Micelle Studies.—In two recent studies[28,29] detergent micelles have been used to evaluate the effect of urea on hydrophobic bonds. The main finding of these studies was that urea raises the critical micelle concentration (c.m.c.). Although no quantitative estimates were made, both groups of workers implied that urea has rather little ability to break hydrophobic bonds. From measurements of c.m.c. dependence on urea concentration at two temperatures, Mukerjee and Ray also concluded that there is no temperature dependence in the hydrophobic bond-breaking tendency of urea. Our present results are at variance with these conclusions. Although micelle formation most certainly does involve hydrophobic bonds, it appears to us that it does not provide a suitable model system for this type of study. The reason for our objection is that the micelle is not the same as a solid crystalline phase in the sense of having constant composition, constant structure, and especially constant free energy. Thus, when we write an equation for micelle formation: n detergent $\leftrightarrows$ $(Det)_n + \Delta F$, and consider how change of solvent composition affects the equilibrium, we must assume that a change in the equilibrium is due only to change in

(28) W. Bruning and A. Holtzer, J. Am. Chem. Soc., **83**, 4865 (1961).
(29) P. Mukerjee and A. Ray, J. Phys. Chem., **67**, 190 (1963).

the chemical potential of the "free-swimming" detergent molecules (those on the left side of the equation) and not of the micelles, if we are to calculate the change in ΔF from the change in c.m.c. Since it is generally accepted that the capacity of micelles to vary in structure is an important feature of detergency, this assumption is dubious. In other words, we question that the chemical potential of $(Det)_n$ does indeed remain constant with a change in solvent composition. Even if the foregoing objection is met, we submit that a change in the chemical potential of the free-swimming molecules will have contributions from both the polar and nonpolar parts of the molecules. Arriving at this point, one must evaluate the relative contributions from both parts of the molecule to get an estimate of the interaction between the nonpolar part of the molecule and the solvent. Since the micelle studies cited did not account for these considerations, we believe that their interpretation is subject to much uncertainty.

COMMUNICATIONS TO THE EDITOR

A New Univalent Cobalt Complex

Sir:

Previously cobalt(I) ion was found by polarographic means to exist in solution as a stable ion.[1]

We have now succeeded in isolating *in vacuo* the phenanthroline cobalt(I) perchlorate from the solution as dark brown crystals. It was found to be the hexacoordinated complex, $[Co^I(phen)_3]ClO_4$.[2]

A reaction apparatus fitted with fritted joints to allow a series of procedures such as mixing, filtering, washing, and sealing *in vacuo* was attached to the usual type vacuum line with an oil diffusion pump which could obtain a pressure of 10^{-7} mm. Sodium borohydride was used as the reducing agent. All procedures were carried out *in vacuo*.

Tris(phenanthroline)cobalt(II) perchlorate (1 g.) was dissolved in about 200 ml. of 10% ethanol–water mixture and it was frozen with liquid nitrogen. The space above the frozen solid was evacuated. After the stopcock was shut, the frozen solid was melted with an electric air drier. The air which was dissolved in the solution bubbled vigorously. The solution was again frozen and the space above the solid was evacuated. This procedure was repeated three times. Under these conditions all oxygen was removed from the reaction mixture.

Similarly the aqueous solution of sodium borohydride (0.5 g.) and the wash solution, containing no dissolved oxygen, were prepared in the vessels connected to the reaction flask. The luteo-salt and the borohydride ion were allowed to react gently at $-5°$. The color of the solution changed from yellow to brown and a brownish black powder separated from the solution. This was filtered and washed *in vacuo*. The product

(1) N. Maki, T. Hirano, and S. Musha, *Bull. Chem. Soc. Japan*, **36**, 756 (1963).
(2) phen = 1,10-phenanthroline. This result was presented at the 13th Symposium on Coordination Compounds, Nagoya University, Nagoya, Japan, Oct. 15, 1963.

on the glass filter (G3) was recrystallized by dissolving in the deaerated 80% ethanol–ether mixture. The solvent was evaporated by suction and lusterous dark brown crystals deposited on the wall of the vacuum tube.

Anal. Calcd. for $[Co^I(phen)_3]ClO_4$: Co, 8.43; C, 61.86; N, 12.02; H, 3.46. Found: Co, 8.32; C, 61.97; N, 11.92; H, 3.21.

The complex is soluble in ethanol and ether and insoluble in water. The aqueous solution of the complex was oxidized with 10% hydrogen peroxide and polarographic studies indicated it to be the $[Co^I(phen)_3]^{+3}$ ion.

