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Kinetics of the Low Temperature Thermal Decomposition of Ammonium Perchlorate and Its Catalysis by Copper Ion

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The low temperature thermal decomposition of ammonium perchlorate is found to be initiated by a single stage nucleation process at a lattice defect site on the surface of the crystal. An aging effect in the form of a decrease in the decomposition rate with storage time at room temperature was observed. Sample impurities and as little as 0.04% copper chloride significantly accelerate the decomposition but do not alter the nucleation process or the rate-determining step. The reaction stoichiometry is changed by copper chloride but not by recrystallization. It is suggested that catalysis occurs through the formation of ammine complexes which tie up the ammonia on the crystal surface and thereby prevent the reversal of the proton transfer reaction.

Introduction

The thermal decomposition of ammonium perchlorate has been extensively studied because of its intrinsic chemical interest and more recently because of its application in solid propellants. Two comprehensive reviews (*1*, *2*) have appeared recently. The low temperature decomposition (200–240°), which terminates after approximately 30% of the original material is consumed, is of interest both as a possible precursor to the combustion process and as a means of gaining insight into the problem of thermal stability during storage.

The ammonium perchlorate low temperature decomposition takes place through the formation and subsequent growth of nucleation centers. Nucleation occurs at only a limited number of crystal surface sites which consist of imperfections or strained regions (*3–10*). There has, however, been much discussion as to whether these nucleation sites are due to crystal dislocations and defects, or to impurities (*1*, *2*, *10*, *11*).

The purpose of this investigation was twofold. First, to determine the primary step responsible for the initiation of the decomposition, and secondly to establish a proper procedure for the evaluation of catalysts. Previous investigators have obtained conflicting results as to the effect of particular catalysts.

Both the uncatalyzed and copper chloride catalyzed reactions were investigated kinetically between 210 and 235°. Various rate parameters in the acceleratory region of the decomposition were determined as functions of the purity of the uncatalyzed sample, the temperature of sample evaporation, and the concentration of the copper chloride additive.

Experimental Procedure

Fisher Certified anhydrous copper chloride and ammonium perchlorate were used. For uncatalyzed runs the ammonium perchlorate was recrystallized from demineralized water at various temperatures given later. For catalyzed runs, the samples were prepared by evaporating to dryness an aqueous solution containing the ammonium perchlorate and copper chloride weighed to within 0.1 mg. In both cases, the solid sample was then dried at 85°, ground in a mortar, sieved to retain particles within the range 74–149 microns (μ), and stored over silica gel.

Nephelometric and *p*H measurements showed that the evaporation procedure did not affect the chloride ion content or *p*H of the initial sample. High-resolution proton magnetic resonance (PMR) spectrometric analysis showed that the drying procedures removed water to less than 0.02% by weight. Complete details of this procedure have already been published (*12*).

The PMR technique was also used to check the copper chloride content of catalyzed samples after evaporation from aqueous solution. The solid samples were dissolved in *N,N*-dimethylformamide (DMF) which formed a complex with the copper ion. The width at half-height of the PMR absorption of this complex was found to be proportional to the copper content with an average deviation of 0.036% absolute. Using this technique, it was shown that the copper content of a catalyzed ammonium perchlorate sample, after evaporation from an aqueous solution, agreed within 0.05% with the amount of copper initially added.

For the rate studies, approximately 0.8 ± 0.01 g samples were immersed in a lithium–potassium–sodium nitrate fused salt bath (*13*) controlled by a Sargent Model S Thermonitor to ±0.05°. The differential rate method employing a soap-film flowmeter following KOH traps, as described previously (*14*) was used. The 0.5 ml flowmeter was graduated to 0.01 ml. The fraction of ammonium perchlorate decomposed (α) was determined from the weight loss of the reaction at various stages of decomposition. The total amount of permanent gases evolved up to each such point was obtained by integrating the periodic rate readings taken from the soap-film meter. A "mole factor" was then calculated as the ratio of the moles of ammonium perchlorate decomposed per mole of permanent gases evolved. For a given sample, the mole factor was found to be unchanged both throughout a particular decomposition and over the temperature range investigated. Thus, α could be calculated at any stage of reaction.

