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Report No. L2801-8

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Aerojet-General CORPORATION

AZUSA, CALIFORNIA

IN F O R M A L R E P O R T O F P R O G R E S S

Copy No. 71

28 July 1954

TO: Office of Naval Research
Department of the Navy
Washington 25, D. C.

VIA: Bureau of Aeronautics Representative
Aerojet-General Corporation
6352 N. Irwindale Avenue
Azusa, California

SUBJECT: Investigation of Liquid Rocket Propellants

CONTRACT: N7onr-462, Task Order III
Project NR 092-023

PERIOD COVERED: 1 June through 15 July 1954

This is the eighth in a series of informal progress reports, submitted between quarterly reports, in partial fulfillment of the contract.

AEROJET-GENERAL CORPORATION

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Report No. L2801-8

A. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

1. It was observed that if nitrogen dioxide was present among the products of the thermal decomposition of nitromethane, the following inconsistencies occurred in the mass-spectrometer analyses:

- a. The carbon-to-nitrogen ratio of the products was usually greater than one.
- b. The total nitrogen content of the products was not always reproducible.
- c. The distribution of nitrogen and its oxides showed considerable variation.

2. In order to overcome these difficulties, experiments are being conducted to determine the effects of the following factors:

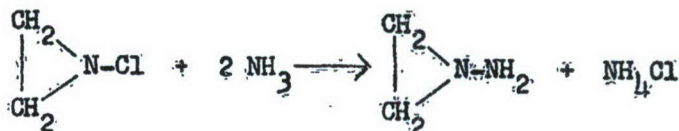
- a. Conditioning of the mass-spectrometer source with nitrogen dioxide or fuming nitric acid prior to analysis. Although a conditioning procedure had been worked out previously, it may have to be modified under the present circumstances.
- b. Pressure dependence of the cracking pattern of nitrogen dioxide. The cracking pattern of nitrogen dioxide, as determined in a Consolidated Engineering Corporation mass spectrometer, changes considerably below 13 microns pressure. This phenomenon was confirmed with the General Electric Company mass spectrometer at the Aerojet-General plant.
- c. Influence of nitrogen dioxide or nitric acid conditioning on the cracking pattern of other compounds. It was found that the extent of conditioning by nitrogen dioxide or nitric acid affects the cracking pattern of nitromethane, acetonitrile, carbon dioxide, hydrogen cyanide, nitrous oxide, and others.
- d. Influence of other compounds on the cracking pattern of nitrogen dioxide. If nitrogen dioxide is run in the mass spectrometer immediately before and after nitromethane, the two cracking patterns of nitrogen dioxide are noticeably different.

B. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

1. Mixtures of liquid ammonia and N-chloroethylenimine (mole ratio 43:1) were allowed to react in stainless steel (304) tubes in an attempt to prepare N-aminoethylenimine:

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The reaction mixtures were analyzed for reducing function (presumably N-aminoethylenimine) by titration with standard potassium iodate; for positive halogen through the addition of excess potassium iodide followed by the titration of the iodine formed with standard potassium thiosulfate; and for halide ion, where desirable, by the method of Fajans.*

2. It was found that the yield of reducing function is not appreciably temperature-dependent in the range from 25 to 110°C. The maximum yield at 25°C was 10%, based on a four-electron change in the iodate analysis for N-aminoethylenimine, while the maximum yield at 50, 75, and 110°C was 12.5%. However, the rate of reaction increased markedly with temperature. At 110°C the reaction was completed in about 5 minutes, at 75°C in about 20 minutes, while at 25°C the reaction was not completed in 6 hours.

3. In the Raschig synthesis of hydrazine, the yield is markedly increased if a small amount of gelatin is added to the reaction mixture. This results from the ability of gelatin to form a complex with copper ion, a specific catalyst for the decomposition of hydrazine. The use of gelatin in the present reaction was found to be without effect on the yield of reducing function. However, gelatin may be too insoluble in liquid ammonia to be effective, or gelatin may not form a complex with copper ion in this medium. For this reason other complexing agents for copper, such as 8-hydroxyquinoline, are being considered.

4. Since the ethylenimine ring is opened readily in acid solution, it was considered desirable to neutralize the ammonium chloride formed in the above reaction. The addition of either sodium hydroxide or barium hydroxide did not affect the yield of reducing function; hence, in future large scale runs, one of these bases will be employed.

5. Future work will be concerned with the effect of the mole ratio of ammonia to chloroethylenimine on the yield of reducing function. In addition, the reaction will be carried out on a scale large enough to permit the isolation and identification of the reaction products.

C. PERFORMANCE CALCULATIONS FOR THE N-AMINOETHYLENIMINE AND LIQUID OXYGEN SYSTEM

Calculations were made of the theoretical specific impulse for the N-aminoethylenimine and liquid oxygen system at 300 psia under conditions

*I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, The MacMillan Company, New York, 1948, p. 474.

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of shifting equilibrium. The heat of formation of N-aminoethylenimine was estimated to be +48 kcal/mole, and the tentative impulse data are:

<u>Mixture ratio, w_{ox}/w_f</u>	<u>Specific impulse, lb-sec/lb</u>
0.80	264.8
1.00	273.4
1.30	272.9
1.928 (stoichiometric)	261.1

Complete performance data will be presented in the next quarterly report.

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