the product as white needles, m.p. 319.5–321°, weighed 10.6 g. (48%).

Anal. Calcd. for $C_{48}H_{40}P_4N_4$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 797. Found: C, 72.6; H, 5.2; P, 15.5; N, 7.1; mol. wt., 833 (b.p. elevation of benzene).

The filtrate (remaining after removal of the tetramer) was concentrated to about 100 ml. and then extracted with three 50-ml. portions of hot 0.08 *N* NaOH. The filtrate was washed with water until neutral to litmus. After setting overnight, a precipitate of trimer was collected. Further concentration of the filtrate yielded, after cooling and filtration, a second precipitate. The two precipitates were combined and recrystallized three times from benzene to give a 7% yield of trimer, m.p. 230–232°.

Anal. Calcd. for $C_{36}H_{30}P_3N_3$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 597. Found: C, 72.3; H, 5.0; P, 15.4; N, 7.0; mol. wt. 585 (f.p. depression of $CHBr_3$).

The Reaction of Diphenylphosphorus Trichloride with Ammonium Chloride.—To a slurry of 11 g. (0.206 mole) of ammonium chloride in 200 ml. of *sym*-tetrachloroethane was added under nitrogen 27.8 g. (0.095 mole) of diphenylphosphorus trichloride. The mixture was heated at 130–135° for 18 hours. Hydrogen chloride, which formed during the course of the reaction, was removed on a current of nitrogen. The mixture was filtered to remove excess ammonium chloride and then concentrated at reduced pressure. The product mixture was dissolved in 300 ml. of benzene. After standing overnight, a precipitate of tetrameric diphenylphosphinic nitrite was collected. Concentration of the filtrate yielded a second precipitate of tetramer. The two precipitates were combined and recrystallized from benzene to give a 7% yield of tetramer, m.p. 314–318°. Two additional recrystallizations from benzene gave needles, m.p. 319–321°.

Anal. Calcd. for $C_{48}H_{40}P_4N_4$: mol. wt., 796. Found: mol. wt., 796 (60° Nier mass spectrometer).

The filtrate that remained after removal of the tetramer (described above) was concentrated to near dryness. After standing overnight, the precipitated trimeric diphenylphosphinic nitride was collected, and then stirred with 50 ml. of 2.5% NaOH solution for 2 hours to remove moisture-sensitive by-products. The trimer was collected, washed with water and then recrystallized from benzene. The product, m.p. 233–234°, as white needles, weighed 0.8 g. (4%).

Anal. Calcd. for $C_{36}H_{30}P_3N_3$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 597. Found: C, 72.2; H, 5.3; P, 14.7; N, 7.0; mol. wt., 597 (60° Nier mass spectrometer).

Acknowledgments.—The authors wish to thank Dr. Fred L. Mohler of the National Bureau of Standards, Washington, D. C., for determining the mass spectra. We also are grateful to Mrs. Catherine Douglas who made the other molecular weight determinations.

CORONA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Triphenylphosphonium Salts

BY JOHN C. SHELDON AND S. Y. TYREE, JR.

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Triphenylphosphonium salts of HCl, $HClO_4$, HI, $HSbCl_4$, $HFeCl_4$, H_2SnCl_6, $HFeBr_4$ and H_2SnBr_6 have been prepared and characterized briefly. It is suggested that absorption spectroscopy is the most definitive means of establishing the presence of the -onium structure.

Introduction

While studying reactions of substituted phosphines with metal halides, it was observed that triphenylphosphine forms a number of stable crystalline complexes with metal halides and the corresponding hydrohalic acids. The ternary complexes can be formulated as $(C_6H_5)_3PHMX_4$ and $[(C_6H_5)_3PH]_2MX_6$, suggesting immediately that they are phosphonium salts and that, as a class, they may exhibit greater stability than hitherto suspected. Previous examples of triphenylphosphonium salts are rare. $(C_6H_5)_3PHBr$ and $[(C_6H_5)P]NiBr_2{\cdot}HBr$ have been mentioned in the patent literature.[1] $(C_6H_5)_3PHI$ and $[(C_6H_5)_3PHCl]_2PtCl_4$ were reported in 1885.[2]

A variety of triphenylphosphine–metal halide addition compounds are known, specifically those of cobalt, nickel and platinum. In spite of the low donor strength of the phosphorus atom in the environment of three phenyl groups, the stability of such addition compounds appears to be considerable. The unexpected stability can be ascribed to π-bonding between a filled d orbital of the metal and a vacant d orbital of the phosphorus atom. Such π-bonding would augment the σ-type coördinate bond formed using the lone pair on the phosphorus. Triphenylphosphonium compounds might well be considered unstable since no d-d π-bonding is possible between phosphorus and a proton.

