO_4. Under these conditions perchlorate ion is not affected. The method is accurate to ± 1% when tested on synthetic solutions of NO_3^-. The apparent error when used with real product solutions was ~ ± 10%. The loss in accuracy is due, at least in part, to a Cl^- induced sensitivity of Fe^{++} to air oxidation. Within the cited error the NO_3^- yield by Fe^{++} reduction agreed with the HNO_3 yield by acid-Cl^- titration. Identification of the unknown acid as HNO_3 is assumed to hold for all our experiments with one exception. At 325°C, the decomposition of pure AP results in high yields of HNO_3 (titration analysis), high recovery of N, and low recovery of Cl. These three facts suggest that at this temperature $HClO_4$ is in fact a product of decomposition with a yield comparable to that of HNO_3. The reported yield of HNO_3 is then the sum of the two. The appearance of $HClO_4$ as a probable reaction product at 325°C is assumed to be related to the erratic kinetic behavior at that temperature.

The nonvolatile reaction products are reported in the form found by analysis--HCl and HNO_3. Conceivably, NO_2Cl, if present, on hydrolysis would ultimately form the observed species HCl and HNO_3. However, the individual acid yields while comparable were not equal. The solution contained only traces of ClO^-, and no detectable NO_2^-. So we assume that HCl and HNO_3 are real reaction products, not derived products.

The analytic results obtained by the methods described are shown in Table I. The generally good recovery of N and Cl indicate that the reaction products are those reported, except as noted in Table I or in the text. A comparison of our product yields for the uncatalyzed decomposition of AP at ~ 275°C with those reported in Ref. 1 is shown in Table II. The comparison shows comparable yields in the case of O_2, N_2, and Cl_2. However, our measured yield of N_2O is smaller and our yield of acid is greater than those reported in Ref. 1. It is likely that these differences are due to the presence of HCl in the volatile fractions analyzed by Bircumshaw and Newman. If the HCl is not removed and the volatiles are analyzed by reaction with Hg, the HCl will be reported as N_2O. If the volatile fraction is analyzed by reaction with a neutral solution of I^-, the oxidation of I^- will take place in weakly acidic solution. Some I^- will be oxidized to IO_3^- by Cl_2[16], and it will be concluded that ClO_2 is a reaction product. The presence of NOCl or NO_2Cl in the volatile fraction would lead to a similar result. The reported yields of ClO_2 may have originated in this way.

As indicated earlier, the decomposition catalyzed by CC is limited to the early stages of reaction and disappears as CC is oxidized by a product of the catalyzed decomposition. The over-all product yields can, therefore, be regarded as the sum of two reactions, one associated with the catalyzed reaction and another with the uncatalyzed reaction. The relative contribution of each can be estimated at 275°C from the data in Table I if it is assumed that the degree of decomposition due to the uncatalyzed reaction is constant and equal to the value measured in the absence of CC (26.5 to 26.8 wt%). The amount of decomposition associated with the catalyzed decomposition is then the difference between the measured value and the value in the absence of CC. In this manner it is found that the measured yields of N_2O correspond to the amount expected for the uncatalyzed decomposition. Consequently, it may be concluded that N_2O is not a product of the catalyzed decomposition. The yield of HCl is even less than that expected if HCl is a product only of the uncatalyzed reaction. The deficiency is revealed by a decrease in the ratio HCl/N_2O with the addition of CC. At both 250°C and 275°C the ratio HCl/N_2O has a minimum at about 1.8% CC. The presence of CC has apparently resulted in a decrease in the yield of HCl or in partial destruction of HCl by secondary reactions. The remaining product yields indicate that O_2, N_2, Cl_2, HNO_3, and NO (as NO_xCl) are products of both the uncatalyzed and the catalyzed reactions. The approximate increments in relative product yield* associated with catalysis by 3.9 wt% CC at 275°C are: HCl, $N_2O \approx 0$, $Cl_2 \approx 0.49$, $N_2 \approx 0.24$, $HNO_3 \approx 0.32$, $O_2 \approx 0.55$, and NO (as NO_xCl) $\geqq 0.04$.

Although CC was the decomposition catalyst of principal interest, a few experiments were carried out using Fe_3O_4/AP and cobalt oxide/AP mixtures. As shown in Table I, Fe_3O_4 caused no major changes in product distribution or in the extent of decomposition. A slight degree of catalytic activity is suggested by minor increases in the yields of O_2, N_2, and NO. The effective catalyst may be Fe_2O_3, the form into which Fe_3O_4 is converted during the early stages of reaction. Like the other catalysts, cobalt oxide is chemically attacked during decomposition, with a color change from dark gray to light gray. The implied change in catalyst

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* Difference between number of moles of product formed relative to total moles of AP decomposed in presence of catalyst and that due to the uncatalyzed reaction.

composition does not destroy catalytic effectiveness as it does in the case of CC.

Unlike either Fe_3O_4 or CC, cobalt oxide causes complete decomposition of the sample (see Table I) and noticeably reduces the amount of sublimation.

Catalysis by cobalt oxide also causes large changes in product yields compared to those for pure AP. The high yield of NO and obvious orange color in the condensed products reveal that NOCl is a major product. A faint blue ring in the entry section of the cold trap reveals that N_2O_3 is a trace product. Finally, the poor recovery of both N and Cl indicates that NO_2Cl or NO_3Cl is also a major product but only a portion of the N is recovered as NO after reaction with Hg.

