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ON THE COPPER (II) - CATALYZED LOW
TEMPERATURE DECOMPOSITION OF
AMMONIUM PERCHLORATE

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Ballistic Research Laboratories

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June 1974

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Previous workers speculated that the copper (II) catalyzes the low-temperature decomposition of ammonium perchlorate either by promoting proton transfer or by forming ammine complexes which inhibit the back reaction above. Recent measurements were made of the catalyzed decomposition using small amounts of copper (0.013 to 0.2 percent by weight copper (II) chloride). The rate of reaction doubled with addition of 0.04 percent by weight CuCl_2 but addition of further CuCl_2 caused little further catalysis. These results cannot be explained by previous mechanisms. We suggest the catalysis results from formation of a copper-ammine complex which is more reactive than the uncomplexed ammonia. The rate law derived from this mechanism is shown to fit the recent copper (II) catalysis experiments. The complexed ammonia reacts three times faster than the uncomplexed ammonia. The formation constant for the copper-ammine complex is $2.1 \times 10^4 \text{ M}^{-1}$ defining concentration as moles of complex in a liter of AP.

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I. INTRODUCTION

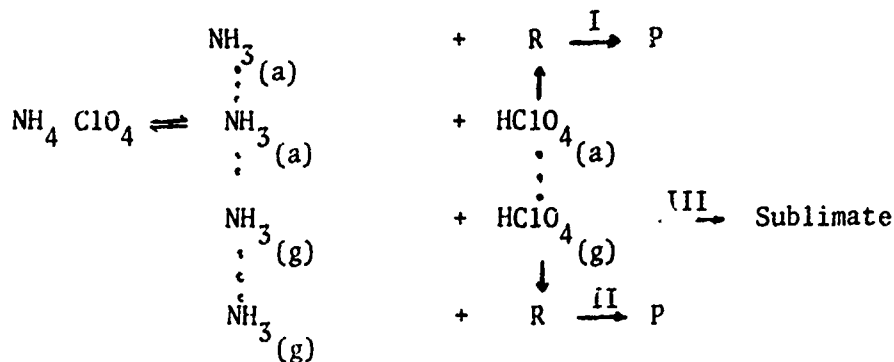
Since ammonium perchlorate is used as an oxidizing agent in many solid propellants, extensive research has been conducted on the thermal decomposition of ammonium perchlorate in order to gain insight into the ignition and combustion of solid propellants.^{1-3*} Although the mechanism of the thermal decomposition of pure ammonium perchlorate seems well established, the mechanism by which certain materials catalyze the rate of decomposition is not as clear. A recent publication by Keenan and Siegmund on the catalysis of the low-temperature decomposition of ammonium perchlorate by copper (II)⁴ contain results which we think provides further evidence that a modification of the currently accepted mechanism is in order. In this report the mechanisms of the catalyzed and uncatalyzed decomposition of ammonium perchlorate are briefly reviewed, Keenan and Siegmund's results are presented, and the modification to existing mechanistic interpretations is discussed.

II. THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

Ammonium perchlorate (AP) begins to decompose measurably at atmospheric pressure above 420 K. Below approximately 570 K the AP decomposes via an autocatalytic reaction which stops after about thirty per cent decomposition. This is designated the "low-temperature" decomposition, as opposed to the "high-temperature" decomposition which takes place between 570 and 720 K at a conveniently measurable rate. In addition to these two decomposition modes, AP undergoes sublimation. The high temperature reaction is not autocatalytic and proceeds to complete decomposition. Above 720 K deflagration of the AP takes place. At first three mechanisms were proposed for the overall decomposition,^{5,6} namely electron transfer, proton transfer, and breakdown of the anion. The low temperature decomposition was ascribed to electron transfer, the sublimation process to proton transfer, and the high temperature decomposition to perchlorate ion breakdown.