The four-coordinated complex, $[Co^I(phen)_2]ClO_4$, could not be obtained under any reaction conditions reported for the dipyridyl cobalt(I) complex.[3,4]

(3) A. A. Vlček, *Nature*, **180**, 573 (1957); *Z. physik. Chem. Sonderheft* (Internationales Polarographisches Kolloquium, Dresden), 143 (1958).
(4) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).
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RADIATION CENTER OF OSAKA PREFECTURE   NOBUFUMI MAKI
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The Reaction of Trialkyl Phosphites with Aliphatic Aldehydes. P³¹ and H¹ Nuclear Magnetic Resonance Spectra of Tetraoxyalkyl Phosphoranes[1,2]

Sir:

We wish to report the isolation and characterization of a tetraoxyalkyl phosphorane(I) from the reaction of 3 moles of anhydrous propionaldehyde with 1 mole of trimethyl phosphite at 20°. The 2:1 adduct

(1) (a) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *J. Am. Chem. Soc.*, **85**, 3056 (1963); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (c) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963); **82**, 2652 (1960).
(2) Acknowledgment is made to the Cancer Institute of the National Institutes of Health (CY-04769) and to the National Science Foundation (G19509) for support of this research.

I was obtained in *ca.* 60% yield based on reacted phosphite (*ca.* 60%) after 14 days.

Ia, *trans*
Ib, *cis*
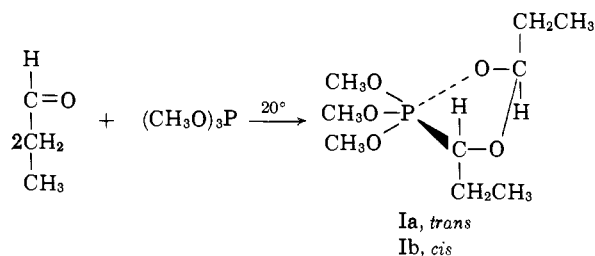
The 2:1 adduct I had b.p. 50–51° (0.2 mm.), $n^{25}D$ 1.4313. *Anal.* Calcd. for $C_9H_{21}O_5P$: C, 45.0; H, 8.7; P, 12.9; mol. wt., 240. Found: C, 44.9; H, 8.8; P, 12.9; mol. wt., 275. There were strong infrared bands at 9.10, 9.30, and 9.43 μ due to CH_3OP vibrations; no CO or PO absorption; H^1 n.m.r. (neat, 60 Mc., τ): multiplets at 5.4 and 6.3 due to methine protons, a doublet at 6.53 (J_{HP} = 12.0 c.p.s.) due to the three methoxyls, multiplet at 8.4 (methylenes), and triplet at 9.06 (methyls).

TABLE I

CHEMICAL SHIFTS IN THE P^{31} N.M.R. SPECTRA OF OXYPHOSPHORANES[a]

III   IV

V   VI
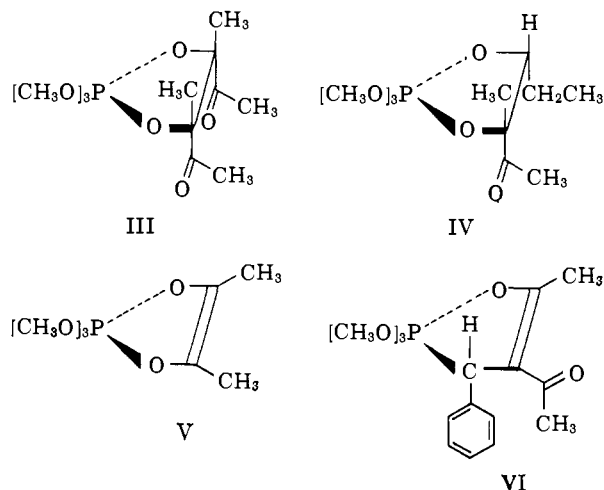
Cyclic Oxyphosphorane		δP^{31}
Pentaoxy 1,3-dioxaphospholane	III[b]	+54.83
	IV[c]	+51.27
Pentaoxy 1,3-dioxaphospholene	V[d-f]	+48.92
Tetraoxyalkyl 1,4-Dioxaphospholane	I[g]	+34.16
Tetraoxyalkyl Δ^4-Oxaphospholene	VI[h-j]	+27.89