Qualitative identification of the unknown product in the volatile fraction as NO_2Cl can be made if it is assumed that H is present in the products only as acid and H_2O. The yield of H_2O can then be deduced from the yield of acid; the quantity of missing O from the yields of O-containing species. The ratio of missing O/N is found to be 2. Inasmuch as partial conversion of NO_xCl to NO on reaction with Hg would tend to increase the ratio of missing O/N, the deduced ratio of 2 suggests that the missing volatile product is NO_2Cl and that reaction with Hg results primarily in conversion to solids, although some conversion to NO_2 and then to NO must occur in order to account for the color changes during analysis. By this view, the yield of NO includes the yield of NOCl and a fraction α of the yield of NO_2Cl. The measured yield of Cl_2 is, therefore, high by an amount that depends on $1-\alpha$.

Kinetic studies[17, 18] of the decomposition of NO_2Cl to NO_2 and Cl_2 indicate that some decomposition will occur during passage of the products through the hot reaction cell (transit time 2 to 3 sec). The presence of trace quantities of N_2O_3 in the trapped products also indicates that decomposition has occurred. Because the volatility of $NO_2(N_2O_4)$ at $-80^{\circ}C$ is low, any NO_2 so produced will remain in the nonvolatile fraction and will not be detected unless specifically sought. The NO_2, as well as its precursor NO_2Cl, satisfies the mass-balance criterion of missing O/N = 2.

B. Adiabatic Studies

Because of sample self-heating associated with the exothermicity of AP decomposition, measurements of the product spectrum do not provide a precise description of the rate of reaction in a form suited to the analysis of combustion and ignition phenomena. Consequently, an adiabatic method[19] was employed for kinetic studies in which all the heat released by reaction is retained by the sample and the rate of temperature rise dT/dt is given by

$$\frac{dT}{dt} = \frac{\dot{q}}{c\rho} \qquad (1)$$

where $\dot{q}$ is the rate of heat release per unit volume, c is the specific heat of the material, and ρ is the density. Measurement of dT/dt as a function of T(°K) is equivalent to measuring the rate of reaction as a function of temperature. The details of the apparatus have been described.[19]

Samples for adiabatic study, wafers 30 mm in diameter and $\sim$ [illegible] mm thick, were prepared by pressing $\sim$ 5 gm of NH_4ClO_4/additive mixtures at $\sim$ 25,000 psi. This procedure results in a hard, durable wafer with a porosity of about 4-5% in the case of pure AP. In each wafer a small radial hole near the center of the sample was drilled to accommodate a glass-sheathed chromel-alumel thermocouple (3 mil lead, $\sim$ 10 mil bead).

P[illegible] NH_4ClO_4 for use in pressing samples was prepared by ball milling [illegible] fractions. Sieved material was then mixed lightly with the desired amou[illegible] powdered additive and the mixture lightly ground with mortar and [illegible] to deagglomerate. The compositions used are listed in Table III[illegible]

Adiabatic experimen[illegible]arried out using the apparatus shown schematically in Fig. 4. The[illegible]le is clamped between the heater plates and held in position by sprin[illegible]ed bolts. The heating elements were made from two lengths of nic[illegible]/ire appropriately coiled and connected in parallel. Equality of he[illegible]of the two plates is obtained by suitable adjustment of the rela[illegible]sistance of the two wires. During an experiment, the sample ther[illegible]e e.m.f. is recorded on a strip-chart recorder while the e.m.f. difference between the block and sample thermocouple is usually displayed on the indicating meter of a microvolt amplifier.

In a typical experiment the block assembly is placed in a small furnace held at a temperature of about 250°C. The temperature of the sample is raised, in a period of about ten minutes, to a temperature a few degrees greater than 240°C, by supplying electrical power to the resistance heaters. The power is then reduced in order to establish within the assembly a constant temperature in the range 240-250°C. Several minutes were required for this process. As the sample begins to decompose, the temperature of the sample rises above that of the plates. Consequently, electrical power is supplied to the heater plates by hand control of a variable transformer at a rate sufficient to maintain a uniform temperature in the plates and sample. As the reaction rate increases, the rate of power supply is correspondingly increased. Under these conditions, the temperature of the sample increases at a rate that depends only on the rate of decomposition. The sample temperature is recorded on a strip-chart recorder until the experiment is terminated either because the sample ignites or explodes or because the rate of temperature rise exceeds about 100°C/min, the highest rate at which our system is able to supply the power required to maintain adiabatic conditions within the sample.

All samples eventually ignite or explode, although at different temperatures, depending on the amount and nature of the additive. Other studies[20] indicated that ignition or explosion results from a gas phase reaction within the pores of the sample. Necessarily, decomposition of the sample is the source of the gaseous reactants.

The experimental data for a given experiment consist of a chart record of sample temperature T(°K) against time, and the physical properties of the sample. Each chart record of T against time was converted to a tabulation of dT/dt against T by graphical methods. Analysis of the adiabatic rate data was made by a Prout-Tompkins equation when the reaction was autocatalytic, and by a simple Arrhenius equation when the reaction was not autocatalytic. The theoretical aspects of this analysis have been described in our earlier study of the adiabatic decomposition of pure NH_4ClO_4.[19]

In our recently completed arc image study[20] of propellant ignitability, the principal additive was copper chromite. Consequently, we devoted considerable time and effort to studying the adiabatic decompositions of AP/CC mixtures. Three concentrations of CC were used for each particle-size range of AP (see Table III). In general, the data were less reproducible than similar data for pure AP, partly because of the difficulty in establishing isothermal starting conditions, and partly because the samples fragment during decomposition. However, a progressive change in the character of the reaction with increasing CC content is noticeable. Decomposition of pure AP and of a mixture containing 1 wt% CC is clearly autocatalytic. Decomposition of samples containing 3 wt% CC is erratic, a behavior we attribute to a nonreproducible degree of mixing of the reactants. Mixtures containing 5 wt% CC were apparently not sensitive to the thoroughness of mixing and as shown in Figure 5 the rate of decomposition is Arrhenius in form. For the range 1 to 100 deg/min, our data can be described by the expressions shown in Table IV. All AP/CC samples ignited or exploded at temperatures greater than 300°C. Ignition temperature decreased with increasing CC content.

