(U) KINETICS OF DECOMPOSITION OF AMMONIUM PERCHLORATE**

W. A. Rosser, S. H. Inami, and H. Wise
Stanford Research Institute
Menlo Park, California

September 29, 1966

Reproduction of this report in whole or in part is permitted for any purpose of the United States Government.

This work was sponsored by the Office of Naval Research, Department of the Navy, under Contract Nonr-3415(00), Authority NR 002-507/10-13-64.
DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>II. EXPERIMENTAL</td>
<td>4</td>
</tr>
<tr>
<td>A. Studies at Constant Temperature</td>
<td>4</td>
</tr>
<tr>
<td>B. Adiabatic Studies</td>
<td>13</td>
</tr>
<tr>
<td>III. DISCUSSION</td>
<td>17</td>
</tr>
<tr>
<td>A. The Decomposition of Pure AP</td>
<td>17</td>
</tr>
<tr>
<td>B. The Decomposition of $\text{NH}_4\text{ClO}_4$ Catalyzed by Copper Chromite</td>
<td>19</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>23</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Products of the Decomposition of NH₄ClO₄</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Product Yield Comparison</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Compositions Used in Adiabatic Studies</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Summarized Results of Adiabatic Studies</td>
<td>28</td>
</tr>
</tbody>
</table>

LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Apparatus Used for Constant Temperature Experiment</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>The Rate of Decomposition of Pure NH₄ClO₄</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>The Rate of Decomposition of NH₄ClO₄ Catalyzed by Copper Chromite</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>Schematic Diagram of the Adiabatic Apparatus</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>The Adiabatic Decomposition of NH₄ClO₄/CC Wafer</td>
<td>33</td>
</tr>
</tbody>
</table>
ABSTRACT

The decomposition of \( \text{NH}_4\text{ClO}_4 \) and of \( \text{NH}_4\text{ClO}_4 \)-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 \( \text{NH}_4\text{ClO}_4 \). 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\textsuperscript{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 \( \text{NH}_3 \) and \( \text{HClO}_4 \).

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.\textsuperscript{1,5} In the absence of a mass balance, the results obtained by Bircumshaw and Newman\textsuperscript{1} indicated that the major products of the low temperature reaction are: \( \text{N}_2 \), \( \text{O}_2 \), \( \text{ClO}_2 \), \( \text{N}_2\text{O} \), \( \text{Cl}_2 \), \( \text{HCl} \), and \( \text{HClO}_4 \). However, the identity of \( \text{HClO}_4 \) was assumed and identification of \( \text{ClO}_2 \) 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 \( \text{Cl}_2 \).

The reaction mechanism usually proposed for the decomposition involves electron transfer from \( \text{ClO}_4^- \) to \( \text{NH}_4^+ \) with the formation of either a molecular complex\textsuperscript{6} \( \text{NH}_4\text{ClO}_4 \) or the radicals\textsuperscript{2} \( \text{NH}_4^* \) and \( \text{ClO}_4^- \) 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\textsuperscript{7}, Cr\textsubscript{2}O\textsubscript{3}\textsuperscript{8,9}, MnO\textsubscript{2}\textsuperscript{9,10}, and Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{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\textsubscript{4}ClO\textsubscript{4}. Consequently, the present study of the decomposition of NH\textsubscript{4}ClO\textsubscript{4} was carried out with three major aims: (1) to obtain reaction rate data for analysis of combustion phenomena involving NH\textsubscript{4}ClO\textsubscript{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\textdegreeC, the temperature at which NH\textsubscript{4}ClO\textsubscript{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 \( \text{NH}_4\text{ClO}_4 \) (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 \( \text{CuO} \cdot \text{Cr}_2\text{O}_3 \) (Harshaw Cu 0202), (2) cobalt oxide (J. T. Baker Co., Reagent Grade, 71.2 wt% Co ~ Co_2O_3), and (3) \( \text{Fe}_3\text{O}_4 \) (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 \( \text{N}_2 \), 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 \( \text{O}_2 \) and \( \text{N}_2 \) concentrations in the effluent from the monitoring detector. Accessory devices included a vaporizer for introducing \( \text{H}_2\text{O} \) into the carrier gas, and flow controls for introducing \( \text{NH}_3 \) 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