[a] In p.p.m. ±0.04 relative to 85% H_3PO_4; see ref. 3. [b] Ref. 1b. [c] Ref. 1a. [d] Ref. 1c. [e] (a) G. H. Birum and J. L. Dever (Abstracts, Division of Organic Chemistry, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 101-P) mention the range +47 to +68 p.p.m. for a series of 1:1 α-diketone tertiary phosphite and dialkylalkyl phosphonite adducts; (b) *ibid.*, U. S. Patents 2,961,455 (1960) and 3,014,949 (1961). [f] The following references do not mention P^{31} n.m.r. of 1:1 adducts of type V: (a) V. A. Kukhtin, *Dokl. Akad. Nauk. SSSR*, 121, 466 (1958); (b) V. A. Kukhtin and K. M. Kirillova, *J. Gen. Chem. USSR*, 32, 2755 (1962); (c) V. A. Kukhtin, K. M. Kirillova, R. R. Shagidullin, Yu. Samitov, N. Lyazima, and N. F. Rahova, *Zh. Obshch. Khim.*, 32, 2039 (1962). [g] This communication. [h] Crystalline adduct VI was made from trimethyl phosphite and 3-benzylidene-2,4-pentanedione at 20° in methylene chloride (F. Ramirez, O. P. Madan, and S. R. Heller, submitted to *J. Am. Chem. Soc.*). [i] The following references offered no satisfactory evidence for the pentacovalency of phosphorus in adducts of type VI: (a) G. Kamai and V. A. Kukhtin, *J. Gen. Chem. USSR*, 27, 2431 (1957); (b) V. A. Kukhtin and K. M. Orekhova, *ibid.*, 30, 1539 (1960). [j] R. G. Harvey and E. V. Jensen (Abstracts, Division of Organic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 61-M) suggested structures of type VI but gave no P^{31} n.m.r. data.
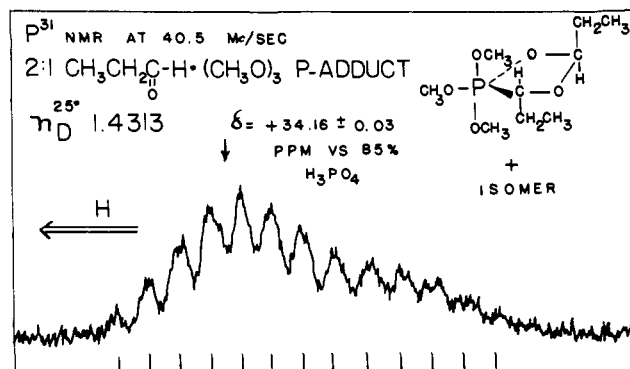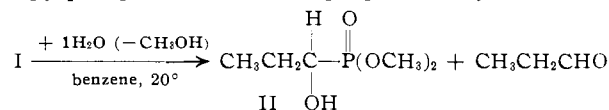

Figure 1.

Further examination of the methoxy doublet at 100 Mc./sec. disclosed the presence of two doublets, both with J_{HP} = 12.0 c.p.s. and separated by 0.5 c.p.s. This is attributed to the presence of two diastereoisomers, Ia and Ib, for the following reasons. (1) The relative proportion of the isomers could be altered somewhat by fractional distillation. (2) The P^{31} n.m.r. spectrum[3] (Fig. 1) showed an unsymmetrical multiplet, suggesting the presence of two very similar phosphorus nuclei. The multiplet due to the major isomer is centered at +34.16 ± 0.03 p.p.m. *vs.* 85% H_3PO_4; that of the minor isomer at +32.8 p.p.m. Data for other oxyphosphoranes[4] are summarized in Table I. The positive shifts of these compounds with pentacovalent phosphorus should be noted.[5] (3) The 2:1 adduct I underwent rapid hydrolysis to dimethyl 1-hydroxypropylphosphonate (II) and propionaldehyde.

$$I \xrightarrow[\text{benzene, 20°}]{+ 1H_2O\ (-CH_3OH)} CH_3CH_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}\overset{\overset{\displaystyle O}{\|}}{P}(OCH_3)_2 + CH_3CH_2CHO$$

II

The hydroxy phosphonate II had b.p. 100–103° (0.5 mm.), $n^{25}D$ 1.4438. *Anal.* Calcd. for $C_5H_{13}O_4P$: C, 35.8; H, 7.8; P, 18.4. Found: C, 36.2; H, 7.9; P, 17.7. Bands were present at 3.08 (OH), 8.00, and 8.16 μ (PO). δP^{31} = −31.1 p.p.m.