A similar progressive change in the course of decomposition with additive content was noted with AP/Cr_2O_3 samples. Decomposition of the $97\frac{1}{2}/2\frac{1}{2}$ mixture is noticeably autocatalytic. The samples ignite or explode at about 305°C. Decomposition of 95/5 mixtures may involve a slight degree of autocatalysis. Because the samples ignite at about 280°C, the total temperature rise prior to ignition is small ($< 30°C$) and autocatalysis is difficult to detect. The rate of decomposition for the range 2 to 100 deg/min is shown in Table IV.

The decomposition of three carbon-containing mixtures (Norit A) was also studied: AP/C ($97\frac{1}{2}/2\frac{1}{2}$), AP/CC/C ($95/2\frac{1}{2}/2\frac{1}{2}$), and $AP/Cr_2O_3/C$ ($95/2\frac{1}{2}/2\frac{1}{2}$). Experimental records for the ternary mixtures were not usable. Ignition occurred at about 260°C, a temperature corresponding to a dT/dt of only a few degrees/min immediately prior to ignition.

Adequate records were obtained with the AP/C mixture. Extensive fragmentation of the samples limited the data to the range 1 to 30 deg/min. In that range the rate of decomposition is that shown in Table IV. The samples ignited but ignition temperatures could not be determined because of thermal disturbances associated with pellet fragmentation. Similar but less reproducible results were obtained on substitution of Cabot carbon for Norit A.

Hematite is commonly used as a burning rate promoter. Consequently, we studied the decomposition of two AP/Fe_2O_3 mixtures, each containing 5 wt% Fe_2O_3. Ignition temperatures were high ($T_{ig} > 300°C$). Results for the range $1 < dT/dt < 100$ are shown in Table IV.

Of the remaining compositions, AP/ZnO, AP/CuO, AP/ferrocene, and AP/cobalt oxide, only data for AP/CuO were analyzable. The decomposition was found to be autocatalytic and ignition occurred at temperatures between 280 and 300°C. The decomposition of the AP/ZnO mixture is also autocatalytic but thermal disturbances beginning near the melting point of $ZnCl_2$ (262°C), prevented us from obtaining analyzable records. Decomposition records for the AP/ferrocene mixture were erratic. Because of the high vapor pressure of ferrocene, a portion of the additive escapes from the sample, and another portion decomposes or reacts with NH_4ClO_4 with the probable formation of carbon and Fe_2O_3, both active materials. The samples ignite at temperatures > 300°C. Decomposition records for AP/cobalt oxide were not analyzable because decomposition began too quickly and it was not possible to establish an isothermal initial condition.

It is apparent that a variety of additives alter the course of decomposition of NH_4ClO_4 and cause ignition or explosion of the material. There is, however, no common type of behavior. There does appear to be a tendency for sufficient concentration of additive to eliminate the autocatalytic feature of the decomposition of pure NH_4ClO_4. In such cases, the rate of decomposition follows Arrhenius-type behavior.

III. DISCUSSION

A. The Decomposition of Pure AP

At reaction temperatures of 240-300°C, the major nitrogen-containing products resulting from the decomposition of NH_4ClO_4 are nitrous oxide, nitric acid, and N_2. The production of N_2O and HNO_3 suggests that the decomposition of NH_4ClO_4 may include some of the features of ammonium nitrate (AN) decomposition, for which nitrous oxide is a major product and HNO_3 an intermediate.[21] The decomposition of AN, a reaction dependent on the dissociation products NH_3 and HNO_3, is strongly promoted by HNO_3, strongly inhibited by NH_3, and weakly inhibited by H_2O. Analogous effects in the case of AP decomposition are: (1) the length of the induction periods that precedes decomposition is shortened by trace quantities of adsorbed $HClO_4$[1]; (2) NH_3 suppresses decomposition; and (3) H_2O inhibits the reaction, but to a lesser degree than NH_3.

In view of the cited facts, we propose that the decomposition of NH_4ClO_4 includes the following reactions:

$$NH_4^+ + ClO_4^- \rightleftarrows \underset{\underset{NH_{3(g)}}{\downarrow\uparrow}}{NH_{3(s)}} + \underset{\underset{HClO_{4(g)}}{\downarrow\uparrow}}{HClO_{4(s)}} \tag{2}$$

$$2\,HClO_{4(s)} \rightleftarrows ClO_3^+ + ClO_4^- + H_2O_{(s)} \tag{3}$$

$$ClO_3^+ + NH_{3(s)} \rightarrow \text{intermediates} + \text{products} \tag{4}$$

Reactions 2 and 3 are the initial chemical reactions associated with nucleation. Inhibition by NH_3 is attributed to the reversal of reaction 2 and inhibition by H_2O to the reversal of reaction 3. Reaction 3 must be the critical step because decomposition ceases after about 30 percent while dissociative evaporation to $NH_{3(g)}$ and $HClO_{4(g)}$ continues.[12] Presumably, reaction 3 only occurs at favorable locations, such as defect sites, within or on the AP crystals.

