76. *Phosphonitrilic Derivatives. Part IV.*[1] *The Heats of Formation of the Trimeric and Tetrameric Phosphonitrilic Chlorides.*

By S. B. HARTLEY, N. L. PADDOCK, and H. T. SEARLE.

The heats of formation of trimeric and tetrameric phosphonitrilic chlorides have been determined by combustion; $\Delta H_f°(PNCl_2)_3(c) = -194{\cdot}1$ kcal. mole^{-1}, $\Delta H_f°(PNCl_2)_4(c) = -259{\cdot}2$ kcal. mole^{-1}. The average P–N bond-energy terms of the two compounds are almost identical, that of the tetramer being slightly the higher; both are greater than expected for a single bond.

COMPARATIVELY few determinations of the heats of formation of compounds of phosphorus and nitrogen have been reported.[2,3] In this connection, the phosphonitrilic compounds $(PNX_2)_n$ are of special interest in that they are formally unsaturated and possess many of the attributes of aromatic character, the theoretical basis of which has been developed by Craig.[4] The energetics of the cyclic phosphonitrilic skeleton may be studied conveniently with the chlorides, which burn to simple products. The present paper describes the determination, by combustion, of the heats of formation of the trimeric and tetrameric chlorides.

EXPERIMENTAL

Preparation of Compounds.—The trimeric chloride $(PNCl_2)_3$ was prepared from the commercial material by recrystallisation from light petroleum, followed by a double sublimation (m. p. 112·8°). The tetrameric chloride was obtained pure (m. p. 122·8°) and free from a more stable polymorphic form [5] by a double sublimation followed by recrystallisation from benzene at 25°. The crystals were dried *in vacuo* below 25°, the form so obtained being that of known crystal structure.[6] Its crystallographic purity was established by *X*-ray diffraction, and absence of solvent by a combustion experiment in which no carbon dioxide was formed.

Experimental Method.—The calorimeter used was of the standard type (Baird and Tatlock, Ltd.), and incorporated a 300 ml. stainless-steel bomb of the single-valve type. It was modified so as to ensure more exact control of the jacket temperature and more rapid attainment of thermal equilibrium. All combustions were carried out in 30 atm. of oxygen in a dry bomb; water was avoided throughout, since its use in the experiments with the phosphorus compounds would have given products hydrated to an uncertain extent. Temperatures were measured with a mercury-in-glass thermometer which had been calibrated to ±0·001°. The observed temperature rise was corrected in all the experiments by the method of Regnault and Pfaundler. The energy equivalent of the calorimeter was determined (within 0·1%) with benzoic acid (B.D.H. Thermochemical Standard), allowance being made for the formation of nitric acid in its combustion.

All samples were burned in a shallow platinum dish, the amount being adjusted to give a temperature rise of 1·8—2°, with a final temperature in the range 24° ± 1°. Samples were ignited by an electrically heated platinum wire; complete combustion of the phosphonitrilic chlorides was ensured by tying a small fragment of hair to the platinum fuse and allowing it just to touch the surface of the sample.

Combustion Process.—The phosphonitrilic chlorides were found to burn essentially according to the equation:

$$(PNCl_2)_n(c) + \frac{5n}{4}O_2(g) \longrightarrow \frac{n}{4}P_4O_{10}(c) + \frac{n}{2}N_2(g) + nCl_2(g)$$

The solid and the gaseous products of combustion were both analysed; no significant difference (either qualitative or quantitative) could be detected between the products of combustion of

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[1] Part III, Chapman, Paddock, Paine, Searle, and Smith, *J.*, 1960, 3608.

[2] Neale and Williams, *J.*, 1956, 422.

[3] Fowell and Mortimer, *J.*, 1959, 2913.

[4] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997; "Theoretical Organic Chemistry," Butterworths Sci. Publ., London, 1959, p. 20.

[5] Lund, Paddock, Proctor, and Searle, *J.*, 1960, 2542.

[6] Ketelaar and de Vries, *Rec. Trav. chim.*, 1939, **58**, 1081.

the two chlorides. The phosphorus pentoxide was shown by *X*-ray powder photography to be the metastable, hexagonal form. Its heat of formation was taken to be that of a crystalline form of the oxide (probably hexagonal) as determined by Giran [7] and re-interpreted by Rossini *et al.*[8] The small amount of residue insoluble in water (0—0·3% of sample weight) was found to be a highly polymeric form of phosphonitrilic chloride. Its weight was subtracted from the initial sample weight, no correction being made for the heat of polymerisation. In early experiments phosphorous and hypophosphorous acids were determined iodometrically, but the amounts found were too small for accurate estimation. Phosphorus was therefore determined as orthophosphoric acid by the quinoline molybdate method,[9] both before and after oxidation with bromine and nitric acid. The phosphorus recovered in each case was 99·7 ± 0·3% (average of six measurements) and 100·2 ± 0·2% (average of seven measurements); the difference between the two figures was taken as tervalent phosphorus, and a correction applied.

