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AFRPL-TR-69-111

(TITLE UNCLASSIFIED)

**INVESTIGATION OF THE THERMODYNAMIC
PROPERTIES OF PROPELLANT INGREDIENTS**

QUARTERLY PROGRESS REPORT AFRPL-TR-69-111

(1 January 1969 to 31 March 1969)

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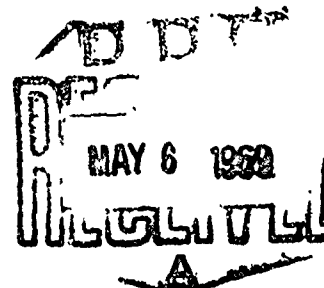
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Report Nr. T0025-1Q-69

QUARTERLY PROGRESS REPORT (U)
(1 January 1969 to 31 March 1969)

April 1969

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This quarterly report covers the work performed during 1 January 1969 through 31 March 1969. The Dow Report Number is T0025-1Q-69.

This work was performed by Dr. G. C. Sinke and Dr. J. L. Curnutt, under the technical supervision of Dr. D. R. Stull and Dr. Harold Prophet and management supervision of Dr. K. O. Groves.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

(C) The heat of formation of methylene bisoxyamine diperchlorate ($\text{CH}_6\text{N}_2\text{O}_2 \cdot 2\text{HClO}_4$) dissolved in ethylene glycol was determined by oxygen bomb calorimetry as -104.4 kcal/mole. The heat of solution in glycol will be measured in order to derive the heat of formation of neat methylene bisoxyamine diperchlorate.

(C) Other work in progress includes the heat of combustion of free methylene bisoxyamine and the heat of explosion of $\text{CF}_2(\text{ONF}_2)_2$ with oxygen and a promoter such as propane.

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A. THE HEAT OF FORMATION OF METHYLENE BISOXYAMINE DIPERCHLORATE (C)**1. Introduction (U)**

(C) A sample of methylene bisoxyamine diperchlorate ($\text{CH}_3\text{N}_2\text{O}_2 \cdot 2\text{HClO}_4$) was received from Dr. Claude Merrill of the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The material was a white crystalline solid. According to Dr. Merrill, elemental analyses for carbon, hydrogen, and nitrogen are in good accord with theory. The compound is somewhat hygroscopic, and all transfer operations were carried out in a dry nitrogen atmosphere.

2. Method (U)

(C) Organic perchlorates can be thermochemically characterized by the heat of combustion technique. Zimmer et al. (1) determined the heat of formation of hydroxylammonium perchlorate by combustion calorimetry. Diethyl oxalate was used as an additive to provide a fuel for the excess oxygen. A determination of the heat of combustion of aniline hydrochloride in this laboratory (2) showed good agreement with a value based on solution thermochemistry. The technique adopted for methylene bisoxyamine diperchlorate was similar to these two investigations.

3. Equipment (U)

(U) A rotating bomb calorimeter and a platinum lined combustion bomb were employed.

4. Procedure (U)

(U) A long narrow bag open on both ends was fabricated from 0.5 mil polypropylene film and accurately weighed. A clamp was fastened across the middle of the bag and the assembly weighed. An appropriate amount of sample was added to one side of the bag in a dry nitrogen atmosphere and the end of the bag was sealed. The bag and contents were weighed. An appropriate amount of ethylene glycol was added to the other side of the bag which was then sealed and the assembly weighed. The clamp was removed and by gentle manipulation the sample was dissolved in the ethylene glycol.

(U) The bag was next placed in a platinum crucible which was suspended in a gimbal in the combustion bomb. A cotton thread fuse was strung from a fine platinum ignition wire to the bag. Approximately 11 g of 0.08 M As_2O_3 solution was accurately metered to the bomb by means of a weight buret. The bomb was closed and charged with purified oxygen to 30 atm pressure. After thermal

equilibrium was established, the charge was fired by electrical heating of the fuse wire and the resulting temperature rise was accurately monitored by an automatic resistance bridge. After the calorimetry the bomb was carefully discharged, opened, and the solution recovered for analysis for nitrate, unoxidized arsenious oxide, and platinum.

(U) The heat of combustion of the polypropylene film and ethylene glycol was determined separately by standard oxygen bomb calorimetry. The calorimeter equivalent was determined by combustion of benzoic acid standard sample 391 from the National Bureau of Standards.

