AD 744658

ANNUAL REPORT No. 11 for the period ending: 31 May 1972 Contract Nonr - N00014-67-A-0201-0014 submitted to Office of Naval Research Material Sciences Division J.

JUL In.

1972

MECHANISMS OF REACTIONS OF OXIDIZERS

e by i

A. G. Keenan

Department of Chemistry University of Miami 'Coral Gables, Florida 33124

NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Contimarce Springfield VA 22151

Reproduced by

DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited

<pre>resurr classified of the bedra states in and indexing accessing much to entropy in classified of the bear include to the</pre>	DOCUMENT CONT	ROL DATA - R	&,D		1
University of Miami Department of Chemistry Repartment of Chemistry Mechanisms of Reactions of Oxidizers determine more indeparted devolute daws Annual Report, June 1, 1971 to May 31, 1972 Annual Report, June 1, 1971 to May 31, 1972 Annual Report advecting internet Keenan, A. G. Report Ogle, 1972 Contract on Contact to Contact and	Security classification of title, body of abstract and indexing ORIGINATING ACTIVITY (Corporate author)	annotation must be a	ntered when the o	verall report is c	Inszilled)
Department of Chemistry Mechanisms of Reactions of Qxidizers Determined method metho	University of Miami	ę • ł	None		
Mechanisms of Reactions of Qxidizers Descentrive notes (Dye of report and inclusive 2014) Annual Report, June 1, 1971 to May 31, 1972 Avioanty (Christmann, Middle Initial, Estimane) Keenan, A. G. May 31, 1972 Contrast of GRANTINO. NO0014-67-A-0201-0014 Annual Report No. 11 b. Offer affort No. 11 b. Offer af	³ Department of Chemistry	(26. GROUP	······	•
Mechanisms of Reactions of Oxidizers Determine Mortes (Provide all Notifies Care) Annual Report, June 1, 1971 to May 31, 1972 Xeenan, A. G. Totation of Grantino. NOO014-67-A-0201-0014 Project No. 11 Noor for the second	acput emente of enemisery		<u> </u>	<u> </u>	1
Mechanisms of Reactions of Qxidizers Annual Report, June 1, 1971 to May 31, 1972 Annual Report, June 1, 1971 to May 31, 1972 Annual Report and mechanics category Keenan, A. G.	REPORT TITLE :	•			
Descriptive Hores (Type of report and inclusive 2.000) Annual Report, June 1, 1971 to May 31, 1972 Xeenan, A. G.	Mechanisms of Reactions of Oxidiz	ers	:		ı
Automatis (First and addition internation) Keenan, A. G. AMAY SI, 1972 CONTRACT ON GRANT NO. NUODIA-67-A-0201-0014 PROJECTING. CONTRACT ON GRANT NO. NUODIA-67-A-0201-0014 PROJECTING. CONTRACT ON GRANT NO. NUODIA-67-A-0201-0014 PROJECTING. CONTRACT ON GRANT NO. CONTRACT ON CONTRACT ON CON	DESCRIPTIVE NOTES (Type of report and inclusive dates) Annual Report, June 1, 1971 to Ma	v 31 ¹ 1972	;, <i>.</i>	<u>````</u>	
Keenan, A. G. May 51, 1972 CONTRACT OR CRANT NO. NOOO14-67-A-0201-0014 PROJECT NO. OUTIGE REPORT NOISI (Any other quantum may be explored min Apont No. 11 Disymmetric quantum and point of the report from DDC Supplementary Notes Supplementary Notes Sup	AUIHOR(S) (First name, middle initial, last name)	<u>, 01, 10/10</u>			+
REMONT 2415 19. NO. OF PAGES 10. NO. OF PAGES CONTRACT ON GRANT NO. 10. NO. OF PAGES 0 NO0014-67-A-0201-0014 Annual Report No. 11 DESTRIBUTION STATEMENT 0 0 Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES 0 SUPPLEMENTARY NOTES 11. SPONSORING MULTIARY ACTIVITY Office of Naval Research Power Program, Code 473 Arlington, Virginia 22217 Assistance 11. SPONSORING MULTIARY ACTIVITY Office of Naval Research Power Program, Code 473 Arlington, Virginia 22217 Assistance 11. Sponsoring the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorate summarized ¹ : Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammoni perchlorate decomposition by copper ion, measurement of electrical inductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrate and measurement of selectivity ratios and ion exchange unstants for Pyrex membranes in fused nitrates. Publications issued an inding are listed. Promu 1472 1	Keenan, A. G.	1 1 1	;	, ,	:
May 31, 1972 CONTRACT OR GRANT NO. NO0014-67-A-0201-0014 PROJECT NO. DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of the report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of the report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of the report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES DISTRIBUTION STATEMENT Qualified requesters may obtain copies of the mechanisms of de- MOVER Program, Code 473 Arlington, Virginia 22217 Arigona, Code 473 Arlington, Virginia 22217 DISTRIBUTION STATEMENT Summarized, Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, visible spectra of mine, nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an Inding are listed.	!	•		1	
CONTACT OF GRATING. N00014-67-A-0201-0014 PROJECT NO. 11 PROJECT NO. 11 PR	May 31, 1972	7. TOTAL NO. OF	F PAGES	76. NO. OF REF	·s !
Annual Report No. 11 Annual Report No. 11 b. OTHER REPORT NOUS (Any other numbers that may be explored miniformal and the investigation of this report from DDC SUPPLEMENTARY NOTES II: SPONSORIME MULTIARY ACTIVITY Office of Naval Research Power Program, Code 473 Arlington, Virginia 22217 Arlington, Virginia 2	CONTRACT OR GRANT NO.	94. ORIGINATOR	S REPORT NUMB	ER(S)	
DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEMENTARY SUPPLEME	N00014-67-A-0201-0014	Annual R	eport No.	11	1 1
Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEME		SP. OTHER REPOI	RT NO(5) (Any of	et numbers that	may be essioned
Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES Dispresent the search power Program, Code 473 Arlington, Virginia 22217 Arlington, Virginia 22217 Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized Areas of investigation include computer simulation calcu- in perchlorate decomposition by copper ion, measurement of electrical inductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and chloro complexes of copper, nickel and cobalt in nergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange instants for Pyrex membranes in fused nitrates. Publications issued an inding are listed.		this feport)			
Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTARY NOTES SUPPLEMENTARY SUPPLEMENTA	۰ ا	•	1	1	
Qualified requesters may obtain copies of this report from DDC SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES SUPPLEMENTARY NOTES Supplementary contained and an antipation of the mechanisms of de- Power Program, Code 473 Arlington, Virginia 22217 Ariangton, Virginia 22217 Ariangton, Virginia 22217 Ariangton of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorate summarized? Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammonian perchlorate decomposition by copper ion, measurement of electrical onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and chloro complexes of copper, nickel and cobalt in registically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	DISTRIBUTION STATEMENT			1 '	_ <u></u>
SUPPLEMENTARY NOTES (12. SPONSORING MILITARY ACTIVITY Office of Naval Research Power Program, Code 473 Arlington, Virginia 22217 Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized. Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammonia perchlorate decomposition by copper ion, measurement of electrical inductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato' and chloro complexes of copper, nickel and, cobalt in nergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	Qualified requesters may obtain c	opies of t	his repor	t from D	DC ,
SUPPLEMENTARY NOTES Office of Naval Research Power Program, Code 473 Arlington, Virginia 22217 Arlington, Virginia 2217 Arlington, Virginia 22217 Arlington, Virginia 2217 Arlington, Virginia 2	· · · · · · · · · · · · · · · · · · ·	:	······	1	
Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized. Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammoni onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and chloro complexes of copper, nickel and cobalt in nergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	SUPPLEMENTARY NOTES	112. SPONSORING N	MLITARY ACTIV	Pecearch	
Arlington, Virginia 22217 Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized. Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammoni a perchlorate decomposition by copper ion, measurement of electrical inductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and chloro complexes of copper, nickel and cobalt in nergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an nding are listed.		Power P	rogram. C	lode 473	
Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized. Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammoni perchlorate decomposition by copper ion, measurement of electrical onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and, chloro complexes of copper, nickel and, cobalt in rergistically catalyzed fused ammonium nitrate, emf studies in fused umonium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.		Arlingt	on, Virgi	nia 2221	7
Progress during the year in the investigation of the mechanisms of de- mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized!" Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammoni perchlorate decomposition by copper ion, measurement of electrical onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and, chloro complexes of copper, nickel and, cobalt in rergistically catalyzed fused ammonium nitrate, emf studies in fused umonium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	ABSTRACT	1			·····
mposition of oxidizers such as ammonium nitrate and ammonium perchlorat summarized. Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammonia perchlorate decomposition by copper ion, measurement of electrical onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato' and chloro complexes of copper, nickel and cobalt in mergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	Progress during the year in the in	vestigatio	n of the	mechanis	ms of de-
summarized Areas of investigation include computer simulation calcu- tions of defects in ammonium perchlorate crystals, catalysis of ammonius a perchlorate decomposition by copper ion, measurement of electrical onductivity of doped ammonium perchlorate crystals, visible spectra of mine, nitrato and chloro complexes of copper, nickel and cobalt in mergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	mposition of oxidizers such as ammo	nium nitra	te and am	monium p	erchlorat
D FORM 1472	summarized, Areas of investigatio	n include (computer	simulati	on 'calcu-
D FORM 1472	nerchlorate decomposition by comp	lorate cry	stals, ca	talysis	or ammon1
mine, nitrato and chloro complexes of copper, nickel and cobalt in rergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange enstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	nductivity of doped ammonium perch	lorate: crv	stals, vi	sible sp	ectra of
nergistically catalyzed fused ammonium nitrate, emf studies in fused monium nitrate and measurement of selectivity ratios and ion exchange onstants for Pyrex membranes in fused nitrates. Publications issued an ending are listed.	mine, nitrato' and, chloro complexes	of copper	, nickel	and, coba	lt in
D FORM 1472	nergistically catalyzed fused ammo	nium nitraj	te, emf s	tudies i	n fused
D FORM 1472	monium nitrate and measurement of	selectivit	y ratios	and ion	exchange
D FORM 1/72	onstants for Pyrex membranes in fus	ed nitrate:	s. Publi	cations	issued an
	ending are listed.	1	×	,	
	· ·				*
D FORM 1/72	· · · · · · · · · · · · · · · · · · ·	•	• •	1	
D FORM 1/72	1 1	1		`J *	
D FORM 1/72	· .	ı	-		
D FORM 1/72	· · · · ·	-	, it ,		Ť
D FORM 1/72	· · · ·	ı	τ.	t	
D FORM 1/72	а ^с І ,		1		
D FORM 1/72		I		8	i
D FORM 1/72	4 ³				
		•			

