ANNUAL REPORT No. 8

for the period ending: 31 May 1969 Contract Nonr - 4008(07)

submitted to

Office of Naval Research

18689

Power Program

MECHANISMS OF REACTIONS OF OXIDIZERS

by A...G. Keenan

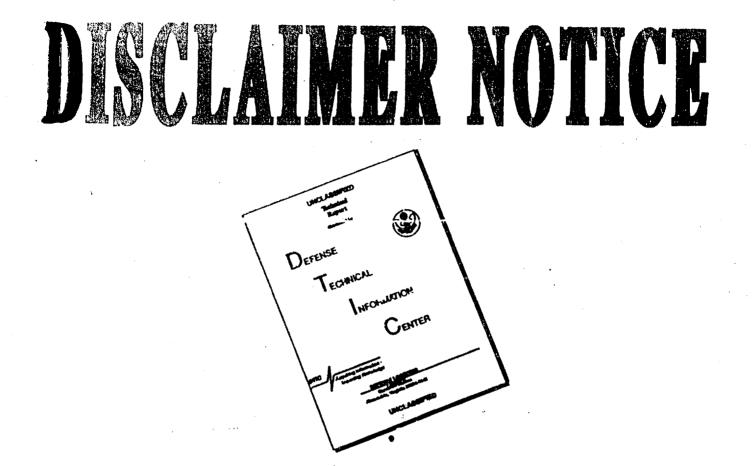
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Department of Chemistry University of Miami Coral Gables, Florida 33124

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Currently four graduate students are working on the contract. Mr. Siegmund has continued his study of the cupric chloride catalyzed decomposition of ammonium perchlorate by the differential rate method. Catalyst concentrations from 1.3 to 10 weight % and a temperature range from 210 to 235°C have been employed. The catalyst is incorporated by crystallization from aqueous solution and the crystals are ground and sieved to lie in the range 714 to 149 microns. Two computer programs have been written in which the input consists of raw experimental data and the output gives all the reaction parameters and their mean deviations evaluated by least square methods. The programs evaluate n and a for the curve $(-\log(1-a))^n = kt$, average these for the different runs, compute reaction rate constants, plot these according to the Arrhenius function and evaluate activation energies. The determination of an activation energy from the time to rate maximum is also incorporated.

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It is hoped that the above work on ammonium perchlorate decomposition will contribute to a resolution of the controversies in the literature over the electron-transfer versus proton-transfer mechanisms and over the effect of impurities as against lattice defects on the initiation of the decomposition.

A new student, Mr. Mark Goldstein, joined the research group during the year and has begun an investigation of the stoichiometry and mechanism of the copper-catalyzed thermal decomposition of ammonium perchlorate using gas chromatographic, infrared, X-ray and other techniques. The stoichiometry of the decomposition of pure AP at 218° gave an O_2/N_2 ratio of 8/1which agrees with that found by others. With 3% CuCl₂, the ratio was 4/1 which is comparable to the results reported in the literature for copper chromite catalyzed AP at 275°. Indications are that the stoichiometry depends on the presence of the catalyst as well as on its concentration but this work is still in a very preliminary stage.

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The standard potential of the Cu/CuO electrode versus a Ag/Ag' reference has been found to be -675.8 mV at 350° in KNO₃. This again is believed to be much more accurate than any value available in the literature. The measurements were made by adding weighed amounts of potassium oxalate to provide oxide ion. The quantitative conversion to oxide has been checked analytically. The slopes of the six emf plots checked the Nernst value for a 2-electron electrode reaction within 0.3%. The least squares standard error of estimate averaged 2.9 mV as determined by a computer program. Using this standard potential, the equilibrium constant for the reaction $Cr_2O_7^2 + O^2 = 2 CrO_4^2$ can now be calculated to be 6.67 x 10⁸ at 350° in KNO₃.

The variation of standard potential with temperature has also been determined over the range 350 to 400°. The standard free energy change for the above reaction at 350° has been calculated to be -25.17 kcal/mole, the enthalpy change -46.06 kcal/mole and the entropy change -27.10 eu.

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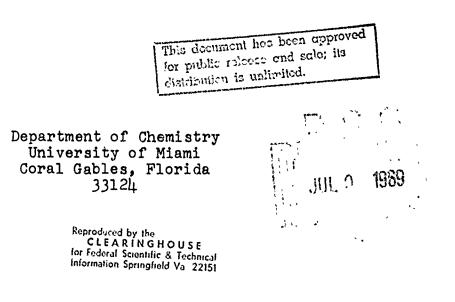
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University of Miami	None
Department of Chemistry	26 GROUP
REPORT TITLE	
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Annual Report, June 1,	1960 to May 31, 1969
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SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
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nitrate and ammonium pe	ecomposition of oxidizers such as ammonium erchlorate is summarized. Research has
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lytic and mechanistic s	studies, and electrometric measurements.
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D 150RM 1473	None
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Security Classification

None							
Security Classification							
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