polyphosphate, respectively. For sample No. T-143B, with a Na/P ratio of 1.002,[33] the corresponding figures were 0.66 and 1.48. It is apparent that approximately two titratable hydrogen ions have been produced for every end-group. These results serve as a final proof that the rapid initial hydrolysis actually occurs at branch points.

NEW BRUNSWICK, N. J.

---

[33] For the preparation and properties of this sample, see reference 10.

[CONTRIBUTION FROM CHEMICAL AND RADIOLOGICAL LABORATORIES]

Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

BY NORBERT MULLER, PAUL C. LAUTERBUR AND JEROME GOLDENSON

RECEIVED DECEMBER 15, 1955

Results of chemical shift measurements for sixty-three phosphorus compounds are presented. In general, shielding increases as one passes from trivalent phosphorus compounds to thiophosphoryl compounds, and then to phosphoryl compounds. The chemical shifts depend in a complicated way on the nature of the molecule involved; a modification of the theory of Saika and Slichter is given, in terms of which the main features of the data may be understood.

Introduction

Chemical shifts in the nuclear magnetic resonance (NMR) of P^{31} were discovered by Knight.[1] Subsequent measurements, particularly those by Gutowsky and his co-workers[2,3] indicate that NMR spectroscopy can become a valuable tool for chemical studies involving phosphorus compounds. To extend the usefulness of the method in this direction, we have obtained chemical shift values for a much larger variety of compounds than has previously been investigated.

Chemical shifts may be used simply as empirical constants characteristic of particular materials. In addition it is possible in principle to deduce from them information as to the bond properties of the molecules studied. Phosphorus compounds present a rather complex problem in this regard, but by introducing suitable simplifications we have been able at least to develop a conceptual framework in terms of which the main features of the results may be understood.

Experimental

The basic theory and experimental details of nuclear magnetic resonance are described in several excellent review articles.[4] The apparatus used in this research was a Bloch-type high-resolution NMR spectrometer (model V-4300), purchased from Varian Associates, Palo Alto, California. It consists of a twelve-inch electromagnet (V-4012) with power supply and current regulator (V-2100 and 2101) and the associated radiofrequency circuits. Resonances were observed at a fixed radiofrequency of 17 mc./sec. and fields in the neighborhood of 9850 gauss.

Chemical shifts were measured by applying an audiofrequency signal from a Hewlett-Packard model 202A function generator to a set of coils wound in the same sense as the coils used to sweep the magnetic field for oscilloscope display. With a single resonance, this causes side-bands to appear on either side of the main resonance, just as if the 17 mc. r-f signal had been replaced by a set of frequencies each differing from 17 mc. by integral multiples of the audiofrequency used.[5] Viewing the sample and a standard alternately, one may adjust the audiofrequency until the nth side-band of the standard falls in the same place as the resonance to be measured. Then if ν is the audiofrequency, the chemical shift, δ, is given by the equation

$$\delta = \frac{(H_{\text{sample}} - H_{\text{standard}})}{H_{\text{standard}}} \times 10^6 = \frac{\nu n}{17}$$

The audio-oscillator was calibrated using a Hewlett-Packard 100-D low-frequency standard. Results were reproducible to about ±1%. Additional errors result from neglecting the bulk diamagnetic susceptibility corrections[6]; on the basis of available susceptibility data, we conclude that these errors should not exceed one-half unit of δ.

Many of the materials studied were furnished by a number of chemical companies (see Table I), whose kindness we gratefully acknowledge. We should also like to thank the personnel of the Organic Branch of these Laboratories, who furnished other samples, and Dr. G. F. Svatos who helped with a number of the syntheses carried out in our own group. Chemical shifts are not sensitive to the presence of small amounts of impurities, so the samples were used without further purification. In some cases the structures were verified by infrared spectroscopy and proton nuclear resonance spectra. Observations were made using 1 to 2 ml. of material sealed off under vacuum in Pyrex tubes of 8 mm. outside diameter.

The reference signal used in determining chemical shifts was that of Merck reagent grade 85% aqueous H_3PO_4. We also examined a number of samples made by adding various amounts of distilled water to H_3PO_4 purified by fractional crystallization by R. H. Schumm at the National Bureau of Standards. There was no detectable shift between any of these samples.