3

.

None

ľ.

Security Classification

14 KEY WORDS		LINK A		LINK B			
	ROLE	ΨT	ROLE	₩Т	ROLE	₩T	
Ammonium							
Nitrate							
Perchlorate							
Propellant							
Oxidizer							
EMF							
Fused Salts							
Computer Simulation							
Spectrophotometry	•						
			*				
						-	
	1						
			Í	ĺ	1		
	1		1				
				l			
	None						
		Security	Classific	ation			

Annual Report No. 11 - 31 May 1972

Office of Naval Research - Contract N00014-67-A-0201-0014

MECHAN SMS OF REACTIONS OF OXIDIZERS

A. G. Keenan

Chemistry Department, University of Miami Coral Gables, Florida 33124

A paper entitled "Kinetics of the Low Temperature Thermal Decomposition of Ammonium Perchlorate and Its Catalysis by Copper Ion", by A. G. Keenan and Robert F. Siegmund, ha. appeared in the Journal of Solid State Chemistry, 4, 362 (1972). This material is taken from the Ph.D. Dissertation of Robert F. Stegmund. Reprints will be distributed shortly as Special Report No. 10.

Two manuscripts have been submitted for publication. "The Computer Simulation of Defects in Ammonium Perchlorate", by Mark Goldstein and A. G. Keenan, is based on work taken from the Ph.D. Dissertation of Dr. Goldstein. "The Synergistic Catalysis of Ammonium Nitrate Decomposition -Visible Spectra of Ammine, Chloro and Nitrato Complexes of Copper, Nickel and Cobalt in Fused Ammonium Nitrate", by A. G. Keenan and I. J. Ferrer, is taken from the M.S. Thesis of I. J. Ferrer. The contents of these theses were summarized in the previous Annual Report. Reprints of the papers will be issued as Special Reports when available.

