tron density from the rings to the extent that occurs when strongly covalent, high molecular orbital overlap bonding is present. Induced ring currents in the relatively electron-rich rings would tend to deshield the ring hydrogens to an extent comparable to benzene and this is consistent with the observed shifts of τ 3.8.

TABLE I

N.M.R. SPECTRA OF THORIUM DERIVATIVES

Compd.	Solvent	Peak position (τ)[a]	Assignment
$Th(C_5H_5)_3OC_4H_9$	Benzene	3.90 (singlet)	$-C_5H_5$
		6.25 (triplet)	$-OCH_2-$
		8.52 (multiplet)	$-CH_2-CH_2-$
		8.94 (triplet)	$-CH_3$
$Th(C_5H_5)_3OCH_3$	Benzene	3.70 (singlet)	$-C_5H_5$
		6.11 (singlet)	$-OCH_3$
$Th(C_5H_5)_3Cl$	Benzene	3.80 (singlet)	$-C_5H_5$
$Th(C_5H_5)_3Cl$	$CDCl_3$	3.70 (singlet)	$-C_5H_5$

[a] Measured relative to $(CH_3)_4Si$ on a Varian 4300 spectrometer at 60 Mc.

TABLE II

INFRARED SPECTRA (CM.$^{-1}$) OF ACTINIDE DERIVATIVES[a]

$Th(C_5H_5)_3Cl$	$Th(C_5H_5)_3$-OCH_3	$Th(C_5H_5)_3$-OC_4H_9	$U(C_5H_5)_3$-OC_4H_9	$U(C_5H_5)_3$-OCH_3
...	...	...	4000 s	3970 s
3060 w	3060 w	3060 w	3060 w	3050 w
2930 m	2920 m	2900 s	2900 s	2910 s
2880 m	2870 s	...	...	2870 s
2820 m	2800 s	2830 s	2775 s	...
1785 w	1730 s	1760 w	1735 m	1768 w
1680 m	1650 m	1645 w	1655 m	1650 w
...	...	1450 m	1462 m	...
1439 m	1440 s	1440 m	1443 m	1439 s
1379 w	1372 s	1372 s	1372 m	1360 w
1118 m	1125 s	1123 s	1121 s	1106 s
...	1092 s	1092 s	1078 s	...
1070 w	1072 m	...	...	1066 w
...	1034 m	1032 m	1033 m	1042 w
1013 s	1012 s	1010 s	1012 s	1010 s

[a] s, strong; m, medium; w, weak. Spectra were taken with carbon tetrachloride as solvent.

The tricyclopentadienylthorium and uranium butoxides appear to be isostructural according to X-ray powder patterns.[5] The great similarity in *d*-values and their relative intensities indicate the two compounds have the same type of unit cell and molecular symmetry. In addition, molecular similarity is indicated by infrared spectra (Table II). Although structural similarity is proposed for the thorium and uranium complexes, an absolute structure determination is lacking without additional information. However, it is most probable that the cyclopentadienyl rings and the alkoxide or chloride are arranged symmetrically about the central atom at the corners of a distorted tetrahedron in the manner proposed for tricyclopentadienyluranium chloride.

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[5] The X-ray powder diffraction data which include intensities and *d*-values for tricyclopentadienylthorium and uranium butoxide have been deposited as Document Number 8047 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Solvent Effects on the Phosphorus-31 Chemical Shift in Triphenylphosphine Oxide[1]

BY GARY E. MACIEL AND RONALD V. JAMES

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Some recent work on the effect of solvents on the C^{13} chemical shift of the carbonyl group of acetone[2] and other carbonyl-containing compounds[3] indicates that the shift is quite sensitive to an environment consisting of proton donors and relatively insensitive to the environment if proton donors are not present. The effect of major importance appears to be associated with the ability of the molecules of moderately acidic solvents to donate a proton in a hydrogen-bonded complex, or the ability of highly acidic solvents to produce a cationic protonated carbonyl group. The relatively larger range of chemical shifts observed in P^{31} magnetic resonance studies[4–11] and the higher natural abundance of P^{31} than C^{13} (100% *vs.* 1.1%), as well as the generally smaller line widths of P^{31} resonance lines,[4] usually result in greater precision and sensitivity in P^{31} n.m.r. studies compared with similar C^{13} work. These considerations have prompted us to undertake a solvent-shift study of the P^{31} resonance of triphenylphosphine oxide to see if a behavior similar to that found in the $>C^{13}{=}O$ case,[2,3] but more sensitive to solvent and more precisely defined, would obtain. Some previous data on the effect of solvents on P^{31} chemical shifts have been reported, and hydrogen bonding was mentioned as a likely influence.[4,12,13]

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The P^{31} chemical shifts of triphenylphosphine oxide were obtained in 1:20 mole ratio (solute:solvent) solutions of the oxide in a variety of reagent grade or Eastman White Label solvents. A measuring frequency of 15.1 Mc./sec. and the absorption mode were employed. Shifts were measured in a concentric-sphere sample container,[14] to eliminate bulk susceptibility effects, with respect to an external reference of 85% phosphoric acid in the center sphere, using the side-band technique.