\(^*\) 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 A molecular sieve to separate O₂ from N₂, 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 O₂ and N₂ 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 NH₄ClO₄, 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 O₂ \( (r_{O₂}) \) and N₂ \( (r_{N₂}) \). The mass loss of the sample due to decomposition was obtained from the total weight loss. A correction based on equilibrium vapor pressure data was applied for mass loss owing to sublimation. The chart record of the gas chromatography detector output yields rates of production of O₂ \( (r_{O₂}) \) and of N₂ \( (r_{N₂}) \) 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, \(~(r_{O₂} + r_{N₂})~\), 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 precipitously 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$_2$O, 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$_4^{2-}$. 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$_4^{2-}$ 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 $\sim 275^\circ$C was determined. It was found that a pressure of NH$_3$ of $\sim 2$ torr completely suppressed decomposition for the hour of observation. Water vapor also inhibited decomposition but to a lesser degree. A pressure of $\sim 500$ torr of H$_2$O 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 $\sim 25$ percent decomposition.

Ammonia (at a partial pressure of about 2 torr) does not inhibit the decomposition of AP/CC (5 wt%) at $\sim 275^\circ$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 $\sim 275^\circ$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$^\circ$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 ($\sim 80^\circ$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\textsuperscript{13} yields unambiguous results only if Cl\textsubscript{2}, N\textsubscript{2}O, and NOCl are present. Cl\textsubscript{2} is completely absorbed, N\textsubscript{2}O is inert, and NOCl yields NO. The procedure \textsuperscript{13} consisted essentially of measuring the quantity of gas before reaction with Hg, Cl\textsubscript{2} + N\textsubscript{2}O + NOCl, the quantity of gas after reaction with Hg, N\textsubscript{2}O + NO, and the quantity of gas volatile at -160\textdegree C\textsuperscript{*} 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 all, but detectable quantities of H\textsubscript{2}O and acid, presumably HCl, into the system.

The volatile product fraction usually consisted primarily of Cl\textsubscript{2} and N\textsubscript{2}O. 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\textsubscript{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\textsubscript{2} or a material that reacts with Hg to give NO\textsubscript{2} as an intermediate, such as HNO\textsubscript{3} or NO\textsubscript{x}Cl \textsubscript{1} (x = 2,3). Because the volatility of NO\textsubscript{2} and HNO\textsubscript{3} at the transpiration temperature (-80\textdegree C) is low (p \sim 0.01 torr), their presence in the volatile fraction in significant quantities is unlikely. Both NO\textsubscript{2}Cl and NO\textsubscript{3}Cl 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\textsubscript{2}Cl or NO\textsubscript{3}Cl. These observations apply both to the decomposition of pure AP and to the catalyzed decomposition.

Major quantities of NO\textsubscript{2} and ClO\textsubscript{2} must not be present in the volatile fraction if unequivocal results are to be obtained. NO\textsubscript{2} reacts to form (1/2)NO\textsubscript{3}, while ClO\textsubscript{2} is absorbed.\textsuperscript{1} The separation by volatility insures the absence of NO\textsubscript{2} but not of ClO\textsubscript{2}. However, solid ClO\textsubscript{2} is orange in