The nature of the product spectrum indicates that the over-all reaction will involve oxidation states of nitrogen from -III (NH_3) to +V (NO_3^-, HNO_3, NO_2^+). Similarly, oxidation states of chlorine from -I (Cl^-, HCl) to +VII (ClO_3^+, $HClO_4$, ClO_4^-) will be involved. Because of its complexity, the reaction mechanism cannot be completely specified. The formation of N_2O is attributed to:

$$NO_2^+ + NH_3 \rightarrow N_2O + H_3O^+ \tag{5}$$

and of HNO_3 and of HCl to:

$$NH_4^+, H_3O^+ + NO_3^- \rightarrow NH_3, H_2O + HNO_3 \tag{6}$$

$$NH_4^+, H_3O^+ + Cl^- \rightarrow NH_3, H_2O + HCl \tag{7}$$

The N^{V} species are presumably kinetically coupled in the same manner as they are in the AN decomposition.[21]

$$NO_2^+ + H_2O + NO_3^- \rightleftarrows 2HNO_3 \tag{8}$$

The proposed partial mechanism is consistent with the fact that nucleation involves a large activation energy[19] (40 to 50 kcal) because of the endothermicity of reaction 2 in the forward direction. The activation energy associated with nucleus growth[19,22] (~ 17 kcal) is much less than that associated with nucleus formation, and this difference suggests that the rate of nucleus growth is not dependent on the dissociative reaction, reaction 2, for $HClO_{4(s)}$. The growth reactions must, therefore, include reactions that regenerate ClO_3^+ or $HClO_4$. If $HClO_4$ is the regenerated intermediate, then the activation energy associated with nucleus growth will depend to a great extent on the activation energy of reaction 3 in the forward direction.

Of the remaining N-containing products (NOCl and N_2), NOCl need not be a product of the solid decomposition. The yield is small and may result from gas reactions involving the gaseous dissociation products NH_3 and $HClO_4$. The yield of N_2 is too great to be explainable in this manner. It is presumably a product of the solid decomposition. If NOCl (and NO_2Cl) are excluded because of their probable origin in gas reactions, the spectrum of Cl-products is simple and includes only HCl and Cl_2.

At reaction temperatures less than 300°C, the decomposition of NH_4ClO_4 ceases after about 25 to 30 percent of the material has decomposed. To account for this unique feature of the reaction, it is usually assumed that decomposition is limited to disordered regions of the crystal, the residue remaining after decomposition consisting of small AP crystallites $(d \sim 3\mu)^6$ with few crystal imperfections. The dissociative sublimation of NH_4ClO_4 can occur even after decomposition has ceased.[12] Reactivity can be restored by exposure of the cooled residue to solvent vapors, H_2O in particular, presumably because of lattice reorganization.[1] No reasonable alternative to this qualitative explanation for the limited degree of reaction has been proposed.

The sudden appearance of $HClO_4$ as a reaction product and the reduced but variable extent of decomposition at a reaction temperature of 325°C (see Table I) suggests that desorption of $HClO_{4(s)}$ can be competitive with reaction 3. It seems likely that such a desorption is involved in both the autocatalytic behavior and the limited degree of decomposition. By analogy to the decomposition of AN, the accumulation of adsorbed $HClO_4$ in the early stages of reaction will be reflected in an accelerating rate of reaction. If it is supposed that the reactivity of strained NH_4ClO_4 is indeed greater than that of unstrained NH_4ClO_4, consumption of the former would eventually result in a situation in which desorption of $HClO_4$ proceeds more rapidly than does reaction 3. Loss of $HClO_4$ would then accentuate the decrease in reaction rate resulting from consumption of reactive material. The ability of water at a high concentration to reduce the extent of decomposition indicates that desorption can be induced by increasing the rate of reaction 3 from right to left. A high reaction temperature, $T \geq 325°C$, also appears to favor desorption of $HClO_4$ and quenching of the decomposition.

B. The Decomposition of NH_4ClO_4 Catalyzed by Copper Chromite

A number of features of the decomposition catalyzed by CC indicate that the mechanism differs profoundly from that of the uncatalyzed decomposition. These are:

1. N_2O and HCl are not products of the catalyzed decomposition.
2. The catalyzed reaction produces a short-lived oxidizer able to oxidize the Cr^{III} in CC to $CrO_4^{=}$.
3. The gaseous reaction products are under some circumstances explosive.
4. Ammonia, an inhibitor of the uncatalyzed decomposition, can at sufficiently high concentration prevent the oxidation of Cr^{III} to $CrO_4^{=}$ and the associated decrease in catalytic activity.

The cited observations suggest a different mechanism for the catalyzed reaction. For example, it may involve electron transfer and the formation of free radicals, such as:

$$NH_4^+ + ClO_4^- \xrightarrow{CC} NH_4^{\cdot} + ClO_4^{\cdot} \qquad (9)^*$$

Here the electronic properties of the catalyst (CC) may play an important role. Decomposition of $NH_4^{\cdot}$ and $ClO_4^{\cdot}$ would be expected to result in the products NH_3, O_2, ClO_2, ClO_3, and H_2. The chlorine oxides may then decompose to Cl_2 and O_2, react with NH_3 and H_2, attack the CC with the formation of $CrO_4^{=}$, or accumulate within or near the decomposing NH_4ClO_4. In such a mixture Cl_2 would readily attack NH_3 and H_2 with the production of N_2 and HCl. Nitrogen, but not HCl, is indeed a major product of the catalyzed reaction. We attribute the absence of HCl in the final products to a rapid oxidation of HCl by chlorine oxides to water and Cl_2 in reactions analogous to the oxidation[24] of HCl by NO_2. It is noteworthy that decomposition catalyzed by cobalt oxide yields very little HCl (see Table I). Inasmuch as some of the HCl produced by the uncatalyzed decomposition can also be oxidized by chlorine oxides, there will be a tendency for the yield ratio HCl/N_2O to be less than the value associated with the uncatalyzed reaction. The data in Table I reveal such a decrease.

