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MECHANISMS OF REACTIONS OF OXIDIZERS

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13. ABSTRACT

Progress during the year in the investigation of the synergistically catalyzed decomposition of oxidizers such as ammonium nitrate and ammonium perchlorate is summarized. Research has been done in the areas of electrometric measurements, UV and visible spectrophotometry, and quantum mechanical computer simulation calculations of defects in ammonium perchlorate crystals. New programs on the direct measurement of cation mobility ratios in Pyrex membranes and on the electrical conductivity of ammonium perchlorate crystals have been initiated.

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MECHANISMS OF REACTIONS OF OXIDIZERS

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The work described in this report under the subject contract is a direct continuation of research which was under way on Contract Nonr-4008(07) when it terminated as of 31 August 1970. The last Annual Report under that contract was No. 9, dated 31 May 1970. A Final Report dated 31 August 1970 was also written. In order to preserve continuity of reporting, the numbering sequence for Annual Reports under the earlier contract will be retained.

U. S. Patent No. 3,553,039 entitled "Ammonium Perchlorate-Ammonium Nitrate Explosive Composition Containing Excess Chloride Ion", A. G. Keenan and Robert F. Siegmund inventors, was issued 5 January 1971.

Mr. Mark Goldstein completed his Ph.D. Oral Defense of Dissertation on 4 May 1971. The title and formal abstract of the dissertation follow:

The Computer Simulation of Defects in Ammonium Perchlorate (April 1971)

Abstract of a Doctoral Dissertation by
Mark Goldstein at the University of Miami

The high temperature thermal decomposition and the electrical conductance of ammonium perchlorate have been theoretically investigated by a computer simulation technique using a polarizable point-ion model. The cohesive energy of the crystal was obtained from an extended Hückel molecular orbital calculation. The Born-Mayer repulsive parameter was obtained from the crystal binding energy. The relaxation of approximately 50 ions was accounted for by exact calculation of the repulsive, electrostatic and polarization energies. Twenty-one defect calculations were performed in all.

Based on these calculations, a novel turnstile mechanism involving slow synchronous rotations of the perchlorate ions to allow passage of ammonium ions is proposed for vacancy migration which accounts for the high temperature electrical conductance.

The energy of formation of a Schottky defect pair was calculated to be 1.66 ev and the activation energy for migration of a vacancy was found to be 4.53 ev. Both of these values are in good agreement with experiment.

The isomorphically substituted foreign ions Li^+, Na^+ and K^+ were chosen as prototypes for predicting the catalytic efficiency of foreign ions on the thermal decomposition of ammonium perchlorate. Using the activation energy for migration of the foreign ions as a measure of their catalytic efficiency, it was found that their activity decreased in the order given. This again agrees with experiment.

This material has been written up as a manuscript for submission to Physical Review. Photocopies of the dissertation will also be available from University Microfilms, Ann Arbor, Michigan.

Mr. Ferrer is terminating his employment with the contract as of 15 June 1971, because he has been drafted into the army. His research, which consisted of a spectrophotometric study of the transition metal complexes involved in the synergistic catalysis of ammonium nitrate decomposition, was aimed at an eventual Ph.D. dissertation. The partial results obtained to date present some interesting data and will be written up as an M.S. thesis.

The absorption spectra of ammino, nitrato, and chloro complexes of copper, nickel, and cobalt have been obtained at temperatures of about 175°. Preliminary spectrophotometric measurements on the synergistic catalysis of ammonium nitrate decomposition have been performed at temperatures of 175° and 185°. The systems investigated were AN-M-Cl^- - $CO_3^=$ where M was copper, nickel or cobalt ion. The absorption of the NO_3^- ion in the ultraviolet region and the decomposition of the solvent presented some difficulties in obtaining the spectra of some species.

It was found that ammine complexes of copper(II) and nickel(II) can exist in ternary nitrate eutectic and ammonium nitrate melts. No amminocobaltates were obtained, but cobalt(III) ammine complexes were observed in these melts. The number of ammine ligands was not determined. However, it was observed that the ability of these metals to complex with NH_3 increased as follows: $Cu(II) > Ni(II) > Co(II)$. Octahedral configuration is expected for all of the ammine complexes.