The gaseous reaction product was examined for oxides of nitrogen and of chlorine, for nitrosyl chloride, and for phosphorus oxychloride. The chlorine and other products were frozen out of the bomb gases; no oxide of nitrogen or of chlorine or nitrosyl chloride was detected on infrared spectroscopic examination of the condensed gases, nor was nitrosyl chloride detected, either by its volatility or on absorption of the concentrated bomb gases in alkali. No phosphorus oxychloride was detected after evaporation of the more volatile constituents. A very small amount of nitrogen dioxide was found by absorption on a mixture of silica gel and potassium dichromate in concentrated sulphuric acid,[10] followed by reduction with Devarda's alloy and estimation as ammonia. The quantities found, however, were small (0·002—0·022 g. of NO_2), and an average correction was applied to all the heat measurements. Elemental chlorine was estimated by absorption in alkali, followed by reduction to chloride with sulphur dioxide and determination by Volhard's method. The average recovery was 99·6 ± 0·2% (five measurements). Nitrogen was determined after further absorption of oxygen in sodium dithionite solution. The average recovery was 100·4 ± 0·4% (six measurements).

Heat Measurements.—All thermal quantities are given in terms of the thermochemical calorie (=4·1840 abs. joules). The mean of six measurements of the heat of combustion of the trimeric chloride was 345·3 kcal. mole^{-1}, and of the tetrameric chloride 460·0 kcal. mole^{-1}. These figures were corrected for the small amount of partly burned phosphorus (0·5%) by assuming it to be in the tervalent state, and its heat of oxidation to correspond to the formation of phosphoryl bonds having a bond dissociation energy of 120 kcal. mole^{-1}. The corrections to the evolved heat were +0·90 kcal. mole^{-1} for the trimeric chloride, +1·20 kcal. mole^{-1} for the tetrameric chloride. The presence of nitrogen dioxide (an average of 0·010 g. for an average sample weight of 4·5 g.) necessitated a further correction (+0·12, +0·18 kcal. mole^{-1}), and with the appropriate allowance for the increase in the number of gaseous molecules on combustion (−0·45, −0·60 kcal. mole^{-1}), we find, finally, $\Delta H_c(PNCl_2)_3(c) = -345{\cdot}9$ kcal. mole^{-1}, $\Delta H_c(PNCl_2)_4(c) = -460{\cdot}8$ kcal. mole^{-1}. The accepted value [8] for $\Delta H_f^\circ(P_4O_{10})(c)$ is −720·0 kcal. mole^{-1}, leading to the heats of formation $\Delta H_f^\circ(PNCl_2)_3(c) = -194{\cdot}1$ kcal. mole^{-1}, $\Delta H_f^\circ(PNCl_2)_4(c) = -259{\cdot}2$ kcal. mole^{-1}.

It is necessary to take into account errors (i) in the thermal measurements, (ii) arising from incomplete reaction or inexact knowledge of it, (iii) in the calibration experiments, and (iv) in the heat of formation of phosphorus pentoxide (the reliability of which is not here assessed). The standard deviations of the means of the thermal measurements corrected as described were 0·2, 0·4 kcal. mole^{-1} for the trimer and tetramer. The chemical error is more difficult to estimate, but is probably comparable. For a comparison between the two polymers (one of the main purposes of this paper) no further errors need be considered, and the standard deviations of the mean heats of formation are therefore taken as 0·4, 0·8 kcal. mole^{-1} for this purpose. Inaccuracies in the calibration introduce the further uncertainties 0·3, 0·4 kcal. mole^{-1}.

The heat of sublimation of the trimeric chloride is known [11] (18·2 ± 0·2 kcal. mole^{-1}) but only the heat of vaporisation of the liquid tetrameric chloride [12] (15·5 kcal. mole^{-1}). Its heat of fusion was determined indirectly by measuring its heat of solution in benzene and correcting,

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[7] Giran, *Ann. Chim. Phys.*, 1903, **30**, 203.
[8] Rossini *et al.*, National Bureau of Standards, Circular 500, Washington D.C., 1952.
[9] Wilson, *Analyst*, 1951, **76**, 65.
[10] Koshun and Klimova, *Zhur. analit. Khim.*, 1949, **4**, 292.
[11] Steinman, Schirmer, and Audrieth, *J. Amer. Chem. Soc.*, 1942, **64**, 2377.
[12] Moureu and de Ficquelmont, *Compt. rend.*, 1941, **213**, 306.

