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HEATS OF FORMATION OF PHOSPHORUS OXIDES

Progress Report on Work Performed in the Period December 1, 1962,
to May 31, 1963, Under Contract CMLMC-PA-2B-RFP-129

Tennessee Valley Authority

Office of Agricultural and Chemical Development

Division of Chemical Development

Fundamental Research Branch

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By

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Wilson Dam, Alabama

Tennessee Valley Authority
Office of Agricultural and Chemical Development
Wilson Dam, Alabama
June 10, 1963

Director,
Directorate for Industrial and Engineering Services
Edgewood Arsenal, Maryland

Attention: Contract Project Officer

Gentlemen:

We transmit herewith the second semiannual progress report on our work on the determination of the heats of formation of phosphorus oxides. The report covers work performed under contract CMLMC-PA-2B-RFP-129 during the period December 1, 1962, to May 31, 1963.

We are distributing copies as follows:

Director, Directorate for Industrial and Engineering Services, ATTN: Contract Project Officer, Edgewood Arsenal, Maryland: 13 copies plus 1 reproducible copy.

Commander, Armed Services Technical Information Agency, ATTN: TIPDR, Arlington Hall Station, Arlington 12, Virginia: 10 copies.

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Very truly yours,

K. L. Elmore

K. L. Elmore, Chief
Fundamental Research Branch

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HEATS OF FORMATION OF PHOSPHORUS OXIDES

Progress Report on Work Performed in the Period December 1, 1962, to May 31, 1963, Under Contract CMLMC-PA-2B-RFP-129

This is the second semiannual report on the determination of the heat of formation from the elements of phosphoric oxide, $P_4O_{10}(c)$, in a bomb calorimeter. The first report, which covered the period June 1 to November 30, 1962, contained descriptions of the bomb calorimeter, the operation of the calorimeter, the measurement of temperature, and the calibration of the calorimeter with standard benzoic acid. Results were reported for the combustion of phosphorus that had been purified by a wet-chemical method (1) and sealed in thin-walled glass ampoules, and of phosphorus coated with a film of Lucite.

Combustions of phosphorus in glass ampoules were not satisfactory because part of the glass entered into the combustion chemistry. Phosphorus purified only by the wet-chemical method was used to establish satisfactory conditions of combustion.

Combustion of Distilled Phosphorus with Lucite Coating

Phosphorus purified by the wet-chemical method was vacuum distilled in a glass apparatus at about 150° C. A portion of the distilled phosphorus was caught in a 9-mm. glass tube and allowed to solidify under vacuum. The glass tube was sealed, separated from the still, and opened under water; the stick of phosphorus was removed and sliced into sections that weighed 0.6 gram each. The distilled phosphorus was "water-white" when molten and translucent when solid. It was observed that the distilled phosphorus was affected by the laboratory fluorescent lights and developed a yellow-to-orange coating on exposure to the lights for a few hours, so that it was necessary to store the phosphorus in the dark.

The phosphorus was coated with Lucite by the procedure described in the previous report, but the rough edges on the sliced phosphorus sections made it difficult to get a Lucite covering that did not "smoke" during drying. When about half of the chloroform of the Lucite solution was replaced with acetone, the drying characteristics of the Lucite film were improved. A glass bulb of about the diameter of a phosphorus sample required about 20 hours to dry to constant weight when coated with Lucite from a chloroform solution, but when half of the chloroform in the Lucite solution was replaced with acetone, a coated glass bulb dried in 3 hours. When weighed phosphorus samples were taken from water and dipped successively in acetone, chloroform, and the chloroform solution of Lucite, a faint trace of smoke was visible for an hour or more after three successive coatings with Lucite. When the chloroform dip was omitted and acetone was added to the chloroform solution of Lucite, the samples smoked only faintly for a few minutes and came to constant weight in a few hours.

