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THE CATALYSIS OF THERMAL DECOMPOSITION AND
BURNING REACTIONS OF FUEL-OXIDANT COMPOSITIONS

Final Report

by

E. S. Freeman and W. Rudloff

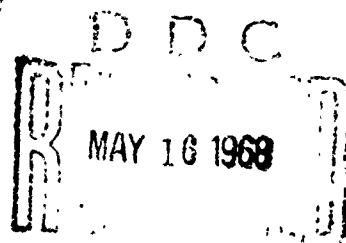
May 1968



DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Chemical Research Laboratory
Edgewood Arsenal, Maryland 21010

Contract No. DAA15-67-C-0119

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FOREWORD

The work described in this report was authorized under Project 1C014501B71A, Life Sciences Basic Research in Support of Materials, Chemical (U). This work was started on October 3, 1966 and completed September 30, 1967.

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ACKNOWLEDGMENTS

The authors wish to acknowledge the experimental work of Mr. Maurice Henry, Miss Anne O'Donnell, Miss Sue Spreckelmeyer and Mr. Brent Boldt.

DIGEST

The effects of defect structure and of doping potassium chlorate on its chemical reactivity with respect to its self-propagative reactions with sulfur were investigated.

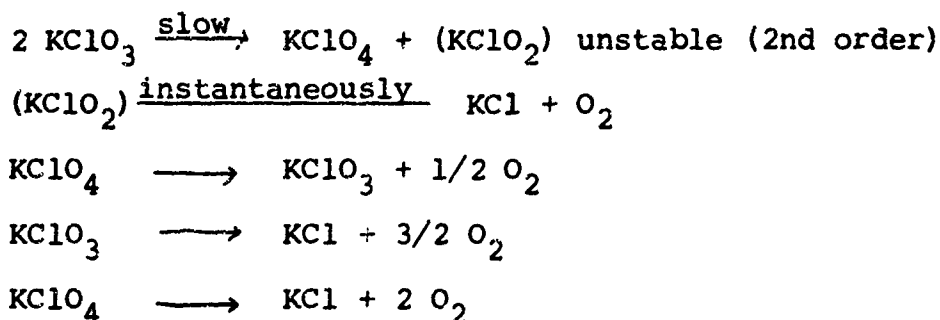
The preparations of doped single crystals of potassium chlorate continued throughout the entire program. Selected single crystals were analyzed for their dopant contents. The influence of doping, irradiation and mechanical shock on the thermal decomposition of potassium chlorate was investigated by differential thermal analysis (DTA) and thermogravimetric analysis, (TGA). Intimate mixtures of sulfur and doped potassium chlorates were also investigated with respect to their combustion properties by means of DTA and TGA.

The effects of potassium perchlorate and potassium chloride as an intermediate reaction product on the thermal decomposition of potassium chlorate were studied. These experiments were necessary for establishing the basis for evaluating the reactivity of KClO_3 with sulfur.

Electrical conductivity studies were conducted to correlate electronic defect structure with the reactivity behavior of KClO_3 . Low temperature isothermal investigations were conducted to evaluate possible reaction mechanisms.

The results of the investigations are summarized as follows:

1. The results indicate that the decomposition of potassium chlorate occurs in the following steps:



The first disproportionation reaction is consistent with a second order mechanism. This reaction is inhibited at low temperatures by excessive amounts of KCl. At higher temperatures, KCl catalyzes the reaction.

KClO_4 does not catalyze decomposition of KClO_3 . At higher concentrations, the decomposition of KClO_3 is inhibited in the presence of KClO_4 .

2. The order of dopants with respect to decreasing the decomposition temperatures of doped KClO_3 was found to be: the most effective, $\text{FeCl}_3 > \text{CuCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{CdCl}_2 > \text{LiNO}_3 > \text{LiCl} \sim \text{KCl} \sim \text{CsCl} \sim \text{No Dopant}$. This order may be correlated to charge density or to charge transfer. Doping KClO_3 with nitrates reduces the temperature of the DTA endotherm for melting.

3. Gamma irradiation and mechanical shock influences the decomposition path of KClO_3 . Low temperature weight loss and smell of chlorine and/or chlorine oxides point to defect creation of possible radicals such as ClO_3 within the crystalline lattice due to irradiation. An exotherm appears at about 75°C in the DTA curve for the mechanically shocked sample which does not appear in the untreated sample.

4. Doping of KClO_3 significantly influences the ignition of mixtures of KClO_3 and sulfur. Two effects are apparent: The order of ignition temperatures with reference to the dopants is: lowest for $\text{CuCl}_2 \ll \text{KCl} \sim \text{undoped} \sim \text{CsCl} \sim \text{Pb}(\text{NO}_3)_2 < \text{FeCl}_3 \sim \text{CdCl}_2 < \text{LiCl} \sim \text{LiNO}_3 \sim \text{CaCl}_2$.

The extent of total weight loss as measured in the TGA experiment is dependent on the rate of combustion since the rapid ignition forces material out of the reaction vessel. This appears to be true particularly for the FeCl_3 doped samples. Fe^{+++} and Cu^{++} doped KClO_3 appears to react slowly at room temperature with sulfur.

5. The reactivity of sulfur- KClO_3 mixtures is especially affected by the presence of Fe_2O_3 catalyst. In oxygen the ignition temperature of the sulfur-potassium chlorate mixture is significantly lowered in the presence of the Cr_2O_3 and Fe_2O_3 catalysts.

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THE CATALYSIS OF THERMAL DECOMPOSITION AND BURNING REACTIONS OF FUEL-OXIDANT COMPOSITIONS

I. INTRODUCTION

In a previous study sponsored by Edgewood Arsenal, Contract No. DA-18-035-AMC-341(A), "Mechanistic Investigation of Catalysis of Thermal Decomposition Reactions" the importance of defect structure in relationship to the heterogeneous catalytic decomposition of potassium chlorate was investigated. This research was extended in the present program to consider the catalytic effects resulting from the presence of small quantities of foreign ions crystallized out of solution with potassium chlorate and to consider the effects of defect structure introduced by doping and various physical treatments. It was shown in previous studies conducted by Dr. Eli S. Freeman^{1,2} that doping with cationic and anionic impurities and exposure to high energy radiation profoundly altered the chemical reactivity of oxidants and fuel such as ammonium perchlorate, potassium perchlorate, and magnesium powder. Another interesting effect in the case of the potassium perchlorate-magnesium mixture is that reproducibility with respect to time to ignition was improved by doping.

The objective of this program was to investigate the relationships between the defect structure of potassium chlorate and its chemical reactivity with respect to thermal decomposition and its reaction with sulfur. The long range goal is to provide information which would establish the basis for the improvement of pyrotechnic compositions.

In this present program two methods of doping were used. The first was evaporation of solutions to dryness and the other principal method was crystallization from aqueous solutions. The crystallization procedures involved the collection of crops of crystals as a function of time in solutions of varying concentrations. Spectroscopic procedures were used to analyze for the dopant ion concentrations.

Some of these doping ions will form oxides and chloride phases during decomposition which may serve as nuclei for decomposition. Another result of crystallizing potassium chlorate in the presence of small quantities of impurity ions will be the formation of defect structure in the potassium chlorate crystal. It was of interest to investigate the effect that crystal defects including lattice vacancies, dislocations and strains can have in catalyzing the decomposition of potassium chlorate. Another interesting aspect of the research was to investigate the possible electron transfer processes on the surfaces of the crystal and molten oxidant and fuel such as sulfur. The catalytic effects resulting from exposure to high energy radiation, such as gamma rays on the propagative reactions between oxidants and fuels as well as defects introduced by mechanical shock was also included in this program.

The experimental methods for investigating the decomposition rates of the oxidants, the oxidation of the fuels and pre-ignition reactions of the oxidant-fuel mixtures were principally thermogravimetry and differential thermal analysis and electrical conductivity measurements.

II. EXPERIMENTAL

A. Preparation and Standardization of Samples

1. Preparation and Standardization of Heterocrystalline Doped Samples of Potassium Chlorate

The following doped chlorates were prepared by evaporating solutions of KClO_3 containing 1 mole percent of the dopants to dryness on a hot water bath:

- (a) KClO_3 - 1 mole % LiCl
- (b) KClO_3 - 1 mole % KCl
- (c) KClO_3 - 1 mole % CsCl
- (d) KClO_3 - 1 mole % CaCl_2
- (e) KClO_3 - 1 mole % CdCl_2
- (f) KClO_3 - 1 mole % CuCl_2
- (g) KClO_3 - 1 mole % FeCl_3
- (h) KClO_3 - 1 mole % LiNO_3
- (i) KClO_3 - 1 mole % PbNO_3

The crystallized samples were crushed gently in a mortar, sieved, and sieve fractions between 240 and 270 mesh sieves, US standard stainless steel sieves, and stored in a desiccator for further use.

2. Preparation of Doped Single Crystals of Potassium Chlorate by Slow Crystallization Procedures

Preliminary crystallization procedures were done as follows: Various reagent grade chlorates obtained from K & K Laboratories were put in solution with KClO_3 in varying concentrations. The concentrations of doping impurities were 0.1, 1, and 10 mole percent. These solutions were then transferred

into large dishes and subjected to slow crystallization at room temperature as well as at lower temperatures.

Saturated solutions of KClO_3 at room temperature were prepared with 0.1, 1 and 10 mole % of the following dopants: NaClO_3 , $\text{Ba}(\text{ClO}_3)_2$, AgClO_3 , $\text{Ca}(\text{ClO}_3)_2$, and $\text{Cu}(\text{ClO}_3)_2$.

Crystallization took place slowly over several weeks and resulted in large single crystals. These single crystals were separated from solution, washed with water, and dried and stored in a desiccator for further use.

Further crystallization procedures were developed which involved slow crystallization from doped solutions in large beakers, and crop collection at different stages of crystallization.

Initial crops were collected, dried in a desiccator and submitted for analysis. These crystallizations were in progress until the end of the program. The following dopants were used:

- a. NaClO_3
- b. $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$
- c. $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$
- d. AgClO_3
- e. $\text{Cu}(\text{ClO}_3)_2$

3. Gamma Irradiation and Shock Treatment of Reagent Grade Potassium Chlorates

Portions of 240-270 mesh KClO_3 (reagent grade) were subjected to Co^{60} gamma irradiation of varying doses. The irradiation cell has been described previously.³ Portions of the irradiated samples were dried in a desiccator at room temperature, and also in an oven at 110°C . Portions were also used for DTA/TGA experiments directly after they were taken from the hot cell.

Some KClO_3 was subjected to mechanical shock by pounding and vigorous crushing in a mortar.

4. Preparation of Pellets

Pellets of KClO_3 were pressed with the hydraulic press under 20,000 psi pressure. These were eventually used in our conductivity experiments.

5. Preparation of Mixtures

In order to investigate the influence of doping and of various oxides on the combustion of KClO_3 with sulfur, mixtures were prepared of different compositions.

Doped KClO_3 was mixed with sulfur corresponding to the stoichiometry of the overall reaction:



some mixtures were prepared with excessive KClO_3 .

The KClO_3 in all mixtures was sieved to screen fraction 240 270 for standardization and then stored in a desiccator.

Tertiary mixtures of various mole ratios were also prepared from reagent grade KClO_3 with several oxides and with

sulfur. The sieve-fractions of KClO_3 and the oxides between 240 and 270 mesh were used. These mixtures were also stored in a desiccator.

B. Differential Thermal Analysis, Thermogravimetric Analysis and Isothermal Experiments

DTA and TGA experiments were done on a combined DTA/TGA Chevenard thermobalance which has been described previously.³ For some combustion experiments of doped potassium chlorates with sulfur, a Moseley X-Y Recorder with a fast time base was connected to a Stone-Cahn Thermobalance.

The DTA experiments involving combustion of KClO_3 -S mixed with oxides were done on IITRI designed DTA equipment⁴ where thermocouples are placed in capillaries below the sample and reference material. Provisions are made for constant gas flows. Isothermal runs were performed on the Chevenard Thermobalance.

C. Electrical Conductivity Experiments and Mass Spectrometric Analysis

Initial conductivity experiments were done in the conductivity cell described previously.³ The cell was connected via a vacuum rack to a Bendix Time-of-Flight mass spectrometer to permit simultaneous conductivity measurements and mass spectrometric analysis.

This particular instrument configuration was later found to be impractical, since high background developed in the mass spectrometer due to the presence of stopcock grease in the vacuum rack. The conductivity cell has been redesigned to

avoid these difficulties. Conductivity runs were performed separately in various gaseous atmospheres including water and sulfur vapor. Provisions were made for drying the gases over an activated bed of molecular sieves before they enter the conductivity cell.

Separate mass spectrometric analysis was initiated to investigate products formed during the reaction between doped KClO_3 and sulfur.

D. Additional Analytical Methods

Analyses were performed on the residues of low temperature isothermal experiments which took place over several days. Cl^- was titrated according to the Mohr method. In a second sample ClO_3^- was reduced by Fe^{++} . The Cl^- content (from $\text{Cl}^- + \text{ClO}_3^-$) was again determined by the Mohr method. ClO_3^- and ClO_4^- were then reduced to Cl^- by ignition with NH_4Cl , and again the overall Cl^- content (from Cl^- , ClO_3^- and ClO_4^-) determined by titration after Mohr. In order to check these results, K^+ was determined independently in a separate batch. Table 1 summarizes the results.

Analyses were also performed on initial crops of doped KClO_3 which were used in the thermal decomposition studies. Copper was colorimetrically determined with neocuproine, sodium by flame photometry and Ca^{++} and Ba^{++} were initially analyzed titrimetrically with EDTA against Eriochrome Black T. Poor reproducibility in the titration results for Ca^{++} and Ba^{++} due to the low concentrations present made it advisable to use a different indicator (Metab-Indicator) in order to check the rather low concentrations. Titration against Eriochrome

Table 1

ANALYSIS OF KClO_3 REACTION PRODUCTS AFTER ISOTHERMAL
DECOMPOSITION FOR SEVERAL DAYS AT 480°C

Method

- A. Cl^- -Mohr titration
- B. $\text{Cl}^- + \text{ClO}_3^-$ -Reduction of ClO_3^- with Fe^{++} ,
Mohr-titration of total Cl^-
- C. $\text{Cl}^- + \text{ClO}_3^- + \text{ClO}_4^-$ -Reduction of ClO_3^- and ClO_4^-
by ignition with NH_4Cl , Mohr
titration of total Cl^-

Synthetic Sample: KCl - 0.852 meq; KClO_3 - 0.114 meq;
 KClO_4 - 0.913 meq.