\textsuperscript{*} 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 ClO₂ might be formed as an intermediate, an AP sample was decomposed under vacuum at ~275°C, a temperature at which ClO₂ is reported to be a major product. The products were condensed on a nearby cold finger cooled by liquid N₂. The only visible color was that of solid Cl₂. Consequently, we concluded that ClO₂, 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. The residue was first dissolved in 100 cc H₂O. 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 Cl₂ 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 AgNO₃ to a Ag₂CrO₄ endpoint. The yield of unidentified acid is obtained by difference. Identification of the unknown acid, believed to be HNO₃, 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 adapted to milligram quantities of NO₃⁻ (5 cc aliquot of original solution). The method involves the reduction of NO₃⁻ to NO by Fe²⁺ in hot, strong H₂SO₄. Under these conditions perchlorate ion is not affected. The method is accurate to ±1% when tested on synthetic solutions of NO₃⁻. 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 Fe²⁺ to air oxidation. Within the cited error the NO₃⁻ yield by Fe²⁺ reduction agreed with the HNO₃ yield by acid-Cl⁻ titration. Identification of the unknown acid as HNO₃ is assumed to hold for all our experiments with one exception. At 325°C, the decomposition of pure AP results in
high yields of HNO₃ (titration analysis), high recovery of N, and low recovery of Cl. These three facts suggest that at this temperature HClO₄ is in fact a product of decomposition with a yield comparable to that of HNO₃. The reported yield of HNO₃ is then the sum of the two. The appearance of HClO₄ 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 HNO₃. Conceivably, NO₂Cl, if present, on hydrolysis would ultimately form the observed species HCl and HNO₃. However, the individual acid yields while comparable were not equal. The solution contained only traces of ClO⁻, and no detectable NO₂⁻. So we assume that HCl and HNO₃ 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 O₂, N₂, and Cl₂. However, our measured yield of N₂O 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 N₂O. 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 IO₃⁻ by Cl₂¹⁶, and it will be concluded that ClO₂ is a reaction product. The presence of NOCl or NO₂Cl in the volatile fraction would lead to a similar result. The reported yields of ClO₂ 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 N₂O correspond to the amount expected for the uncatalyzed decomposition. Consequently, it may be concluded that N₂O 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/N₂O with the addition of CC. At both 250°C and 275°C the ratio HCl/N₂O 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 O₂, N₂, Cl₂, HNO₃, and NO (as NOₓCl) 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, N₂O = 0, Cl₂ = 0.49, N₂ = 0.24, HNO₃ = 0.32, O₂ = 0.55, and NO (as NOₓCl) ≥ 0.04.

Although CC was the decomposition catalyst of principal interest, a few experiments were carried out using Fe₃O₄/AP and cobalt oxide/AP mixtures. As shown in Table I, Fe₃O₄ 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 O₂, N₂, and NO. The effective catalyst may be Fe₂O₃, the form into which Fe₃O₄ 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

---

* 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 Fe₃O₄ 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 N₂O₃ is a trace product. Finally, the poor recovery of both N and Cl indicates that NO₂Cl or NO₃Cl 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 NO₂Cl can be made if it is assumed that H is present in the products only as acid and H₂O. The yield of H₂O 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 NOCl 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 NO₂Cl and that reaction with Hg results primarily in conversion to solids, although some conversion to NO₂ 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 NO₂Cl. The measured yield of Cl₂ is, therefore, high by an amount that depends on 1-α.

Kinetic studies of the decomposition of NO₂Cl to NO₂ and Cl₂ 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 N₂O₃ in the trapped products also indicates that decomposition has occurred. Because the volatility of NO₂(N₂O₄) at -80°C is low, any NO₂ so produced will remain in the nonvolatile fraction and will not be detected unless specifically sought. The NO₂, as well as its precursor NO₂Cl, 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 was employed for kinetic studies in which all the heat released by reaction is retained by the sample and the rate of temperature rise \( \frac{dT}{dt} \) is given by

\[
\frac{dT}{dt} = \frac{\dot{q}}{cp}
\]

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

Samples for adiabatic study, wafers 30 mm in diameter and ~1 mm thick, were prepared by pressing ~5 gm of \( \text{NH}_4\text{ClO}_4 \)/additive mixtures at ~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, ~10 mil bead).

Prepared \( \text{NH}_4\text{ClO}_4 \) for use in pressing samples was prepared by ball milling into \( 250 \) to 400 fractions. Sieved material was then mixed lightly with the desired amount of powdered additive and the mixture lightly ground with mortar and pestle to deagglomerate. The compositions used are listed in Table III.