The reaction of butyraldehyde with trimethyl phosphite was slower, but the course of the reaction was analogous.

We conclude that the phosphorus of the phosphite adds slowly to the carbonyl carbon[6] of aliphatic aldehydes to form a 1:1 adduct VII, which reacts further with a second molecule of aldehyde to give the precursor VIII of the oxyphosphorane I. There is no alkyl group translocation at the 1:1 stage (VII) or at the 2:1 stage (VIII). However, we found evidence for a further reaction between VIII and the aldehyde to give a 3:1 adduct (similar to VIII) which underwent an alkyl group translocation to a 3:1 acetal phosphonate (IX).

VII   VIII

IX
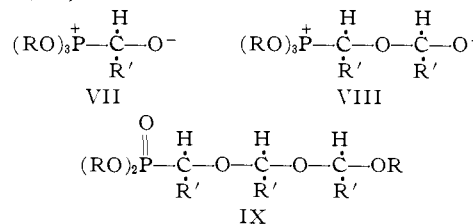
(3) Varian HR100 spectrometer at 40.5 Mc./sec.

(4) In all the cases of Table I, except compound I, the P^{31} n.m.r. spectra were symmetrical, indicating the presence of one type of P-nucleus.

(5) See also Q. E. Thompson, *J. Am. Chem. Soc.*, 83, 845 (1961).

(6) Addition of the phosphorus of a phosphite to the carbonyl oxygen of a quinone was first observed by F. Ramirez and S. Dershowitz: (a) *J. Org. Chem.*, 22, 856 (1957); (b) *J. Am. Chem. Soc.*, 81, 4338 (1959); (c) see also, *ibid.*, 78, 5614 (1956).

The reaction of triethyl phosphite with o-nitrobenzaldehyde,[7] with benzaldehyde,[8] and with aromatic ketones[9] has been reported. Epoxides and 1:1 adducts (analogous to VII) have been isolated from the reaction of a phosphorus triamide with aldehydes.[10]

Acknowledgment.—We are grateful to Prof. P. C. Lauterbur of this department for advice on P^{31} n.m.r. spectroscopy and to Dr. E. M. Banas (American Oil Co.) and Prof. E. Eliel (University of Notre Dame) for some of the earlier H n.m.r. spectra.

(7) (a) V. A. Kukhtin and K. M. Kirillova, *J. Gen. Chem. USSR*, **31**, 2078 (1961); (b) *Zh. Obshch. Khim.*, **31**, 2226 (1961).

(8) A. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1030 (1960).

(9) A. C. Poshkus and J. E. Herweh, Abstracts, Division of Organic Chemistry 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17-O.

(10) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963).

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Radical and Molecular Yields in the γ-Radiolysis of D_2O and H_2O Vapor

Sir:

Recent work[1,2] on the γ-radiolysis of water vapor in the presence of scavengers for H and OH has led to estimates of the 100-e.v. yield $G(H)$ which are different when D_2 is used[1] from those obtained using organic scavengers.[2] The reactions involved are

$$H_2O \longrightarrow H, HO$$
$$H + RH \longrightarrow H_2 + R$$
$$H + D_2 \longrightarrow HD + D$$
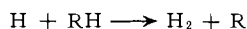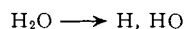
and it is assumed that $G(H_2)$ or $G(HD)$ are measures of $G(H)$. The observations[2] also showed the formation of H_2 with a yield of 0.5, even in the presence of benzene which should remove all H without forming H_2, and suggested that, as with liquid water, there is a yield of molecular as well as atomic hydrogen. This we have now confirmed by observations on D_2O radiolysis, and we also confirm that higher $G(D)$ are found using H_2 than using organic scavengers.
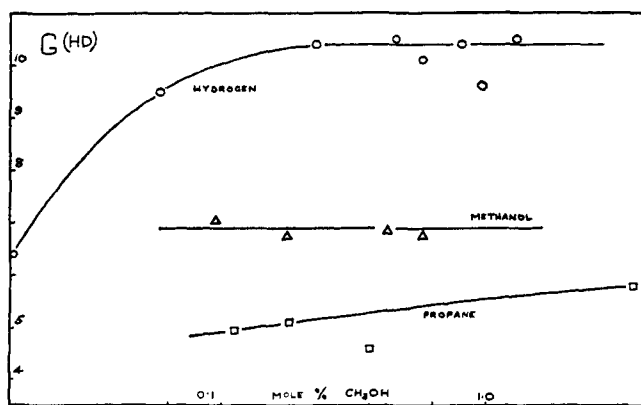

Figure 1.