<u>Analysis</u>	<u>Theoretical</u>	<u>Found</u>
A. Cl^-	0.852 meq	0.850
B. $\text{Cl}^- + \text{ClO}_3^-$	0.967 meq	0.977
C. $\text{Cl}^- + \text{ClO}_3^- + \text{ClO}_4^-$	1.88 meq	1.84

Sample Under Investigation

Cl^-	0.748 meq/total sample = 55.8 mg KCl
ClO_3^-	0.071 meq/total sample = 8.7 mg KClO_3
ClO_4^-	0.760 meq/total sample = 105.4 mg KClO_3
	<u>1.579 meq</u> <u>169.9 mg</u>

Sample Wt. given 172.7 mg

K^+	61.2 mg	61.4 mg $\pm$ 0.2 mg
	61.6 mg	
	61.4 mg = 1.57 $\pm$ 0.005 meq K^+	

Black T proved to be very difficult at low concentrations of Ca and at all concentrations of Ba, because the titration end point was rather difficult to detect. Tables 2 and 3 summarize the analytical results for Na^+ , Cu^{++} , Ba^{++} and Ca^{++} . Other auxiliary methods included x-ray analysis done with a Phillips X-ray diffractometer and microscopic investigations with a Zeiss polarizing microscope.

III. EXPERIMENTAL RESULTS

A. Analysis of Doped Samples of Potassium Chlorate

Potassium chlorate samples which were prepared by evaporating solutions of 1 mole % dopant with KClO_3 at 100°C to dryness, were heterocrystalline; and with the exception of FeCl_3 and CuCl_2 doped samples, were white. Since the samples were obtained by way of evaporation, no analysis for the dopant content was necessary

A method for the preparation of doped single crystals was developed which involved evaporation of the solutions and crop collection in stages. Initial crops were analyzed for their dopant contents. The results are listed in Tables 2 and 3. Crops of crystals at higher concentrations were collected during the latter stages of the program.

The growth of the single crystals from water solutions was influenced by the amount and type of dopants. Large single crystals in the form of plates were obtained from solutions containing 0.1% or less of dopant.

Table 2

EDTA TITRATION OF KClO_3 SINGLE CRYSTALS FOR Ca AND Ba AGAINST
METALS AND/OR ERIochrome BLACK T INDICATORS

<u>Crop No.</u>	<u>% Dopant in Original Mother Liquid</u>	<u>% Dopant Against Metal</u>	<u>% Dopant Against Black Eriochrome</u>
Ca			
1.1	5%	--	0.0042
1.2	5%	0.0064	0.0060
1.3	5%	--	0.0112
2.1	1%	0.0020	--
2.2	1%	0.0037	--
3.1	0.1%	0.0007	--
3.2	0.1%	0.0017	--
Ba			
1.1	5%	0.0013	
1.2	5%	0.0024	
1.3	5%	0.0020	
2.1	1%	0.0015	
3.1	0.1%	0.0003	

Table 3

ANALYSIS OF DOPED KClO_3 CROPS FOR Na^+ BY FLAME PHOTOMETRY, AND
FOR Cu WITH NEOCUPROINE

<u>Sample</u>	<u>% Cu in Original Mother Liquid</u>	<u>% Cu</u>
Crop #1	0.1%	0.000086%
Crop #2	0.1%	0.000086%
Crop #1	1%	0.00018%
Crop #2	1%	0.00014%
Crop #1	5%	0.0069%
Crop #2	5%	0.010%
Crop #3	5%	0.0076%

<u>Sample</u>	<u>% Na in Original Mother Liquid</u>	<u>% Na</u>
Crop #1	0.1%	0.0021%
Crop #2	0.1%	0.0027%
Crop #1	1%	0.0036%
Crop #2	1%	0.0071%
Crop #1	5%	0.0028%
Crop #2	5%	0.0056%
Crop #3	5%	0.0092%

If higher percentages of dopants were used the crystals were smaller in size. An exception was NaClO_3 where the single crystals formed in solutions of higher NaClO_3 concentrations were as large as the KClO_3 crystals. Observations with a polarizing microscope showed gross surface defects which are possibly due to etching by water during the washing process. Aside from this, structural defects were observed in some cases as judged from the birefringence pattern of the crystals under the crossed polarizer and analyzer of the microscope.

B. X-Ray Analysis of Some Doped Samples of KClO_3

Attempts were made to analyze doped samples by X-ray, and investigate whether gross structural defects could be detected. No significant differences were observed which, in essence means that the different phases are too small to be detected or that the dopants were incorporated substitutionally into the lattice. The exceptions are, perhaps the LiNO_3 -doped sample which exhibit slightly lower intensities of the major peaks at a diffraction angle of about 20.9° and 21.8° , the lead nitrate-doped sample which shows additional lines and CdCl_2 -doped samples which also show an additional peak.

C. The Thermal Decomposition of KClO_3 at Low Temperatures

The low temperature isothermal decomposition studies of pure KClO_3 which were initiated during a previous program³ were continued in order to obtain further insight into the disproportionation kinetics as the first stage of decomposition.

To this end, samples of undoped KClO_3 were isothermally decomposed at about 480°C . This reaction took place over several days. The final weight loss was approximately 33% of the overall weight loss at higher temperatures. The residue was analyzed as described in the experimental section. The results are summarized in Table 1. It may be seen that the mole percents of KCl and KClO_4 are approximately equal which is of significance for the proper interpretation of the overall decomposition reaction.

D. The Decomposition of Potassium Chlorate in the Presence of Potassium Perchlorate

Mixtures of potassium chlorate and potassium perchlorate were prepared in the mole ratios, $\text{KClO}_4:\text{KClO}_3 = 1:1$ and $1:5$. The purpose of these experiments was to investigate the possible catalytic influence of KClO_4 on the thermal decomposition of KClO_3 . Some authors⁵ deduced from isothermal experiments that KClO_4 catalyzes the isothermal decomposition of KClO_3 . Unfortunately, their experiments were conducted with bare chromel-alumel thermocouples imbedded in the samples. Their experimental findings, therefore, must be considered unreliable since chromel-alumel thermocouples catalyze the thermal decomposition of both, potassium perchlorate⁶ and potassium chlorate.³

Figure 1 shows the combined DTA/TGA curves of pure potassium chlorate, pure potassium perchlorate, and mixtures of potassium chlorate and potassium perchlorate in the mole ratios mentioned

above. The total weights of the mixtures were adjusted in such a way that the overall weight loss was approximately the same for all samples. This permitted more direct comparisons between the weight loss curves.

The thermal stability of the mixture having a mole ratio of $\text{KClO}_4:\text{KClO}_3 = 1:5$ does not appear to differ appreciably from that of pure KClO_3 as indicated from the weight loss curves. The DTA curves for the mixture show a small endotherm at about 300°C due to the phase transition of the perchlorate. An increase in the relative amount of KClO_4 (Ratio 1:1) increases the magnitude of the transition endotherm and decreases the relative magnitude for the melting endotherm of KClO_3 at about 365°C . This double endotherm could be due to the formation of a eutectic between some reaction products and residual KClO_3 . The higher the amount of KClO_4 in the mixture, the greater is the shift in the decomposition curves to higher temperatures. In addition, a sharp endotherm occurs at about 610°C where KClO_4 melts before it undergoes further decomposition.

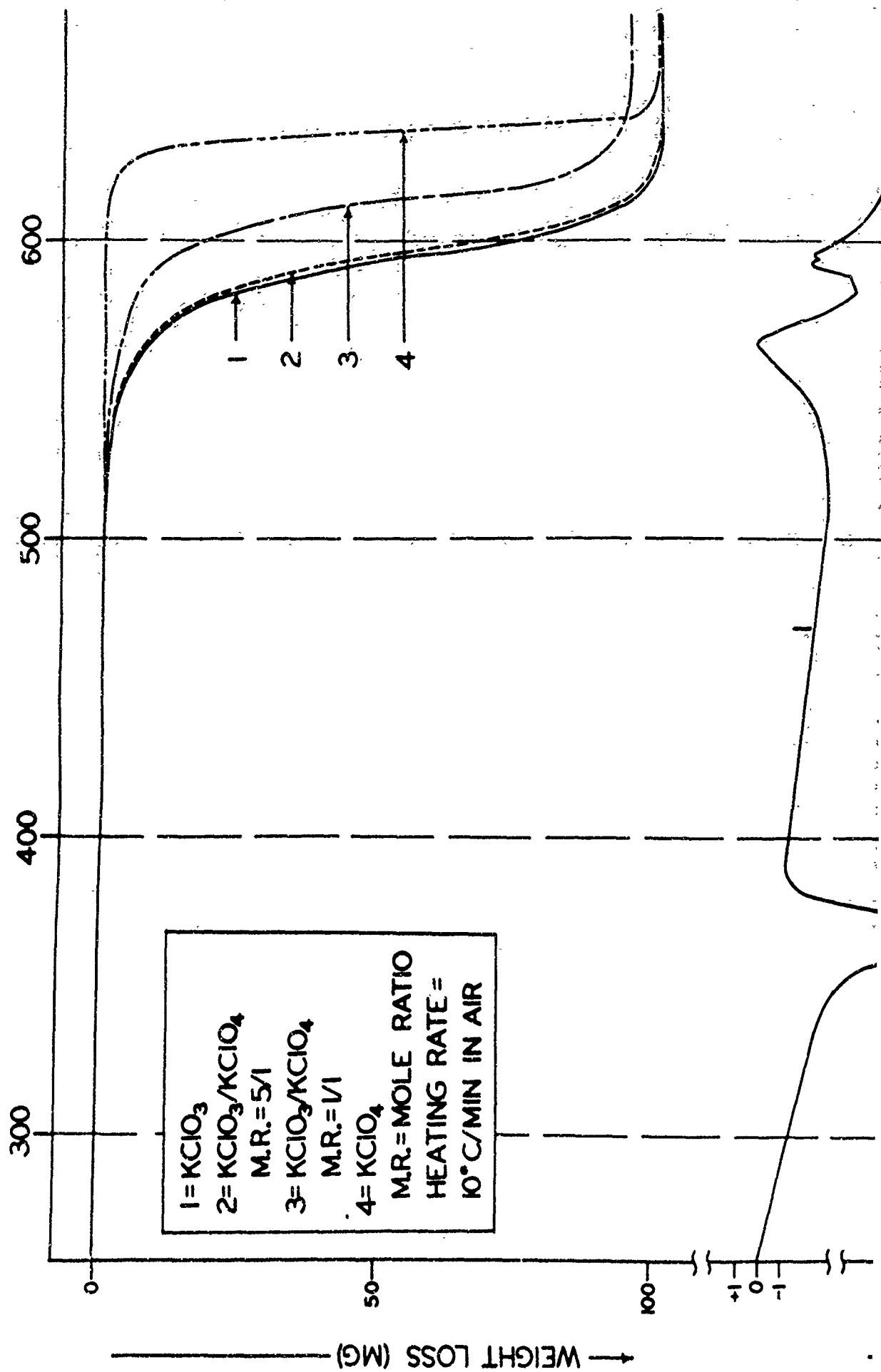
E. The Influence of the Final Decomposition Product, KCl , on the Thermal Decomposition of KClO_3

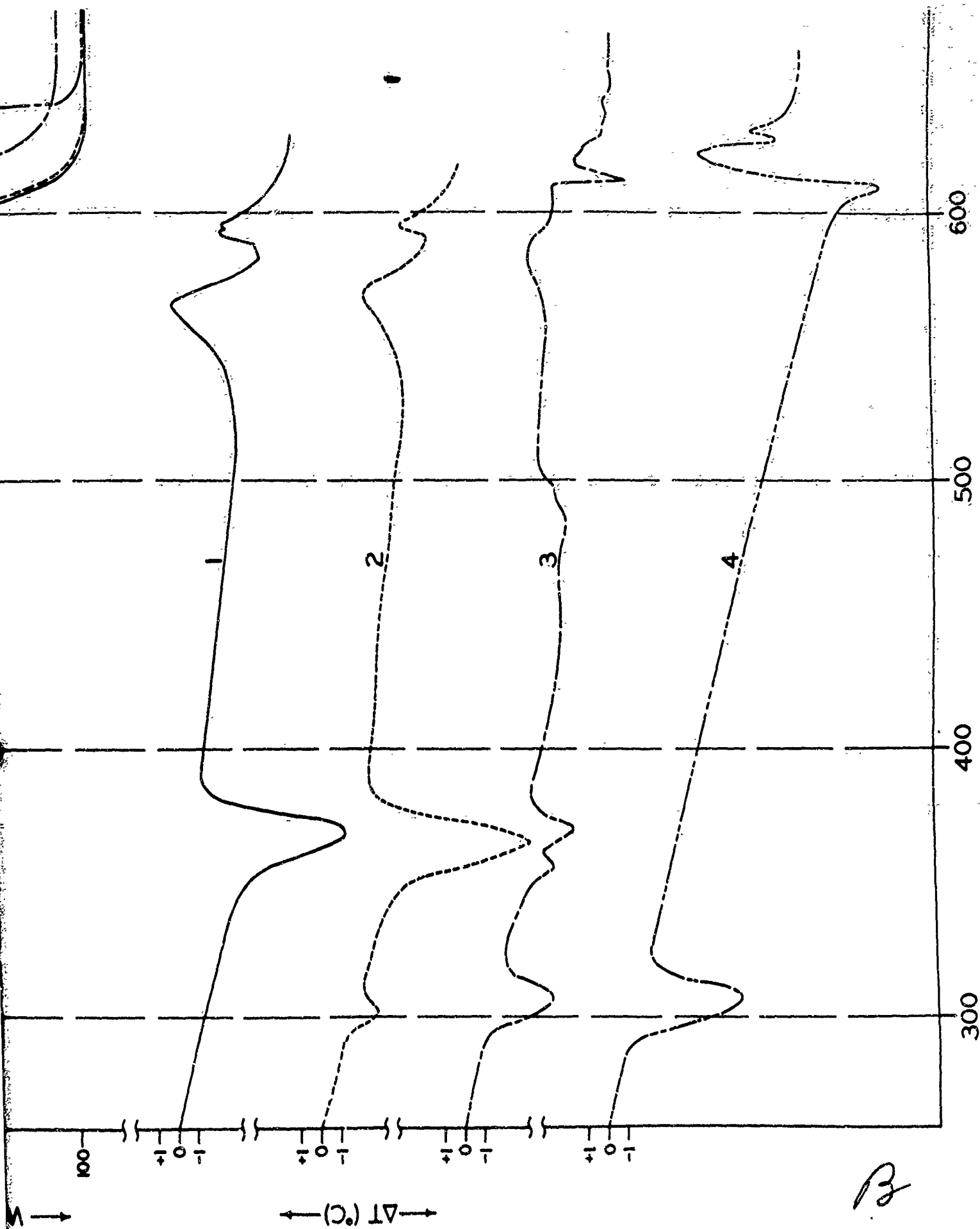
As in case of KClO_4 , it is of importance to establish the role played by potassium chloride on the decomposition of KClO_3 , since it is the final decomposition product.

