Phosphorous Oxide, a New Standard for Phosphorus Nuclear Magnetic Resonance

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WE suggest that phosphorous oxide, P_4O_6, should become the primary standard for the referencing of chemical shifts in phosphorus nuclear magnetic resonance. This compound melts at 23·8° to a mobile liquid which gives the expected[1] single-line n.m.r. spectrum, and because of the low viscosity the line is extremely narrow (Figure 1a). The liquid readily supercools to 16°. By means of the sideband interpolation technique, careful measurements have been made of the chemical shift between the phosphorous oxide line and that of the previous standard, 85% orthophosphoric acid, using both phosphorous oxide in the central capillary with phosphoric acid in the outer tube, and *vice versa*. The audio-oscillator was calibrated with an electronic counter. The mean result from a large number of spectra is that the shift of P_4O_6 from phosphoric acid is -2812 ± 2 c./sec. at 25 Mc./sec., *i.e.*, $-112{\cdot}5 \pm 0{\cdot}1$ p.p.m. The resonance therefore falls in a spectral region convenient for referencing the majority of phosphorus compounds. This fact, its high phosphorus content, and its small line-width make it an ideal standard for phosphorus n.m.r. The difficulties experienced with phosphoric acid (Figure 1b), of a weak signal necessitating large capillaries which displace considerable volumes of sample, and of a

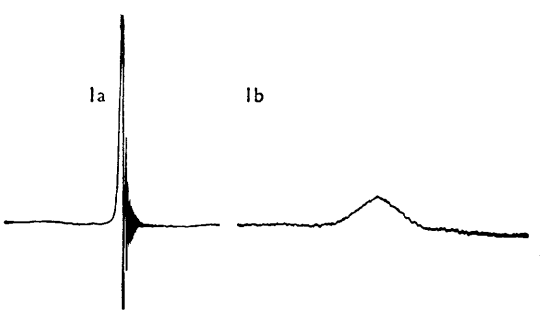

FIG. 1. (a) *The spectrum of* P_4O_6 *recorded at* 25 Mc./sec. (*A.E.I. RS2 spectrometer*). *The line width is about* 0·3 c./sec.
(b) 85% *phosphoric acid recorded under the same conditions as* (a), *except that the gain is increased by four times. The line width is about* 3·5 c./sec.

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[1] G. C. Hampson and A. J. Stosick, *J. Amer. Chem. Soc.*, 1938, **60**, 1814.

broad line preventing accurate measurement, are avoided by the use of phosphorous oxide.

The strong narrow line also makes phosphorous oxide the ideal sample to use for signal location and setting up resolution in phosphorus n.m.r. The signal may be scanned fairly rapidly and adjustments to resolution made by observing the wiggle-beat pattern. In the case of other samples which have been used for this purpose, such as trimethyl phosphite, not only does the greater line width (Figure 2) limit the attainment of resolution, but the spectrum must be scanned slowly, so that the process takes very much longer.

FIG. 2. *The spectrum of trimethyl phosphite and a sideband* (678 c./sec.) *from a capillary of* P_4O_6 (*bore approximately* 1·5 *mm.*), *showing the narrower line from the latter compound.*

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