The times to maximum rate and induction periods were found to be reproducible to within 1%. To determine these parameters, zero time was taken as the instant when a reactor and its charge of salt, both preheated to 85°, were inserted into the fused salt bath at reaction temperature. The termination of the induction period was arbitrarily defined by a short extrapolation of the nearly vertical initial portion of the rate *vs.* time curve to the zero-rate axis.

Variations in sample weight of ±10 mg, and in particle size of ±38 μ, were found to have no observable influence upon any of the reaction rate parameters. In preliminary work, using apparatus and procedures previously described (*15*), it was established that no deflagration occurred at any catalyst concentration within the range used and at furnace temperatures not exceeding 240°.

Results and Discussion

The rate curve which was obtained directly in terms of cm^3/min as a function of the reaction time, was integrated to give the typical α against t sigmoid curve. The kinetic data for the acceleratory region were fitted to several well-known solid-state kinetic expressions. In both the uncatalyzed and catalyzed decompositions the results were found to fit best the Avrami–Erofeyev equation over the entire acceleratory region, i.e., from $\alpha = 0$ to $\alpha = 0.14$ approximately, regardless of temperature and mode of precipitation. Thus,

$$-\log(1-\alpha) = (kt)^n, \qquad (1)$$

where

$$n = \lambda + r. \qquad (2)$$

The symbol r represents the number of molecular decompositions required to obtain formation of a stable nucleus and λ signifies the number of dimensions in which nuclei grow. In the acceleratory region of the reaction direct visual observation has shown (*3*) both the uncatalyzed and catalyzed low temperature thermal decompositions to grow three dimensionally into the crystal ($\lambda = 3$). Thus Eq. (1) can be written

$$-\log(1-\alpha) = (kt)^{r+3}. \qquad (3)$$

Rate constants and the best fit of n for Eq. (1), and activation energies and Arrhenius preexponential factors were determined by least-squares analysis on a computer.

Crystal Impurities

It was found that successive recrystallizations, by allowing nearly saturated solutions of ammonium perchlorate at 80° to cool to room temperature, had no observable effect on the mole factor to the extent of six recrystallizations. A value of 0.655 ± 0.005 was obtained for samples decomposed approximately 20%. This means that in the acceleratory region of the decomposition, the stoichiometry remains unchanged regardless of sample purity. This is in contrast, however, to the rate of decomposition which decreased with increasing purity. This is shown in Fig. 1, in which the maximum rate of decomposition decreases steadily as the number of recrystallizations increases. This occurred over the entire temperature range of decomposition investigated. All the rate parameters demonstrated the inhibiting effect of recrystallization on the decomposition. As the sample impurities were removed both the induction periods and times to maximum rate increased while the rate constants and the maximum rates decreased. The value of the exponent n, however, remained fairly constant at approximately three. This indicates that for uncatalyzed ammonium perchlorate the nucleation