It was observed during our previous program³ that at sufficiently low temperatures chloride appeared to inhibit decomposition, but at higher temperatures it appeared to

Figure 1

DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRIC ANALYSIS OF PURE POTASSIUM CHLORATE AND MIXTURES OF POTASSIUM CHLORATE WITH POTASSIUM PERCHLORATE





accelerate the reaction. Isothermal experiments were also carried out at temperatures below 500°C. It was found that at these low temperatures the decomposition mechanism of KClO_3 essentially involves complete disproportionation to KCl , KClO_4 and O_2 . In addition, chloride was added to the KClO_3 in varying amounts so that the initial mixtures in the molten phase will vary in KClO_3 concentration. This is important because it was already demonstrated that chloride ion at sufficiently high concentrations as produced during the decomposition of KClO_3 can affect the rate of decomposition.

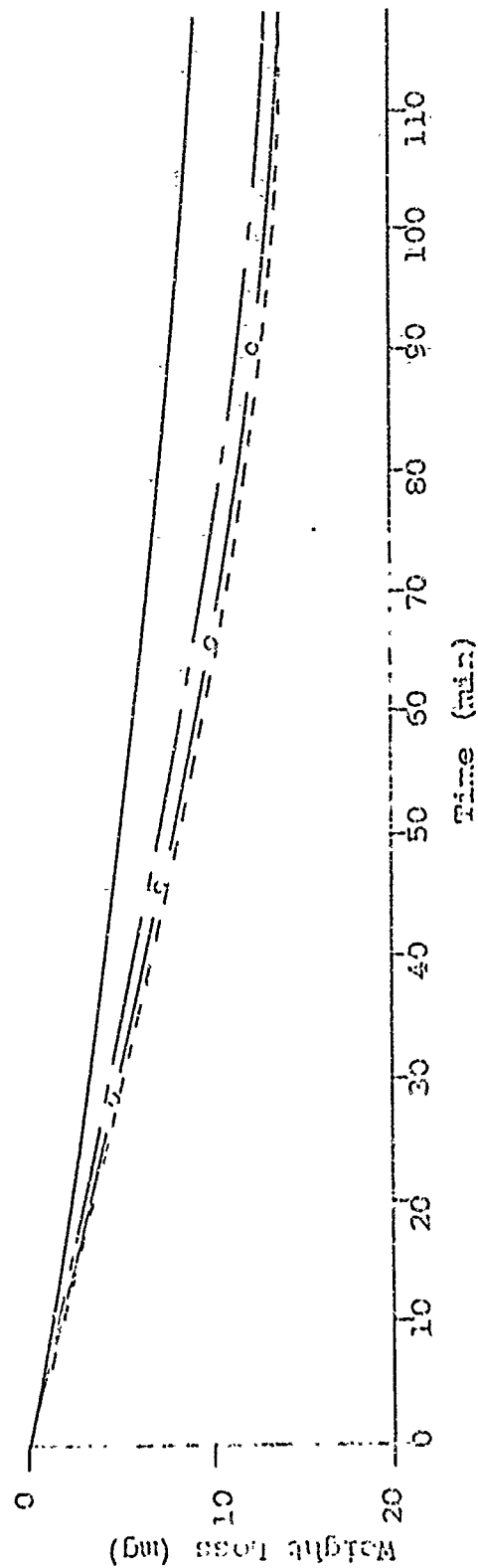
Figure 2 shows typical isothermal curves for the decomposition of undoped KClO_3 in varying concentrations with potassium chloride diluent. It is clearly seen that at sufficiently high concentrations of chloride the rate of decomposition is appreciably reduced in mixtures with chloride.

F. Effects of Doping on Chemical Reactivity

Thermogravimetric analysis and combination differential thermal analysis-thermogravimetric analysis experiments were performed on doped and undoped potassium chlorate. The combined DTA/TGA apparatus was described previously.³ The heating rate was nominally 10 C per minute. Figure 3 shows comparisons of the thermal decomposition characteristics of pure KClO_3 with those of the doped materials. The results indicate that chloride salts did not appreciably influence its thermal decomposition characteristics. The chloride dopants included LiCl , KCl , and CsCl .

Figure 2

INITIAL WEIGHT LOSS DURING ISOTHERMAL DECOMPOSITION OF PURE KClO_3
AND IN MIXTURES WITH KCl
(Temperature About 480°C)



Mole Ratio

KCl/KClO_3

Symbol

1:1

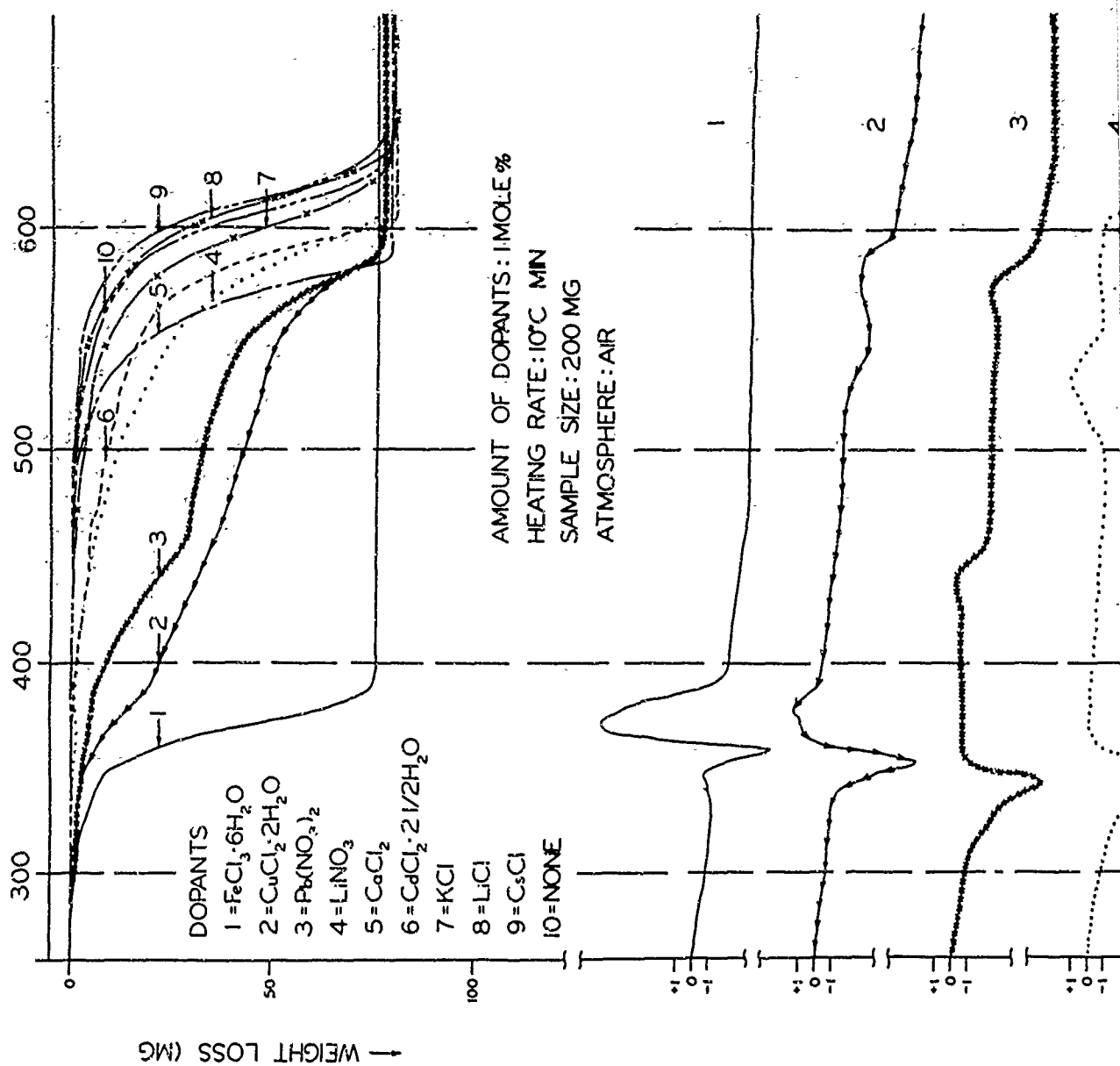
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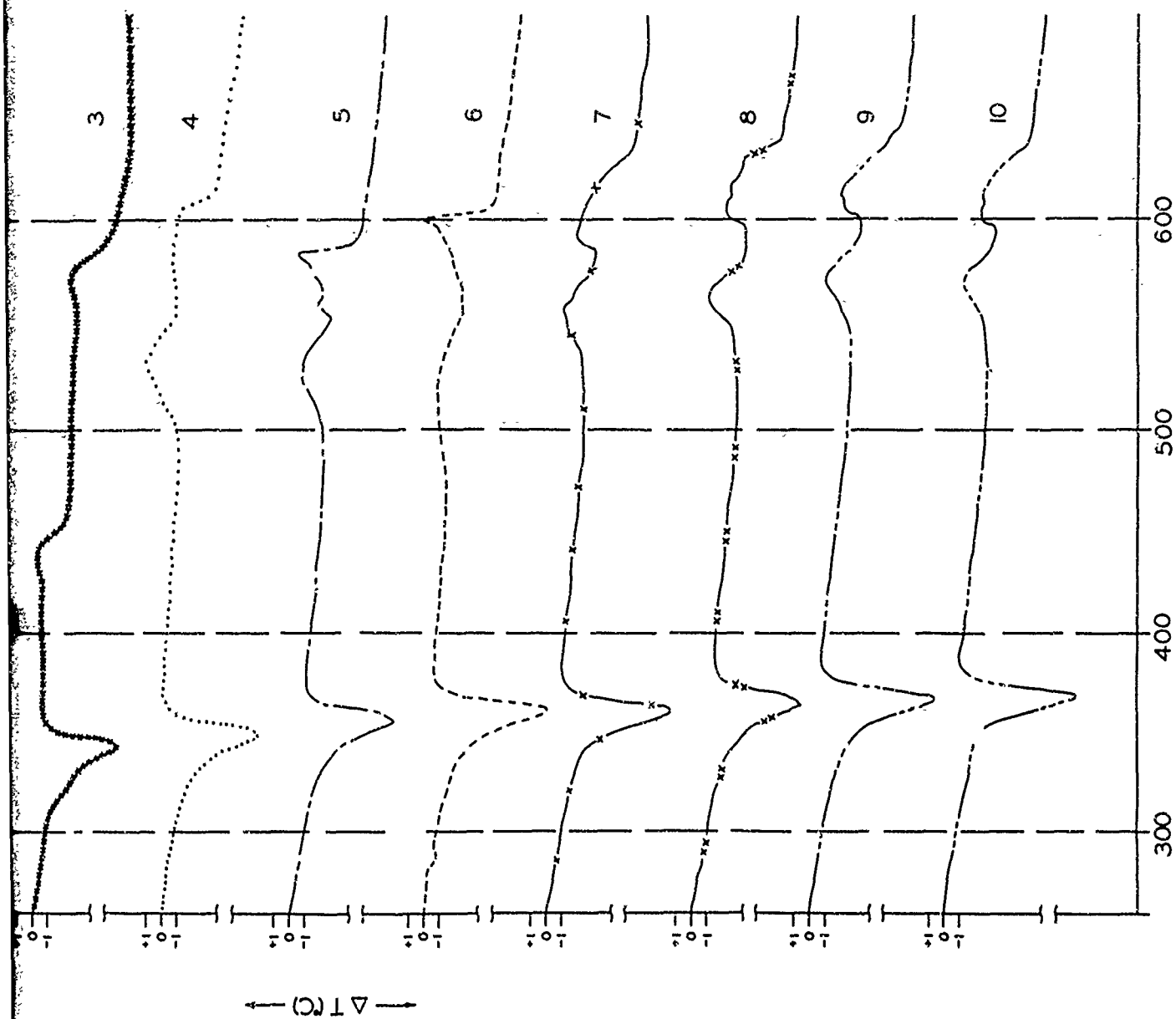
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Figure 3

THERMOGRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS
OF DOPED POTASSIUM CHLORATES





The data based on the experiments are tabulated in Table 4 and reveal several interesting points.

1. The average temperatures of the endothermal minimum at the melting point of KClO_3 are only slightly decreased upon addition of chloride. The decreases in temperature is much more pronounced upon addition of the nitrate impurities.

2. Doping with the nitrates has the effect of decreasing the average decomposition temperatures from 25° to 50° below the temperatures of decomposition of the pure and chloride doped chlorates.

3. The most effective dopants are FeCl_3 and CuCl_2 . In particular, doping with FeCl_3 causes appreciable thermal decomposition of KClO_3 to occur below the temperature of the melting endotherm as is seen in Figure 3.