Adiabatic experiments were carried out using the apparatus shown schematically in Fig. 4. The sample is clamped between the heater plates and held in position by spring-loaded bolts. The heating elements were made from two lengths of nichrome wire appropriately coiled and connected in parallel. Equality of heating of the two plates is obtained by suitable adjustment of the relative resistance of the two wires. During an experiment, the sample thermoe.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 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$_4$ClO$_4$.\textsuperscript{19}

In our recently completed arc image study\textsuperscript{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$_2$O$_3$ samples. Decomposition of the 97\%/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\%/2\%), AP/CC/C (95/2\%/2\%), and AP/Cr$_2$O$_3$/C (95/2\%/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$_2$O$_3$ mixtures, each containing 5 wt% Fe$_2$O$_3$. Ignition temperatures were high (T$_{ig}$ > 300°C). Results for the range $1 < \text{dT/dt} < 100$ 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$_4$ClO$_4$ with the probable formation of carbon and Fe$_2$O$_3$, 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$_4$ClO$_4$ 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$_4$ClO$_4$. 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 NH₄ClO₄ are nitrous oxide, nitric acid, and N₂. The production of N₂O and HNO₃ suggests that the decomposition of NH₄ClO₄ may include some of the features of ammonium nitrate (AN) decomposition, for which nitrous oxide is a major product and HNO₃ an intermediate.²¹ The decomposition of AN, a reaction dependent on the dissociation products NH₃ and HNO₃, is strongly promoted by HNO₃, strongly inhibited by NH₃, and weakly inhibited by H₂O. 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 HClO₄; (2) NH₃ suppresses decomposition; and (3) H₂O inhibits the reaction, but to a lesser degree than NH₃.

In view of the cited facts, we propose that the decomposition of NH₄ClO₄ includes the following reactions:

\[
\text{NH}_4^+ + \text{ClO}_4^- \rightarrow \text{NH}_3(g) + \text{HClO}_4(g) \quad \text{(2)}
\]

\[
2 \text{HClO}_4(s) \rightarrow \text{ClO}_4^+ + \text{ClO}_4^- + \text{H}_2\text{O}(s) \quad \text{(3)}
\]

\[
\text{ClO}_3^+ + \text{NH}_3(g) \rightarrow \text{intermediates} + \text{products} \quad \text{(4)}
\]

Reactions 2 and 3 are the initial chemical reactions associated with nucleation. Inhibition by NH₃ is attributed to the reversal of reaction 2 and inhibition by H₂O to the reversal of reaction 3. Reaction 3 must be the critical step because decomposition ceases after about 30 percent while dissociative evaporation to NH₃(g) and HClO₄(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 (NH₃) to +V (NO₃⁻, HNO₃, NO₂⁺). Similarly, oxidation states of chlorine from -I (Cl⁻, HCl) to +VII (ClO₃⁺, HClO₄, ClO₄⁻) will be involved. Because of its complexity, the reaction mechanism cannot be completely specified. The formation of N₂O is attributed to:

\[ \text{NO}_2^+ + \text{NH}_3 \rightarrow \text{N}_2\text{O} + \text{H}_3\text{O}^+ \]  
(5)

and of HNO₃ and of HCl to:

\[ \text{NH}_4^+ + \text{H}_3\text{O}^+ + \text{NO}_3^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{HNO}_3 \]  
(6)

\[ \text{NH}_4^+ + \text{H}_3\text{O}^+ + \text{Cl}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{HCl} \]  
(7)

The N⁺ species are presumably kinetically coupled in the same manner as they are in the AN decomposition.²¹

\[ \text{NO}_2^+ + \text{H}_2\text{O} + \text{NO}_3^- \rightarrow 2\text{HNO}_3 \]  
(8)