Results and Discussion

a. Table of Chemical Shifts.—The chemical shifts obtained for sixty-three phosphorus compounds are given in Table I. In those cases where the resonance is split by indirect spin–spin interactions[2] the value given is that for the center of the resonance pattern. The results may be summarized in the following generalizations.

1. With a few exceptions, the chemical shifts of trivalent phosphorus compounds, compounds containing the phosphoryl linkage, and compounds containing the thiophosphoryl linkage fall into distinct ranges.

Thus the trivalent phosphorus compounds usually have δ's below -95 and ranging down to about -230. The exceptions are PH_3, found by Gutowsky and McCall[3] to have $\delta = +241$, and the trialkyl or triaryl phosphites which have δ's slightly above zero.

---

[1] W. D. Knight, *Phys. Rev.*, **76**, 1259 (1949).

[2] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[3] H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954).

[4] For example, J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955); also R. E. Andrew, "Nuclear Magnetic Resonance," Cambridge, 1955.

[5] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[6] W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).

Table I

Results of Chemical Shift Measurements

$$\delta = \frac{(H_{\text{sample}} - H_{\mathrm{H\,PO_4}}) \times 10^6}{H_{\mathrm{H_3PO_4}}}$$

Material	Source[a]	δ, p.p.m.
Br_3PS	A	111.8
Br_3PO	B	102.9
$\{[(CH_3)_3SiO]_2P{=}O\}_2O$	A	32.7
$[(CH_3)_3SiO]_3PO$	A	26.5
$(C_2H_5)_3P$	A	20.4
$(m\text{-}CH_3C_6H_4O)_3PO$	C	17.9
$(C_6H_5O)_3PO$	D	17.3
$(p\text{-}CH_3C_6H_4O)_3PO$	C	17.2
$(o\text{-}CH_3C_6H_4O)_3PO$	C	17.1
$(HO)_2POOPO(OH)_2$ (aq.)	E	10.6
$(C_6H_5)_3P$	C	5.9
$(CF_3CH_2O)_3PO$	B	4.0
NaH_2PO_4 (aq.)	F	1.3
$(CCl_3CH_2O)_3PO$	G	1.3
$(C_2H_5O)_3PO$	C	0.9
H_3PO_4	H	0.00 (std.)
Cl_3PO	I	−1.9
$(C_2H_5O)_2ClPO$	B	−2.8
$(i\text{-}C_3H_7O)_2HPO$	B	−4.2
$H_2(OH)PO$	J	−12.0
$[(CH_3)_2N]_3PO$	K	−23.4
$(C_2H_5O)_2(C_2H_5S)PO$	B	−26.4
$(C_2H_5O)_2(C_3H_7S)PO$	B	−26.5
$(C_2H_5O)_2(C_4H_9S)PO$	B	−26.6
$(C_2H_5O)_2(C_5H_{11}S)PO$	B	−26.6
Cl_3PS	M	−28.8
$(C_8H_{17})(C_8H_{17}O)_2PO$	N	−30.7
$(C_4H_9)(C_4H_9O)_2PO$	N	−30.9
$(C_2H_5)(C_2H_5O)_2PO$	N	−32.8
$(C_6H_5)Cl_2PO$	O	−34.5
$(C_4H_9)_3PO$	B	−43.2
CH_3Cl_2PO	B	−44.5
$(C_2H_5)_3PSe$	A	−45.8
$(C_2H_5)_3PO$	A	−48.3
$(CH_3)_2(C_2H_5O)PO$	B	−50.3
$(o\text{-}CH_3C_6H_4O)_3PS$	C	−52.2
$(C_6H_5O)_3PS$	A	−53.4
$(p\text{-}CH_3C_6H_4O)_3PS$	C	−54.0
$(C_2H_5)_3PS$	A	−54.5
$(C_2H_5S)_3PO$	B	−61.3
$(C_2H_5O)_3PS$	K	−68.1
$(C_2H_5O)_2ClPS$	B	−68.1
$(C_4H_9O)_3PS$	N	−69.2
$(i\text{-}C_8H_{17}O)_3PS$	N	−69.5
$(C_6H_5)Cl_2PS$	O	−74.8
$[(C_2H_5)_2N]_3PS$	A	−77.8
CH_3Cl_2PS	B	−79.8
$(C_2H_5S)_3PS$	B	−92.9
$(C_2H_5O)_2(C_2H_5S)PS$	B	−94.2
$(C_2H_5)Cl_2PS$	B	−94.3
$(C_2H_5S)_3P$	N	−115.6
$(C_3H_7S)_3P$	N	−118.2
$[(C_2H_5)_2N]_3P$	A	−118.2
$(C_6H_5O)_3P$	C	−126.8
$(p\text{-}CH_3C_6H_4O)_3P$	C	−127.6
$(C_2H_5O)_3P$	B	−136.9
$(i\text{-}C_3H_7O)_3P$	B	−136.9
$(ClCH_2CH_2O)_3P$	M	−138.7
$(C_6H_5)Cl_2P$	O	−161.6
$(CH_3O)Cl_2P$	B	−180.5
CH_2Cl_2P	B	−191.2
Cl_3P	I	−219.4
Br_3P	C	−227.4