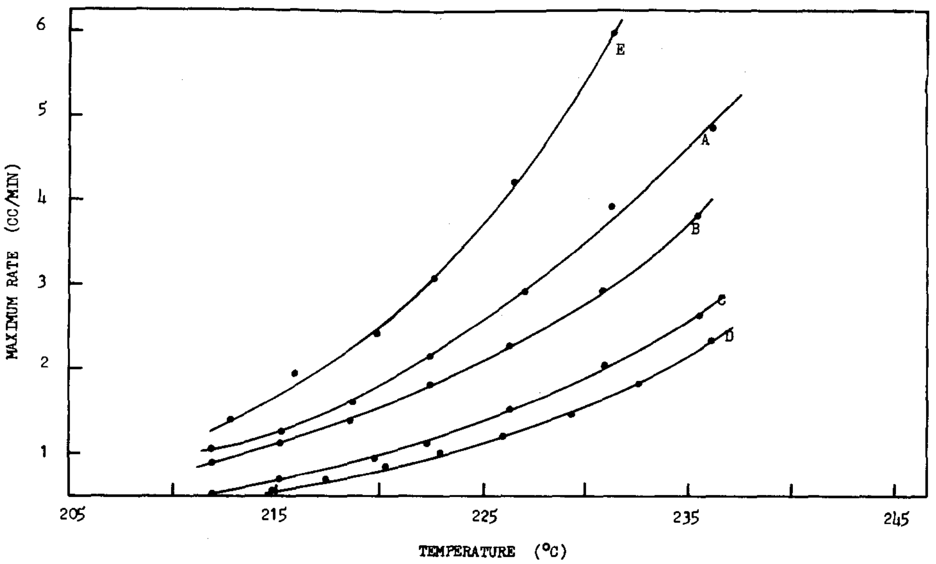

FIG. 1. Effect of recrystallization on maximum rate of decomposition of ammonium perchlorate. Number of crystallizations: A, 0; B, 2; C, 4; D, 6. For comparison, curve E shows effect of 0.66 wt % of $CuCl_2$ on unrecrystallized material.

process occurs extremely rapidly and only during the initial stage of the reaction and that the kinetics of the acceleratory region are governed principally by the growth of existing nuclei. Therefore, r, when averaged over the entire acceleratory region, is effectively equal to zero.

Thus, although sample impurities do not alter the reaction stoichiometry, they do increase the rate and amount of decomposition up to the rate maximum. In addition, impurities do not appear to affect the nucleation process.

Variation of the Sample Evaporation Temperature

In an effort to elucidate which particular type of crystalline imperfection, defects and dislocations or impurities, initiates nucleation, samples were prepared by allowing solutions of ammonium perchlorate to evaporate down partially at various constant temperatures from 60 to 96°. Increasing the temperature at which crystal growth occurs increases the dislocations and defects formed in the growing crystal without altering the concentration of impurities.

The results for a decomposition temperature of 233° are given in Table I. Identical trends were obtained at the other decomposition temperatures. Considering first the entries for a constant crystal "age" of 20 hr (the time from drying to the beginning of a decomposition run), it is seen that as the evaporation temperature is increased from 60 to 85°, both the induction period and time to maximum rate (R_t) decrease. This indicates an increase in the rate of the reaction initiation process. The value of the exponent also decreases from over four to three, substantiating that an increase in the rate of the nucleation process has occurred. For a sample evaporated near 80°, nucleation is apparently completed very rapidly during the beginning of the decomposition so that $r = n - \lambda = 0$. For a sample evaporated at 60°, on the other hand, nucleation occurs throughout the acceleratory region of the decomposition giving an overall value of $r = 1$, approximately.

The reaction rate constants and maximum rates (R_m), however, vary randomly indicating no change in either the rate or amount of decomposition up to the rate maximum. In light of the previous results obtained during the sample recrystallization studies, this also confirms that sample impurities are not appreciably altered by a change in the evaporation temperature.

From the changes observed in r, discussed earlier, it may be hypothesized that nucleation is promoted by an increase in the number of dislocations and defects contained within the crystal lattice. These crystalline imperfections, however, do not appear to otherwise influence the decomposition.

The above trends in induction period and maximum rate show anomolies above 85°. This is seen more clearly for the induction period in Fig. 2 which gives the data for one out of five independent and entirely reproducible series of runs. The value

TABLE I

EFFECT OF EVAPORATION TEMPERATURE AND AGING
(DECOMPOSITION TEMPERATURE 233°)

Evaporation temperature (°C)	Age (hr)	Induction period (sec)	Maximum rate		n	Rate constant ($sec^{-1} \times 10^{-4}$)	
			R_t (sec)	R_m (cm^3/min)		$n = 3$	$n = 4$
60	20	345	1348	3.42	4.25	3.36	3.67
70	20	248	1162	3.02	3.21	3.26	3.55
	90	260	1130	3.19	3.38	3.44	3.72
	114	260	1155	3.32	3.38	3.45	3.76
	186	300	1220	3.26	3.79	3.43	3.73
	210	320	1230	3.22	3.92	3.45	3.78
75	20	235	1050	3.27	2.98	3.41	3.73
80	20	230	1033	3.36	2.98	3.46	3.78
85	20	223	1008	3.25	2.97	3.31	3.60
88	20	235	1030	3.50	3.07	3.56	3.86
90	20	250	1155	3.17	2.98	3.14	3.41
96	20	225	1088	3.36	2.91	3.32	3.63

of n, however, remains unchanged at about three, indicating no change in the crystal defect structure. These anomolous effects are explained as being due to the desorption of water from the lattice during crystallization between 85 and 90°.

