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MECHANISMS OF REACTIONS OF OXIDIZERS

A. G. Keenan

Miami University

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MECHANISMS OF REACTIONS OF OXIDIZERS

by

A. G. Keenan

Department of Chemistry
University of Miami
Coral Gables, Florida
33124

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13. ABSTRACT

Progress during the year in the investigations of the mechanism of decomposition of oxidizers such a ammonium nitrate and ammonium perchlorate is summarized. Areas of investigation include the study of the electrical conductivity of single crystals of ammonium perchlorate, measurement of mobility ratios, ion exchange constants and selectivity ratios of cations in Pyrex immersed in fused nitrates and the study of the electrode reactions at both Cu/CuO and Pt/PtO_2 electrodes in carbonate containing fused nitrates exposed to atmospheres of O_2, CO_2, N_2 and H_2O. Publications issued and pending are listed.

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MECHANISMS OF REACTIONS OF OXIDIZERS

A. G. Keenan

Chemistry Department, University of Miami
Coral Gables, Florida 33124

Special Report No. 10, comprised of a reprint of the paper "Kinetics of the Low Temperature Thermal Decomposition of Ammonium Perchlorate and Its Catalysis by Copper Ion" by A. G. Keenan and Robert F. Siegmund, Journal of Solid State Chemistry, 4, 362 (1972), was distributed during the year. This work was taken from the Ph.D. Dissertation of R. F. Siegmund.

Special Report No. 11, comprised of a reprint of the paper "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, Journal of Physical Chemistry, 76, 2844 (1972), was also distributed during the year. This was taken from the M.S. Thesis of Mr. Ferrer.

A publication entitled "Computer Simulation of Defects in Ammonium Perchlorate" by M. Goldstein and A. G. Keenan will appear in the Journal of Solid State Chemistry, 7, No. 3, July (1973). This material is taken from the Ph.D. Dissertation of M. Goldstein. Reprints will be distributed as Special Report No. 12 as soon as available.

A brief manuscript entitled "The Decomposition of Oxalate in Fused Nitrate" by A. G. Keenan and Carlos G. Fernandez has been submitted to the Journal of the Electrochemical Society and a second brief manuscript entitled "The Stability of Carbonate Ion in Fused Nitrate" by A. G. Keenan, Carlos G. Fernandez and Thomas R. Williamson has just been completed.

Research on this project during the year has been in two relatively unrelated areas in the general field of "Mechanisms of Reactions of Oxidizers". One of these deals with the solid state decomposition of ammonium perchlorate, the experimental approach being a study of the electrical conductivity of single crystals both pure and when doped with transition metal ions or exposed to various atmospheres. The other area concerns an electrometric study of acidity in fused nitrates, with a view to understanding further the mechanism of their decomposition reactions and explaining the synergistic catalytic system discovered earlier.

The work on ammonium perchlorate decomposition follows the earlier theoretical calculations by Dr. Goldstein referenced above. During the year, an enclosed glass system has been built which allows the electrical conductance of single crystals to be measured at temperatures from ambient to 300°C while pumped under high vacuum or exposed to variable pressures of gases such as N_2, O_2, HCl, H_2O and others. Crystals of ammonium perchlorate, pure or doped with various transition metal ions such as Cu and Ni have been grown by crystallization from aqueous solution.

It has been shown that H_2O and NH_3 individually do not affect the conductivity at room temperature significantly, but when the AP crystal is exposed to both gases in succession a remarkable 15,000% increase in conductivity results. Previous workers have studied the effect of NH_3 but have not apparently noted the significant effect produced when H_2O and NH_3 are combined. It is believed that some of the oversight may be due to the fact that others have not pumped their AP to the degree of dryness attained in the present work.

The above phenomenon is most readily explained on the basis that the charge carriers in AP are NH_4^+ produced in the experiment described above by the reaction

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Combining this with the fact that H_2 is a known cathode product of the conduction process, a reasonable cathode reaction may then be postulated as

$$NH_4^+ + e \rightleftharpoons NH_4$$

$$2\ NH_4 \rightleftharpoons 2\ NH_3 + H_2$$

A parallel anode reaction which explains the known depression of conductivity by O_2 is

$$ClO_4^- \rightleftharpoons ClO_4 + e$$

$$2\ ClO_4 \rightleftharpoons 2\ ClO_3 + O_2$$

Other work which has also been done includes determining the ratio of surface to bulk conductance by use of a guard ring method. Preliminary results indicate that 99% may be surface. A coulometer has been built to collect and analyze electrode products. A higher voltage than initially estimated will be required and a power supply for 20,000 volts is now under construction. Conductivity measurements on a pure AP crystal with varying temperature give two very accurate linear regions in log (sigma T) plotted against 1/T. The lower range from 25 to 75° has a correlation coefficient of 0.996 and gives an activation energy of 0.13 eV. The range from 75 to 135° has a correlation coefficient of 0.998 and gives E_a equal to 1.1 eV.

These experiments will be continued. Ammonium perchlorate doped with various cations and exposed to partial pressures of various known atmospheres, as well as rubidium and cesium perchlorates will be used. The purpose of this research is to elucidate the conduction mechanism and hence discover which ions are mobile and what kinds of defects may be present. Such information in turn should contribute to an understanding of the thermal decomposition mechanism.