The present work is directed toward enlarging the scope of triphenylphosphonium salts and to developing means of their characterization.

Experimental

Preparation of Compounds. Triphenylphosphonium Chloride.—The compound cannot be isolated from aqueous solutions even when present in high concentrations. When dry hydrogen chloride is passed into a dry ethereal solution of triphenylphosphine, a white oily suspension is produced, which crystallizes on stirring. After filtration and drying in a stream of dry air, the crystals are homogeneous, short, deliquescent needles. The crystals melt over a range of 70–73°, and recrystallization is very slow. The crystals are easily and irreversibly soluble in polar organic solvents. They are only slowly decomposed by water, due, we believe, to the formation of the insoluble triphenylphosphine on the crystal surfaces.

Anal. Calcd. for $(C_6H_5)_3PHCl$: Cl, 11.9; P, 10.35. Calcd. for $[(C_6H_5)_3PHCl]_3{\cdot}HCl$: Cl, 15.2; P, 9.95. Found: Cl, 15.1; P, 10.05.

Triphenylphosphonium Iodide.—$(C_6H_5)_3PHI$ has been reported previously.[2] The original method of preparation was followed. Triphenylphosphine dissolves readily in hot, concentrated hydriodic acid. On cooling the solution, colorless needles slowly separate. The crystals can be washed with small portions of cold glacial acetic acid and sucked dry with air. Like the other salts described below (though unlike the chloride), the crystals are not hygroscopic. They decompose slowly at 100°, more rapidly at higher temperatures. No melting occurs when a melting point tube containing some of the crystals is placed in a

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(1) German Patent 824,047, *C. A.*, **49**, 6998a (1955).

(2) A. Michaelis and H. v. Soden, *Ann.*, **229**, 295 (1885).

bath at 215°. On heating to 217° the crystals in the tube melt to a dark red effervescing liquid (215° is the recorded melting point[2]).

Anal. Calcd. for $(C_6H_5)_3PHI$: I, 32.5; P, 7.95; H, 4.14; C, 55.3. Found: I, 31.7; P, 8.0; H, 4.12; C, 55.3.

The same crystals can be prepared by adding concentrated hydriodic acid to a solution of triphenylphosphine in concentrated hydrochloric acid. It was not possible to prepare the bromide by the above procedures.

Triphenylphosphonium Perchlorate.—When 70% perchloric acid is added to a solution of triphenylphosphine in concentrated hydrochloric acid an oil separates. The oil crystallizes to square ended needles. The needles decompose slowly at 100° and melt at 165–167°. The crystals could not be safely washed with solvents without some decomposition. Consequently they were sucked dry on the filter and analyzed while still not in a "free-flowing condition."

Anal. Calcd. for $(C_6H_5)_3PHClO_4$: ClO_4, 27.4; P, 8.55. Found: ClO_4, 25.3; P, 8.2.

Using the above procedure triphenylphosphonium sulfate could not be prepared. Triphenylphosphine recrystallizes unchanged from glacial acetic acid.

Triphenylphosphonium Chloroantimonate(III).—Equimolar quantities of triphenylphosphine and antimony(III) chloride are dissolved in cold, absolute alcohol. The solution is saturated with dry hydrogen chloride with continued cooling. At first a large amount of white, amorphous precipitate is produced, which dissolves completely upon continued passage of the hydrogen chloride. One or two drops of water are added to the solution, whereupon some white precipitate forms. The precipitate dissolves upon stirring, and, simultaneously, colorless, square-ended needles crystallize from the solution. The crystals melt over a range of 115–135°, and recrystallize upon cooling.

Anal. Calcd. for $(C_6H_5)_3PHSbCl_4$: Cl, 26.9; Sb, 23.2; P, 5.9. Found: Cl, 26.9; Sb, 23.0; P, 5.45.

Triphenylphosphonium Tetrachloroferrate(III).—The substance is prepared in a manner similar to that of the chloroantimonate. The crystals are yellow needles, melting at 104°, with decomposition.

Anal. Calcd. for $(C_6H_5)_3PHFeCl_4$: Cl, 30.8; Fe, 12.1; H, 3.50; P, 6.7; C, 46.8. Found: Cl, 30.6; Fe, 11.7; H, 3.75; P, 6.3; C, 46.6.