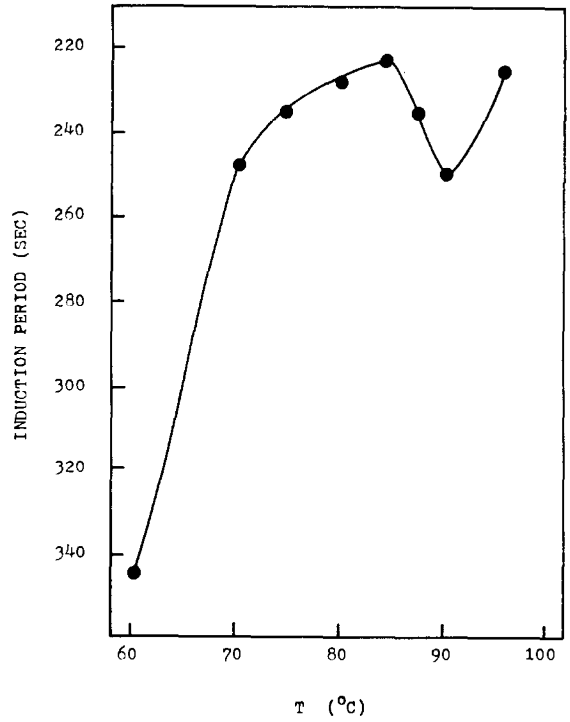

FIG. 2. Variation of induction period with sample evaporation temperature. Average for 18- and 24-hr-old samples.

The parameters discussed above were also studied as a function of crystal age for samples evaporated at 70°. As seen from the entries under 70° in Table I, the rate constant and extent of decomposition to the rate maximum remained unchanged and the exponent n increased with age. The induction period and time to maximum rate also increased markedly. Thus, although the rate of decomposition remained unchanged, the rate of the nucleation process decreased as a function of time. This supports an early theory by Maycock *et al.* (*16*, *17*) which attributed an increase in the induction period with time to an annealing out of defects and dislocations from the crystal lattice. The increase in n from three to four substantiates this postulate indicating that the rate of the nucleation process has indeed been reduced.

In summary then, for the low temperature uncatalyzed decomposition of ammonium perchlorate, crystal defects and dislocations promote nucleation without otherwise affecting the decomposition, while sample impurities accelerate the reaction without altering the nucleation process. Thus, as a result of these phenomena, sample purity and method of preparation must be strictly reproduced in order to obtain meaningful reaction evaluations.

Copper Chloride Catalyzed Decomposition

The addition of copper chloride was found to have a profound influence on all the measured parameters of the low temperature decomposition

TABLE II

EFFECT OF COPPER CHLORIDE ON DECOMPOSITION (EVAPORATION TEMPERATURE 70°, DECOMPOSITION TEMPERATURE 228°)

$CuCl_2$ wt %	Mole factor	Maximum rate cm^3/min	n	Rate constant ($sec^{-1} \times 10^{-4}$) $n = 3$	$n = 4$
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

of ammonium perchlorate. Preliminary experiments showed that equal amounts of chloride added as ammonium chloride had no effect. As seen from Table II, the mole factor (which was independent of α) changes appreciably at the very low catalyst concentration of 0.04 wt %. It then remains essentially constant up to the highest concentration tried, namely 10%. This change in mole factor confirms previous observations (*18–23*) that addition of a catalyst alters the product distribution.