The adequacy of the Lucite coating was tested by placing a coated sample, that had dried to constant weight, in the bomb for 2 hours under 30 atmospheres of oxygen. The weight of the exposed sample was the same as the initial weight, showing that the Lucite coating was impervious to oxygen.

Five samples of distilled phosphorus that were dried in a stream of deoxidized nitrogen and weighed under water were found to contain 99.96 ± 0.08 per cent P_4. The arsenic contents of two 0.5-gram samples of distilled phosphorus were below the limit of detection (0.002 mg.).

Results of 14 combustions of distilled phosphorus coated with Lucite are given in Table I. The average value for the heat of combustion is 713.59 kcal. per mole P_4, but the average deviation, ± 0.26 per cent, is larger than is acceptable for the determination of the heat of formation of $P_4O_{10}(c)$. The deviation is decreased if no correction is made for HPO_3 formation from the water from the combustion of Lucite, which indicates that the assumed formation of HPO_3 is not adequate, but there is no satisfactory substitute for this assumption. Errors of only a few milligrams in the sample weights would account for the deviations, but there is no reason to suspect the weights.

A plot of the values for ΔE_c (substance), the total calories developed in the combustion without corrections for impurities, against the total combustibles (phosphorus and Lucite) is a straight line for which the equation is

$$\Delta E_c(\text{sub.}) = 107.88 - 5937.97 \, [m(\text{sub.})]$$

with a deviation of ± 0.22 per cent. A plot of the corrected temperature rise against the total combustibles also is a straight line which is represented by the equation

$$\Delta T = 2.5251 \, [m(\text{sub.})]$$

with an average deviation of 2.7 millidegrees. The deviations from both equations include the observed deviations in the calculated heats of combustion listed in Table I. Other attempts to correlate the observed spread in measured heats of combustion with the impurity contents also failed to improve the calculated values.

TABLE I

Heat of Combustion of Lucite-Coated Distilled Phosphorus

Run No.	Weight, grams P_4	Weight, grams Lucite	Weight, grams P_4 equiv. of P_4O_6	ΔT, °C.	$-\Delta E_c$, cal. Substance	$-\Delta E_c$, cal. Lucite	$-\Delta E_c$, cal. HPO_3	$-\Delta E_c$, cal. P_4O_6	$-\Delta E_c$, cal. P_4	$-\Delta E_c$, kcal./mole P_4
56	0.49391	0.00330	0.00166	1.25063	2856.961	21.015	3.703	2.638	2834.881	711.118
57	0.67482	0.00248	0.00227	1.70593	3898.279	15.793	2.782	3.152	3882.855	712.882
58	0.59653	0.00323	0.00201	1.51924	3471.287	20.570	3.624	2.791	3449.884	716.517
59	0.76396	0.00626	0.00285	1.95616	4470.558	39.866	7.024	3.957	4427.626	718.050
60	0.60270	0.00478	0.00195	1.53262	3501.877	30.440	5.363	2.707	3468.781	713.067
61	0.65215	0.00310	0.00211	1.65538	3782.655	19.742	3.478	2.930	3762.365	714.773
62	0.65987	0.00144	0.00213	1.66895	3813.691	9.170	1.616	2.957	3805.862	714.577
63	0.63014	0.00600	0.00204	1.60298	3662.792	38.210	6.732	2.832	3620.683	711.882
64	0.63546	0.00260	0.00205	1.61089	3680.896	16.558	2.917	2.846	3664.267	714.420
70	0.67981	0.00413	0.0026	1.72912	3947.908	26.301	4.634	3.610	3920.583	714.525
71	0.63146	0.00332	0.0023	1.60633	3667.299	21.143	3.725	3.193	3645.625	715.280
72	0.56846	0.00707	0.0021	1.45371	3318.557	45.024	7.932	2.916	3268.517	712.369
73	0.61131	0.01101	0.0022	1.56613	3575.418	70.115	12.353	3.054	3496.005	708.541
74	0.72697	0.01083	0.0030	1.86438	4256.987	68.969	12.151	4.165	4180.032	712.390

Three samples of the gaseous combustion products from runs 60, 61, and 62 (Table I) were analyzed on the mass-spectrometer at the CBR Agency, Research and Development Laboratory, Edgewood Arsenal.