Nitrato complexes of Ni(II) and Co(II) were obtained in ternary nitrate eutectic and ammonium melts. They were only observed in ternary nitrate eutectic for Cu(II) due to the ability of this metal to bind to NH_3 ligands in ammonium nitrate. It is believed that the symmetry of the complexes is tetrahedral for Co(II) and octahedral for the Cu(II) and Ni(II) cases.

The presence of chloro complexes in fused ternary nitrate eutectic and ammonium nitrate was confirmed for the metal(II) ions of copper, nickel and cobalt. Tetrahedral tetrachlorocobaltate was found in both solvents. Also, it seems that the copper(II) and nickel(II) species present in these melts are tetrahedral in symmetry.

The decomposition studies were not rigorous due to time limitations; therefore not too many conclusions can be drawn. Nevertheless, spectroscopic evidence for the presence of ammine complexes for the metals studied was found when the medium was basic. As the acidity increased the formation of chlorocomplexes took place. Several species already observed during the spectral studies of metals in ternary nitrate eutectic and ammonium nitrate melts were present in the decomposition. These conclusions agree with previous studies on synergistic catalysis of ammonium nitrate.

After some further work on the EMF of the Cu/CuO electrode in mixed $NaNO_3/KNO_3$ melts and in pure $NaNO_3$ using $K_2C_2O_4$ as a source of oxide ion, Mr. Fernandez has turned his efforts toward clarifying the exact stoichiometry of the thermal decomposition of oxalate in fused nitrate melts.

Addition of oxalate has been accepted in the past, both in the literature and in the present research program, as a way of adding oxide ion to melts. A few recently published papers suggest that oxalate may decompose at least partially to carbonate. Another complication which has recently been suggested is the possible presence of nitrite in the nitrate melts. The effect of this on the EMF of the Cu/CuO electrode is presently being investigated.

Titrations with HCl of quenched melts to which oxalate had been added previously show that the oxalate has been converted stoichiometrically to carbonate. Schlegel has subsequently demonstrated that oxalate decomposes to carbonate and CO_2 in these melts.

A standard spectrophotometric method due to Swofford and McCormick gives a concentration of nitrite of about 1.64×10^{-4} m in a sample of KNO_3 which had been molten at 350°C for 72 hours. The effect of nitrite ion on the EMF has not been determined yet. Recent information in the literature is in agreement with the results obtained in this laboratory regarding oxalate and nitrite.

The EMF work has been continued using potassium carbonate instead of oxalate. The results of only one run to date indicate that the copper electrode developed in this laboratory responds linearly with added carbonate with a two-electron slope. Equilibration time is reached sooner than with oxalate, and the EMF becomes steady in less than 24 hours after the addition of carbonate.

Future work calls for the investigation of the effect of nitrite ion on the EMF of this electrode and of the type of copper oxide coating the copper electrode. Also, more EMF work will be continued varying the sodium to potassium molar ratios and at different temperature ranges and further purification of these melts will be undertaken to see if any change occurs in the standard potential of this electrode.

Two new graduate students have elected to do their research on this project. Mr. Roberto Martin will continue the study of membrane potentials which was begun by Dr. Notz and continued by Mr. Wilcox and Dr. Lane. He plans to design and build apparatus for the direct measurement of cation mobility ratios in Pyrex membranes using the method of Eisenman and Conti. This work is directed toward a better understanding of Pyrex electrodes in fused salts and their role in studying oxidizer decomposition mechanisms.

Mr. Michael Ohanian will begin an experimental investigation of ammonium perchlorate decomposition starting with a study of the variation of electrical conductivity as a function of the adsorption of various gases such as ammonia and water vapor. He has had prior experience with adsorption measurements. This research will tie in with the theoretical calculations performed by Dr. Goldstein. The new students began their research actively on 1 February 1971, and there are no results of any consequence to report as yet.