Mr. Ohanian has continued his research on the electrical conductivity of single crystals of ammonium perchlorate, both pure and doped with various metallic additives and in various atmospheres. This work is designed to follow the results of the theoretical calculations performed by Dr. Goldstein, referred to above. The aim of the program is to gain further understanding of the mechanism of decomposition of oxidizers.

The experimental work has not yet progressed far enough to produce significant results. Various pieces of apparatus have been built, some checks with literature values have been obtained, and it has been established that mercury vapor and variations of total pressure of inert gas have no effect on the conductivity. Thus a standard vacuum system open to mercury manometers etc. may be used to measure conductivity

1

as a function of the pressure of reactive gases. Some preliminary experiments in ammonia atmospheres have been carried out. These show a marked variation in conductivity.

In the research on ammonium nitrate as a prototype oxidizer for mechanistic studies, Mr. Fernandez has now established that the stoichiometry of potassium oxalate decomposition in fused KNO3 at 350° is

$$K_2C_2O_4 + KNO_3 \longrightarrow CO_2 + K_2CO_3 + KNO_2$$

Qualitative analysis of the CO₂ was done with a mass spectrometer. No CO was detected and only a trace of O₂, presumably from decomposition of KNO3. The CO₂ was determined qualitatively in a gas buret. The NO₂⁻ was determined quantitatively by UV spectrometry and the CO₃²⁻ by titration with HC1 in aqueous solution. The latter technique has been described previously. A mass balance within experimental error was obtained.

It has further been shown that the decomposition of the oxalate is complete in 2 hrs. The CO₂ flashes off as it is formed and the CO_3^{2-} and NO_2^{-} concentrations remain constant up to at least 21 hr. This allows adequate time for equilibration of electrodes for EMF studies.

The Cu/CuO electrode gives the same two-electron slope and the same intercept on a Nernst plot for oxalate additions to pure KNO3, pure NaNO3 and an equimolar NaNO3/KNO3 mixture. Furthermore, direct additions of carbonate also give the same slope and intercept.

It may therefore be considered proven that the stoichiometry given above holds for oxalate decomposition in all three solvents, that the Cu/CuO electrode responds to CO_3^2 whether the carbonate is added directly or comes from the decomposition of oxalate, and that NO₂⁻ does not interfere in this reaction. The obvious electrode reaction to fit these facts is then

$$Cu + CO_3^{2^-} - Cu0 + CO_2 + 2 e.$$

Although the CO₂ evaporates completely out of the melt within analytical experimental error, there is presumably enough residual solubility to maintain the above electrode reaction equilibrium.

These results are of some importance in the fused salt emf field since oxalate has in the past been considered to be a standard source of 0^2 ion. This has been questioned lately but a complete and definite stoichiometry has not been presented. These results are being written up for publication.

2

Mr. Fernandez has also begun work with emf's produced by NO_2^- and peroxide additions to the above melts but no definite results are yet available.

Emf studies in fused nitrates using a Pt/PtO electrode have also been initiated by Mr. Williamson. So far results with addition of carbonate show a Nernstian slope which is 14% higher than the predicted two-electron value. This requires further study.

In work directed toward a better understanding of the mechanism of operation of Pyrex membrane electrodes in the study of the acidity of fused nitrate oxidizers, Mr. Martin has been carrying out measurements of the voltage/current ratios observed across such membranes. These measurements will provide a means of evaluating the cation mobility ratios and ion exchange constants for the membranes, following the theoretical model of Conti and Eisenman.

This work is also in its early stages and not many results are yet available. For the Ag^+/Na^+ system in fused KNO_3 at 350°, an ion exchange constant of 0.67 was obtained. This agrees favorably with a value of 0.62 at 305° in the literature. Selectivity constants for Ag^+ , Li⁺ and K⁺ relative to Na⁺ have also been obtained but need to be checked further before being quoted. This work is continuing.