The experiments were carried out as described previously[2] using doses of 1.5–5.5 $\times$ 10^{19} e.v. delivered to the vapor at 116° and about 60-cm. pressure in a 5-l. vessel.

The values of $G(HD)$ obtained with various amounts of H_2, CH_3OH, and C_3H_8 present are shown in Fig. 1.

(1) R. Firestone, *J. Am. Chem. Soc.*, **79**, 5593 (1957).

(2) J. H. Baxendale and G. P. Gilbert, *Discussions Faraday Soc.*, in press.

They attain limiting values of 10.5 with H_2 but appear to approach only about 7.0 with CH_3OH or C_3H_8.

Furthermore, we have observed the formation of D_2 which in the presence of the high concentrations of H_2 or C_3H_8 can only originate as molecules from D_2O. For the six experiments with H_2 present, where $G(HD)$ has reached the maximum, we find $G(D_2) = 0.56 \pm 0.07$, and for the four experiments with C_3H_8 present, we observe $G(D_2) = 0.48 \pm 0.05$. Higher values, $viz.$, $G(D_2) = 0.80 \pm 0.02$, are found in the methanol experiments, but we believe the increase over 0.5 can be attributed to the reaction

$$D + CH_3OD \longrightarrow D_2 + CH_3O$$
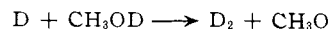
occurring to a small extent.

The molecular hydrogen may be formed by an excitation process or perhaps from the ion H^-, as proposed by Platzman[3]

$$H_2O + e \longrightarrow H^- + OH$$
$$H^- + H_2O \longrightarrow H_2 + OH^-$$
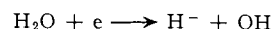
but if this is the only source, the yield of H^- would need to be about twice the value he suggested.

(3) R. L. Platzman, Abstracts of the Second International Congress of Radiation Research, Harrogate, 1962, p. 128.

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Inclusion Compounds Containing Macromolecules

Sir:

Although several inclusion compounds have been extensively studied recently,[1] little is known about inclusion compounds containing macromolecules. Brown and White[2] succeeded in polymerizing 1,3-butadiene and other monomers when included in urea or thiourea; nevertheless, no direct experimental evidence as to the formation of inclusion compounds with the polymers produced has been given. Recently, Parrod and others[3] verified the formation of an inclusion compound of urea with polyoxyethylene glycol, but attempts to include polyethylene and 1,4-polybutadiene into the same host structure were unsuccessful.

We have now found that several kinds of linear macromolecules such as polyethylene, cis-1,4 polybutadiene, $trans$-1,4 polybutadiene, and polyoxyethylene glycol give rise to very stable inclusion compounds with a host molecule of a new kind, the $trans$-$anti$-$trans$-$anti$-$trans$-perhydrotriphenylene (PHTP) (I). This com-

$I\ a$ $I\ b$
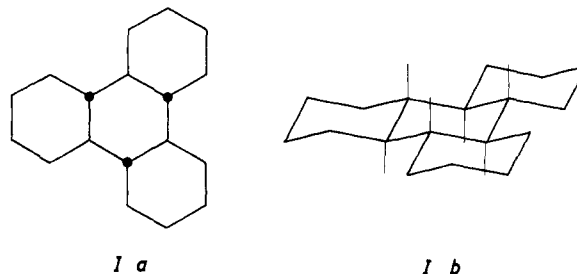
pound, recently synthesized in our Institute,[4] has shown a very strong tendency to include, in the crys-

(1) S. M. Hagan, "Clathrate Inclusion Compounds," Reinhold Publishing Co., New York, N. Y., 1962; for detailed studies on Channel-like structures: W. Schlenk, Jr., *Fortschr. Chem. Forsch.*, **2**, 92 (1951); D. Lawton and H. M. Powell, *J. Chem. Soc.*, 2339 (1958).

(2) J. F. Brown and D. M. White, *J. Am. Chem. Soc.*, **82**, 5671 (1960); D. M. White, *ibid.*, **82**, 5678 (1960).

(3) J. Parrod and A. Kohler, *Compt. Rend.*, **246**, 1046 (1958); *J. Polymer Sci.*, **48**, 457 (1960); A. Kohler, G. Hild, and J. Parrod, *Compt. Rend.*, **255**, 2763 (1962).

(4) M. Farina, *Tetrahedron Letters*, in press.