In Figure 4 the effect of cation doping on the thermal characteristics of doped single crystals is demonstrated. It is seen that dopants such as Na^+ and Ba^{++} have, if at all, only little influence on the thermal decomposition characteristics of KClO_3 . Even crystals which were crystallized from solutions containing 10% Na^+ (which coincides with the curve obtained from 1% Na^+), and 10% Ba^{++} do not differ appreciably in their thermal behavior from the undoped material. In case of Na^+ this is not unexpected, since Na^+ is in the same group of the periodic system as K^+ . The decomposition behavior of 10% Ca^{++} doped KClO_3 is significantly different from the behavior of pure KClO_3 . The most pronounced differences in thermal

Table 4

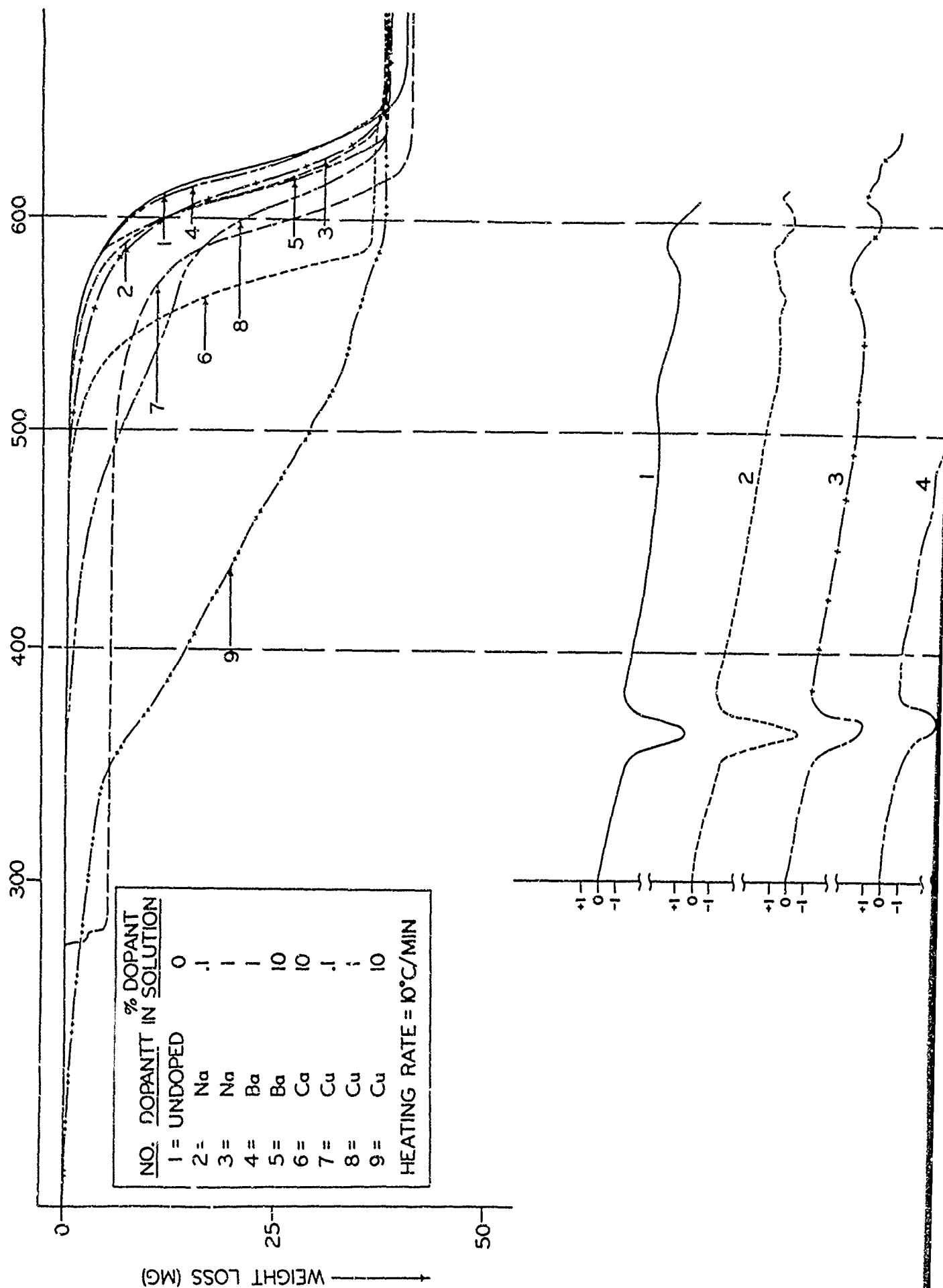
SUMMARY OF THERMAL ANALYSIS RESULTS

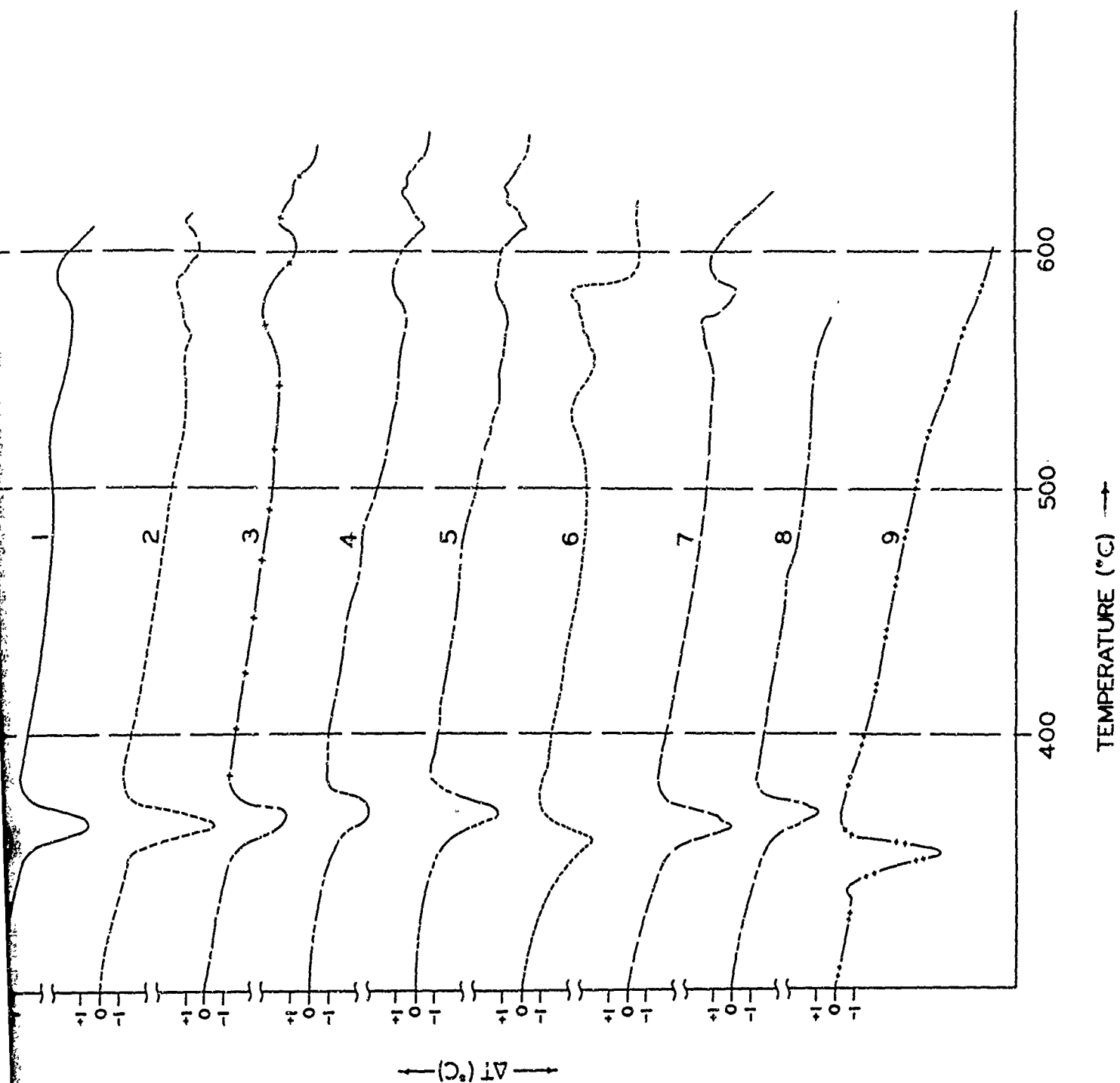
<u>Dopant</u>	<u>Average Peak Endothermal Temperature</u>	<u>Average De- composition Temperature at 25% wt Loss</u>	<u>Average De- composition Temperature at 50% wt loss</u>	<u>Charge Density of Cationic Dopant_{o2} Electrons/A²</u>
LiCl	363 ± 2.6	588.7 ± 8.1	607.3 ± 2.6	0.69
KCl	360 ± 0.0	581.5 ± 2.1	606.5 ± 0.7	0.179
CsCl	367.7 ± 2.5	601.7 ± 7.6	618 ± 5.3	0.114
CuCl ₂	353.3 ± 1.5	398.3 ± 2.9	485 ± 5.0	1.240
CdCl ₂	360.7 ± 9.3	562.3 ± 6.8	586 ± 7.9	0.678
CaCl ₂	355.3 ± 19.6	554.3 ± 14.3	568.3 ± 12.8	0.650
FeCl ₃	357.5 ± 3.5	354 ± 1.4	375 ± 0.0	2.42
Pb(NO ₃) ₂	342.5 ± 0.7	441.5 ± 0.7	543.5 ± 9.2	0.442(1.800)*
Li(NO ₃)	349 ± 15.5	549 ± 8.5	585 ± 7.1	0.69
NONE	368 ± 4.2	606.5 ± 2.1	620 ± 2.8	0.0

* Second number refers to four-valent lead

Figure 4

THE EFFECT OF CATION DOPING ON THE THERMAL CHARACTERISTICS OF SINGLE CRYSTALS





B

characteristics are found, if the solutions were doped with .1, 1, and 10% Cu^{++} . The single crystals obtained from 10% solutions were most reactive. Slow decomposition begins much below the melting point of KClO_3 and the melting point is shifted towards lower temperatures. At least two steps are seen in the weight loss curves of Cu^{++} doped KClO_3 . Initial weight loss of the sample doped with 0.1 Cu^{++} occurs below 300°C .

G. The Effect of Gamma-Irradiation and Mechanical Shock on the Thermal Decomposition of KClO_3

Experiments were initiated to elucidate possible effects of irradiation and mechanical shock on the thermal decomposition of potassium chlorate. The results are very interesting. It was observed that the data appeared to be poorly reproducible, if time and atmospheric conditions during storage were not kept under very careful control. If the irradiated samples were taken directly from the hot cell, a chlorine odor was discernible, and the samples were of tannish color. If the samples were dried at about 110°C , the color faded and the smell disappeared.

A DTA/TGA experiment on a sample placed on the thermobalance immediately after it was taken from the hot cell, showed exothermal and endothermal decomposition steps at low temperatures. Partial weight loss is observed at ambient temperatures (Figure 5). This low temperature weight loss is approximately 18.5% of the total weight. The total weight loss after complete decomposition is approximately 60%.

If the sample is dried in a desiccator or if it is stored for a longer period of time, the low temperature weight loss is no longer observable. A sample dried in an oven at 110°C loses its tannish color and again, low temperature weight loss is no longer apparent. The melting endotherm of irradiated KClO_3 shows two pronounced shoulders, while the higher temperature exotherms appear similar to those of unirradiated material. One sample of KClO_3 which had been subjected to mechanical shock showed a similar but smaller weight loss at low temperatures as the irradiated material directly after irradiation. (Figure 5).

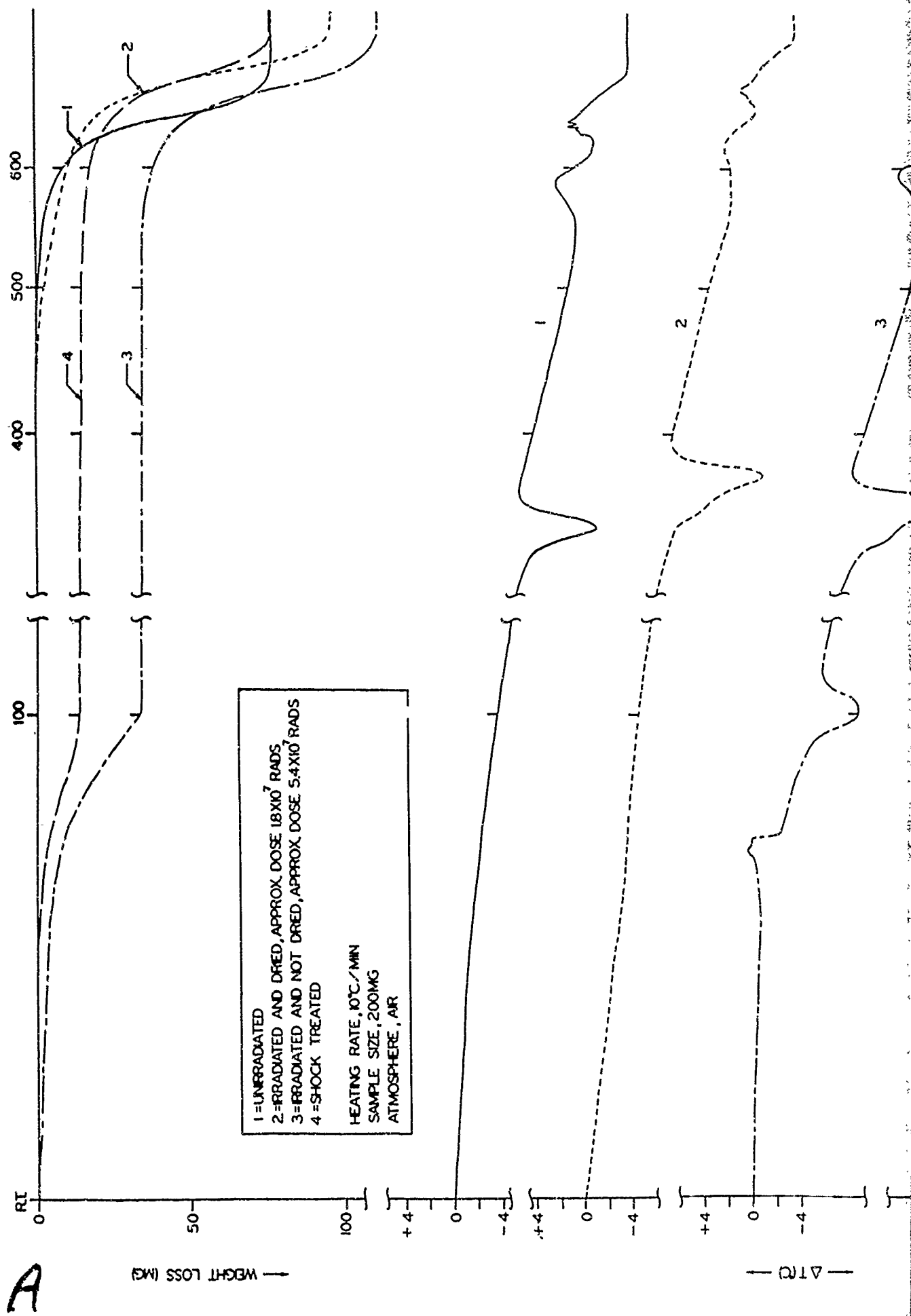
H. Electrical Conductivity Studies and Mass Spectrometric Analysis of Potassium Chlorate

Preliminary electrical conductivity experiments were started to test the conductivity cell which was set up in conjunction with a Bendix Time-of-Flight mass spectrometer. This has the advantage of combining the electrical conductivity setup with a sensitive analytical tool to determine the gaseous reaction products. KClO_3 was pressed at 20,000 psi to form a cylindrical pellet. The opposite surfaces were ground parallel to provide for smooth contact with the platinum electrodes of the conductivity cell.

