630. *The Heat of Formation of Disodium Methylphosphonate.*

By Raymond Thompson.

The heat of combustion of disodium methylphosphonate has been determined in a commercial bomb calorimeter, and a value of 226·6 ± 0·5 kcal./mole obtained. The equation for the bomb reaction has been established quantitatively to be $CH_3{\cdot}PO(ONa)_2(c) + 2O_2(g) = \frac{1}{2}Na_4P_2O_7(c) + CO_2(g) + \frac{3}{2}H_2O(l)$, from which the heat of formation of disodium methylphosphonate (c) is calculated to be 350 kcal. (1465 abs. k-joules)/mole.

Evaluation of heats of formation from heats of combustion of organic compounds containing elements other than carbon, hydrogen, nitrogen, and oxygen is not readily accomplished owing to difficulties involved in ascertaining the precise stoicheiometry of the bomb

reaction. The products of combustion often include acids of the other elements (*e.g.*, sulphur and the halogens) in various states of hydration and oxidation. Uniformity of hydration is guaranteed only by the use of a rotating bomb such as that used by Sunner (*Svensk Kem. Tidskr.*, 1946, **58**, 71); oxidation is dependent to some extent on the presence and action of nitric and other acids (*e.g.*, Huffman and Ellis, *J. Amer. Chem. Soc.*, 1935, **57**, 41), and the fixation and subsequent analysis of a mixture of chemically similar acids can introduce considerable practical problems. There is no record of the combustion of organophosphorus compounds, and it was considered that, in view of the numerous oxy-acids of phosphorus and their various polymeric forms, the bomb reaction might in this case be even more complex. A difficulty encountered in the actual combustion of such compounds was the low volatility of the acids produced. For example, attempts to burn methylphosphonic acid were unsuccessful, for the acid produced damped combustion, and only by using an accelerator in proportion so large as to render the heat contribution due to the methylphosphonic acid relatively small (with consequent reduced accuracy) could the substance be induced to burn completely.

The experiments now described were therefore designed with a view to the complete elimination of liquid and gaseous phosphorus compounds as products of combustion. This has been achieved by burning disodium methylphosphonate, which was found (following J. K. Leary's qualitative observation) to be converted quantitatively into sodium pyrophosphate according to the equation

$$CH_3{\cdot}PO(ONa)_2(c) + 2O_2(g) = \tfrac{1}{2}Na_4P_2O_7(c) + CO_2(g) + \tfrac{3}{2}H_2O(l)$$

Sodium pyrophosphate remained within the crucible after combustion as a crystalline white solid. Under optimum conditions combustion was complete and no carbonaceous residue remained. The water formed condensed in droplets on the walls of the bomb; a trace of phosphate was detectable in this aqueous phase.

The heat of combustion was found to be 226·6 ± 0·5 kcal./mole (weighed in air) at 21°, and the value was assumed to be the same as 25°. By using the value of 760·8 kcal./mole for the heat of formation of sodium pyrophosphate (c) ("Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., 1950) and 94·05 and 68·32 for carbon dioxide (g) and water (l) respectively (Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143), the heat of formation of disodium methylphosphonate is seen to be 350 kcal. (1465 abs. k-joules)/mole.

That the solid remaining after combustion was sodium pyrophosphate was revealed by qualitative tests and verified by an *X*-ray powder photograph. The stoicheiometry of the bomb reaction was established as follows. The sodium salt burned was perfectly pure and anhydrous, and a phosphate determination on the combined solid and liquid reaction products gave P, 22·10% [Calc. for $CH_3{\cdot}PO(ONa)_2$: P, 22·13%]. The weight of sodium pyrophosphate remaining in the crucible in those experiments in which scattering did not occur (see below) corresponded with the above equation and the weight of disodium methylphosphonate taken. The following results are typical:

	Calc.	Expt. 1	Expt. 2
Weight ratio $2CH_3{\cdot}PO(ONa)_2/Na_4P_2O_7$	1·054	1·052	1·053

Fused sodium pyrophosphate is not readily hydrated and has a high vapour pressure in equilibrium with the hydrated salt (there are no lower hydrates than the decahydrate). In view of this and the facts that (*a*) water formed during combustion condenses preferentially on the cold walls of the bomb, (*b*) the vapour pressure of water within the bomb is small, and (*c*) the crucible was weighed immediately following the determination, it was expected that the degree of hydration would be slight. This was confirmed by a determination of the phosphorus content of the solid within the crucible (Found: P, 23·08. Calc. for $Na_4P_2O_7$: P, 23·29%). The close proximity of the above ratios to the theoretical is therefore due to the mutually compensating effects of this small degree of hydration and of slight volatilisation. A ratio of 1·056 could be obtained by withdrawing the crucible 2—3 minutes after firing.

It is thus established that, within the precision of the apparatus used, the heat evolved during the combustion of disodium methylphosphonate is entirely that due to the reaction indicated by the above equation.