5. Calculations (U)

(U) A number of corrections must be applied to the bomb calorimeter data in order to derive true heats of formation. These corrections are calculated by means of a computer program based on the outline of Hubbard et al. (3) for C-H-O compounds and of Baroody et al. (4) for C-H-O-N-Cl compounds. Parameters for C-H-O compounds are reasonably well established, but for C-H-C-Cl samples some estimates have to be made (2). Constant factors specific for the individual compounds treated here are given in Table I.

(U) The calorimeter equivalent determined by benzoic acid combustion is $E(\text{calor}) = 3427.20 \text{ cal/deg}$. This value is an average of numerous determinations over the past year. There is no discernible trend with time.

6. Results (U)

(C) Calorimetric data for ethylene glycol are given in Table II. The average value of $-\Delta E_c^\circ/M$ is used in correcting for the glycol in the methylene bisoxamine diperchlorate runs. The glycol was a shelf sample which contained some water, and the results are not intended to define the heat of combustion of pure glycol.

(C) Calorimetric data for the heat of combustion of the solution of methylene bisoxamine diperchlorate are given in Table III. The average value of $-\Delta E_c^\circ/M$ and a molecular weight of 278.988 yield:

$$\Delta E_c^\circ = -276.86 \text{ kcal/mole}$$

for the reaction:

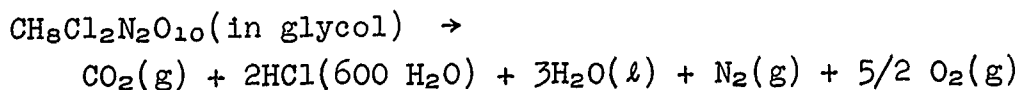


TABLE I

(C) Constant Factors in Calorimetry of Ethylene Glycol and
Methylene Bisoxamine Diperchlorate^{a,b}

Empirical formula, glycol	$C_2H_6O_2$
Empirical formula, perchlorate	$CH_8Cl_2N_2O_{10}$
Density of glycol, g/cc	1.115
Density of perchlorate, g/cc	(1.85)
Bomb volume, liter	0.349
Water added to bomb for glycol experiments, ml	1.0
Initial oxygen pressure at 25°C, atm	30.3
Reference temperature, °C	25.00
Final ratio, H_2O/HCl	600
$(\delta E/\delta P)_T$ of glycol, cal/g/atm	-0.00397
$(\delta E/\delta P)_T$ of perchlorate, cal/g/atm	(-0.001)
C_p of glycol, cal/g/°C	0.577
C_p of perchlorate, cal/g/°C	(0.26)
$E(\text{Calor})$, cal/°C	3427.20
Additional platinum parts, g	47.33

^aQuantities in parentheses are estimated.

^bFor data on polypropylene film and cotton fuse,
see Reference 2.

TABLE II
(U) Heat of Combustion of Ethylene Glycol

Parameter	Experiment Number				
	1	2	3	4	5
Sample mass, g	1.36266	1.36609	1.35999	1.36760	1.35481
Polypropylene, g	0.05588	0.06923	0.05754	0.06102	0.06519
Cotton fuse, g	0.00400	0.00378	0.00392	0.00346	0.00400
t_i , °C	22.96673	22.96669	22.96672	22.96684	23.00462
t_f , °C	25.01884	25.06089	25.01880	25.03658	25.06574
$\Delta t_{corr.}$, °C	0.06934	0.06544	0.06950	0.06488	0.05931
Ign. energy, cal	0.35	0.36	0.36	0.28	0.32
Corr. to std. states, cal ^a	3.425	3.493	3.425	3.460	3.444
ξ_i (cont.), cal/°C	5.681	5.687	5.680	5.685	5.679
ξ_f (cont.), cal/°C	6.186	6.206	6.186	6.197	6.191
$-E_c^\circ/M$, cal/g	4526.4	4523.0	4521.6	4525.5	4524.9

Average $-\Delta E_c^\circ/M = 4524.3$ cal/g

^a Includes Items 81-85 and 87-94 of reference 3.