[a] The following code is used for the various sources: A, prepared by personnel of NMR laboratory; purity 90% or better, checked by NMR only; B, prepared by personnel of Organic Branch, Chemical and Radiological Laboratories, Army Chemical Center, Maryland; C, Eastman Kodak Company; D, Paragon Testing Laboratories; E, Eimer and Amend, C.P. Grade; F, J. T. Baker Analyzed Grade; G, Aldrich Chemical Co.; H, Merck Reagent Grade; I, Mallinckrodt Analytical Reagent; J, J. T. Baker, 50% Aqueous, "Differs from U.S.P. in Assay"; K, Monsanto Industrial Sample; L, Sample obtained from National Bureau of Standards; M, Westvaco; N, Virginia Carolina Chemical Corporation; O, Victor Chemical Works.

The thiophosphoryl compounds generally have δ's in the range from −100 up to −50. The only exception found was $PSBr_3$, with the surprising value $\delta = +110.8$.

The range of δ's for the phosphoryl compounds somewhat overlaps the thiophosphoryl region; it extends upward from about −60. Only one phosphoryl compound has δ above +40; it is $POBr_3$, with $\delta = +101.9$.

2. As would be expected, the chemical shift depends most strongly on the nature of the atoms directly bonded to the phosphorus atom, and the kind of bond involved. Thus one can readily distinguish between such isomeric pairs as $(C_2H_5O)_3P$ ($\delta = -136.9$) and $(C_2H_5O)_2(C_2H_5)PO$ ($\delta = -32.8$) or $(C_2H_5O)_3PS$ ($\delta = -68.1$) and $(C_2H_5O)_2(C_2H_5S)PO$ ($\delta = -26.4$). Substitution at some distance from the phosphorus atom has a relatively small effect; for example, $(C_2H_5O)_3PO$ has $\delta = 0.9$, and $(ClC_2H_4O)_3PO$ has $\delta = 1.3$.

3. There is no convenient quantitative correlation between the chemical shift and the nature of the atoms or groups bonded to phosphorus. We expected, for example, that $(C_2H_5O)_2(C_2H_5S)PS$ would have a chemical shift intermediate between those of $(C_2H_5O)_3PS$ ($\delta = -68.1$) and $(C_2H_5S)_3PS$ ($\delta = -92.9$). However, we found for the "mixed" compound $\delta = -94.2$, which clearly shows that one cannot assign an additive "shift constant" to groups such as C_2H_5O– and C_2H_5S– for purposes of predicting chemical shifts as was done for phosphoryl infrared absorption wave lengths.[7]

In this connection, two further trends may be noted. First, in nearly every case measured, the chemical shift of a "mixed" compound (example A_2BPO) is more negative than the value obtained by interpolating between the related symmetrical compounds (A_3PO and B_3PO). Secondly, the difference between chemical shifts found and those expected from such an interpolation is considerably greater in thiophosphoryl compounds than in phosphoryl compounds.

b. Solvent Effects on the Chemical Shift.—Table II shows the changes in chemical shift when various liquid phosphorus compounds are diluted with an equal volume of solvent. While our work along this line has been quite limited, the absence of any detectable effect with CS_2 or CCl_4 as the solvent suggests that solvent effects on the chemical shift are associated with hydrogen bonding, and might form a useful basis for quantitative hydrogen

---

(7) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, This Journal, **76**, 5189 (1954).

bonding studies.[8] It is also apparent that any measurements of chemical shifts of solid phosphorus compounds made using solutions in hydrogen bonding solvents would be subject to uncertainties of several units of δ.