*References are listed on page 17

A "unified" mechanism involving solely proton transfer was formulated in 1967 by Jacobs and Russell-Jones⁷ and later shown to account successfully for the complex product distribution observed in the decomposition of AP.⁸ Decomposition begins with proton transfer from the ammonium ion to form adsorbed ammonia and perchloric acid. The following diagram shows how the three decomposition modes are accounted for from the initial proton transfer step:



where

- I = low temperature mechanism
- II = high temperature mechanism
- III = sublimation process
- a = adsorbed
- g = gas phase
- R = radical intermediates
- P = final products

The low-temperature reaction results from heterogeneous decomposition of perchloric acid followed by oxidation of adsorbed ammonia. The cessation of reaction after only thirty per cent decomposition may be explained by incomplete oxidation of the adsorbed ammonia which eventually covers the crystal surface to halt further reaction.

The high-temperature decomposition occurs in the gas phase and competes with the sublimation process. These processes are strongly pressure dependent as one would expect. The reader interested in a detailed description of the unified proton transfer mechanism is referred to reference 8.

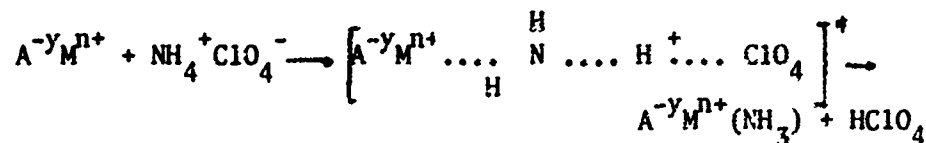
The effect of additives on the thermal decomposition of ammonium perchlorate has received considerable attention in an effort to understand the decomposition of ammonium perchlorate, and to be able to modify the burning properties of ammonium perchlorate-based propellants. A list of some of these additives is given in Table I taken from Reference 3. From these experiments the catalysts have been divided into three groups. One group is the metal oxides which do not react with ammonium perchlorate, such as NiO, Cr₂O₃, Co₂O₃, and CuO. Presumably these compounds provide a surface for perchloric acid to decompose and thereby explain the observed catalysis of the high-temperature thermal decomposition. The second group comprises the metal oxides which react with ammonium perchlorate to form the corresponding metal perchlorate, such as MgO, CdO, ZnO, and PbO. The mechanism proposed to explain the catalysis involves fusion of the metal perchlorate with the more facile proton transfer occurring in the melt. These metal oxides have been observed to catalyze both the low and high-temperature decomposition. The third group of catalysts is comprised of compounds substituted isomorphically in the ammonium perchlorate crystal. They catalyze only the low temperature thermal decomposition, and both cations and anions may fall into this group. Silver (I) and Cu (II) are examples of cations; permanganate, chlorate, iodide, and bromide, are examples of anions. The mechanism by which the group catalyzes AP decomposition is the least understood. No reasonable explanation has been tendered to explain the role of the anions in catalyzing the decomposition; for the cations, the formation of metal-ammonia complexes has been invoked to account for the catalysis of the low temperature decomposition.

The mechanisms involving metal-ammine complexes have been tendered to explain this latter mode of catalysis as follows. Jacob and Russell-Jones⁷ first suggested such complexes may account for the catalysis but they offered no further explanation of how such complexes could catalyze the decomposition. Dauerman⁹ proposed that the metal-ammine complex facilitated proton-transfer as follows:

Table I.

List of Compounds Studied as Additives on the
Thermal Decomposition of Ammonium Perchlorate

<u>Halides</u>	<u>Oxides</u>	<u>Oxy Salts</u>
NH ₄ Cl	MgO	LiClO ₄
NH ₄ Br	CaO	AgClO ₄
NH ₄ I	ZnO	Ca(ClO ₄) ₂
NaCl, KCl, MgCl ₂ , CaCl ₂	CdO	TlClO ₄
CuCl	Al ₂ O ₃	Cu(ClO ₄) ₂
CuCl ₂ ·2H ₂ O	PbO	Fe(ClO ₄) ₂
FeCl ₃	Cu ₂ O, CuO	Zn(ClO ₄) ₂
	Cr ₂ O ₃	Cd(ClO ₄) ₂
	MnO ₂	Mg(ClO ₄) ₂
	Fe ₂ O ₃	K ₂ CrO ₄
	NiO	(NH ₄) ₂ CrO ₄
	Cobalt oxides	CaCrO ₄
	TiO ₂	K ₂ Cr ₂ O ₇
	V ₂ O ₅	KMnO ₄
	Copper chromite	KIO ₃ , KIO ₄
		KClO ₃
		CuCO ₃
		(NH ₄) ₂ SO ₄ , (NH ₄) ₂ C ₂ O ₄