TABLE III
(C) Heat of Combustion of Methylene Bisoxayamine Diperchlorate

Parameter	Experiment Number				
	1	2	3	4	5
Sample mass, g	0.50090	0.49822	0.51089	0.49928	0.50170
Glycol mass, g	1.21373	1.09178	1.13825	1.14813	1.14898
Polypropylene mass, g	0.09441	0.09461	0.07988	0.08772	0.09170
Cotton fuse mass, g	0.00442	0.00387	0.00344	0.00408	0.00340
n^i (H ₂ O), mole	0.6522	0.5952	0.6410	0.6116	0.6169
n^i (As ₂ O ₃), mole	0.001243	0.001135	0.001227	0.001170	0.001174
n^f (As ₂ O ₃), mole	0.001162	0.001019	0.001144	0.001106	0.001125
n^f (HNO ₃), mole	0.000516	0.000520	0.000508	0.000504	0.000540
n^f (H ₂ PtCl ₆), mole	0.000011	0.000011	0.000010	0.000009	0.000007
t_i , °C	22.96678	22.96678	22.96677	22.96033	22.96677
t_f , °C	25.08450	24.93516	24.94820	24.97982	24.99362
$\Delta t_{corr.}$, °C	0.06302	0.07472	0.07138	0.07469	0.06758
Ign. energy, cal	0.39	0.36	0.37	0.39	0.39
Corr. to std. state, cal ^a	7.736	6.746	7.142	7.076	7.147
$\mathcal{E}^i$ (cont.), cal/°C	16.422	15.332	16.173	15.656	15.753
$\mathcal{E}^f$ (cont.), cal/°C	16.821	15.685	16.534	16.031	16.136
$-\Delta E_c^\circ/M$, cal/g	499.2	492.5	507.4	493.6	499.2

Average $-\Delta E_c^\circ/M = 498.4$ cal/g

^aIncludes Items 81-85, 87-89, 93, and 94 of Reference 3.

Correcting to constant pressure conditions:

$$\begin{aligned}\Delta H_c^\circ &= -276.86 + 9/2 RT \\ &= -274.20 \text{ kcal/mole}\end{aligned}$$

(C) With auxiliary heats of formation in kcal/mole of -94.052 for $\text{CO}_2(\text{g})$, -39.823 for $\text{HCl}(600 \text{ H}_2\text{O})$, and -68.315 for $\text{H}_2\text{O}(\text{l})$, there is derived for the heat of formation of methylene bisoxyamine diperchlorate dissolved in ethylene glycol:

$$\Delta H_{298}^\circ = -104.4 \pm 1.2 \text{ kcal/mole.}$$

The heat of solution is expected to be a small positive value, so the heat of formation of neat methylene bisoxyamine diperchlorate will be slightly more negative.

B. WORK IN PROGRESS (U)

(C) A sample of methylene bisoxyamine of higher purity than the last reported work (2) has been received and its heat of combustion will be determined. The heat of solution of methylene bisoxyamine diperchlorate in glycol will also be determined.

(C) The heats of solution of methylene bisoxyamine and methylene bisoxyamine diperchlorate in dilute perchloric acid are being run. These data will serve to interrelate the two compounds and provide a check on the accuracy of the heats of combustion.

(C) Some work on the heat of explosion of mixtures of CF_3CN , C_3H_8 , and O_2 indicates that satisfactory heats of formation of gaseous C-F-N-O-H compounds can be obtained by explosion with a promoter, such as C_3H_8 , and oxygen. Time permitting, this approach will be used to measure the heat of formation of a sample of $\text{CF}_2(\text{ONF}_2)_2$ received from Rocketdyne Corporation.

REFERENCES

1. M. F. Zimmer, E. E. Barody, G. A. Carpenter, and R. A. Robb, J. Chem. Eng. Data, 13, 212 (1968).
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3. W. Hubbard, D. W. Scott, and G. Waddington, Chapt. 5 of "Experimental Thermochemistry," Vol. I, Interscience, New York, 1956.
4. E. E. Barody, G. J. Wynne, and M. F. Zimmer, U. S. Naval Propellant Plant, Indianhead, Md., NavWeps Report 8686, Technical Report 154, August 17, 1964.

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13 SUPPLEMENTARY NOTES (C) The heat of formation of methylene bisoxamine diperchlorate ($\text{CH}_3\text{N}_2\text{O}_2 \cdot 2\text{HClO}_4$) dissolved in ethylene glycol was determined by oxygen bomb calorimetry as -104.4 kcal/mole. The heat of solution in glycol will be measured in order to derive the heat of formation of neat methylene bisoxamine diperchlorate. (C) Other work in progress includes the heat of combustion of free methylene bisoxamine and the heat of explosion of $\text{CF}_2(\text{ONF}_2)_2$ with oxygen and a promoter such as propane.		

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