Both the reaction rate constant, as calculated from the Avrami–Erofeyev equation, and the maximum rate were increased by $CuCl_2$. Again Table II shows the extent to which small catalyst concentrations accelerated the decomposition. Figure 3 shows the maximum rate as a function of copper chloride. Beyond 0.8% there was no further change up to 10%. The exponent n also varied rapidly from 3 to 4 at extremely low catalyst concentrations (Table II). Beyond 0.2%, no further change occurred up to 10%.

In contrast to the results in Table I, it was found that the various reaction parameters for the catalyzed reaction became insensitive to changes in sample evaporation temperature for catalyst concentrations exceeding 0.2%. Therefore, for the catalyzed decomposition, nucleation apparently occurs throughout the acceleratory region and gives an average value $r = n - \lambda = 1$.

Arrhenius Parameters

In a solid-state decomposition, the preexponential factor A represents the concentration of reactant at the reaction interface. Increasing the concentration and, thus, the frequency factor can be accomplished through the formation of an intermediate species which, by tying up reactant molecules, acts as a preferential site for decomposition. The shifting of an equilibrium process either toward the production of a particular reactant, or against the formation of an inhibiting species also results in an increase in the frequency factor.

Activation energies for the low temperature decomposition of ammonium perchlorate were calculated for both the uncatalyzed and $CuCl_2$ catalyzed reactions. Table III summarizes the results. The numerical values were obtained by least-squares analysis of Arrhenius plots of times to maximum rate and of rate constants as calculated from Eq. (1) for n equal to both 3 and 4.

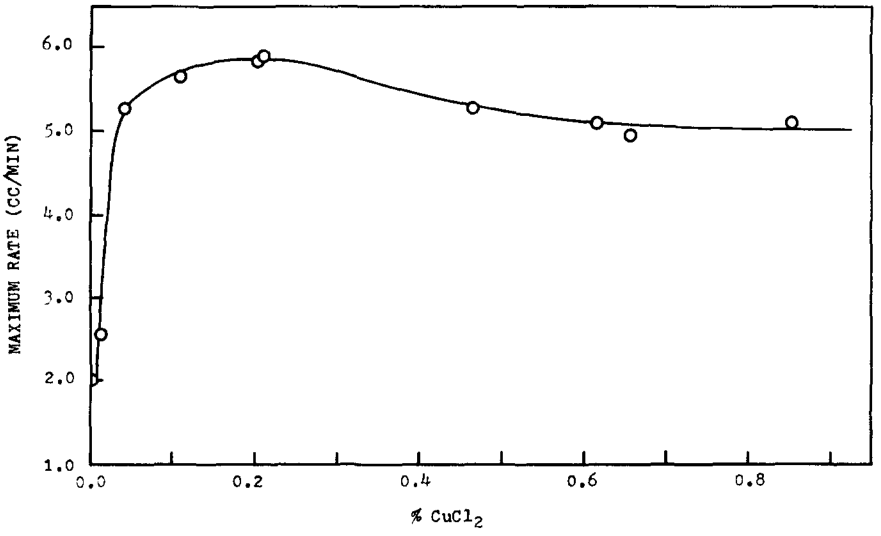

FIG. 3. Maximum reaction rate as a function of copper chloride concentration.

TABLE III

DECOMPOSITION KINETICS OF AMMONIUM PERCHLORATE (EVAPORATION TEMPERATURE 70°)

Uncatalyzed				
		Activation energy (kcal/mole)		
			From Avrami–Erofeyev equation	
Number of recrystallizations	Best fit n value	From maximum rate	$n = 3$	$n = 4$
0	2.91	26.70	27.83	27.45
0[a]	3.62	30.25	30.31	29.77
2	2.99	28.74	31.32	30.97
2	2.76	29.28	30.75	30.36
3[b]	3.98	—	28.06	27.51
4	3.04	28.57	27.75	27.06
4	3.34	26.10	27.24	26.42
Avg	3.01	28.27 ± 1.25	29.04 ± 1.51	28.51 ± 1.60
Copper chloride catalyzed				
% $CuCl_2$				
0.20	3.95	30.53	31.18	31.20
0.85	3.80	27.36	30.18	29.79
1.31	4.05	29.83	31.65	31.82
3.67	3.91	29.57	30.79	30.97
5.24	3.56	27.81	28.22	27.90
10.14	3.79	29.87	28.85	28.47
Avg	3.84	29.16 ± 1.05	30.15 ± 1.07	30.03 ± 1.31

[a] Evaporation temperature 50°.