The proposed partial mechanism is consistent with the fact that nucleation involves a large activation energy¹⁹ (40 to 50 kcal) because of the endothermicity of reaction 2 in the forward direction. The activation energy associated with nucleus growth¹⁹,²² (∼ 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 HClO₄(s). The growth reactions must, therefore, include reactions that regenerate ClO₃⁺ or HClO₄. If HClO₄ 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 N₂), 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 NH₃ and HClO₄. The yield of N₂ is too great to be explainable in this manner. It is presumably a product of the solid decomposition. If NOCl (and NO₂Cl) are excluded because of their probable origin in gas reactions, the spectrum of Cl-products is simple and includes only HCl and Cl₂.
At reaction temperatures less than 300°C, the decomposition of NH₄ClO₄ 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 ~ 3μ)⁹ with few crystal imperfections. The dissociative sublimation of NH₄ClO₄ can occur even after decomposition has ceased.¹² Reactivity can be restored by exposure of the cooled residue to solvent vapors, H₂O 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 HClO₄ 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 HClO₄(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 HClO₄ in the early stages of reaction will be reflected in an accelerating rate of reaction. If it is supposed that the reactivity of strained NH₄ClO₄ is indeed greater than that of unstrained NH₄ClO₄, consumption of the former would eventually result in a situation in which desorption of HClO₄ proceeds more rapidly than does reaction 3. Loss of HClO₄ 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 ≥ 325°C, also appears to favor desorption of HClO₄ and quenching of the decomposition.

B. The Decomposition of NH₄ClO₄ 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$_2$O 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$_4^{2-}$.

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$_4^{2-}$ 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:

$$\text{NH}_4^+ + \text{ClO}_4^- \rightarrow \text{CC} \rightarrow \text{NH}_4^+ + \text{ClO}_4^-$$  \hspace{1cm} (9)\text{)*}

Here the electronic properties of the catalyst (CC) may play an important role. Decomposition of NH$_4^+$ and ClO$_4^-$ 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$_4^{2-}$, or accumulate within or near the decomposing NH$_4$ClO$_4$. 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$_2$O 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$_2$O is a product) and to the catalyzed reaction (N$_2$O is not a product).
All the chlorine oxides are extremely reactive substances able to oxidize NH₃. The products NOCl, NO₂Cl, and HNO₃ presumably originate in this way. The high yield of HNO₃ is surprising but plausible inasmuch as N₂O₄ can also oxidize NH₃ to HNO₃ in the gas phase. Traces of NH₃ might escape attack by either Cl₂ or chlorine oxides but would not have been detected as a product by our analytical methods.

The probable formation of NH₃ 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/MnO₂ powder proceeds without an accompanying sublimation. 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 NH₃ can be effective.

A variety of substances that catalyze the decomposition of AP (Fe₂O₃, MnO₂, Cr₂O₃, 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 NH₄⁺ and ClO₄⁻, the details of the over-all reaction will vary with the nature of the catalyst.

The catalyzed decomposition of NH₄ClO₄ 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, 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.\textsuperscript{20} Ignition of a loose powder, however, will be sudden but not explosive and will only result in deflagration of the material.
REFERENCES