by Hildebrand's solubility theory,[13] for the heat of mixing of the two liquids. The calorimeter consisted of a Dewar vessel immersed as completely as possible in a thermostat bath maintained at 25°c. It contained a stirrer, heater coil for calibration, and a Beckmann thermometer capable of being read to within $\pm 0{\cdot}002°$. The powdered chloride was equilibrated at the temperature of the benzene, and mixed rapidly with it. The temperature changes recorded were of the order of $-2{\cdot}4°$; small corrections were made for heat losses during the short solution period. The heat of solution at 25° was found to be 7·75 kcal. mole^{-1}; the heat of mixing was calculated to be 0·15 kcal. mole^{-1}, leading to a value for the heat of fusion of $7{\cdot}60 \pm 0{\cdot}1$ kcal. mole^{-1}, and the heat of sublimation of the tetrameric chloride at 25° is therefore assessed at $23{\cdot}1 \pm 0{\cdot}2$ kcal. mole^{-1}. The heats of formation of the two compounds in the vapour phase are, therefore, $\Delta H_f^\circ(\mathrm{PNCl_2})_3(\mathrm{g}) = -175{\cdot}9$ kcal. mole^{-1}, $\Delta H_f^\circ(\mathrm{PNCl_2})_4(\mathrm{g}) = -236{\cdot}1$ kcal. mole^{-1}.

DISCUSSION

The heats of formation of the $\mathrm{PNCl_2}$ unit in the gas phase are $-58{\cdot}63$ kcal. mole^{-1} for the trimeric chloride, and $-59{\cdot}03$ kcal. mole^{-1} for the tetrameric chloride. Energetically, therefore, there is little difference between the two molecules. From the known heats of formation of the gaseous atoms (phosphorus [14] 75·3, nitrogen [15] 112·9, chlorine [16] 28·9 kcal. g.-atom^{-1}) the heats of atomisation may be calculated as 913·9 kcal. mole^{-1} (trimeric chloride) and 1220·1 kcal. mole^{-1} (tetrameric chloride). If, in a particular molecule, all the P–N bonds are assumed equal, and all the P–Cl bonds are assumed equal, the sum of the bond energy terms $\bar{E}$(P–Cl) + $\bar{E}$(P–N) is 152·3 kcal. mole^{-1} for the trimer, 152·5 kcal. mole^{-1} for the tetramer. If $\bar{E}$(P–Cl) can be taken to be the same in both molecules, the difference of 0·2 kcal. can be taken as a measure of the strengthening of the ring bonds in the tetramer as compared with the trimer. The difference is too small compared with its standard deviation (0·12 kcal.) to be considered significant. By contrast, it may be deduced from the heats of combustion in the gas phase of benzene [17] (788·4 kcal. mole^{-1}) and of cyclo-octatetraene [18] (1095·2 kcal. mole^{-1}) that the increase in ring size here entails a decrease in $\bar{E}$(C–C), averaged over all ring bonds, of 2·75 kcal., provided $\bar{E}$(C–H) remains unchanged. This difference demonstrates a clear distinction between the two series of compounds.

The length of the P–Cl bond in trimeric phosphonitrilic chloride [19] is 1·98 Å, and it is therefore reasonable to take $\bar{E}$(P–Cl) as 80 kcal. mole^{-1}, the value estimated by Neale and Williams [20] for phosphorus oxychloride, in which the length of the P–Cl bond [21] is 1·99 Å. For the trimeric and tetrameric chlorides, we therefore obtain $\bar{E}$(P–N) = 72·3, 72·5 kcal. mole^{-1} respectively. Both values are higher than expected for a single bond, a value of 66·8 kcal. mole^{-1} having been obtained by Fowell and Mortimer [3] for $\bar{E}$(P–N) in trisdiethylaminophosphine. The difference seems, however, to be less than would be expected from the difference in the lengths of the P–N bonds in the trimer chloride [19] (1·60 Å) and the phosphoramidate ion [22] $\mathrm{NH_2PO_3^{2-}}$ (1·78 Å).

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ALBRIGHT & WILSON (MFG.) LTD.,
OLDBURY, BIRMINGHAM.

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[13] Hildebrand and Scott, " The Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, 3rd edn., 1950.

[14] Cottrell, " The Strengths of Chemical Bonds," Butterworths Sci. Publ., London, 2nd edn., 1958, p. 162.

[15] Cottrell, ref. 13, p. 160.

[16] Cottrell, ref. 13, p. 165.

[17] Prosen, Gilmont, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 65.

[18] Springall and White, *Trans. Faraday Soc.*, 1954, **50**, 815.

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