Calibration standards were not available for these mixtures, so that only the relative peak intensities were reported. The results are listed in Table II; the original report of the analyses is attached as an appendix to this report.

TABLE II

Mass Spectrometer Analysis of Gaseous Combustion Products

Run No.	Relative intensity			
	O_2	N_2	CO_2	CO
60	9000	600	180	81
61	7600	800	120	67
62	8200	1200	126	65

The data in Table II do not correlate well with other known information on these samples. Chromatographic analysis of the cylinder oxygen and the oxygen from a bomb that had gone through the normal flushing and filling procedure to 30 atmospheres pressure for a bomb initially containing air at 1 atmosphere showed significantly less than 1 per cent nitrogen in both samples. The weights of Lucite-coated phosphorus in runs 61 and 62 were essentially the same, so that the relative intensities of oxygen in the combustion gases should have been about the same. The weights of Lucite in the three runs were 5, 3, and 1 mg., respectively, and the combined CO_2 plus CO from these runs should have been in the same order.

The presence of even traces of carbon monoxide in the combustion gases indicates incomplete combustion of the Lucite. The gases from the first eight combustions of Lucite-coated phosphorus were shown by a Mine Safety Appliances carbon monoxide detector to contain no carbon monoxide. The gases from runs 60, 61, and 62 were not tested.

The possibility that a systematic error developed in the calorimetric technique was explored by calibrating the bomb again with benzoic acid after the results in Table I were calculated. The result of 5 calibrations was 2278.18 (± 0.03%) calories per degree, a value slightly less than that (2280.129 cal./degree, ± 0.019%) obtained in the original series of calibrations because a small amount of metal had been machined from the bomb in preparation for the attachment of an oxygen jacket. The results in Table I were obtained before the bomb was machined. The consistency in the results of the two calibrations indicated that the observed deviations of the values listed in Table I resulted not from errors in the calorimetric measurements but from variations in the chemistry of the combustion process--either some of the assumed side reactions did not occur, or unknown side reactions took place.

Jacketed Combustion Bomb

Nuttall, Wise, and Hubbard (4) of the Argonne National Laboratory modified a bomb for the combustion of organic compounds in an atmosphere of fluorine by placing a double-walled jacket around the bomb. The jacket was filled with fluorine under a pressure of about 150 p.s.i., and the fluorine was admitted to the bomb through a quick-opening valve to supply a pressure of 50 p.s.i. of fluorine in the bomb. Our bomb was modified similarly, with the assistance of shop drawings supplied by the Argonne National Laboratory (except that the wall thickness of the jacket was increased to permit a working pressure of 600 p.s.i. (40 atm.) of oxygen pressure in the jacket), so that uncoated phosphorus could be placed in the bomb in an inert atmosphere, and oxygen could be admitted for the combustion when thermal equilibrium was attained. This modification is intended to eliminate the undesirable water that is formed by combustion of the Lucite on coated phosphorus samples.

The jacketed bomb is shown in Figure 1. The jacket valve and packing gland and the seal ring in the combustion chamber failed to function properly because of the high pressure. When the packing gland on the jacket valve was tightened sufficiently to hold the increased oxygen pressure, the valve would not operate smoothly. The valve was closed by a screw which pushed against the hinge of a knuckle joint to which the valve stem was attached. When the screw was backed off, the gas pressure was supposed to open the valve by bending the knuckle joint. It was necessary to double the thickness of the knuckle-joint members and to provide a positive connection between the joint and the screw and its driving pulley wheel, so that the valve was pulled open when the screw was backed out. The valve is closed by tightening the pulley wheel with a small torque wrench, so that the pressure on the valve seat is the same each time the valve is closed.