TABLE II

SOLVENT SHIFTS OF P^{31} MAGNETIC RESONANCES

All solutions were 50% by volume.

Solute	Solvent	$H_{\text{soln.}} - H_{\text{solute}} / \times 10^6 H_{\text{solute}}$
$(C_2H_5O)_2(C_2H_5)PO$	CS_2	0
	$CHCl_3$	−1.0
	C_2H_5OH	−1.0
	H_2O	−4.2
$(C_2H_5O)_3PO$	CCl_4	0
	$CHCl_3$	0
	H_2O	−0.6
$PSCl_3$	CS_2	0
	$CHCl_3$	+1.9
	Dioxane	−2.6
$[(CH_3)_2N]_3PO$	CCl_4	0
	C_2H_5OH	+2.4
	Dioxane	−0.6

c. Structure of the "Acid Phosphites."—The chemical shift of isopropyl acid phosphite was found to be −4.2, which alone would indicate that the compound contains a phosphoryl group. In addition, the resonance is split into a doublet with a separation of 687 c.p.s. (40.4 parts per million at 17 mc./sec.), which shows that one hydrogen must be bonded directly to the phosphorus atom. These results definitely exclude the structure $(RO)_2P(OH)$, and confirm the structure $(RO)_2HPO$, in agreement with deductions from infrared spectra[9] and with NMR work[2] on the analogous acid $(HO)_2HPO$.

d. Indirect Spin-Spin Coupling.—Except in the compounds just discussed, the splittings due to indirect spin–spin coupling were quite small. We observed splittings in compounds containing protons bonded to neighbors or second neighbors of the phosphorus atom, as for example in P–C–H, P–S–C–H, P–O–C–H and P–N–C–H chains. The separations between multiplet components were difficult to measure precisely. They are of the order of 10 c.p.s., and only slightly larger for P–C–H than for the other configurations. With the large sample volume used, the structure of the phosphorus signal is usually only partly resolved, so that the main effect of the spin–spin coupling is to determine the effective line width, and thus to limit the sensitivity and resolution obtainable.

No interaction was found between phosphorus and hydrogen nuclei in P–O–H groups, presumably because of chemical exchange of the acidic proton with traces of water present as an impurity.[10]

e. Relation of Chemical Shift and Bond Type.—A theory relating the chemical shifts with the detailed electronic structures of molecules has been developed by Ramsey.[11] The computational difficulties that would be involved in applying this theory to complex molecules are, however, so great that one is usually forced to resort to semi-empirical analysis in order to relate chemical shift data and such commonly used bond properties as hybridization, amount of multiple bond character, and degree of ionic character. This is particularly difficult for a polyvalent atom, such as phosphorus. Thus Gutowsky and McCall[3] relate the chemical shift to an empirical "electron density" at the phosphorus nucleus. We feel that a more satisfactory starting-point for a discussion of chemical shift in terms of the above-mentioned bond properties is found in the work of Saika and Slichter.[12] These authors, dealing with F^{19} chemical shifts, introduced a series of assumptions to achieve a drastic simplification of Ramsey's theory.

The first of these assumptions is that the differences in the amount of shielding for fluorine nuclei in various compounds are determined mainly by differences in a single term in Ramsey's equations, which they call the "second-order paramagnetic term." This assumption should be equally valid for P^{31} nuclei. The problem is thus reduced to that of evaluating this paramagnetic correction (PC). The chemical shift will depend linearly on the PC with δ becoming more negative as the PC increases.

The second assumption is that only the valence (3p) electrons of the phosphorus atom need to be considered in calculating the PC. Saika and Slichter show that s electrons make no contribution to this term, and that electrons in closed shells contribute very little. Valence electrons on other atoms are assumed to be far enough from the P^{31} nucleus to be neglected, and we neglect 3d electrons of the phosphorus atom provisionally. In the compounds considered, the bonds are roughly tetrahedrally oriented around the phosphorus atom, so that the extent of d-orbital hybridization is probably small.