In the area of electrometric studies in fused nitrates, research has been conducted along three lines, all of which are ultimately concerned with the study of acidity and its role in the decomposition kinetics of fused oxidizers. First, the principles of operation of Pyrex membrane electrodes have been studied following the method suggested by Conti and Eisenman. This involves measuring voltage/current ratios across the glass membrane while immersed in fused salt. Cation mobility ratios (u_i/u_j), ion exchange constants (K_{ij}) and selectivity constants (k_i) can then be calculated from the data. An alternative procedure which involves electrolyzing the glass to constant conductivity was also developed. The results by the two methods are given in the tables below.

Experimental Values for K_{ij} and u_i/u_j in Pyrex Glass

$i=Na^+$, $j=K^+$ or Ag^+

T(°C)	325	350			380		413	
	u_i/u_j	K_{ij}	u_i/u_j		u_i/u_j		u_i/u_j	
Na^+-Ag^+	1.22	1.24	0.92	0.86	1.10	0.86	1.0	0.74
Na^+-K^+	--	0.257	7.87	--	16.0	50.5	--	82.0
Method	(b)	(a)	(a)	(b)	(a)	(b)	(a)	(b)

(a) by Conti-Eisenman method
(b) electrolysis measurements

Selectivity Ratios for Na^+, Ag^+ and K^+ at 350°C in Pyrex Glass

Ion	Selectivity, k
Na^+	1.0
Ag^+	0.78
K^+	0.07

For sodium and silver the results of the two methods agree within expected error. For sodium and potassium the results differ by a factor of nearly four. This is believed to be due to the fact that the composition of the glass changes during the Conti-Eisenman procedure. The mobilities of sodium and potassium are sufficiently different so that the results are influenced by this change, whereas the mobilities of sodium and silver are nearly equal.

The data in the table are not yet complete and further work is required. The data obtained so far in many cases check such scattered literature values as are available. In other cases large discrepancies exist. These will have to be investigated further.

The second line of research in the area of electrometric studies in fused nitrates has dealt with the behavior of a $Cu/CuO/CO_3^{2-}$ electrode in the presence of N_2, O_2 and CO_2 atmospheres, pure and in various mixtures. The results indicate that the electrode behaves reversibly in the presence of O_2, CO_2 and mixtures of them. The E° for the electrode at 350° and with KNO_3 in pure O_2 is 695 mV while in pure CO_2 it is 592 mV. When the electrode is subject to mixed gases it behaves according to the respective partial pressures of the gases present. The electrode reaction in accordance with the results so far obtained is:

$$CO_3^{2-} = CO_2 + 1/2\ O_2 + 2e.$$

The mechanism for the electrode reaction may therefore be any of the following three:

$$\begin{array}{llcl}
(A) & \underline{Cu} + CO_3^{2-} & \longrightarrow & CuCO_3 + 2e \\
 & CuCO_3 & \longrightarrow & CO_2 + 1/2\ O_2 + \underline{Cu} \\
(B) & \underline{CuO} & \longrightarrow & Cu^{+2} + 1/2\ O_2 + 2e \\
 & Cu^{+2} + CO_3^{2-} & \longrightarrow & CO_2 + \underline{CuO} \\
(C) & \underline{CuO} + CO_3^{2-} & \longrightarrow & CuCO_3 + 1/2\ O_2 + 2e \\
 & CuCO_3 & \longrightarrow & CO_2 + \underline{CuO}
\end{array}$$

This work will be extended to $NaNO_3$ and mistures and is expected to be concluded shortly.

The third line of research in the area of electrometric studies in fused nitrates is similar to the second except that the electrode used is Pt/PtO_2. In the course of this work it was necessary to study the stability of CO_3^{2-} in fused nitrates because of contradictory statements in the literature. This study was carried out with a pH recorder and constant rate buret to determine the two end points characteristic of carbonate which had been observed previously with colorimetric indicators. Melts were purged with nitrogen or oxygen since these gases have been claimed to remove carbon dioxide from the melt. The results showed no dissociation of carbonate.

It has also been indicated in the literature that addition of dichromate enhances the evolution of carbon dioxide causing the dissociation of carbonate to continue to completion. Results in this laboratory show that while carbon dioxide is evolved, the reaction occurs stoichiometrically as follows:

$$CO_3^{2-} + Cr_2O_7^{2-} \longrightarrow CO_2 + 2\ CrO_4^{2-}$$

These results provide clear evidence that the reaction

$$CO_3^{2-} \longrightarrow CO_2 + O^{2-}$$

does not take place in nitrate melts, and thus that carbonate cannot be considered as a source of oxide ion in these melts.

The work on the Pt/PtO_2 electrode has shown that it behaves in essentially the same manner as the Pt rotating disc electrode previously described by Zambonin. The electrode half-reaction is the same as given earlier for the Cu/CuO electrode, when the atmosphere is a mixture of CO_2 and O_2. However, in an atmosphere of CO_2 only, the reaction is

$$CO_3^{2-} + NO_2^{-} \rightleftharpoons CO_2 + NO_3^{-} + 2e.$$

This has also been proposed by others for a Pt rotating disk electrode. The Pt/PtO_2 electrode was also found to exhibit non-Nernstian behavior with respect to carbonate in a pure oxygen atmosphere and to be irreversible in a nitrogen atmosphere.