**Table 1**

**THE PRODUCTS OF THE DECOMPOSITION OF NH4ClO4**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Catalyst</th>
<th>Cat. Conc. (Wt. %)</th>
<th>Yield (mole/mole)</th>
<th>Recovery</th>
<th>Wt. % Decomp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O₂</td>
<td>N₂</td>
<td>N₂O</td>
</tr>
<tr>
<td>250</td>
<td>--</td>
<td>0</td>
<td>0.61</td>
<td>0.055</td>
<td>0.37</td>
</tr>
<tr>
<td>250</td>
<td>CC</td>
<td>1.79</td>
<td>0.54</td>
<td>0.064</td>
<td>0.32</td>
</tr>
<tr>
<td>250</td>
<td>CC</td>
<td>3.99</td>
<td>0.54</td>
<td>0.078</td>
<td>0.30</td>
</tr>
<tr>
<td>275</td>
<td>--</td>
<td>0</td>
<td>0.55</td>
<td>0.051</td>
<td>0.36</td>
</tr>
<tr>
<td>275</td>
<td>--</td>
<td>0</td>
<td>0.50</td>
<td>0.047</td>
<td>0.35</td>
</tr>
<tr>
<td>275</td>
<td>CC</td>
<td>1.03</td>
<td>0.56</td>
<td>0.073</td>
<td>0.29</td>
</tr>
<tr>
<td>275</td>
<td>CC</td>
<td>1.79</td>
<td>0.47</td>
<td>0.080</td>
<td>0.28</td>
</tr>
<tr>
<td>275</td>
<td>CC</td>
<td>2.73</td>
<td>0.47</td>
<td>0.090</td>
<td>0.26</td>
</tr>
<tr>
<td>275</td>
<td>CC</td>
<td>3.90</td>
<td>0.53</td>
<td>0.12</td>
<td>0.25</td>
</tr>
<tr>
<td>300</td>
<td>--</td>
<td>0</td>
<td>0.53</td>
<td>0.052</td>
<td>0.37</td>
</tr>
<tr>
<td>325</td>
<td>--</td>
<td>0</td>
<td>0.56</td>
<td>0.064</td>
<td>0.34</td>
</tr>
<tr>
<td>325</td>
<td>--</td>
<td>0</td>
<td>0.58</td>
<td>0.061</td>
<td>0.39</td>
</tr>
<tr>
<td>275</td>
<td>CoOx</td>
<td>2.8</td>
<td>0.24</td>
<td>0.030</td>
<td>0.14</td>
</tr>
<tr>
<td>275</td>
<td>Fe₃O₄</td>
<td>2.0</td>
<td>0.66</td>
<td>0.084</td>
<td>0.34</td>
</tr>
</tbody>
</table>

* After Hg analysis
† Believed to be HNO₃ and HClO₄ in comparable amounts
‡ Believed to be derived from both NOCl and NO₂Cl
Table 2

PRODUCT YIELDS FROM THE DECOMPOSITION OF NH₄ClO₄: T ~ 275°C

<table>
<thead>
<tr>
<th>Product</th>
<th>Present Study</th>
<th>Ref. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.50-0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>N₂</td>
<td>.050</td>
<td>.063</td>
</tr>
<tr>
<td>N₂O</td>
<td>.36</td>
<td>.45</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.39</td>
<td>.40*</td>
</tr>
<tr>
<td>Acid</td>
<td>.33</td>
<td>.14</td>
</tr>
<tr>
<td>NO†</td>
<td>01</td>
<td>0</td>
</tr>
</tbody>
</table>

* Reported as Cl₂ + ClO₂ by B & N because Cl₂ and ClO₂ are not distinguishable by Hg analysis.
† After Hg analysis.
### Table 3

**COMPOSITIONS USED IN ADIABATIC STUDIES**

<table>
<thead>
<tr>
<th>NH$_4$ClO$_4$ Additive</th>
<th>Additive (% by wt)</th>
<th>Additive Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>43- 61µ 88-124µ</td>
<td>CC (1,3,5)</td>
<td>Harshaw</td>
</tr>
<tr>
<td>88-124µ</td>
<td>Cr$_2$O$_3$ (21),5</td>
<td>Matheson, Coleman, and Bell (Reagent powder)</td>
</tr>
<tr>
<td>88-124µ</td>
<td>CuO (5)</td>
<td>J. T. Baker Co.</td>
</tr>
<tr>
<td>43- 61µ 88-124µ</td>
<td>Fe$_2$O$_3$ (5)</td>
<td>Matheson, Coleman, and Bell</td>
</tr>
<tr>
<td>88-124µ</td>
<td>ZnO (3)</td>
<td>Mallinckrodt (Analytical Reagent)</td>
</tr>
<tr>
<td>88-124µ</td>
<td>Ferrocene (1)</td>
<td>Matheson, Coleman, and Bell</td>
</tr>
<tr>
<td>88-124µ</td>
<td>C (2/2)</td>
<td>1. Norit A 2. Cabot-Sterling VR</td>
</tr>
<tr>
<td>88-124µ</td>
<td>C/CC (2/2/2)</td>
<td></td>
</tr>
<tr>
<td>88-124µ</td>
<td>C/Cr$_2$O$_3$ (2/2/2)</td>
<td></td>
</tr>
<tr>
<td>88-124µ</td>
<td>Cobalt Oxide (5)</td>
<td>J. T. Baker Company</td>
</tr>
</tbody>
</table>