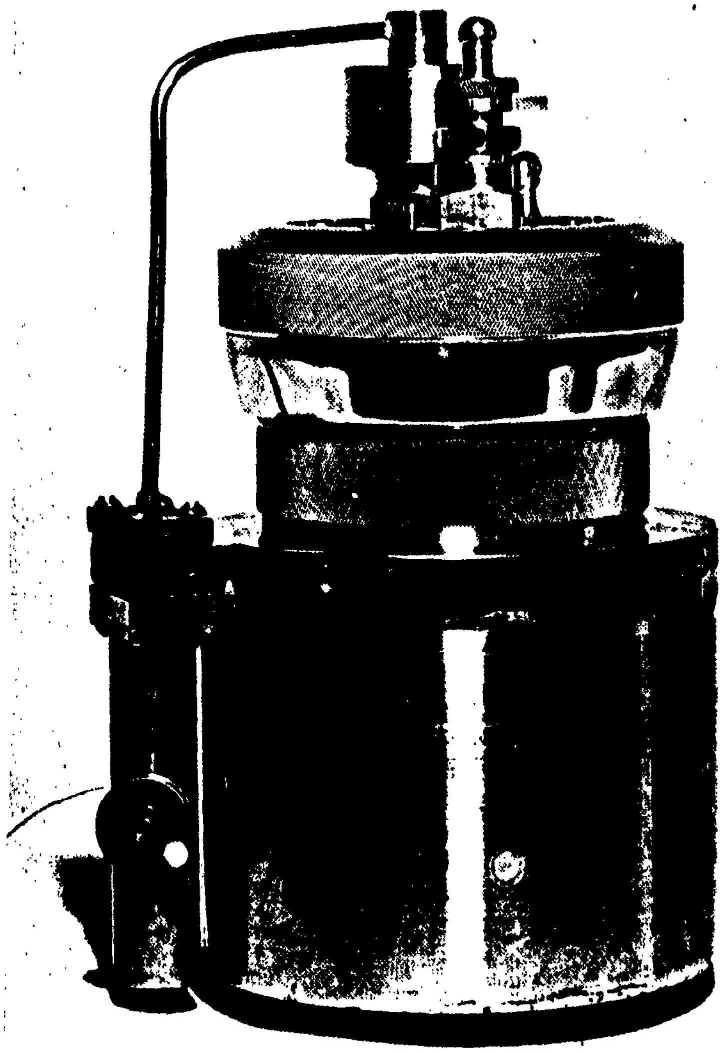

FIGURE I
COMBUSTION BOMB WITH OXYGEN JACKET

The neoprene seal ring in the original combustion bomb was seated by the internal gas pressure. This arrangement was satisfactory when the bomb was filled from an oxygen cylinder, as the gas lost before the internal pressure seated the seal ring was of no consequence. With the oxygen jacket on the bomb, however, a leak could not be tolerated, because the degree of cooling of the oxygen when it expanded from the jacket to the bomb depended on the final pressure in the bomb. The original screw cap on the bomb was modified by addition of a brass tension ring fitted with 8 stainless steel setscrews. With this arrangement, the seal ring was set at 1 atmosphere pressure, and there was no leakage when the oxygen was released into the bomb. The volume of the bomb was 338.1 cc., that of the oxygen jacket to the valve seat 172.7 cc., and that of the interconnecting fittings and gas space 2.9 cc.; the total expanded volume was 513.7 cc.

Combustion of Phosphorus in Jacketed Bomb

Four trial combustions of phosphorus in the jacketed bomb appeared to be essentially complete, but there were small amounts of a yellow-to-orange deposit. The phosphorus for these trial combustions was weighed in water, dried in a stream of deoxidized nitrogen, and loaded into the bomb in a glove bag in an atmosphere of nitrogen. For the final combustion, the phosphorus still will be modified to produce dry phosphorus pellets in small glass bulbs. The weight of the phosphorus sample will be determined by recovering and weighing the glass bulb after it is opened in a dry-box.