---

* Although this type of reaction has been proposed for the decomposition of pure AP, it is unlikely to apply to both the normal reaction (N_2O is a product) and to the catalyzed reaction (N_2O is not a product).

All the chlorine oxides are extremely reactive substances able to oxidize NH_3. The products NOCl, NO_2Cl, and HNO_3 presumably originate in this way. The high yield of HNO_3 is surprising but plausible inasmuch as N_2O_4 can also oxidize NH_3 to HNO_3 in the gas phase.[25] Traces of NH_3 might escape attack by either Cl_2 or chlorine oxides but would not have been detected as a product by our analytical methods.

The probable formation of NH_3 as an intermediate in the catalyzed reaction will tend to reduce both the rate of the normal decomposition and the rate of sublimation. In the case of AP/CC powders, we were unable to verify the reduction in evaporation rate because catalysis is limited to the early stages of reaction. We did observe such a reduction with decomposing AP/cobalt oxide powders. Others have observed that the decomposition of AP/MnO_2 powder proceeds without an accompanying sublimation.[1] A reduction in sublimation rate is most likely at temperatures less than 300°C because the normal dissociation pressure is low and, as a result, a low concentration of NH_3 can be effective.

A variety of substances that catalyze the decomposition of AP (Fe_2O_3, MnO_2, Cr_2O_3, C, cobalt oxide, CuO) probably do so in the same manner as copper chromite. Because the catalyst may also participate in the reactions that follow, the original formation of $NH_4^{\cdot}$ and $ClO_4^{\cdot}$, the details of the over-all reaction will vary with the nature of the catalyst.

The catalyzed decomposition of NH_4ClO_4 involves the formation of potentially explosive intermediates. Ignition, when it occurs, is attributed to a gas phase reaction involving the accumulated intermediates and products. The occurrence of ignition of an AP/CC (or other additive) sample will depend on: (1) the degree of contact between the additive particles and the AP particles; (2) the amount of catalyst; (3) the activity of the catalyst; and (4) the conditions within or near the sample. In the specific case of our arc image study of ignitability,[20] the sample is in contact with a cold atmosphere and ignition of the gases evolved by the solid will depend on the thermal conductivity of the atmosphere and on the rate of movement of the reactants, by convection or diffusion, away from the hot surface of the sample and into the colder atmosphere.

On the other hand, when a pressed wafer is in contact with an atmosphere at substantially the same temperature as the wafer, ignition can occur within the pores of the sample and give rise to a violent explosion.[20] Ignition of a loose powder, however, will be sudden but not explosive and will only result in deflagration of the material.

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Table 1

THE PRODUCTS OF THE DECOMPOSITION OF NH_4ClO_4

Temp. (°C)	Catalyst	Cat. Conc. (Wt. %)	Yield (mole/mole)							Recovery		
			O_2	N_2	N_2O	Cl_2	HNO_3	HCl	NO*	N (Atom %)	Cl (Atom %)	Wt. % Decomp.
250	--	0	0.61	0.055	0.37	0.39	0.14	0.15	0.006	98.7	93.4	19.8
250	CC	1.79	.54	.064	.32	.45	.15	.091	.019	93.8	100.2	29.4
250	CC	3.99	.54	.078	.30	.43	.15	.11	.026	93.6	100.0	31.0
275	--	0	.55	.051	.36	.39	.15	.17	.011	97.8	96.0	26.8
275	--	0	.50	.047	.35	.39	.19	.16	.019	99.1	94.9	26.5
275	CC	1.03	.56	.073	.29	.41	.17	.12	.014	91.7	94.7	35.3
275	CC	1.79	.47	.080	.28	.44	.20	.095	.023	94.9	99.4	36.5
275	CC	2.73	.47	.090	.26	.44	.20	.10	.026	92.9	100.9	36.2
275	CC	3.90	.53	.12	.25	.42	.22	.10	.024	97.6	96.8	38.7
300	--	0	.53	.052	.37	.37	.12	.21	.018	99.0	96.2	22.6
325	--	0	.56	.064	.34	.29	.22†	.28	.035	106	90	10.6
325	--	0	.58	.061	.39	.28	.28†	.28	.029	121	84	16.6
275	CoOx	2.8	.24	.030	.14	.41	.097	.020	.18‡	62	84	100
275	Fe_3O_4	2.0	.66	.084	.34	.40	.15	.13	.023	103.2	93.7	27.0

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* After Hg analysis

† Believed to be HNO_3 and $HClO_4$ in comparable amounts

‡ Believed to be derived from both NOCl and NO_2Cl

Table 2

PRODUCT YIELDS FROM THE DECOMPOSITION OF NH_4ClO_4: T ~ 275°C

	Yield (mole %)	
Product	Present Study	Ref. 1
O_2	0.50-0.55	0.56
N_2	.050	.063
N_2O	.36	.45
Cl_2	.39	.40*
Acid	.33	.14
NO†	01	0

---

* Reported as Cl_2 + ClO_2 by B & N because Cl_2 and ClO_2 are not distinguishible by Hg analysis.

† After Hg analysis.