The observed shifts referred to the resonance line of 85% phosphoric acid are presented in Table I. These shifts are the average results of at least five field scans in both increasing and decreasing senses and can be considered uncertain by less than ±0.2 p.p.m. They cover a total range of 35 p.p.m. with the largest positive shift occurring with dioxane as solvent and the largest negative shift corresponding to a 96% sulfuric acid solvent, in which the triphenylphosphine oxide can be described as a cationic protonated species. The effect of dilution was qualitatively checked with methanol as the solvent, in which case the shifts obtained with mole ratios of 1:20, 1:30, and 1:40 were identical within experimental error. As in the related investigation of the carbonyl group,[2] the shifts obtained with aprotic solvents covered a narrow range (1.2 p.p.m.) at the high-field end of the scale, while in protic solvents capable of forming hydrogen bonds with, or completely transferring a proton to, the solute molecule a large range of about 20 p.p.m. was observed. Thus, qualitatively the solvent effects observed in these two cases appear strikingly similar, as is seen from a comparison of the corresponding P^{31} shifts (triphenylphosphine oxide) with the C^{13} (acetone) shifts[2] in the same solvents listed in Table I. While a strict linear relationship does not exist between these two sets of shifts, a definite monotonic trend is apparent, with 1,4-dioxane the only solvent out of order.

TABLE I

P^{31} CHEMICAL SHIFTS OF $(C_6H_5)_3PO$ IN 1:20 MOLE RATIO SOLUTIONS IN SEVERAL SOLVENTS

Solvent	P^{31} chemical shift, p.p.m. with respect to 85% H_3PO_4[a]	C^{13} chemical shift of acetone in 1:6 mole fraction solutions[b]
1,4-Dioxane	−24.8	0.0
Carbon tetrachloride	−24.9	+1.3
Benzene	−26.1	+0.8
2-Propanol	−29.8	−1.9
Methanol	−32.6	−3.7
Acetic acid	−33.3	−6.2
m-Cresol	−36.4	−8.2
Formic acid	−37.3	−9.1
Dichloroacetic acid	−41.7	−11.9
Trifluoroacetic acid	−48.1	−14.1
Sulfuric acid	−59.8	−37.4

[a] Shifts in the direction of increasing field are considered positive. [b] Taken from ref. 2.

The difference between the shifts obtained in a highly acidic solvent and a moderately acidic or nonacidic solvent can be interpreted most simply in terms of a large change in the position of the equilibrium

$$(C_6H_5)_3PO + HA \rightleftharpoons (C_6H_5)_3POHA \rightleftharpoons (C_6H_5)_3P\overset{+}{O}H + A^-$$

In solutions of triphenylphosphine oxide, a substance which is less basic than water,[15] in solvents which are not highly acidic, the concentrations of the cationic species resulting from proton transfer would be too low to influence significantly the weighted-average chemical shift of the solute involved in the rapid acid–base equilibrium. In such solvents the predominant effect responsible for the downfield trend with increasing solvent acidity appears to be that of an increase in the number and strength of solvent-to-solute hydrogen bonds as represented by the hydrogen-bonded complex in the above equilibrium. There is ample evidence in the literature that such interactions are important in systems containing triphenylphosphine oxide and alcohols, phenols, carboxylic acids, or chloroform,[15–17] the association constant for the phenol–triphenylphosphine oxide complex in carbon tetrachloride solvent at 20° being 1055.[16] Of course, if the acidity of the solvent is high enough, the hydrogen-bonding effect will blend into, or be obscured by, the influence of an appreciable equilibrium concentration of the cationic protonated triphenylphosphine oxide. A distinction between these two types of acid–base interactions with triphenylphosphine oxide was made by Hadzi,[15] whose infrared experiments on crystalline adducts showed that a hydrogen-bonded complex is formed with trichloroacetic acid, while proton transfer may occur with the much stronger acid hydrogen bromide.

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B-Tribromoborazines from the Bromination of Borazine and N-Trimethylborazine

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Wiberg[2] has reported that bromination of borazine using excess bromine in the absence of solvent yields a yellow, unsymmetrical "adduct" which he formulated as B,B′-dibromo-N,N′-dibromocyclotriborazane. He further reported that pyrolysis of the "adduct" gives B,B′-dibromoborazine by splitting out two molecules of hydrogen bromide.

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[1] Taken in part from a thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1964.

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