There was some indication in these trial combustions that an oxide of platinum had formed on the 20-gage platinum wire on which the samples were suspended in the bomb. In combustions with Lucite-coated phosphorus, the ignition of the Lucite coating apparently melted the phosphorus which dropped free of the wire before any significant combustion of the phosphorus occurred. With the uncoated phosphorus, the combustion appears to start at or near the platinum wire with considerable heating of the wire.

Before any measured combustions of phosphorus are made, the energy of ignition and the heat of expansion of the oxygen will be measured, and the system will be calibrated with standard benzoic acid. Since, under the usual conditions of combustion, nitrogen is assumed (2) to obey the same P-V-T relations as oxygen, whereas helium (3) is significantly different, it will simplify the conversion of the gas to standard conditions if nitrogen is used as the inert atmosphere, unless the formation of oxides of nitrogen becomes objectionable.

Four measured expansions of oxygen in the jacket at 40 atmospheres pressure into the combustion bomb gave a temperature drop of 5.28 ± 0.12 millidegrees. Six measurements of the ignition of 5 inches of 30-gage platinum fuse wire gave a temperature rise of 0.38 ± 0.12 millidegrees. The calories equivalent to these temperature changes will be determined when the bomb is calibrated with benzoic acid.

Further Work

The determination of the heat of combustion of phosphorus will be completed under an extension (Contract RFP-129, Amendment 1660.1) of the present contract. The extended contract will cover, in addition to determination of the heat of formation of $P_4O_{10}(c)$, one or more of the following determinations: heat of formation of phosphorus trichloride; heat of formation of a phosphonate; heat of formation of liquid phosphorus oxychloride; heat of formation of a phosphorus sulfide, such as phosphorus thiochloride; and heat of reaction of phosphorus trichloride or oxychloride with an alcohol.

References

(1) Hildebrand, J. H., and Rotariu, G. J., J. Am. Chem. Soc. 73, 2524 (1951).

(2) Hubbard, W. N., Scott, D. W., and Waddington, G., in "Experimental Thermochemistry," Chapter 5, F. D. Rossini, Editor, Interscience Publishers, Inc., New York, 1956.

(3) Keesom, W. H., "Helium," Chapter II, Elsevier Press, New York, 1942.

(4) Nuttall, R. L., Wise, S., and Hubbard, W. N., Rev. Sci. Instr. 32, 1402 (1961).

APPENDIX: Analysis of Gas Samples

SMUCR-WS(PR)2 18 April 1963

MEMORANDUM FOR FILE

SUBJECT: Analysis of Gas Samples from Combustion of Phosphorus under Contract CMLMC-PA-2B-RFP-129, Tennessee Valley Authority

1. The Division of Chemical Development of the Tennessee Valley Authority, Wilson Dam, Alabama submitted three gas samples, labelled HCP 60 (I), HCP 61 (II), and HCP 62 (III) for analysis by mass spectrometry.

2. The mass spectra in the range of m/e from 12 to about 120 displays the mass peaks and relative intensities indicated in the following Table:

Table

Sample No.	M/e = 44	M/e = 34	M/e = 32	M/e = 28		M/e = 18
	CO_2		O_2	N_2	CO	
HCP 60 (I)	180	28	9000	600	81	
HCP 61 (II)	120	26	7600	800	67	75
HCP 62 (III)	126	30	8200	1200	65	90

In addition, the usual peak at M/e = 17 (OH^+) accompanies the M/e = 18 peak (H_2O). The pressure in the inlet system of the spectrometer was the same for all samples so the relative amounts of the constituents are given directly by the numbers in the Table. The presence of carbon monoxide as indicated by the resolution of the mass peak at M/e = 28 into a doublet is to be especially noticed. The mass peak at M/e = 34 is believed to be the $O^{16}O^{18}$ combination rather than an indication of N_2H_6.

LESTER W. DAASCH