

equalled those in the paraffin lubricant. Fig. 1 shows the results for hexadecane (cetane) and straight-chain acids, amines and alcohols. Double bonds seem to fit in with their effective lengths, for example, elaidic is longer than oleic. Similar results were obtained using tetradecane and decane as carriers, when the peaks occurred with 14 and 10 carbon atoms respectively in the (straight-chain) additives.

There is some evidence that this effect is bound up with the peptization of wear debris away from the contact zone. Runs with the discharge-voltage method<sup>1</sup> indicated that scuffing occurred when the discharge voltage across the gap became zero, indicating zero lubricant film thickness.

Investigations are now being carried out using flocculation of iron oxide as an indicator of the interaction of carrier and surface-active agent.

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<sup>1</sup> Siripongse, C., Rogers, P. R., and Cameron, A., *Engineering*, **186**, 146 (1958).

## CHEMISTRY

### Enthalpy of Formation of Phosphorus Oxide

THE thermochemical literature contains a single value<sup>1</sup> for the standard enthalpy of formation  $\Delta H_f^\circ$   $P_4O_{6(c)}$  of  $-540$  kcal/mole. This value was obtained by an indirect route involving accurate measurements of the heat of combustion of red phosphorus in nitric oxide. The products of combustion were reported to be exclusively  $P_4O_6$  and  $P_4O_{10}$ , but the identification of the products was not necessarily definitive.

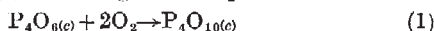
Because of possible ambiguities in this connexion it has seemed to us desirable to measure directly the heat of combustion of a well-defined sample of  $P_4O_6$ .

The sample of  $P_4O_6$  used was synthesized by burning white phosphorus and collecting the lower oxide in the manner described by Thorpe and Tutton<sup>2</sup>. The material was purified by ultra-violet irradiation treatment (to convert residual white phosphorus to involatile red) and by subsequent vacuum distillation. The final solid collected for use had a measured melting point of  $23.9^\circ$  C and on melting gave a clear liquid which could readily be super-cooled by  $2^\circ$ – $3^\circ$ .

Analysis showed the phosphorus content of two of the samples burnt to correspond to 99.95 per cent of that required by the formula  $P_4O_6$ .

For accurate combustion experiments the  $P_4O_6$  was pelleted, preliminary analysis having shown this treatment to give the most complete combustion. The pellets were first allowed to equilibrate to temperature in a conventional bomb calorimeter (previously described<sup>3</sup>) under 1 atm. of carbon dioxide. 35 atm. of oxygen was then added, equilibrated to temperature, and a combustion carried out rapidly. A correction for the small amount of oxidation which occurred prior to the nominal 'firing' was made, and other standard corrections were made as necessary. No evidence of carbon monoxide, which could arise from reaction between  $P_4O_6$  and carbon dioxide, was obtained.

Analysis of the final combustion products indicates that under the best conditions about 95 per cent of the  $P_4O_6$  was oxidized to  $P_4O_{10(c)}$  according to the equation:



The  $P_4O_{10(c)}$  was identified by X-ray analysis.

The combustion products contained small amounts of an insoluble residue, probably red phosphorus—up to 1 per cent by weight in well-combusted samples. Considerable

amounts of trivalent phosphorus also formed in the combustion products. Paper chromatography shows the only trivalent phosphorus species to be phosphite.

It seems likely that the insoluble residue and part of the trivalent phosphorus come from the pyrolysis reaction<sup>4</sup>:



The pyrolysis of small samples of  $P_4O_6$  at  $280^\circ \pm 10^\circ$  C has been investigated separately using differential thermal analysis and it has been shown that assuming complete reaction the overall pyrolysis occurs with an enthalpy change  $\Delta H = -15$  kcal/mole of  $P_4O_6$ . It has not been possible to establish unequivocally that reaction (2) represents the stoichiometry of the pyrolysis.

Experiment No.	1	2	3	4
$P_4O_6$ sample weight (g)	1.185	0.9166	0.8124	0.4570
Heat measured in bomb (cal)	1,364	1,240	1,141	617
Bomb residue (mg)	32	8.7	0.5	2.2
PIT (mg) estimated as $H_3PO_3$	62	26	12.4	8.5
Total P (analytical) (mg)	682	524		251
Theoretical P (mg)	688	517	458	258
$-\Delta U$ kcal/mole $P_4O_6(c)$	318	327.5	318.5	314

Analyses of the trivalent phosphorus contents of the soluble combustion products by iodine titration<sup>4</sup>, when compared with weights of residue, show that the amounts of  $H_3PO_3$  are larger than expected on the basis of the pyrolysis according to equation (2). There are two simple alternative explanations for this: the first that some of the  $P_4O_6$  remains uncombusted, the second (and more likely) that a percentage of  $P_4O_6$  is directly oxidized to  $P_4O_{10}$ . Both these effects have been considered, a figure for the enthalpy of formation of  $P_4O_6$  being estimated as the mean of those for  $P_4O_8$  and  $P_4O_{10}$ . For calculations total amounts of phosphorus in the bomb have been derived from the known mass of  $P_4O_6$  added. In three cases the total soluble phosphorus was estimated after oxidation of the trivalent phosphorus. This estimate together with weighed amounts of residue show agreement of 1–3 per cent between the analytical amounts and the known amounts added; this is probably within the limits of the analysis.

Allowance for the heat of pyrolysis according to equation (2) involves corrections of 1 per cent or less. It has been found that either of the foregoing assumptions about trivalent phosphorus gives substantially the same result for the heat of combustion of  $P_4O_6$ .

The results of four combustions are averaged to give an energy of combustion,  $-\Delta U$  of 320 kcal/mole, from which we calculate (using standard corrections for pressure effects) an enthalpy of formation  $\Delta H_f^\circ$   $P_4O_{6(c)}$  to be  $-392$  kcal/mole (taking  $\Delta H_f^\circ$   $P_4O_{10(c)}$  to be  $-713$  kcal/mole)<sup>5</sup>.

Using values for the heats of sublimation of  $P_4O_6$  and  $P_4O_{10}$  to be respectively<sup>6,7</sup> 16 and 24 kcal/mole, we can calculate the mean bond energy  $\bar{E}(P-O)$  to be 86 kcal/mole and the mean dissociation energy  $\bar{D}(P=O)$  in  $P_4O_{10}$  to be 138 kcal/mole. The latter value now falls better into line with those obtained for other phosphoryl compounds<sup>7</sup> than the value of 115 kcal/mole usually quoted (cf. Neale and Williams)<sup>8</sup>.

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<sup>1</sup> Koerner, W. E., and Daniels, F., *J. Chem. Phys.*, **20**, 113 (1952).

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<sup>3</sup> Holmes, W. S., *Trans. Farad. Soc.*, **58**, 1916 (1953).

<sup>4</sup> Jones, R. T., and Swift, E., *Anal. Chem.*, **25**, 1272 (1953).

<sup>5</sup> Albright and Wilson (unpublished work).

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<sup>7</sup> Paddock, N. L., *Roy. Inst. Chem. Monograph Lecture Series*, No. 2 (1962).

<sup>8</sup> Neale, E., and Williams, L. T. D., *J. Chem. Soc.*, 2485 (1955).