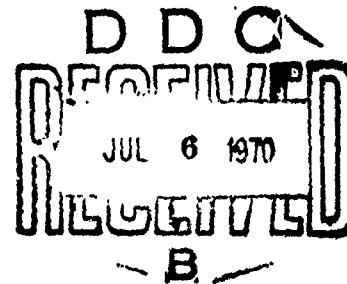


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MECHANISMS OF REACTIONS OF OXIDIZERS

by
A. G. Keenan



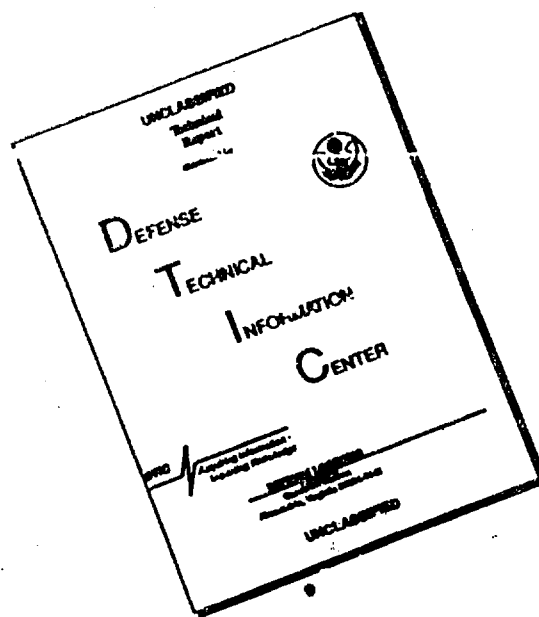
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Annual Report No. 9 - 31 May 1970

Office of Naval Research - Contract Nonr - 4008(07)

MECHANISMS OF REACTIONS OF OXIDIZERS

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The following publications have appeared during the past year:

1. "Thermal Decomposition of Ammonium Perchlorate."
A. G. Keenan and Robert F. Siegmund, Quarterly Reviews (London), 23, 430 (1969). This article was based on Special Report No. 6, dated 1 August 1968.
2. Special Report No. 7, dated 1 May 1969. A reprint of the paper "Silver and Sodium Ion Transport Numbers into Pyrex from Binary Nitrate Melts." A. G. Keenan and W. H. Duewer, Journal of Physical Chemistry, 73, 212 (1969).
3. Special Report No. 8, dated 1 August 1969. A reprint of the paper "Synergistic Catalysis of Ammonium Nitrate Decomposition." A. G. Keenan, K. Notz and N. B. Franco, Journal of the American Chemical Society, 91, 3168 (1969).
4. "Determination of Water in Crystalline Ammonium Perchlorate by High-Resolution Proton Magnetic Resonance." A. G. Keenan and Robert F. Siegmund, Analytical Chemistry, 41, 1880 (1969).
5. Special Report No. 9, dated 1 January 1970. A reprint of the above paper.
6. "An Acidity Scale for Fused Potassium Nitrate." William B. Lane, Ph.D. Dissertation, University of Miami, January 1970.
7. "Kinetics of the Thermal Decomposition of Ammonium Perchlorate." Robert F. Siegmund, Ph.D. Dissertation, University of Miami, June 1970.

A U. S. Patent Application, Serial No. 744,989, entitled "Synergistically Catalyzed Composite Oxidizer," A. G. Keenan and Robert F. Siegmund inventors, filed on July 15, 1968, is still pending. This invention concerns the catalysis of a mixed ammonium nitrate/ammonium perchlorate oxidizer by metal-excess chloride catalysts. A Confirmatory License to the Government has been executed.

Abstracts of the completed doctoral dissertations in items 6 and 7 above, follow. The results are also being written up for journal publication.

An Acidity Scale for Fused Potassium Nitrate.

(January, 1970) Abstract of a Doctoral Dissertation by William B. Lenz at the University of Miami.

An acidity scale based on oxide ion concentration has been developed in fused KNO_3 at 350° . A copper-copper oxide electrode of the second kind has been shown to respond to oxide ion concentration over fourteen orders of magnitude, $10^{-15} < [\text{O}^{2-}] < 10^{-1}$. The standard potential of this electrode was found to be -675.8 mV vs a silver-2.40 wt % silver nitrate reference. Oxide was added as potassium oxalate which was shown to yield stoichiometric amounts of oxide ion on decomposition. Solutions of quenched melts were analyzed titrimetrically to verify the stoichiometry and the validity of the scale in the oxide ion concentration region $10^{-14} < [\text{O}^{2-}] < 10^{-1}$. The equilibrium between chromate, dichromate and oxide ions was investigated and the constant found to be 1.52×10^7 in KNO_3 at 350° . The molal absorptivities of the chromate and dichromate ions were determined in the wavelength region 350 to 400 nm. The electrometric acidity scale was checked in the oxide concentration range $10^{-13.5} < [\text{O}^{2-}] < 10^{-10.5}$ using the value of K and the concentrations of chromate and dichromate ion determined spectrophotometrically. The values of $p\text{O}^{2-}$ determined independently agree to within 3% in each range checked.

Kinetics of the Thermal Decomposition of Ammonium Perchlorate.

(June 1970) Abstract of a Doctoral Dissertation by Robert F. Siegmund at the University of Miami.