Table 3

COMPOSITIONS USED IN ADIABATIC STUDIES*

NH_4ClO_4	Additive (% by wt)	Additive Source
43- 61μ 88-124μ	CC (1,3,5)	Harshaw
88-124μ	Cr_2O_3 (2½,5)	Matheson, Coleman, and Bell (Reagent powder)
88-124μ	CuO (5)	J. T. Baker Co.
43- 61μ 88-124μ	Fe_2O_3 (5)	Matheson, Coleman, and Bell
88-124μ	ZnO (3)	Mallinckrodt (Analytical Reagent)
88-124μ	Ferrocene (1)	Matheson, Coleman, and Bell
88-124μ	C (2½)	1. Norit A 2. Cabot-Sterling VR
88-124μ	C/CC (2½/2½)	
88-124μ	C/Cr_2O_3(2½/2½)	
88-124μ	Cobalt Oxide (5)	J. T. Baker Company

---

* C = carbon, CC = copper chromite.

Table 4

SUMMARIZED RESULTS OF ADIABATIC STUDIES*

Additive	Wt Percent	Particle Size Range (microns)	dT/dt (deg/min)
Copper chromite	5	88-124	$10^{18.3} \exp(-43,000/RT)$
Copper chromite	5	43-61	$10^{19.5} \exp(-46,000/RT)$
Chromic oxide	5	88-124	$10^{27.6} \exp(-68,000/RT)$
Carbon	2.5	88-124	$10^{21.7} \exp(-52,500/RT)$
Ferric oxide	5	88-124	$10^{14.7} \exp(-34,300/RT)$
Ferric oxide	5	43-61	$10^{15.6} \exp(-36,600/RT)$

---

* Average of 4 to 8 experiments.