He argued that the transition state complex depicted above was more stable than the one resulting from proton transfer in the absence of the catalyst. We find this difficult to visualize, since one would expect ammonium ion-metal ion interaction depicted above to be repulsive, hence form a less stable transition-state complex. Jacobs and Pearson⁸ postulated that the metal-ammine complex inhibits the reversal of the proton-transfer step between adsorbed ammonia and adsorbed perchloric acid.

Support for the presence of these complexes comes from other results from Keenan's laboratory where metal-ammine complexes were detected in the melt of decomposing ammonium nitrate doped with copper (II).¹⁰ Ammonium nitrate decomposition is also thought to originate by proton transfer. However, ammonium nitrate decomposition takes place in the liquid phase, where it is easier to comprehend formation of metal-ammine complexes.

The recent results of Keenan and Siegmund will not be examined with the foregoing discussion as background.

III. REVISED MECHANISM

Keenan and Siegmund's experiments merit special attention regarding the mechanism of cation catalysis because:

1. they used smaller concentrations of catalyst than previous investigators
2. they measured the rate of decomposition both gravimetrically and volumetrically. They were then able to calculate a "mole factor", the ratio of moles of ammonium perchlorate decomposed to moles of permanent gases evolved. A change in the mole factor should signal a change in stoichiometry.

Keenan and Siegmund's results are presented in Table II which is also

Table II in reference 4. The n in Table II refers to the exponent in the equation used to represent the fraction of ammonium perchlorate decomposed as a function of time. The specific equation is given below:

$$[-\ln(1-\alpha)]^{1/n} = kt \quad (1)$$

where k represents the rate coefficient. They fitted their data to equation (1) by setting n=3, n=4, and by letting n vary.

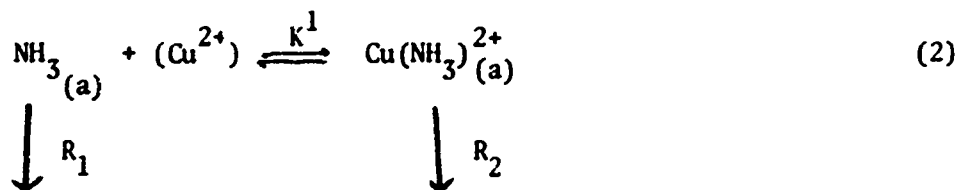
Table II. Effect of Copper Chloride on Decomposition (Evaporation Temperature 70°, Decomposition Temperature 228°)

CuCl ₂ , % by weight	Mole factor	Maximum rate cm ³ /min	variable n	Rate constant (sec ⁻¹ x 10 ⁻⁴)	
				n=3	n=4
0.0	0.64	2.05	3.46	2.53	2.79
0.013	0.65	2.59	3.44	2.88	3.14
0.041	0.70	5.30	3.75	4.08	4.32
0.110	0.71	5.66	3.89	4.14	4.37
0.211	0.70	5.92	4.03	3.87	4.11

Two factors emerge from these results that must be accounted for by any mechanism proposing to explain the role of the copper (II). These are:

1. the rate doubles with the addition of 0.04 percent by weight of CuCl₂ while further addition results in little further increase.
2. The mole factor changes sharply with the same small addition of CuCl₂ but is also insensitive to further addition.