Experimental

Preparation of Materials.—Methylphosphonic acid was prepared by hydrolysis of methylphosphonyl dichloride, 65 g. of which were added, slowly and with constant stirring, to 50 ml. of water. The resultant liquid was then evaporated to dryness, a further 50 ml. of water added, and the process repeated. By this means all traces of hydrogen chloride were removed, and 40 g. of a wax-like solid remained on cooling.

The disodium salt was prepared by dissolving 24 g. of the acid in 50 ml. of dry ethanol and treating the solution with 23 g. of sodium dissolved in 400 ml. of ethanol. A white precipitate formed rapidly, but the mixture was refluxed for ½ hour to complete the reaction. The product was removed by filtration and recrystallised twice from 50% aqueous ethanol, then dried in a vacuum-desiccator. About 30 g. of the solvated product were obtained, purity rather than high yield being the primary consideration.

The salt was prepared for combustion by drying it successively in ovens at 80° (3 hours), 140° (16 hours) and 180° (4 hours). It was then compressed into firm pellets, which were transferred to a weighing bottle and further dried at 180° for 3 hours.

Calorimetry.—Heats of combustion were determined by using a Mahler–Cook bomb calorimeter and standard procedure. The water equivalent of the apparatus was assessed by 12 combustions of benzoic acid (B.D.H. Thermochemical Standard), the heat of combustion of which was taken to be 6·319 kcal./g. (vac.). Temperature measurements were made with a Beckmann thermometer which had been calibrated against a standard. The relative mean deviation of the water equivalent values was calculated to be 0·2%, a deviation high by comparison with modern standards but of adequate precision for present purposes. All combustions were performed under a pressure of 25 atm. and at 21°±1°, and all values corrected to 15°-calories. Washburn corrections were not applied.

The pellets of salt were weighed from the weighing bottle into a silica crucible of 2·5-cm. top diameter and 2 cm. high; this relatively deep crucible was necessary in order to prevent scattering of the contents during combustion. Ignition was effected by means of a 4 × 0·009 cm. platinum wire and a potential of 12 v in conjunction with a fuse (0·005 g.) of oven-dried Whatman No. 1 filter-paper; the heat of combustion of the paper was taken to be 3·99 kcal./g. (C. B. Knowles, Thesis, Manchester, 1951). It was found that complete combustion of the salt was not obtained if the sample exceeded 1·8 g.; the size and shape of the crucible were partly responsible for this critical weight, and a black core resulted if larger quantities were burned. About 1·6 g. were used in obtaining the combustion values quoted. The capacity of the bomb was 300 ml., and no water was introduced before combustion.

The heat of combustion of disodium methylphosphonate was taken as the mean of six determinations whose individual values were: 226·3, 226·7, 227·2, 226·4, 226·9, 225·9 kcal./mole.

On a number of occasions several small pieces of solid sodium pyrophosphate were found on the base of the bomb after combustion. It was seen from their sharp edges, and corresponding crevices in the pyrophosphate within the crucible, that this was due to uneven contraction during cooling and not to scattering at the time of combustion. Silica was known to be soluble in molten phosphate (Yost and Russell, "Systematic Inorganic Chemistry," Prentice Hall, 1944, p. 224) but the amount actually dissolved in the short time during which the sodium pyrophosphate was molten was only about 0·4 mg. It was not possible to assess alkalimetrically the amount of nitric acid produced during the combustion of disodium methylphosphonate because of the large excess of sodium pyrophosphate. The thermal contribution due to nitric acid formation was therefore considered to be the same as in the case of the combustion of benzoic acid (9 cal.), and the heats of combustion recorded have been calculated upon this assumption. Any error incurred thereby (and the results of spectrophotometric analysis suggest that nitric acid formation is the same) is not of significance in comparison with certain other errors attendant upon the present method of calorimetry, and particularly of temperature measurement.

Analysis.—The phosphorus content of the combustion products was determined as magnesium pyrophosphate following double precipitation. It must be emphasised that, contrary to general belief, pyrophosphate is not readily converted completely into orthophosphate by dissolution in water and boiling, even after the addition of hydrochloric acid. In the present work 25-ml. aliquots containing 0·25 g. of sodium pyrophosphate were refluxed for several hours

with 5 ml. of concentrated nitric acid, finally being diluted to 100 ml., and the determination completed in the normal manner.

Spectrophotometric estimation of nitrate present in the bomb after combustion was effected with a Unicam SP 500 spectrophotometer. The ultra-violet-absorbing substances present were pyrophosphate, nitrate, and dissolved silica, of which only the last was found to absorb at 370 mμ. The absorption due to silica at 302·5 mμ was readily calculated by application of data obtained from heating " AnalaR " sodium pyrophosphate in a silica crucible in air and measuring the absorption of the aqueous solution of the product. Knowing the weight of sodium pyrophosphate in the bomb contents and $\varepsilon_{302\cdot5}$ (found by separate experiments for the same concentration of $Na_4P_2O_7$ in water to be 0·07), and employing a value for sodium nitrate of $\varepsilon_{302\cdot5} = 7\cdot01$ (Addison, Gamlen, and Thompson, *J.*, 1952, 338), the amount of nitrate present was readily determined.

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