[b] Evaporation temperature 25°.

A check on self-heating was made by measuring the difference between bath and internal sample temperature with suitably placed thermocouples. For uncatalyzed samples the maximum error in activation energy due to self-heating was found to be 0.31 kcal/mole. For catalyzed samples, the corresponding figure was 1.41.

The activation energy is seen to be independent of both recrystallization and catalyst. Thus, both the catalyzed and uncatalyzed reactions proceed by the same rate-determining step and the acceleration of the reaction by $CuCl_2$ and by sample impurities must be due to an increase in the preexponential factor, that is, to an increase in the effective concentration of reactants at the reaction interface. Preexponential factors were calculated for a number of runs, and while subject to considerable variations due to scatter, they do show the expected trends.

In Table III, the best values of the exponent n have also been tabulated for both the uncatalyzed and catalyzed reactions. An average value of 3.01 was found for the uncatalyzed decomposition, and 3.84 for the catalyzed reaction. This further substantiates the theory that reaction initiation occurs as a result of dislocations and defects while addition of catalyst inhibits nucleation. In two of the uncatalyzed runs, the samples were prepared by evaporation at lower temperatures (50 and 25°) than the standard 70°. In each case, the n value was considerably higher which is consistent with the hypotheses advanced.

Conclusions

As a result of the present investigation and of the previous work by others already cited (*1*, *2*), it seems reasonable to postulate that the low temperature decomposition of ammonium perchlorate is initiated by a single stage nucleation process occurring at a lattice defect site on the surface of the crystal. The rate-determining step in the reaction is generally considered to be the transfer of a proton from an ammonium ion to a perchlorate (*1*, *2*). This yields adsorbed ammonia and perchloric acid.

$$NH_4^+ + ClO_4^- \rightleftharpoons NH_{3(a)} + HClO_{4(a)}. \quad (4)$$

Once formed, these species can either desorb into the gas phase (the sublimation process), decompose on the crystal surface, or undergo the reverse process. The low temperature decomposition occurs as a result of the bi- or unimolecular decomposition of perchloric acid. The intermediates formed then react with the adsorbed ammonia to yield the various reaction products. The presence of sample impurities or of copper chloride accelerates the reaction by increasing the concentration of the reacting species, $HClO_{4(a)}$, on the surface of the crystal. Copper most likely ties up the ammonia by forming amine complexes (*11*, *24*). This inhibits the reversal of reaction (4). The complexing of the ammonia by the copper in addition influences the oxidation of the ammonia by the various intermediates formed in the decomposition of the perchloric acid. This accounts for the observed change in the stoichiometry.

The effect of recrystallization can be attributed to the removal of both metallic impurities such as iron which can act in the same way as copper, and of chlorate which is contained to the extent of 0.003% in the perchlorate and which has been proposed as producing the principal reactive intermediates in the decomposition of perchloric acid (*2*, *25*).

The fact that the low temperature decomposition is markedly suppressed in specially purified ammonium perchlorate (*26*, *27*) has led to the suggestion (*11*) that foreign ions are the prime decomposition initiation sites. This can be readily explained in terms of the above mechanism. Apparently, in the low temperature decomposition range, the reversal of the initial proton transfer process, and sublimation, are energetically preferred over the surface decomposition of the adsorbed perchloric acid. To accomplish thermal decomposition, the presence of chemical additives or sample impurities is required to facilitate the build up of the reacting species on the surface of the crystal.

Finally, this work has shown that to properly evaluate the effectiveness of a catalyst several criteria such as activation energy, induction period, mole factor, rate constant, maximum rate, and time to maximum rate must be determined at a number of catalyst concentrations. The variation in these parameters as a function of the catalyst concentration can then accurately define the behavior of the catalyst. The measurements must also be carried to low catalyst concentrations.

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