Neither Dauerman's nor Jacobs-Pearson's mechanisms can account for either observation, particularly the second which implies a change in stoichiometry. We propose that a mechanism to account for these observations is one in which a copper-ammine complex is formed (as does Jacobs-Pearson), but that the increased observed rate results from the complexed ammonia reacting with the perchloric acid (or perchloric acid decomposition products). Our mechanism may be represented as follows:



where

R_1 = the rate of low-temperature decomposition

R_2 = the rate of low temperature decomposition via oxidation of the copper (II) ammonia complex

K^1 = equilibrium constant for formation of the copper-ammonia complex

(Cu^{2+}) = concentration of copper (II)

In order to compare this mechanism with Keenan and Siegmund's experimental results one must derive a rate law to express the observed rate as a function of R_1 , R_2 and the total concentration of copper (II). This may be done as follows where

A_t = total concentration of ammonia

A = concentration of uncomplexed ammonia

CA = concentration of complexed ammonia

K^1 = stability constant for the copper (II) ammonia complex

(Cu^{2+}) = concentration of copper (II)

R_1 = rate of decomposition of free ammonia

R_2 = rate of decomposition of complexed ammonia

The experimentally observed rate of decomposition, R_{obs} , will be equal to the sum

$$R_{\text{obs}} = (A/A_t) \cdot R_1 + (CA/A_t) \cdot R_2 \quad (3)$$

The uncomplexed ammonia concentration in terms of observed quantities

$$A_t = A + CA, \quad (4)$$

$$A_t = A + K^1(\text{Cu}^{2+}) A, \quad (5)$$

$$A = A_t / (1 + K^1(\text{Cu}^{2+})) \quad (6)$$

For the complexed ammonia concentration

$$CA = A_t - A \quad (7)$$

$$CA = A_t - A_t / (1 + K^1(Cu^{2+})) \quad (8)$$

$$CA = A_t \cdot K^1 \cdot (Cu^{2+}) / (1 + K^1(Cu^{2+})) \quad (9)$$

Substituting for A/A_t and CA/A_t into (3)

$$R_{obs} = \frac{R_1 + R_2 K^1(Cu^{2+})}{1 + K^1(Cu^{2+})} \quad (10)$$

Thus, the observed rate of decomposition reaches a limit corresponding to the rate of decomposition of the copper ammonia complex as the concentration of copper increases. At very low concentrations of copper (II), i.e. where $[K + Cu(II)] \ll 1$, the observed rate of decomposition depends linearly on copper (II). This scheme explains in our mind, Keenan and Siegmund's dependence of maximum rate of decomposition with varying concentrations of copper (II). It may also explain the change in the mole factor, if the stoichiometry of the complexed ammonia-perchloric acid reaction is slightly different. We converted the percent by weight of copper to moles of Cu(II) per liter of ammonium perchlorate. The agreement between experimental rates and the rates calculated from the best-fit values are shown in Figure 1. The best-fit values are:

$$\begin{aligned} R_1 &= 1.8 \pm 0.7 \text{ cm}^3/\text{min} \quad , \\ R_2 &= 6.8 \pm 1 \text{ cm}^3/\text{min} \quad , \\ K &= 2.2 \pm 2 \times 10^4 \text{ l/mole} \quad . \end{aligned}$$

The agreement between the experimental rates and the calculated rates is considered adequate, since the weight of copper chloride could be measured to an average deviation of 0.036 percent absolute. The equilibrium constant for the copper-ammonia complex is of the order of magnitude for such a complex in aqueous solution. A summary of results of the same calculation of R_1 , R_2 , and K for $n=3$, and $n=4$ is presented in Table III.

