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MECHANISMS OF REACTIONS OF OXIDIZERS

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13. ABSTRACT

Progress during the year in the investigation of the mechanisms of decomposition of oxidizers such as ammonium nitrate and ammonium perchlorate is summarized. Areas of investigation include computer simulation calculations of defects in ammonium perchlorate crystals, catalysis of ammonium perchlorate decomposition by copper ion, measurement of electrical conductivity of doped ammonium perchlorate crystals, visible spectra of ammine, nitrato and chloro complexes of copper, nickel and cobalt in synergistically catalyzed fused ammonium nitrate, emf studies in fused ammonium nitrate and measurement of selectivity ratios and ion exchange constants for Pyrex membranes in fused nitrates. Publications issued and pending are listed.

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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, has appeared in the Journal of Solid State Chemistry, 4, 362 (1972). This material is taken from the Ph.D. Dissertation of Robert F. Siegmund. 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

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 KNO_3 at 350° is

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

Qualitative analysis of the CO_2 was done with a mass spectrometer. No CO was detected and only a trace of O_2, presumably from decomposition of KNO_3. The CO_2 was determined qualitatively in a gas buret. The NO_2^- was determined quantitatively by UV spectrometry and the CO_3^{2-} by titration with HCl 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 CO_2 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 KNO_3, pure $NaNO_3$ and an equimolar $NaNO_3/KNO_3$ 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 NO_2^- does not interfere in this reaction. The obvious electrode reaction to fit these facts is then

$$Cu + CO_3^{2-} \rightleftharpoons CuO + CO_2 + 2\ e.$$

Although the CO_2 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 O^{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.

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.