Figure 6 shows electrical conductance curves of undoped KClO_3 in air at atmospheric pressure and in vacuum at less than 10^{-4} mm Hg. The sample was heated at a constant rate of about 10°C/min. The logarithm of the electrical conductance

Figure 5

INFLUENCE OF IRRADIATION AND MECHANICAL SHOCK ON THE DECOMPOSITION OF POTASSIUM CHLORATE



HEATING RATE, 10°C/MIN
SAMPLE SIZE, 200MG
ATMOSPHERE, AIR

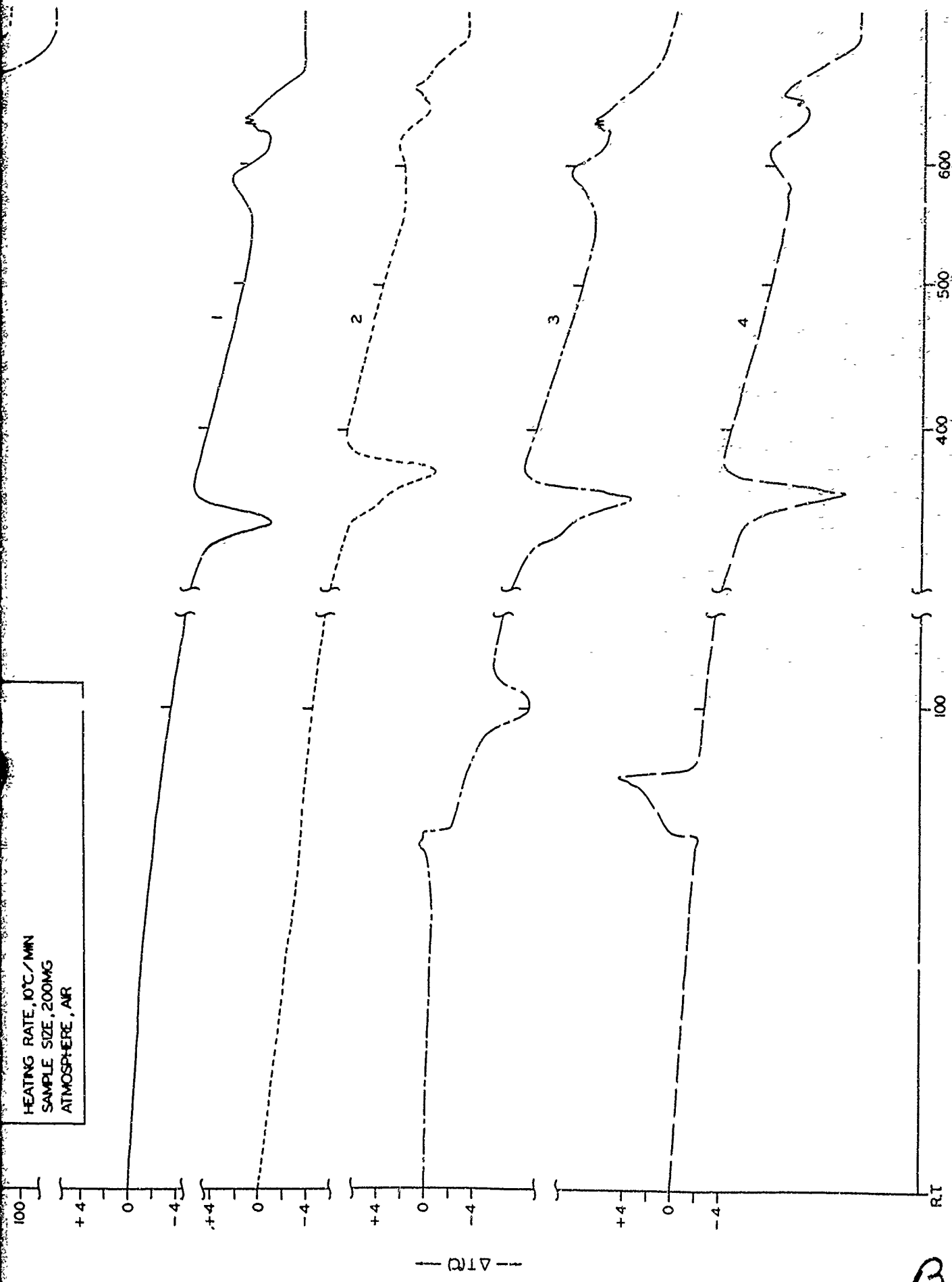
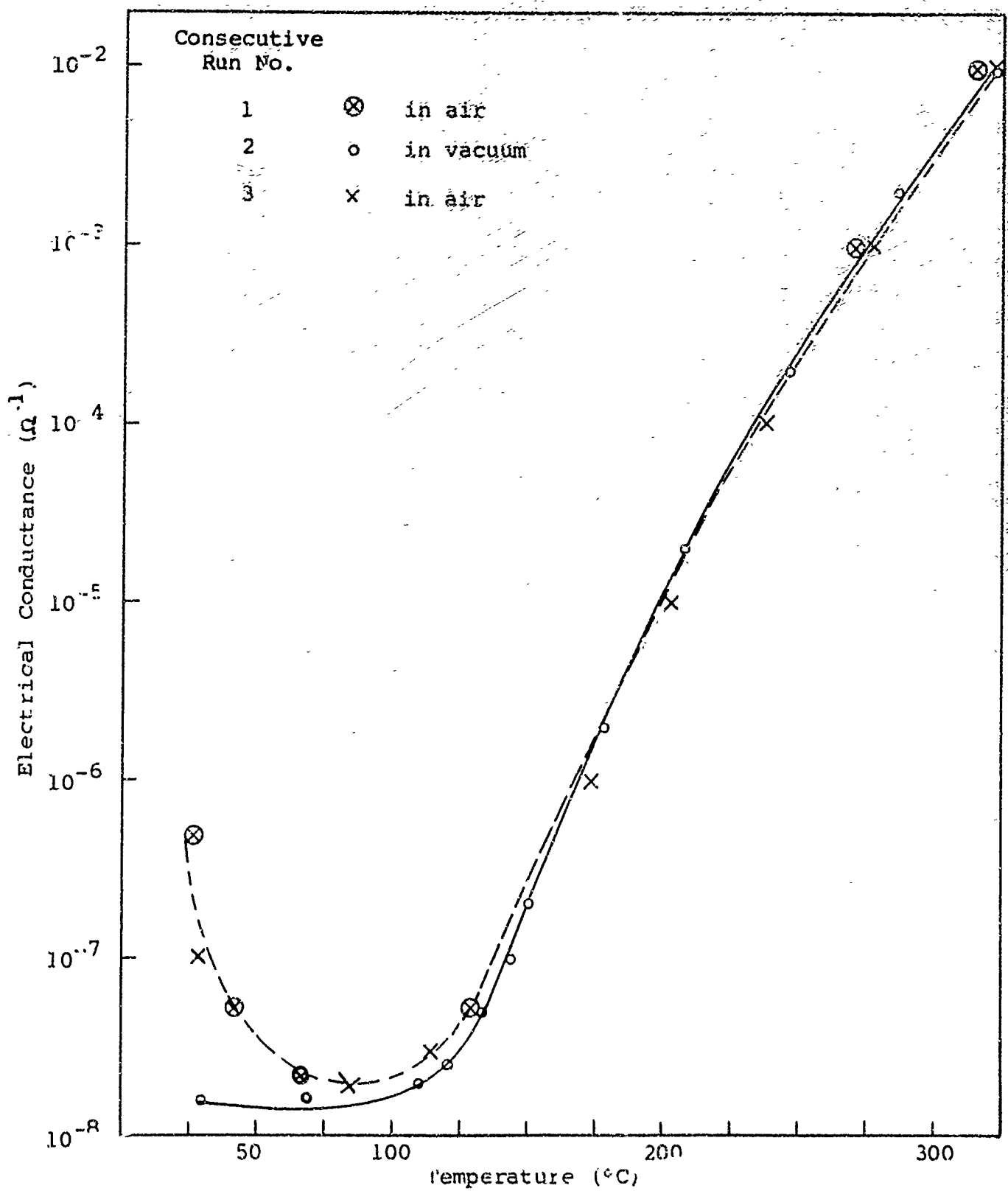


Figure 6

ELECTRICAL CONDUCTANCE OF A KClO_3 PELLET



is plotted as a function of the temperature. This data is taken directly from the recorded curves. It is seen that the conductance is similar at temperatures above 150°C for the sample in air and in vacuum. At lower temperatures, however, the sample in air increases in conductivity with decreasing temperatures. This is not true under vacuum where the conductivity continues to decrease as the temperature is reduced.

In Figure 7 the conductivity is plotted as a function of inverse absolute temperature. The activation energy obtained from the straight portions of these curves is about 32 kcal/mole.

Conductivity runs were also performed in various gas and vapor atmospheres. The results are summarized in Figure 8. It can be seen that water vapor significantly increases the electrical conductivity at low temperatures which explains the fact that preliminary runs (Figure 6) in undried air were found to be non-reproducible at low temperatures. The electrical conductivity in dry oxygen, argon and in air does not appear to be significantly different from the conductivity in vacuum. It was, however, observed that the steady state pressure in the system increases from a value of 10^{-5} at room temperature to 10^{-3} mm Hg at temperatures above 300°C in vacuum. Preliminary attempts of simultaneous mass spectrometric analysis failed, because of a large background problem.

Figure 7

ACTIVATION ENERGY OF THE CHARGE TRANSFER
IN A POTASSIUM CHLORATE PELLET

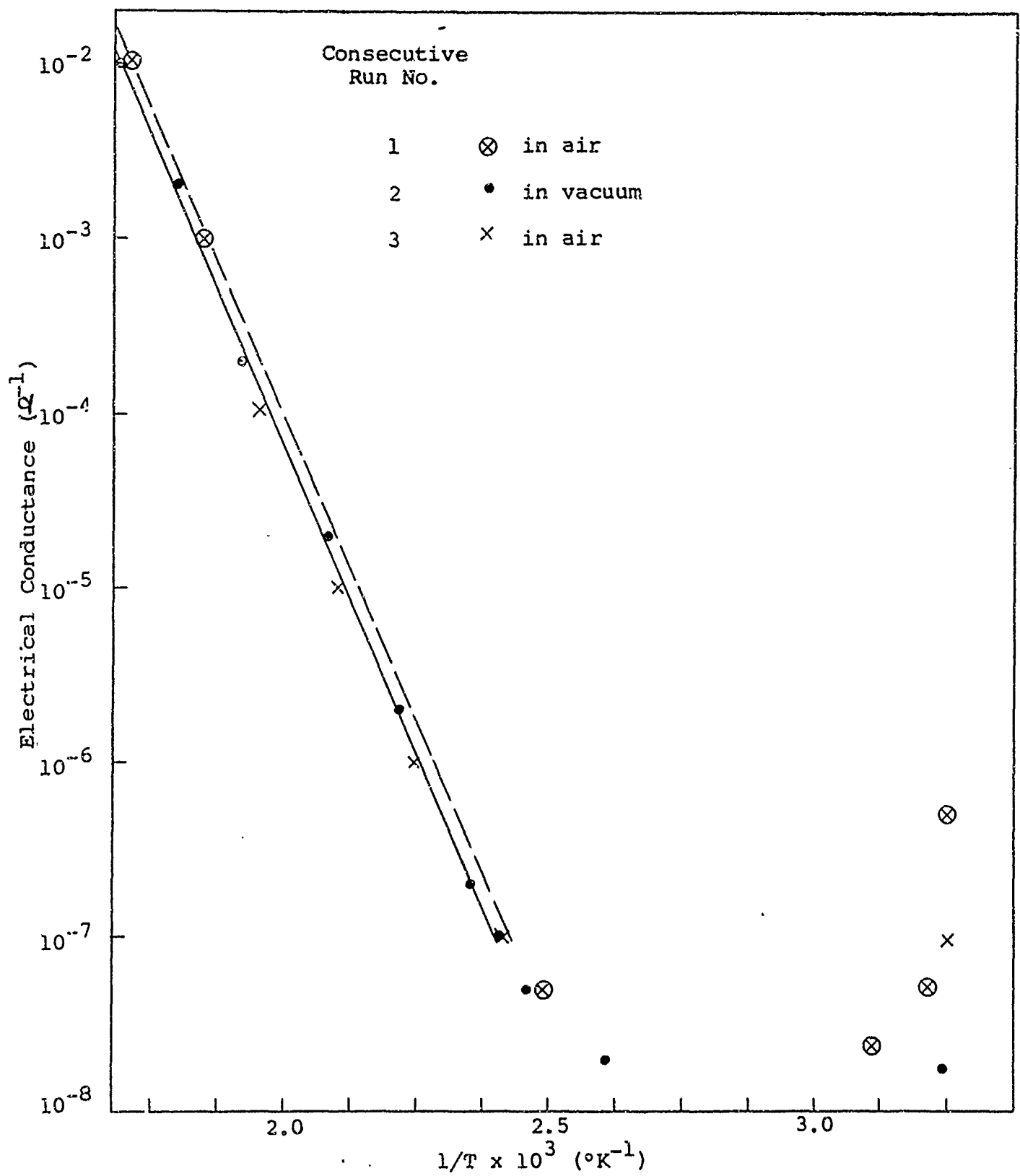
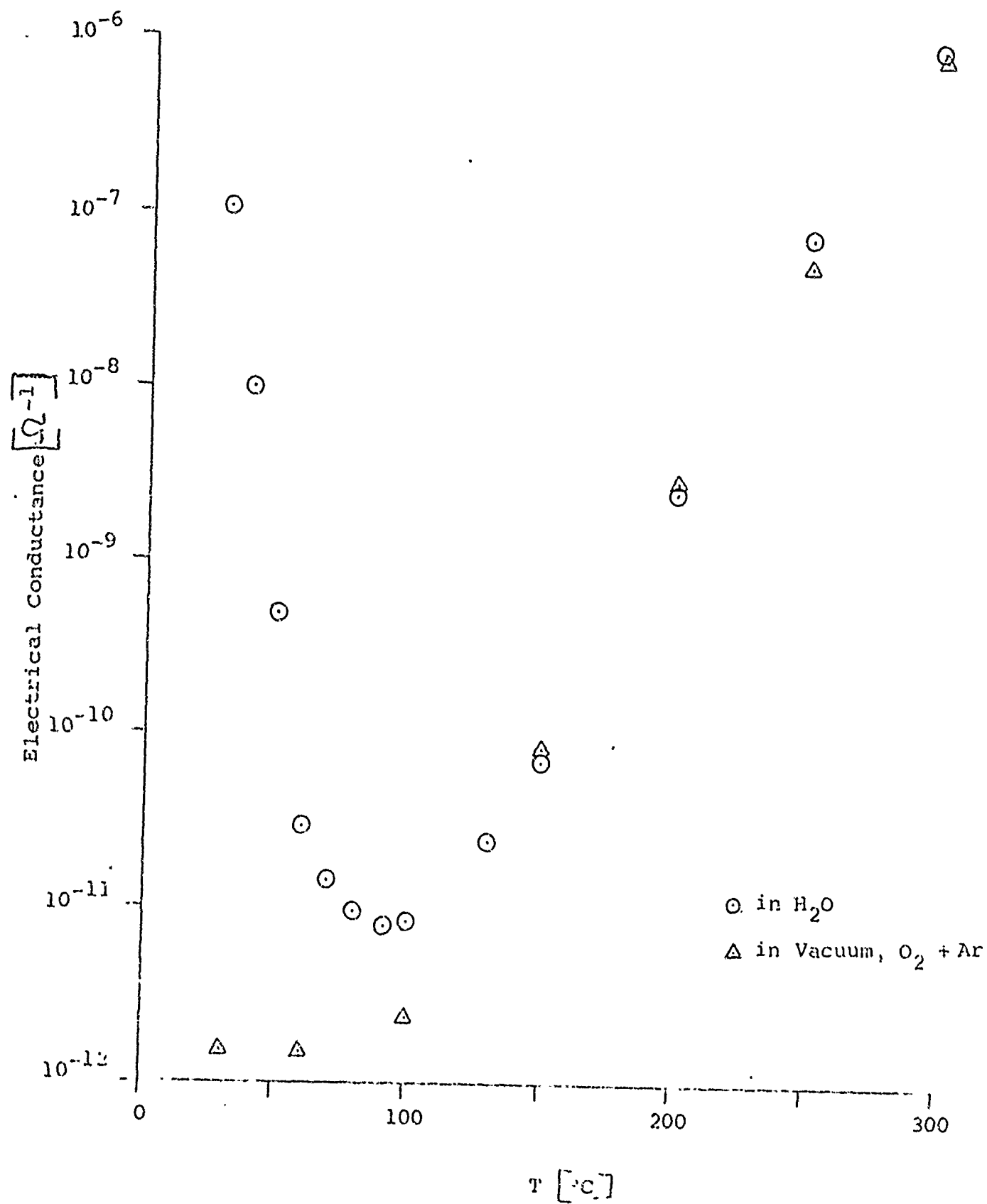