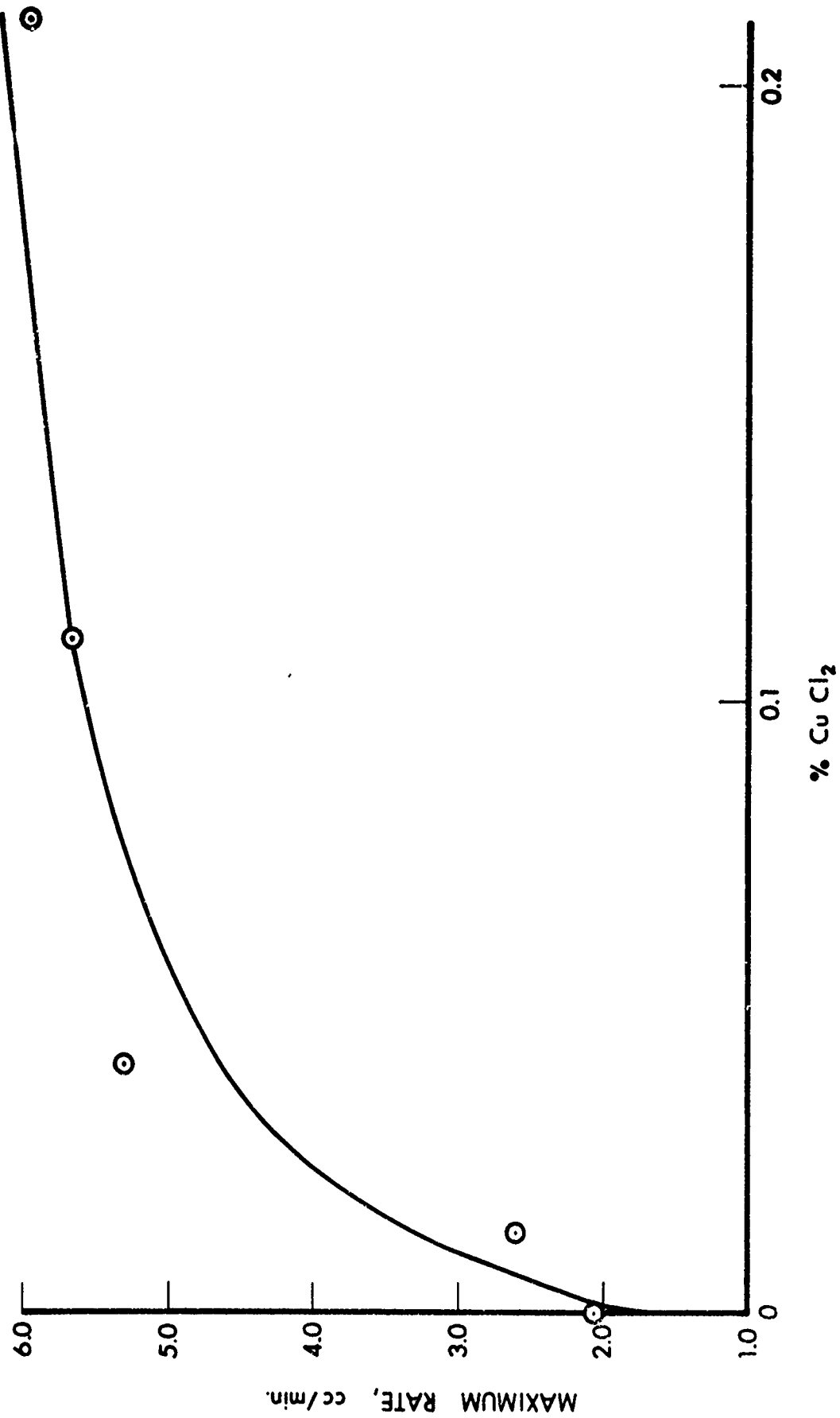


Figure 1. Comparison of Experimental and Calculated Maximum Reaction Rates.

Table III. Best-Fit Values of R_1 , R_2 , and K from Observed Rate Coefficients with $n=3$ and $n=4$

	$R_1 \text{ sec}^{-1} \times 10^4$	$R_2, \text{ sec}^{-1} \times 10^4$	$\frac{K, \text{ mole}}{R, \text{ sec}} \times 10^4$
$n=3$	2.5 ± 0.4	4.3 ± 0.5	4 ± 4
$n=4$	2.7 ± 0.4	4.5 ± 0.5	4 ± 4

IV. CONCLUSION

A new interpretation of the role of copper (II) in catalyzing the low temperature decomposition of ammonium perchlorate is made. Our mechanism proposes that a copper-ammine complex forms which reacts with the free radicals from the perchloric acid decomposition. This mechanism successfully interprets recently published data of copper (II) catalyzed ammonium perchlorate decomposition which previously proposed mechanisms cannot.

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