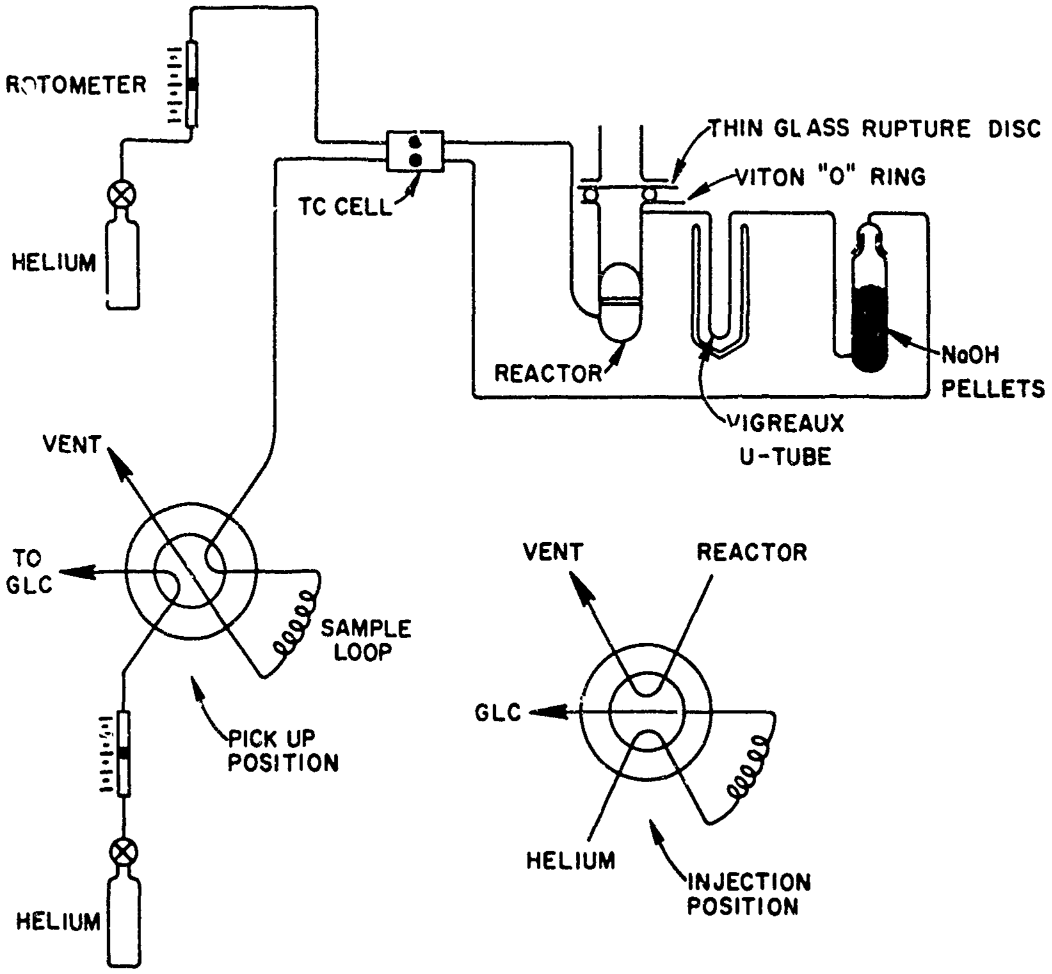

FIG. 1 APPARATUS USED IN CONSTANT TEMPERATURE EXPERIMENTS

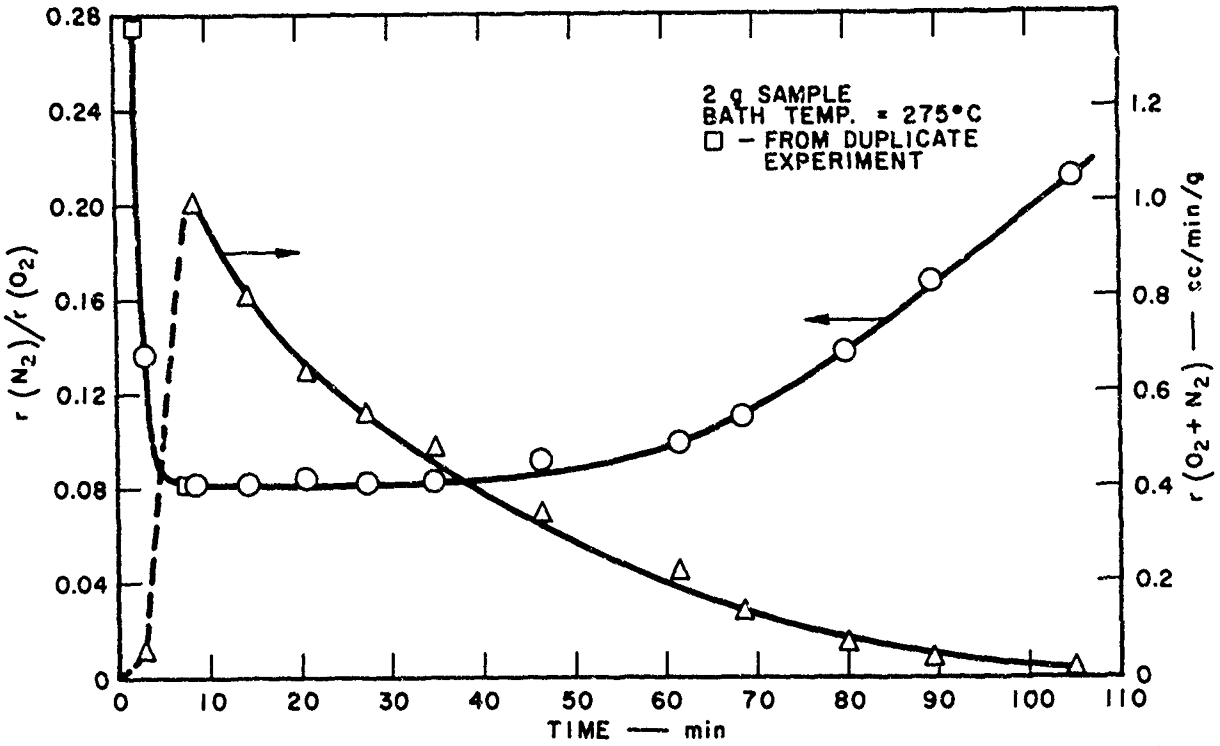

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FIG. 2 THE RATE OF DECOMPOSITION OF PURE NH_4ClO_4

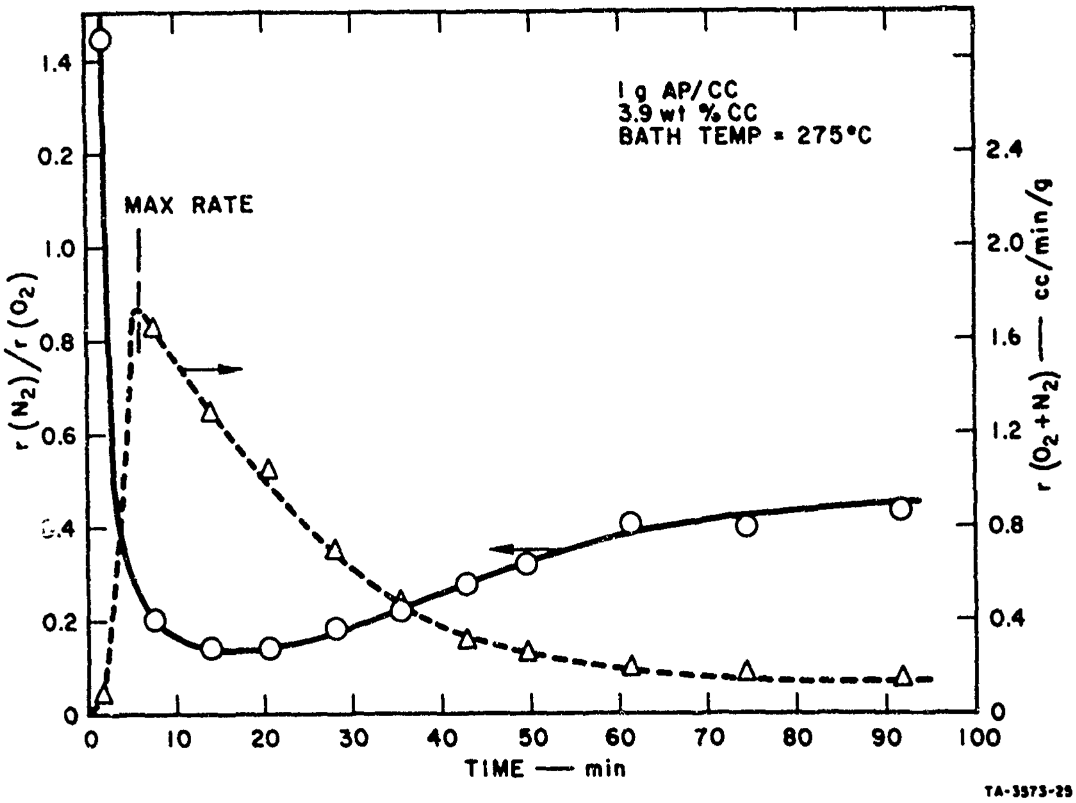

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FIG. 3 THE RATE OF DECOMPOSITION OF NH_4ClO_4 CATALYZED BY COPPER CHROMITE