Figure 8
INFLUENCE OF WATER VAPOR ON THE ELECTRICAL CONDUCTIVITY OF
POTASSIUM CHLORATE



I. Thermal Analysis of the Combustion of Doped KClO₃ in Mixtures with Sulfur

Preliminary DTA/TGA runs were carried out with various mixtures of sulfur and doped potassium chlorates. The potassium chlorate samples were obtained from evaporation of 1% dopant in KClO₃ solutions. This was done to investigate the influence of doped KClO₃ on the combustion of sulfur.

Table 5 summarizes the results in terms of ignition temperature. The average values of the ignition temperatures and corresponding error limits (standard deviations from these values) are compiled in Table 6. The ignition temperature is lowest with KClO₃ doped with 1% CuCl₂. It is reduced by more than 20°C as compared to the ignition temperature of the undoped chlorate. McLain⁷ also showed similar results for Cu⁺⁺ doped mixtures. The effect of the dopants on the ignition temperature is CuCl₂ ~ KCl ~ Undoped ~ CsCl ~ Pb(NO₃)₂ < FeCl₃ ~ CdCl₂ < LiCl ~ LiNO₃ ~ CaCl₂. It is interesting to note that FeCl₃ is much less active as far as the ignition temperature is concerned than CuCl₂. It should, however, be pointed out that the average weight loss is much higher with FeCl₃ than with all the other dopants. The stoichiometric weight loss according to the equation:



is approximately 37.6%. The actual weight losses are much higher.

Therefore, the observed weight losses are significant only in that they showed a more vigorous reaction is taking place in the FeCl₃ doped reaction.

Table 5

THE COMBUSTION OF SULFUR WITH DOPED
SAMPLES OF POTASSIUM CHLORATE

<u>1 mole % Dopant</u>	<u>Ignition Temperature (°C)</u>
Undoped	142
Undoped	141
Undoped	137
FeCl ₃	142
FeCl ₃	145
CuCl ₂	118
CuCl ₂	120
CsCl	138
CsCl	142
LiNO ₃	150
LiNO ₃	155
LiCl	150
LiCl	151
Pb(NO ₃) ₂	145
Pb(NO ₃) ₂	137
Pb(NO ₃) ₂	140
Pb(NO ₃) ₂	138
KCl	137
KCl	142
CdCl ₂	143
CdCl ₂	147
CaCl ₂	155
CaCl ₂	147

Table 6

AVERAGE IGNITION TEMPERATURES FOR THE REACTION OF
SULFUR WITH DOPED POTASSIUM CHLORATES

<u>Dopant</u>	<u>Average Ignition Temperature (°C)</u>
Undoped	140 ± 2.2
FeCl ₃	143.5 ± 2.1
CuCl ₂	119 ± 1.4
CsCl	140 ± 2.8
LiNO ₃	152.5 ± 3.5
LiCl	150.5 ± 0.7
Pb(NO ₃) ₂	140 ± 3.1
KCl	139.5 ± 3.5
CdCl ₂	145 ± 2.8
CaCl ₂	151 ± 5.7

TGA runs were performed using a relatively fast x-y-recorder to elucidate the rates of combustion in KClO_3 -S mixtures with and without additional KClO_3 as diluents, the results indicated that the rate of combustion even in dilute mixtures is too fast to be determined by the x-y-recorder.

J. Catalytic Activity of Metal Oxides on the Ignition of Potassium Chlorate-Sulfur Mixtures

The influence of metal oxide additives on the combustion of mixtures of potassium chlorate and sulfur was probed by differential thermal analysis. The oxides considered were Fe_2O_3 , Cr_2O_3 , and Al_2O_3 . These oxides were selected since the first two were found to be excellent catalysts while Al_2O_3 was relatively inactive. The concentration of the oxides were varied from 5 to 50 mole percent. These runs were generally performed in an argon atmosphere. A few experiments were carried out in an oxygen atmosphere. In an argon atmosphere the possibility of air oxidation is eliminated thereby limiting the oxidation of sulfur to reaction with the KClO_3 in the mixture. Carrying out the reaction in pure oxygen emphasizes the role of air oxidation in the combustion reaction. Table 7 shows the results. It can be seen that the ignition temperature differs significantly depending on the mole ratio of metal oxide to potassium chlorate and is also dependent on the gaseous environment. In Figure 9 the peak temperatures of the ignition exotherms are plotted as a function of mole ratio of the metal oxide to potassium chlorate.

Table 7

COMBUSTION OF SULFUR-POTASSIUM CHLORATE IN
MIXTURES WITH OXIDE CATALYSTS

<u>Catalyst</u>	<u>Atmosphere</u>	<u>Mole Ratio</u>	<u>Ignition Temperature</u>	<u>Relative Peak Height</u>	<u>Remarks</u>
Fe_2O_3	Ar	1:10	157	3.25	
Fe_2O_3	Ar	1:10	158	2.20	
Fe_2O_3	Ar	3:10	164	>2.9	off chart
Fe_2O_3	Ar	3:10	162	1.6	
Fe_2O_3	Ar	1:20	186	2.0	
Fe_2O_3	Ar	1:20	190	0.2	} 2S
Fe_2O_3	Ar	1:20	191	0.7	
Al_2O_3	Ar	1:10	163	2.8	
Al_2O_3	Ar	1:10	170	3.6	
Cr_2O_3	Ar	1:10	173		
Cr_2O_3	Ar	1:10	170	0.7	
Cr_2O_3	O_2	1:10	157		
Fe_2O_3	O_2	1:10	154	>3	off chart

Heating Rate: 10°C/min

Amount KClO_3 : 200 mg

Amount Sulfur: 75 mg (except 2S = 150 mg)

Gas Flow: 300 ml/min

Table 7

COMBUSTION OF SULFUR-POTASSIUM CHLORATE IN
MIXTURES WITH OXIDE CATALYSTS

<u>Catalyst</u>	<u>Atmosphere</u>	<u>Mole Ratio</u>	<u>Ignition Temperature</u>	<u>Relative Peak Height</u>	<u>Remarks</u>
Fe_2O_3	Ar	1:10	157	3.25	
Fe_2O_3	Ar	1:10	158	2.20	
Fe_2O_3	Ar	3:10	164	>2.9	off chart
Fe_2O_3	Ar	3:10	162	1.6	
Fe_2O_3	Ar	1:20	186	2.0	
Fe_2O_3	Ar	1:20	190	0.2	} 2S
Fe_2O_3	Ar	1:20	191	0.7	
Al_2O_3	Ar	1:10	163	2.8	
Al_2O_3	Ar	1:10	170	3.6	
Cr_2O_3	Ar	1:10	173		
Cr_2O_3	Ar	1:10	170	0.7	
Cr_2O_3	O_2	1:10	157		
Fe_2O_3	O_2	1:10	154	>3	off chart

Heating Rate: 10°C/min

Amount KClO_3 : 200 mg

Amount Sulfur: 75 mg (except 2S = 150 mg)

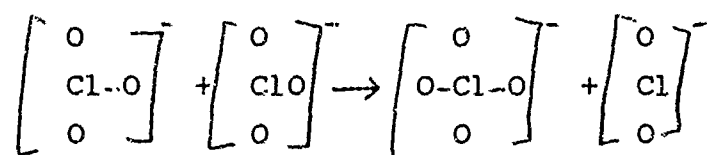
Gas Flow: 300 ml/min

It should be pointed out that there was a rather wide spread of experimental points, and therefore, only general trends can be discussed. Additional experiments would possibly result in data with improved precision. Because of the limited effort most of the work was confined by Fe_2O_3 . If one considers the general trend of the results with the Fe_2O_3 additive, as the concentration is increased from zero to 5 mole % oxide the principle effect is an increase in the ignition temperature. As additional Fe_2O_3 oxide is added and the optimum ratio for catalytic activity is approached there is a minimum in the ignition temperature curve which represents the maximum lowering of the ignition temperature. This occurs at the mole ratio of oxide to KClO_3 of 1/10. There is again an increase in ignition temperature at higher concentrations of oxide. It appears, however, that Al_2O_3 and Cr_2O_3 are significantly less active than ferric oxide at the 1/10 mole ratio. On the other hand, it may be noted that in oxygen the ignition temperature of the mixture containing Cr_2O_3 was appreciably reduced, and was comparable to the Fe_2O_3 containing compositions. There was also a slight decrease in the ignition temperature of the mixture containing Fe_2O_3 in the presence of oxygen. At the mole ratio of 3/10 oxide in KClO_3 it is seen that an increase in concentration of sulfur from stoichiometric to double the stoichiometric amount results in a lower ignition temperature. In summary the most significant findings appear to be those for the compositions containing the Fe_2O_3 catalyst where a minimum in the ignition temperature curve occurs at the mole ratio of oxide to KClO_3 of 1/10.

IV. DISCUSSION

A. Mechanism of the Decomposition of Potassium Chlorate

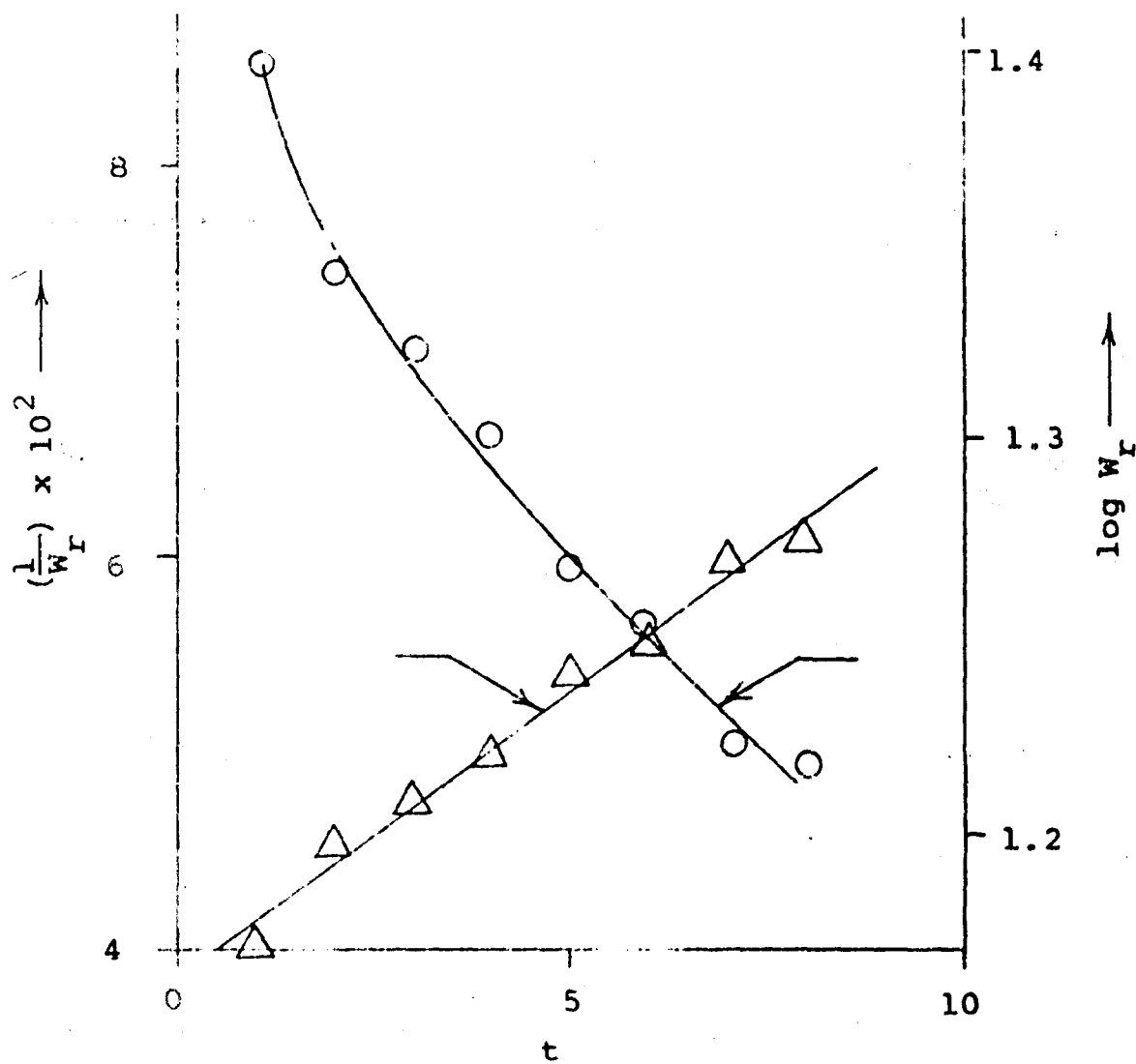
It was tentatively concluded at the termination of our previous investigation³ that the initial disproportionation step during decomposition of KClO_3 involves apparently a direct oxygen transfer between two ClO_3^- anions.



