The Thermal Dissociation of Diphosphoros Tetrafluoride and the Formation of Tetraphosphorus Hexafluoride

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IT is well known that dinitrogen tetrafluoride, N_2F_4, dissociates readily into $\cdot NF_2$ radicals.[1] By analogy, the compound P_2F_4, described by Parry[2] and Colburn,[3] might be expected to dissociate thermally into $\cdot PF_2$ radicals, but only tentative evidence for this has been previously published.[2,4]

In an attempt to demonstrate the formation of $\cdot PF_2$, the thermal decomposition of P_2F_4 has been studied by mass spectrometry. Gaseous P_2F_4, at a maximum pressure of about 2 mtorr, was passed through a 5-mm. bore quartz tube, which could be heated. The gas emerged from the tube into the ionization region of a Bendix time-of-flight mass spectrometer. The conditions were chosen to give rapid escape of unstable species from the quartz tube into the mass spectrometer, but thermodynamic equilibrium was not established within the tube.

As the tube temperature was raised from 25 to 900°, the mass spectrum of the effluent gas, taken at 20 ev, showed only peaks normally present in the spectrum of P_2F_4, but their relative intensities

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changed. Above 350°, the intensity of $P_2F_3^+$ and $P_2F_4^+$ was observed to decrease, and that of PF_2^+ to increase with temperature. By 700°, the ratios of the intensities $PF_2^+:P_2F_3^+$ and $PF_2^+:P_2F_4^+$ had each increased ten-fold over their value in the spectrum of P_2F_4.

At 13 ev, no spectrum was seen for the effluent gas with the tube temperature below 350°. Above 350°, PF_2^+ appeared and increased in intensity with temperature. Up to 900° no other ions were detected.

These results indicate that the $\cdot PF_2$ radical was being formed by dissociation of P_2F_4 at high temperatures and low pressures, and that it was probably the only new species generated under the experimental conditions.

When gaseous P_2F_4 was passed through a quartz furnace at 900° at a pressure of about 3 torr, and thence by a collision-free path to a liquid-nitrogen cooled surface, a transparent yellow solid collected (the e.s.r. spectrum of such a solid in a parallel experiment, showed it contained up to 1% of a free radical, possibly $\cdot PF_2$). On warming the deposit to room temperature, PF_3 and P_2F_4 were pumped off, followed by several highly unstable fractions which deposited yellow phosphorus–fluorine polymers on the walls of the vacuum system wherever they were condensed. From this mixture, low temperature fractional distillation eventually yielded a small amount of a less unstable colourless liquid.

The mass spectrum of this liquid showed that it contained only phosphorus and fluorine. The highest molecular weight ion appeared at m/e 238, corresponding to $P_4F_6^+$, and the PF_2^+ ion was the most intense in the spectrum at 50 ev.

The ^{19}F n.m.r. spectrum (94·1 MHz) of the liquid at −30°, showed a doublet of doublets centred at +88 p.p.m. relative to CCl_3F. The ^{31}P n.m.r. spectrum (40·5 MHz) showed a triplet of doublets of triplets, and a less intense quartet of septets 245 p.p.m. upfield. The area ratio of these two features was three to one. The spectra were those expected for first order P–F, P–P–F, P–P, and P–P–P splittings in a structure $P(PF_2)_3$. However, neither spectrum was simple first-order, as each had impressed upon the above first-order form many other lines of lesser intensity. Fortunately, this second-order form was much less dominant than has been described for P_2F_4,[5] where it was due to the magnetic non-equivalence of the phosphorus and fluorine nuclei. The observed splittings in the ^{19}F and ^{31}P spectra were in agreement, giving approximate coupling-constants (considering only first order interactions), J_{PPP} 36 Hz, J_{PPF} 61 Hz, J_{PP} 323 Hz, and J_{PF} 1225 Hz.

The compound $P(PF_2)_3$ melts at −68°. It decomposes very rapidly in the vapour phase, and in the liquid phase above 10°.

A more detailed study of the high temperature decomposition of P_2F_4 and of the properties of $P(PF_2)_3$ is in progress.

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