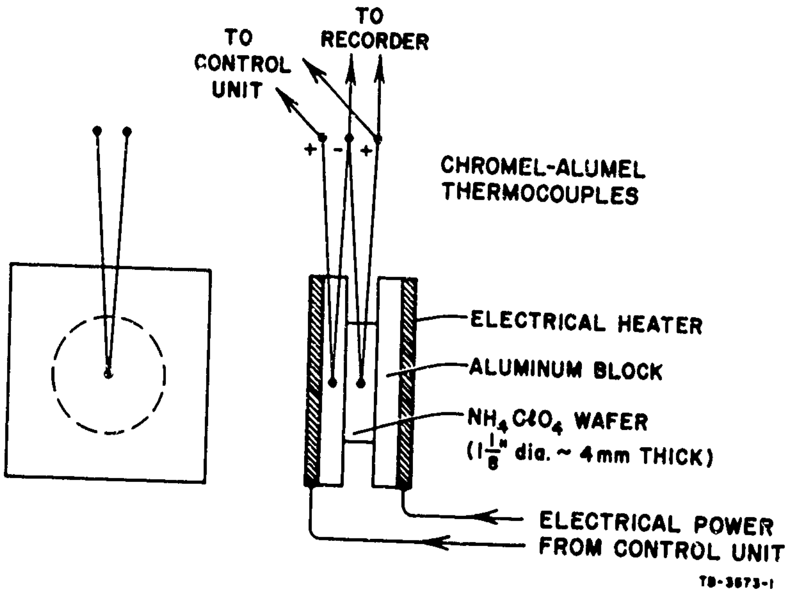

FIG. 4 ADIABATIC APPARATUS

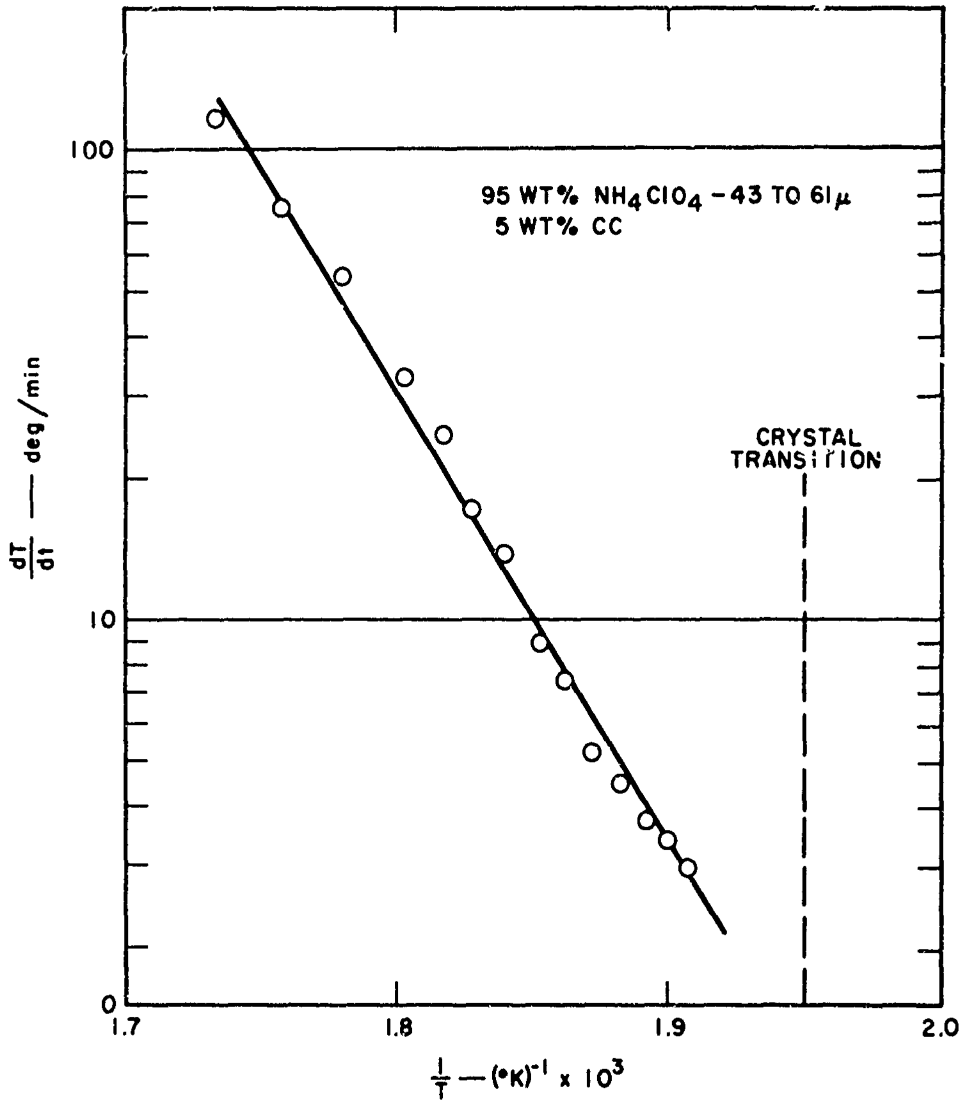

FIG. 5 THE ADIABATIC RATE OF DECOMPOSITION OF AN NH_4ClO_4/CC WAFER

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The decomposition of NH_4ClO_4 and of NH_4ClO_4-copper chromite mixtures has been studied by isothermal and adiabatic methods. Isothermal experiments resulted in identification of the reaction products and provided kinetic details. Adiabatic experiments provided a description of the rate of decomposition in a mathematical form adaptable to the analysis of combustion phenomena involving NH_4ClO_4. Reaction mechanisms for both uncatalyzed and catalyzed decomposition are proposed.

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