For the effect of a single p electron on the shielding, Saika and Slichter calculate

$$-\frac{2}{3}\left(\frac{e^2h^2}{m^2c^2}\right)\left(\left\langle\frac{1}{r^3}\right\rangle_{\text{av}}\right)_{\text{p}} \times \frac{1}{\Delta E}$$

If this expression were constant for all molecules, we would now need only to find the "number of unbalanced p-electrons" (a quantity used in the closely related problem of calculating nuclear quadrupole coupling constants in molecules[13]) for each molecule to be studied, and multiply that number by this constant.

Actually, ΔE will differ for various molecules, though excitation energies for most bonds are of the order of 5 e.v. In the absence of experimental ΔE values, one must try to get along without allowing for this variation explicitly. We shall therefore attempt to correlate chemical shifts by assuming

$$\delta = a - bD \tag{1}$$

where D is the number of unbalanced p electrons,

---

[8] Hydrogen-bonding effects in proton NMR spectra have been reported by C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955), and other authors cited there.

[9] C. I. Meyrick and H. W. Thompson, *J. Chem. Soc.*, 225 (1950).

[10] See ref. 2; also E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

[11] N. F. Ramsey, *ibid.*, **77**, 567 (1950); **78**, 699 (1950); **83**, 540 (1951); **86**, 243 (1952). See also J. F. Hornig and J. O. Hirschfelder, *J. Chem. Phys.*, **23**, 474 (1955).

[12] A. Saika and C. P. Slichter, *ibid.*, **22**, 26 (1954).

[13] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," New York, N. Y., 1953, Sec. 6.2 and chapter 7.

and the values of a and b are to be determined empirically,

To evaluate D, we must first determine the extent of hybridization of the bonding atomic orbitals (AO's). We then include the effect of ionicity by considering the AO to be occupied by one electron for a pure covalent bond (the other electron of the bonding pair "belonging" to the other atom) and by an appropriate "fraction of an electron" for a partly ionic bond.

Compounds of the Type PX_3.—The least complicated problem is presented by the compounds that have three similar atoms or groups (X) bonded to a trivalent phosphorus atom.

We write the phosphorus AO involved in the ith P–X bond (i = 1,2,3) as a hybrid

$$\psi_i = \sqrt{1 - \alpha^2}\,\mathrm{s} + \alpha \mathrm{p}_i$$

where α determines the extent of hybridization, s is the phosphorus 3s orbital, and p_i is a 3p AO directed along the bond axis. Similarly, the lone-pair electrons are in a hybrid AO

$$\psi = \sqrt{1 - \beta^2}\,\mathrm{s} + \beta \mathrm{p}_z$$

where p_z is a 3p AO directed along the symmetry axis of the molecule, designated the z-axis.

If θ represents the X–P–X bond angle, it may be shown[14] that a necessary condition for the ψ's to be orthogonal is

$$\beta^2 = 3\,(1 - \alpha^2) = \frac{-\,3\cos\theta}{1 - \cos\theta} \qquad (2)$$

This allows one to find β if the value of the bond angle is known.

We now define a parameter ϵ such that $(1 + \epsilon)$ is the number of electrons of each P–X bond that belong to the phosphorus atom. $\epsilon = -1$ would correspond to an ionic structure of the type P^+X^-. Except for sign, the parameter ϵ is the same as the fractional ionic character of the P–X bond, and may be estimated from the electronegativity difference between phosphorus and the neighboring atom. A simple formula empirically derived for diatomic molecules (see ref. 14, eq. 33, p. 134) is

$$|\epsilon| = 0.16\,|X_A - X_B| + 0.035\,|X_A - X_B|^2 \quad (3)$$

where X_A is the Pauling electronegativity of atom A. Use of a more refined formula is hardly justified since the uncertainty in the bond angle alone will produce a sizable uncertainty in D.