* C = carbon, CC = copper chromite.
### Table 4

**SUMMARIZED RESULTS OF ADIABATIC STUDIES**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Wt Percent</th>
<th>Particle Size Range (microns)</th>
<th>(\frac{dT}{dt}) (deg/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper chromite</td>
<td>5</td>
<td>88-124</td>
<td>(10^{18.3}) (\exp\left(-43,000/RT\right))</td>
</tr>
<tr>
<td>Copper chromite</td>
<td>5</td>
<td>43-61</td>
<td>(10^{19.6}) (\exp\left(-46,000/RT\right))</td>
</tr>
<tr>
<td>Chromic oxide</td>
<td>5</td>
<td>88-124</td>
<td>(10^{27.8}) (\exp\left(-68,000/RT\right))</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.5</td>
<td>88-124</td>
<td>(10^{21.7}) (\exp\left(-52,500/RT\right))</td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>5</td>
<td>88-124</td>
<td>(10^{14.7}) (\exp\left(-34,300/RT\right))</td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>5</td>
<td>43-61</td>
<td>(10^{15.8}) (\exp\left(-36,600/RT\right))</td>
</tr>
</tbody>
</table>

* Average of 4 to 8 experiments.
FIG. 1 APPARATUS USED IN CONSTANT TEMPERATURE EXPERIMENTS
FIG. 2 THE RATE OF DECOMPOSITION OF PURE $\text{NH}_4\text{CIO}_4$
FIG. 3 THE RATE OF DECOMPOSITION OF NH₄ClO₄ CATALYZED BY COPPER CHROMITE
TO RECORDER

CONTROL UNIT

CHROMEL-ALUMEL THERMOCOUPLES

ELECTRICAL HEATER

ALUMINUM BLOCK

NH$_4$CIO$_4$ WAFER
($1/8$ in. dia. ~ 4 mm THICK)

ELECTRICAL POWER FROM CONTROL UNIT

FIG. 4 ADIABATIC APPARATUS
FIG. 5 THE ADIABATIC RATE OF DECOMPOSITION OF AN \( \text{NH}_4\text{ClO}_4/\text{CC} \) WAFER
The decomposition of $\text{NH}_4\text{ClO}_4$ and of $\text{NH}_4\text{ClO}_4$-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 $\text{NH}_4\text{ClO}_4$. Reaction mechanisms for both uncatalyzed and catalyzed decomposition are proposed.
### Security Classification

<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROLE WT</td>
<td>ROLE WT</td>
<td>ROLE WT</td>
<td></td>
</tr>
</tbody>
</table>

#### INSTRUCTIONS

1. **ORGANIZING ACTIVITY**: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. **RECOMMENDS SECURITY CLASSIFICATION**: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP**: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE**: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in capital letters immediately following the title.

4. **DESCRIPTIVE NOTES**: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S)**: Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE**: Enter the date of the report, day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES**: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES**: Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER**: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b. **& 8c. PROJECT NUMBER**: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S)**: Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S)**: If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES**: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

   1. "Qualified requesters may obtain copies of this report from DDC."
   2. "Foreign announcement and dissemination of this report by DDC is not authorized."
   3. "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through "
   4. "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through "
   5. "All distribution of this report is controlled. Qualified users shall request through "

   If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES**: Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY**: Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. **ABSTRACT**: Enter an abstract giving a brief and factual summary of the document. The abstract should be unclassified. It may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

   It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

   There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS**: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.