By means of the N value in the Avrami-Erofeyev equation, $-\log(1-\alpha) = (kt)^N$, in the acceleratory region, the low temperature ($209-235^\circ\text{C}$) thermal decomposition of ammonium perchlorate was found to be initiated solely at lattice dislocations and defects. The aging effect exhibited by ammonium perchlorate was found to occur as a result of the dislocations and defects annealing out of the crystal lattice with time. The presence of a catalyst, copper chloride, or sample impurities, significantly accelerated the reaction but did not alter the nucleation process or the rate-determining step.

The copper cation was found to be the species responsible for accelerating the decomposition, exerting a maximum catalytic effect at only 0.2% by weight copper chloride. The reaction stoichiometry, although unchanged by recrystallization, was found to be markedly altered by the addition of copper chloride.

It is suggested that catalysis occurs as a result of the formation of ammine complexes which tie up the ammonia on the surface of the crystal and thereby prohibit the reversal of the proton transfer reaction. Studies of the sample preparation procedure as a function of the evaporation temperature, successive sample recrystallizations, and the copper catalyzed decomposition were all found to be consistent with this theory.

In addition, a decrease in the decomposition reaction rate was observed for samples evaporated in the region of 90°C. This is apparently due to the trapping of adsorbed H₂O during the rapid evaporation.

In current research now underway, Mr. Goldstein is carrying out computer calculations of the energy of an ammonium perchlorate lattice, both pure and doped with interstitial atoms. If the calculations are successful, they may possibly be used to predict a priori the effectiveness of metallic catalysts on ammonium perchlorate decomposition and to understand the physical factors which are the cause of catalytic activity in this system.

A model of ammonium perchlorate has been simulated on the IBM 360-65 computer and the effect of substitutional atoms and defects on the crystal lattice energy calculated. The repulsive energies were obtained from the Thomas-Fermi-Dirac (Abrahamson) model of rare gas configurations. Since the spherically symmetric free rotating ammonium and perchlorate ions in the FCC crystal resemble rare gas configurations in their outermost electron shell, it is assumed that the repulsive contributions, at internuclear distances great enough to allow complete rotational freedom, are composed almost entirely of the outer electron shell interactions. The repulsive energies for the substitutional ions K⁺ and Li⁺ were obtained from the same source. Li⁺ was found to lower the energy of the system more than K⁺, which is what would be expected from experimental observations on the rate decomposition.

The activation energy for the migration of a vacant lattice site in FCC ammonium perchlorate has also been calculated using a "defect" program. The repulsive parameters A and B of the Born-Mayer equation were obtained from Wedepohl's equation by fitting the parameters between 0.4 and 0.6 Å. The energies of activation for various types of migrations in various directions were considered. Qualitatively it can be determined which directions would be most likely for vacancy migration. Positive ion vacancy migration in the 110 direction appears to be a likely path. Negative ion vacancy migration in the 110 direction is ruled out because the energy is too large.

Mr. Baier is extending the work of Dr. Siegmund on a thermal analysis study of metallic catalysts for ammonium perchlorate decomposition to other catalysts besides copper chloride. The purpose of this work is to test out the hypotheses put forth by Dr. Siegmund for copper catalysis and to employ the general methods for catalyst evaluation developed by him in a search for the most effective catalyst combination. An attempt will be made to confirm the hypothesis that metal catalysts operate through the formation of ammine complexes by looking for correlations between catalytic activity and stability constants.

Mr. Fernandez is continuing the work of Dr. Lane on electrometric acidity studies in fused salts with the aim of extending the acidity scale, so far developed for KNO_3 at 350° , to mixed nitrate eutectics and lower temperatures. If an acidity scale can be developed at a low enough temperature to be applicable to fused ammonium nitrate, further understanding can be obtained of the decomposition mechanism of this oxidizer. This knowledge in turn may be applicable to other oxidizers.

The measurement of the standard potential of the Cu/CuO electrode has been extended to mixed melts of Na/KNO_3 . In an equimolar melt at 350° the value for the standard potential is -559.0 mV with a two electron Nernst slope of -62.87 mV . The standard potential is a surprising 117 mV more positive than in pure KNO_3 . The effect may be due to the greater polarizing power of the sodium ion or to a change in the solubility product constant of CuO . In any event the large change caused by change in solvent means that an interesting phenomenon is at hand and that the measurements in mixed solvents should prove fruitful. Some difficulty is being experienced due to presumed hydrolysis of the sodium salt but this can be overcome with further experimentation using standard procedures.

Mr. Ferrer is working on a spectrophotometric study of the spectra of copper ammine and chloro complexes in fused nitrates in the visible UV region. This work is a continuation of the studies on synergistic catalysis begun by Drs. Notz and Franco and is aimed at getting a better understanding of the role of copper complexes in the mechanism of the catalyzed decomposition of ammonium nitrate. It has been shown that it would probably be very difficult to obtain sufficient resolution in the spectra of various copper-chloro complexes in nitrate melts to be useful for characterization of these complexes. The difficulty arises from the high absorptivity of nitrate ion below about 350 nm . Even though a blank solvent cell is used, the low transmission strains instrument sensitivity. Attention will next be turned to ammine complexes which in aqueous solution absorb at considerably higher wavelengths.

None

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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 thermal analysis, rate studies, catalytic and mechanistic studies, electrometric measurements, UV and visible spectrophotometry and computer calculations.		

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ammonium Nitrate Perchlorate Propellant Oxidizer EMF Fused Salts						

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