Now taking x- and y-axes perpendicular to the symmetry axis, and expressing each $3p_i$ AO as a combination of $3p_x$, $3p_y$ and $3p_z$, it may be shown that the $3p_x$ and $3p_y$ AO's will each contain $(1 + \epsilon)$ electrons, while the $3p_z$ AO will contain $(1 + \epsilon)(1 - \beta^2) + 2\beta^2$ electrons. Thus the number of unbalanced p electrons is given by the difference

$$D = |(1 + \epsilon)(1 - \beta^2) + 2\beta^2 - (1 + \epsilon)| = |\beta^2(1 - \epsilon)| \quad (4)$$

i. **PH_3.**—This molecule is unique among PX_3 compounds in that it has a large positive value of δ. ($\delta = +241$, measured by Gutowsky and McCall[3].) It is also unique structurally, with the unusually small X–P–X angle of 93° (see ref. 13, Table A.9, p. 372). We calculate $\beta^2 = 0.15$, $\epsilon = 0$, and hence $D = 0.15$, in line with the expectation that a large positive δ correlates with a small value of D.

ii. **PCl_3.**—The Cl–P–Cl angle is 100° and $X_{Cl} - X_P = 0.9$. Thus $\beta^2 = 0.45$, $\epsilon = -0.17$ and $D = 0.53$. This much higher value of D should result in a much more negative δ; we found $\delta = -219.4$.

Using these two molecules, we evaluated a and b in equation 1, which becomes

$$\delta = 4.2 \times 10^2 - 1.2 \times 10^3 D \qquad (5)$$

The value of a, of course, reflects our arbitrary choice of a zero point of the chemical shift scale. The magnitude of b is of the same order as that of the corresponding term calculated for fluorine in reference 12. Since D is intrinsically positive, 4.2×10^2 should represent an upper limit to the possible values of δ. Gutowsky and McCall[3] report $\delta = 4.9 \times 10^2$ for P_4 as the most positive value found[15]; in view of the approximations made, the agreement is good.

iii. **Other PX_3 Molecules.**—The bond angles in most other PX_3 compounds are probably in the neighborhood of 100°, and the corresponding values of ϵ are small. Accordingly we expect δ in the neighborhood of -200, in agreement with observation in most cases. The exceptionally high values for trialkyl and triaryl phosphites could be attributed to abnormally small bond angles, or could arise from a violation of any one of the assumptions listed at the start of this discussion. The derivation of equation 5 also loses validity if there is extensive double-bond character in the P–X bonds, as is most likely in the case of PF_3, for which again the observed δ-value is much higher than the predicted. The attempt to include double bonding quantitatively in the discussion would require the introduction of a further parameter, and such a refinement of this approximate treatment could hardly be justified at present.

Compounds of the Types PX_3O and PX_3S.—These phosphoryl and thiophosphoryl compounds are similar to the PX_3 compounds except that the lone pair of electrons of the PX_3 are now shared with an oxygen or sulfur atom. Defining ϵ_z analogously to ϵ above, so that $(1 + \epsilon_z)$ is the number of electrons in the lone-pair AO which belongs to the phosphorus atom, we find in place of equation 4

$$D = |(1 + \epsilon)(1 - \beta^2) + (1 + \epsilon_z)\beta^2 - (1 + \epsilon)| = |\beta^2(\epsilon_z - \epsilon)| \quad (6)$$

Since three parameters are now required to determine D, equation 6 is of little use in making detailed predictions. However, it helps one to predict correctly the general trend of the chemical shifts. Thus, since ϵ_z will always be less than unity, D should be smaller (other things being roughly equal) for the phosphoryl and thiophosphoryl compounds than for the phosphines. Consequently these pentavalent phosphorus compounds should have more positive chemical shifts; this agrees with the experimental data. Further, the more electronegative oxygen atom should bind the electrons

---

[14] See, for example C. A. Coulson, "Valence," Oxford Press, New York, 1952, pp. 193 ff.

[15] The P_4 molecule is generally assumed to have nearly pure p-type bonds, which because of its geometry must be somewhat bent. For pure p bonds we would have $\beta = 0$, $D = 0$. See ref 14, p. 206, also W. E. Moffitt, *Trans. Faraday Soc.*, **44**, 987 (1948).

more tightly than sulfur, leading to smaller ϵ_2-values, hence smaller D's and more positive δ's for the phosphoryls than for the thiophosphoryls. This again is in agreement with observation, except for the two compounds $POBr_3$ and $PSBr_3$, in which the chemical shifts are completely out of line with those of compounds involving only first and second row elements, and remain unexplained.