This was born out by the observations that the extrapolated initial weight loss was found to be approximately 33% of the total weight loss (See Figure 35 of Ref. 3) and that the relative amounts in the residues are approximately 50 mole % KClO_4 and 50 mole % KCl at the inflection point of the weight loss curve of KClO_3 . In order to obtain further evidence, isotherms were performed at low temperatures, where decomposition of KClO_4 is negligible, and the order of reaction evaluated. In Figure 10, isothermal data at 480°C are plotted in first and second order plots, and in Figure 11 $\log dw/dt$ is plotted versus $\log W_r$. The first figure indicates that the second order plot is approximately descriptive of the mechanism, while the slope (as a measure of the order) of the second graph is evaluated to be about 2.3. Additional evidence for the disproportionation reaction is found in Table 3 which indicates that the low temperature reaction yields approximately the same moles of KCl and KClO_4 .

Figure 10

FIRST AND SECOND ORDER PLOT OF KClO_3
DECOMPOSITION AT LOW TEMPERATURE (480°C)



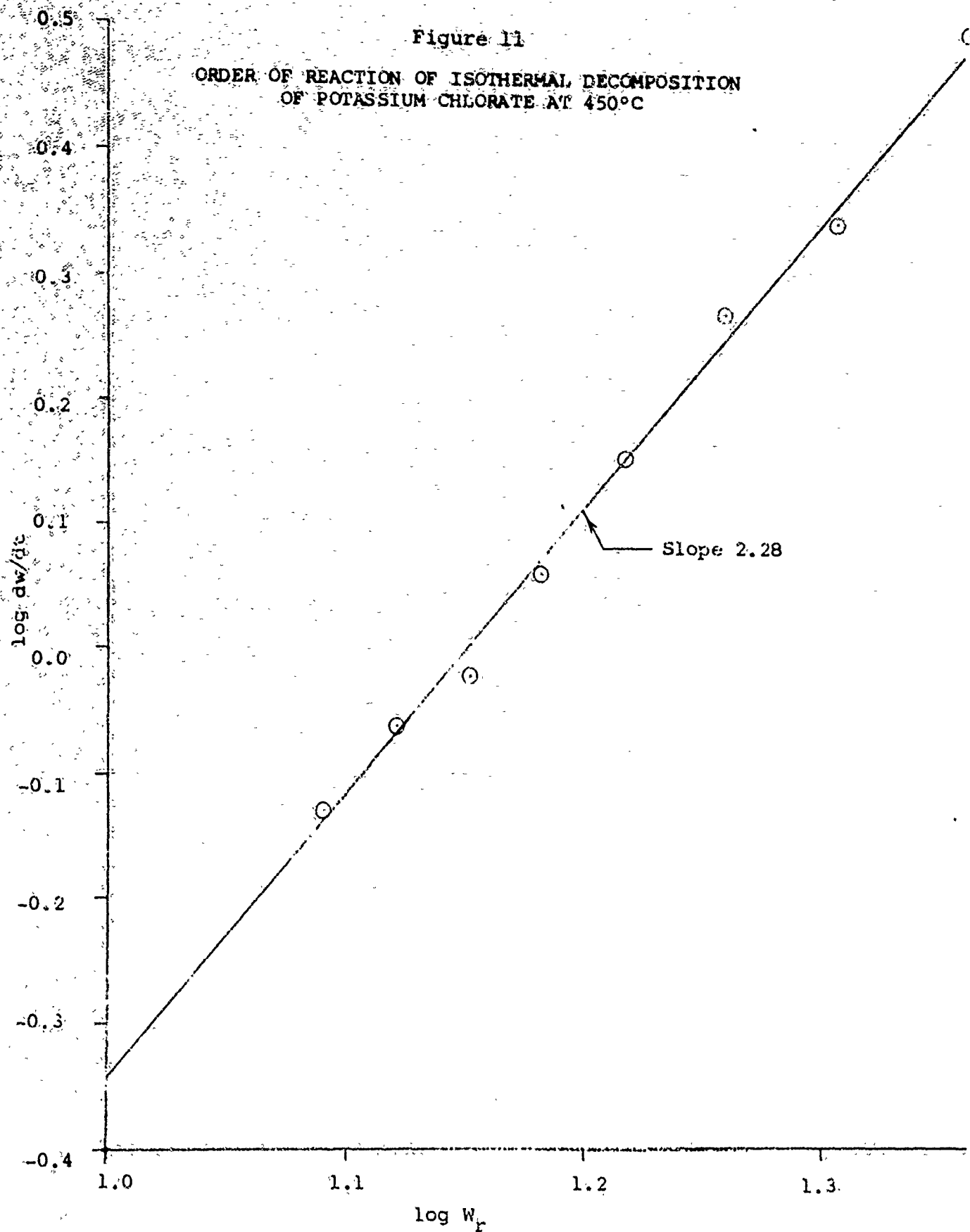
() = 1st order plot

Δ = 2nd order plot

time factor: 1 unit = 16 min

Figure 11

ORDER OF REACTION OF ISOTHERMAL DECOMPOSITION
OF POTASSIUM CHLORATE AT 450°C



The hypothetical ClO_2^- ion is very unstable at the temperature of reaction and decomposes spontaneously to Cl and O_2 .



This is consistent with the finding that KClO_2 decomposes upon heating above 160°C .⁸ The above postulated mechanism is also in agreement with the observation that there is no appreciable change in thermal decomposition characteristics in an oxygen atmosphere, compared to that in an inert atmosphere. (See Figure 10 in Ref. 3).

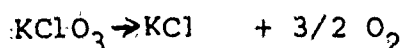
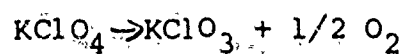
The influence of KCl as a reaction product on the decomposition of KClO_3 was found to vary with concentration. TGA and DTGA experiments indicated that at high relative concentration (mole ratio 1:1) the KCl appears to retard the reaction at lower temperatures. (See Figure 19 of Ref. 3). Isothermal runs (Figure 2) at 480°C confirmed this.

At high temperatures and intermediate mole ratios of KCl/KClO_3 , the KCl appears to accelerate the decomposition of KClO_3 . (See Figure 42 of Ref. 3). One has to conclude that two opposing mechanisms govern the influence of KCl on the decomposition of KClO_3 . At low temperatures and/or high concentrations of KCl , the KCl acts as a diluent, and the reaction is partially suppressed. At high temperatures and intermediate concentrations, the KCl additive acts as a catalyst. This catalytic action of KCl is born out by the observation⁵ that KCl of different histories influences the decomposition of KClO_3 differently. It was found that reagent grade KCl has a

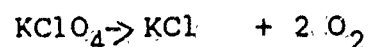
different apparent catalytic effect on KClO_3 decomposition than KCl obtained originally from total decomposition of pure KClO_3 . The maximum apparent catalytic effect is approximately at a mole-ratio of $\text{KCl}:\text{KClO}_3$ of 1:3 to 1:2. This might possibly be an indication that KCl could activate a bimolecular $\left[\begin{array}{cc} \text{O} & \text{O}^{-2} \\ \text{OCl} & \text{---} & \text{OCl} \\ \text{O} & \text{O} \end{array} \right]$ anion to decompose more readily than in case of the pure decomposition. It is quite possible that polarization centers are formed by the additive which distort the electron distribution in the above anion.

It should be of theoretical interest, to compare quantum mechanically the ClO_3^- ions with ClO_4^- and ClO_2^- and the above hypothetical bimolecular transition state. A priori calculations of the energy differences could yield an activation energy comparable to the actual value. The intermediately formed KClO_4 decomposes further via two apparent paths (See Figure 35, Ref. 1):

First



Second



The intermediately reformed (KClO_3) is rather unstable at these higher temperatures and decomposes almost instantaneously to $\text{KCl} + \text{O}_2$.

Some authors claim⁵ that KClO_4 also catalyzes the decomposition of KClO_3 . To verify this, TGA and DTA runs were performed

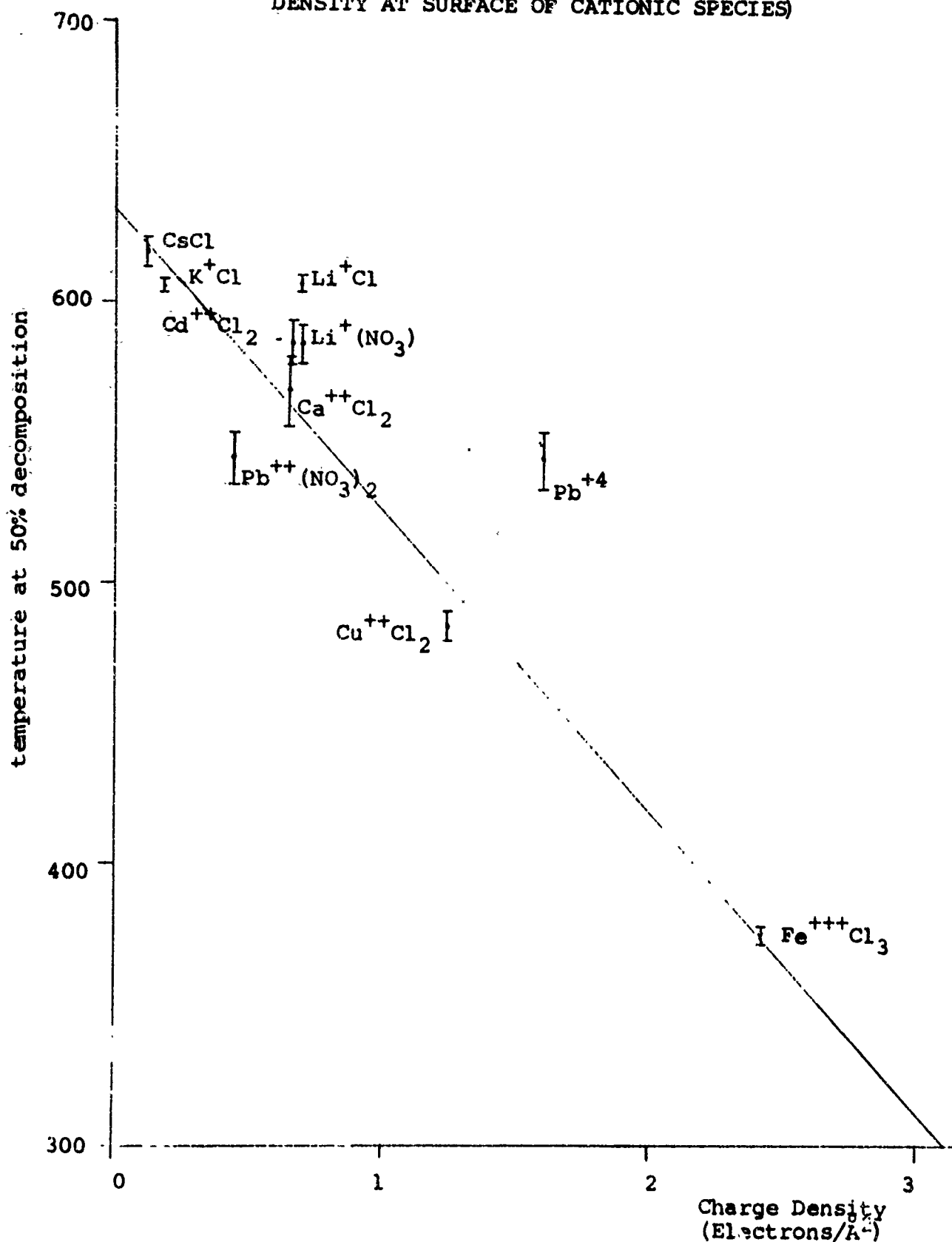
on various mixtures of KClO_3 with KClO_4 . The weights were approximately adjusted in such a way that the total weight loss was approximately the same in all cases. It is seen from Figure 1 that in no case is an acceleratory effect on the decomposition of KClO_3 observed. This and the catalytic action of dopants described below leads us to believe that the above mentioned authors had worked with impure materials which could possibly have acceleratory effects on the decomposition of KClO_3 .

B. Decomposition of Doped, Irradiation, and Mechanically Shocked KClO_3

The decomposition of potassium chlorate is significantly altered by small amounts of impurities. Figures 3 and 4 and Table 4 show that, in particular, cations of transition elements such as Fe^{+++} and Cu^{++} can lower the decomposition temperatures by more than 200°C. In fact both, Cu^{++} and Fe^{+++} doped, samples initiated decomposition in the solid phase before the melting endotherm occurs. In Figure 12, the average decomposition temperatures at 50% reaction are plotted as a function of the charge density. The charge density is obtained by dividing the cationic charge by the surface area of an assumed spherical model of the impurity cations based on the published ionic radii.⁹ It appears that the decomposition temperature is decreased with increasing charge density of the dopant cation. This may indicate that the polarizing power of the doping cation on the asymmetric electron distribution of the ClO_3^- anion is an important factor in the reactivity of the doped potassium chlorate.

Figure 12

REACTIVITY OF DOPED KClO_3
(TEMPERATURE AT 50% DECOMPOSITION AS FUNCTION OF CHARGE
DENSITY AT SURFACE OF CATIONIC SPECIES)

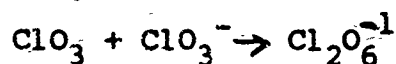


It should be kept in mind that the KClO_3 was in the molten state during this stage of these reactions. Doping with CuCl_2 caused appreciable increases in the chemical reactivity of KClO_3 . In addition, it is also apparent that the first step of decomposition due to disproportionation is significantly more pronounced in the presence of these dopant cations.

In Figure 12 the reactivity of the lead dopant is plotted twice. In one case a doubly charged Pb^{++} ion was assumed and in the other case a valence +4 was assumed, Pb^{+4} ion. The point for the double valent Pb^{+2} ion dopant lies left of the line, while that of the +4 valent Pb^{+4} dopant lies to the right of the line. One interpretation may be that the lower valent lead dopant is partially oxidized to a higher valence state by the strong oxidant host compound.