As to the important question of double-bonding in the P → O or P → S linkages, the data unfortunately allow one to say very little. Presumably such double bonding involves a transfer of p-electrons from the oxygen or sulfur back into the $3p_x$ or $3p_y$ orbitals of phosphorus or possibly into d-orbitals. (The p-orbitals could only accept such electrons if they were partly vacant, as they might be if the group X is highly electronegative.) Such an electron transfer would tend to reduce D and increase δ. Since double bonding is believed to be more important for bonds with first-row than with second-row elements, including this effect would reinforce the prediction that the phosphoryls will have higher δ's than the thiophosphoryls. However, it appears unprofitable to attempt to estimate double-bond character by trying to separate its effect from the effects of varying the other parameters in the discussion.

Acknowledgment.—The authors wish to express their thanks to Mr. Marlan L. Shepard for his help throughout the early stages of this research.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION NO. 1187 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

An Evaluation of the Density of Water at 5° Intervals between 45 and 85°[1]

BY BENTON B. OWEN, JAMES R. WHITE AND JAMES S. SMITH

RECEIVED FEBRUARY 15, 1956

1. Two types of precision dilatometers are described, and it is shown that by using a special platinum-tipped pipet the mercury meniscus, which determines the expansion, can be reproduced with a precision which corresponds to an uncertainty of only 0.2 p.p.m. in the density of water. 2. By means of ten such dilatometers the density of water, as determined by Chappuis, was extended over the range 45 to 85°, and values of the coefficient of expansion of water are reported. 3. It is shown that the use of three times the linear expansion for the volume expansion of "worked" tubular Pyrex vessels can lead to appreciable errors in precision dilatometry.

The values of the density of water given in the International Critical Tables[2] for the range 0 to 40° are the means of the smoothed values of Chappuis[3] and of Thiesen, Scheel and Diesselhorst.[4] These two sets of values differ irregularly, sometimes by as much as 8 parts per million. At temperatures above 40° the values calculated by an equation of Thiesen[5] are given as the best available, but they are expressed to only five decimal places and contain uncertainties in the last place. It is clear that if the I.C.T. densities of water are used to determine the coefficient of expansion of glass vessels, pronounced irregularities will be evident in the sixth decimal place below 40° and in the fifth decimal place above this temperature. These irregularities are of such a nature that they cannot be ascribed to the actual behavior of glass and are too large to be disregarded in precise measurements, such as those required for the determination of the partial molal expansibilities of electrolytes. To overcome this difficulty we have carried out what is in effect an extrapolation of the density data of Chappuis from 40 to 85° by means of ten 110-cc. Pyrex dilatometers. The choice of these particular data for extrapolation was governed by three important considerations.

(1) They are generally accepted as standard in this country and by the International Bureau of Weights and Measures.

(2) They are conveniently represented empirically by the Tilton and Taylor[6] equation

$$1 - d = \frac{(t - 3.9863)^2}{508929.2} \times \frac{(t + 288.9414)}{(t + 68.12963)} \quad (1)$$

to within about one part per million over the whole experimental range, 0 to 42°.

(3) They lead to smooth quadratic temperature variations for the volumes of our dilatometers within the limit of reproducibility of our measurements which is comparable to that of Chappuis. The fulfillment of this last condition is, of course, subsumed in our procedure, because Chappuis expressed the volumes of his glass dilatometers as a quadratic in the temperature.

The two independent series of measurements described below differed in objective as well as in technique. Series S, performed by J. S. Smith, was carried out solely for the calibration of the series S dilatometers. Its aim was a reproducibility of two or three parts per million in the individual dilatometric measurements. When it became clear that it was necessary as well as possible to extend the precise results of Chappuis by means of such measurements, series W was undertaken by J. R. White, and every effort was made to attain a reproducibility of one part per million. The description of the experimental technique and the treatment of the data will, for brevity, be confined almost entirely to series W because of its higher reproducibility and

---

(1) This communication embodies parts of the experimental material presented by James R. White (1944) and James S. Smith (1943) to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) "The International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1931, pp. 24–26.

(3) P. Chappuis, *Trav. et Memoires Bur. International Poids et Mesures*, **13**, D40 (1907).

(4) M. Thiesen, K. Scheel and H. Diesselhorst, *Wiss. Abhandl. physik-tech. Reichsanstalt*, **3**, 67 (1900) 1–70.

(5) M. Thiesen, *ibid.*, **4**, 30 (1904).

(6) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **18**, 205 (1937). The density is expressed as grams per milliliter.