The apparent catalytic effects may be considered from another point of view. This concept is based on the finding that the activation energy for thermal decomposition is about 50-55 kcal/mole. Based on this one would expect that if the rate controlling step in the thermal decomposition of KClO_3 involved the rupture of the Cl-O bond in the ClO_3^- ion, then the marked effects of the Fe^{+3} and Cu^{+2} ions could not be accounted for. However, if the impurity cations could act as bridges in an electron transfer rate controlling mechanism then the marked reductions in decomposition temperatures may be reasonably expected. The reaction involves the formation of an intermediate Fe^{+2} ion with a ClO_3 radical. The radical would

be considerably more reactive than the ClO_3^- ion. The following equations illustrate this mechanism.



A similar mechanism would apply to Cu^{+2} ion dopant. This mechanism can apply to the molten state or solid state decomposition. The activation energy for the interaction of 2 chlorate species would be reduced because of the formation of the intermediate chlorate radical. In the case of solid state decomposition, however, another factor such as defect state also becomes important which determines the concentration and mobility of charge carriers during charge transfer. The addition of higher valent cations may cause a reduction of positive holes or an increase of electrons in the conduction band. Another possibility is that the concentration of cationic vacancies would increase.

An estimate of order of activation energies of the doped potassium chlorates were made from the thermogravimetric curves obtained in the Chevenard DTA/TGA experiments. A method is described in the literature, where the inflection point in the TGA curve is determined.¹⁰ The final equation is as follows:

$$\frac{E^*}{n} = - (RT_1^2/w_1) (dw/dt)_1$$

where E^* is the activation energy, T_1 the temperature at the inflection point, w_1 the weight loss at the inflection point;

n is the order. It should be noted that using this expression we are comparing E^*/n , rather than an activation energy alone. This however, does give information concerning the relative activation energies for comparison purposes.

Table 8 summarizes some of the values of E^*/n . It can be seen that there is wide scatter which is due to the qualitative nature of the Charvenard TGA runs. In particular, $(dw/dt)_i$ is rather difficult to determine.

From Table 8 we can, nevertheless, see certain trends in the activation energies:

The order of activation energies is in the order of dopants: $\text{None} > \text{CsCl} \sim \text{CaCl}_2 > \text{LiCl} > \text{Pb}(\text{NO}_3)_2 > \text{CdCl}_2$.

The activation energy trends for the Cu^{++} and Fe^{++} doped samples were not evaluated, since the transition from solid state to molten state decomposition complicates the TGA-curves.

It is seen from the above equation that an order of two for the disproportionation mechanism, if applied to the doped chlorates would indeed double the apparent activation energies.

Irradiation with gamma rays seems to introduce a change in reactivity with respect to decomposition. The odor of chlorine and/or chlorine oxides indicates that irradiation creates radicals such as ClO_3 which decompose at much lower temperature than the ClO_3^- anion. The radical formation does not

Table 8

APPARENT ACTIVATION ENERGIES OF DOPED KClO_3

<u>Dopant</u>	<u>E*/n</u> <u>Kcal/mole</u>	<u>Average</u> <u>Kcal/mole</u>
None	56.8	56.7
None	62.3	
None	52.3	
None	52.5	
None	50.4	
None	61.4	
CaCl_2	50.7	52.5
CaCl_2	51.9	
CaCl_2	54.8	
CsCl	46.4	52.2
CsCl	61.2	
CsCl	49.1	
LiCl	40.4	41.9
LiCl	32.8	
LiCl	52.5	
$\text{Pb}(\text{NO}_3)_2$	21.3	22.5
$\text{Pb}(\text{NO}_3)_2$	24.5	
CdCl_2	20.8	17.7
CdCl_2	17.1	
CdCl_2	15.1	

appear to be stoichiometric in view of the observation that sufficient KClO_3 is still left to create a large endotherm at around 360°C . This endotherm, however, shows shoulders indicating eutectics formed by the residual KClO_3 and some reaction product.

The nonstoichiometric nature of the low temperature release of gaseous products is also born out by the fact that one sample which underwent mechanical shock shows much less weight loss even though the DTA peak is approximately at the same temperature indicating a similar reaction.

The observation that the samples dried at room temperature in a desiccator, do not show the initial weight loss suggests that the reaction products are either very unstable and of low boiling point, or they are loosely sorbed within the irradiated defect crystalline structure and diffuse slowly to the surface, where they desorb under the force of concentration gradient set up by the drying agent in a desiccator.

C. The Reaction Between Potassium Chlorate and Sulfur, O_2 , Argon and Water

Preliminary DTA/TGA experiments were carried out with various mixtures of sulfur and doped potassium chlorates. The potassium chlorate samples were obtained from evaporation of 1% dopant in KClO_3 solutions. This was done to investigate the influence that doped KClO_3 has on the combustion of sulfur.

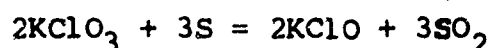
Table 5 summarizes the results in terms of combustion temperature. The average values of the combustion temperatures and the corresponding error limits (standard

deviations from these values) are compiled in Table 6.

The combustion temperature is lowest with KClO_3 doped with 1% CuCl_2 . The ignition temperature is reduced by more than 20°C as compared to the ignition temperature of the undoped chlorate.

The effect of the dopants on the ignition temperature is $\text{CuCl}_2 \ll \text{KCl} \sim \text{Undoped} \sim \text{CsCl} \sim \text{Pb}(\text{NO}_3)_2 < \text{FeCl}_3 \leq \text{CdCl}_2 < \text{LiCl} \sim \text{LiNO}_3 \sim \text{CaCl}_2$.

It is interesting to note that FeCl_3 is much less active as far as the combustion temperature is concerned than CuCl_2 . It should, however, be pointed out that the average weight loss is much higher with FeCl_3 than with all the other dopants. The stoichiometric weight loss according to the equation:



is approximately 37.6%. The actual weight losses are much higher. This is a consequence of the vigorous reaction which forces material out of the crucible. The fact that the average weight loss in case of FeCl_3 as the dopant is much higher than with all other dopants indicates a much faster reaction rate. Unfortunately, the TGA curves show almost instantaneous weight losses so that differences between reaction rates cannot be distinguished. To overcome this difficulty, several trial experiments were run with faster recorder speeds. Even with a recorder speed of 1 sec/inch under dilute conditions, where additional KClO_3 acted as a diluent, we were not able to detect significant differences in combustion rates between doped and undoped KClO_3 mixtures. This indicates that the rates are too fast and that the recorder is the limiting factor.

It had been observed that mixtures of sulfur with Fe^{+++} and Cu^{++} doped KClO_3 slowly released accumulated SO_2 gas which has a distinct odor.

Mass spectrometric analysis of a mixture of KClO_3 -S heated in vacuum above 70°C showed a peak at mass 64 indicating the probable presence of SO_2 and/or S_2 .

Preliminary conductivity measurements on a potassium chlorate pellet in air showed relatively high conductivity at low temperatures which were no longer present in vacuum (Figure 6). It was speculated that moisture in the air was the reason for this behavior. This was verified by experiments in dry atmospheres of air, argon and oxygen and the pellet did not exhibit the high conductivities at low temperatures. Rather, the curves appear to be similar as that in vacuum (Figure 8), and the activation energy calculated for the high temperature charge transfer was about 32 kcal/mole (Figure 7).

If the experiment was run, however, in water vapor, (Figure 8), the low temperature conductance was again observed. This might indicate that H_2O molecules adsorbed on the pellet surface contribute considerably to ionic surface conductivity of perhaps solvated surface ions. This conductance disappeared as soon as the water was removed in vacuum.

Conductivity experiments in dry sulfur vapor did not yield conclusive results.

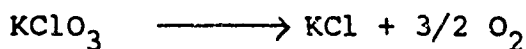
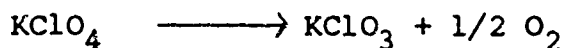
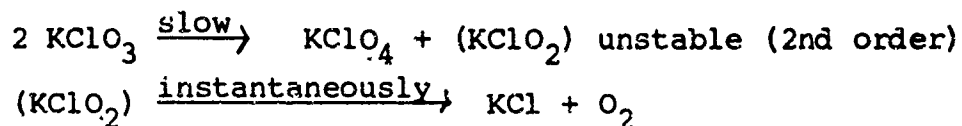
The influence of metal oxide additives on the combustion of mixtures of potassium chlorate and sulfur was probed by differential

thermal analysis. The oxides considered were Fe_2O_3 , Cr_2O_3 and Al_2O_3 . These oxides were selected since the first two were found to be excellent catalysts while Al_2O_3 was relatively inactive. The concentration of the oxides were varied from 5 to 30 mole percent. These runs were generally performed in an argon atmosphere. A few experiments were carried out in an oxygen atmosphere. In an argon atmosphere the possibility of air oxidation is eliminated limiting the oxidation of sulfur to reaction with the KClO_3 in the mixture. Carrying out the reaction in pure oxygen emphasizes the role of air oxidation in the combustion reaction. Table 7 shows the results. It can be seen that the apparent ignition temperature differs significantly depending on the mole ratio of the metal oxide to potassium chlorate. It should be pointed out that there was a rather wide spread of experimental points, and, therefore, only general trends can be discussed. Additional experiments would undoubtedly result in data with improved precision. Because of the limited effort most of the work was confined to Fe_2O_3 . If one considers the general trend of the results with the Fe_2O_3 additive, it appears that with increasing oxide content, to 5 mole % oxide, the principle effect is an increase in the ignition temperature. This would occur if the relative amount of oxide, or active oxide surface was less than optimum. As additional Fe_2O_3 oxide is added and the optimum ratio of catalytic activity is approached there is a minimum in the ignition temperature curve which represents the maximum lowering of the

ignition temperature. This occurs at the mole ratio of oxide to KClO_3 of 1/10. As the optimum amount of catalyst is exceeded, the additional oxide probably acts as a diluent, as evidenced by the increase in ignition temperature. Since only one mole ratio was considered in the cases of aluminum oxide and Cr_2O_3 additives, little interpretation can be given to these results. It appears, however, that these oxides are significantly less active than ferric oxide at the 1/10 mole ratio. On the other hand it may be noted that in oxygen the ignition temperature of the mixture containing Cr_2O_3 was appreciably reduced, and was comparable to the Fe_2O_3 containing compositions. There was also a slight decrease in the ignition temperature of the mixture containing Fe_2O_3 in the presence of oxygen. Possibly Cr_2O_3 and Fe_2O_3 can act as catalysts for the reaction between sulfur and oxygen. At the mole ratio of 3/10 oxide of KClO_3 it is seen that, with an increase in concentration of sulfur from stoichiometric to double the stoichiometric amount, the ignition temperature was reduced. In summary, the most significant findings appear to be those for the compositions containing the Fe_2O_3 catalyst where a minimum in the ignition temperature curve occurs at the mole ratio of oxide to KClO_3 of 1/10. Further experiments, however, will be required before definite conclusions can be reached.

V. CONCLUSIONS

1. The results indicate that the decomposition of potassium chlorate occurs in the following steps:



The first disproportionation reaction is consistent with a second order mechanism and is inhibited at low temperatures by excessive amounts of KCl. At high temperatures, KCl catalyzes the reaction.

KClO_4 does not catalyze decomposition of KClO_3 . At higher concentrations, the decomposition of KClO_3 is inhibited in the presence of KClO_4 .

2. The order of dopants with respect to decreasing the decomposition temperatures of doped KClO_3 was found to be: the most effective, $\text{FeCl}_3 > \text{CuCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{CdCl}_2 > \text{CaCl}_2 > \text{LiNO}_3 > \text{LiCl} > \text{KCl} \sim \text{CsCl} \sim \text{No Dopant}$. This order can be correlated to charge density or to charge transfer. Doping KClO_3 with nitrates reduces the temperature of the DTA endotherm for melting.

3. Gamma irradiation and mechanical shock influences the decomposition path of KClO_3 . Low temperature weight loss and smell of chlorine and/or chlorine oxides point to defect creation of possible radicals such as ClO_3 within the crystalline lattice due to irradiation. An exotherm appears at about 75°C in the DTA curve for the mechanically shocked sample which does not appear in the untreated sample.

4. Doping of KClO_3 significantly influences the ignition of mixtures of KClO_3 and sulfur. Two effects are apparent: The order of ignition temperatures with reference to the dopants is: lowest for $\text{CuCl}_2 < \text{KCl} \sim \text{undoped} \sim \text{CsCl} \sim \text{Pb}(\text{NO}_3)_2 < \text{FeCl}_3 < \text{CdCl}_2 < \text{LiCl} \sim \text{LiNO}_3 \sim \text{CaCl}_2$.

The extent of total weight loss as measured in the TGA experiment is dependent on the rate of combustion since the rapid ignition forces material out of the reaction vessel. This is particularly true for the FeCl_3 doped samples. Fe^{+++} and Cu^{++} doped KClO_3 appears to react slowly at room temperatures with sulfur.

5. The reactivity of sulfur- KClO_3 mixtures is especially affected by the presence of Fe_2O_3 catalyst.

In oxygen the ignition temperature of the sulfur-potassium chlorate mixture is significantly lowered in the presence of the Cr_2O_3 and Fe_2O_3 catalysts.

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13. ABSTRACT The effects of defect structure and doping of potassium chlorate on its chemical reactivity with respect to its propagative reactions with sulfur was investigated. The preparation of doped single crystals of potassium chlorate was continued during the entire program. The crops of single crystals were analyzed for their dopant contents. The influence of doping on the thermal decomposition of potassium chlorate was investigated by DTA and TGA. The effect of potassium chloride and perchlorate as an intermediate reaction product on the thermal decomposition of potassium chlorate was studied. These experiments are necessary for establishing the basis for evaluating the reactivity of potassium chlorate with sulfur. Electrical conductivity studies were initiated to correlate electronic defect structure with the reactivity behavior of potassium chlorate. Low temperature isothermal investigations were conducted to evaluate possible reaction mechanisms. The effect of irradiation and mechanical shock on the decomposition of potassium chlorate was probed. The combustion reaction of mixtures of sulfur with doped potassium chlorate and of mixtures with selected metal oxides was investigated.		

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14. KEYWORDS

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Calcium chloride
Cesium chloride
Combustion temperature
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Differential thermal analysis
Doping
Electrical conductivity
Electronic defect structure
Gamma irradiation
Iron (III) chloride
Lead nitrate
Mechanical shock
Potassium chlorate
Potassium chloride
Potassium perchlorate
Single crystals
Sulfur
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