Triphenylphosphonium Hexachlorostannate(IV).—The substance is prepared in a manner similar to that of the chloroantimonate. The crystallization of the salt is spontaneous, requiring no seeding by the addition of water. The crystals are insoluble in water. It is of interest to note that the water solubilities of the triphenylphosphonium perchlorate and hexachlorostannate are similar to those of the corresponding tetraphenylphosphonium salts.[3] The crystals appear as hexagonal plates. They are stable for short periods at 100°, but lose hydrogen chloride on prolonged heating. The crystals melt over a range of 200–230°, with the evolution of hydrogen chloride. In a sealed tube a somewhat higher range is observed.

Anal. Calcd. for $[(C_6H_5)_3PH]_2SnCl_6$: Cl, 24.8; P, 7.22; Sn, 13.8. Found: Cl, 24.8; P, 7.02; Sn, 13.6.

Triphenylphosphonium Tetrabromoferrate(III).—The iron bromide starting material (which is best described as a mixture of $FeBr_3$ and $FeBr_2$) was prepared by the action of bromine vapor on iron filings with subsequent sublimation of the product in an atmosphere of bromine. Triphenylphosphine in absolute alcohol is added to a solution of the iron bromide in concd. hydrobromic acid. No precipitate forms at first. Upon scratching the sides of the vessel, golden-brown leaflets crystallize. After sucking dry in air, the crystals melt at 105–106°, with the evolution of hydrogen bromide. The crystals contain no divalent iron. Heating at 110° results in some reduction of Fe^{III} to Fe^{II}, presumably by the triphenylphosphine.

Anal. Calcd. for $(C_6H_6)_3PHFeBr_4$: Br, 50.0; Fe, 8.75; P, 4.85. Found: Br, 49.1; Fe, 8.5; P, 4.45.

Triphenylphosphonium Hexabromostannate(IV).—A pale yellow crystalline precipitate separates immediately when alcoholic triphenylphosphine is added to a solution of tin(IV) bromide in concd. hydrobromic acid. The crystals lose hydrogen bromide rapidly at 110°. They melt over a very broad range of 170–240° with the continued evolution of hydrogen bromide.

Anal. Calcd. for $[(C_6H_5)_3PH]_2SnBr_6$: Br, 42.5; P, 5.51. Found: Br, 41.9; P, 5.56.

Applying the above techniques, we have been unable to prepare triphenylphosphonium salts starting with $TiBr_4$, CuCl, $HgCl_2$ and $AlCl_3$. Concentrated hydrochloric acid solutions of Co^{II} and Te^{IV} also failed to yield phosphonium salts. Te^{IV} apparently is reduced to elemental tellurium by the phosphine.

Properties of Triphenylphosphonium Salts.—Ultraviolet absorption spectra were obtained of triphenylphosphine dissolved in 50/50 alcohol-water solvent to which varying amounts of hydrogen chloride had been added. A Beckman DU instrument was used. Infrared absorption spectra were obtained for all compounds prepared above using Nujol mulls in a Baird Associates recording spectrophotometer, Serial No. AB2-193.

Molecular weight determinations of most of the compounds reported above were determined by the freezing point lowering of nitrobenzene.

The dissociation pressures of hydrogen halide over several of the compounds were measured as a function of temperature. The pressures obtained were not rigidly reproducible.

Results and Discussion

Ultraviolet Spectra.—Triphenylphosphine is insoluble in water, but soluble in concentrated hydrochloric acid. This latter solubility is clearly shown to be due to the formation of the phosphonium salt by the ultraviolet spectra shown in Fig. 1. Curve I shows the molar extinction coefficient of triphenylphosphine in the solvent 50/50 alcohol–water. The band at 260 mμ is almost certainly due to conjugation of the phenyl groups through the phosphorus atom.[4] Such conjugation involves delocalization of the lone pair of electrons of the phosphorus atom amongst the phenyl groups. Any degree of donation of these electrons by the phosphorus atom to a proton would prohibit the conjugation, and the spectra would resemble that of single, monosubstituted benzene groups. Curve II is a similar plot with the addition of 0.24 mole/l. of HCl to the solvent. It is apparent that some reaction is taking place even under such conditions. Curve III gives the molar extinction coefficient of the same phosphine in 6 *M* HCl. The intense band at 260 mμ has disappeared. In its place is seen a weaker band of partially resolved character. This latter band is similar to the spectra of triphenylphosphine oxide[5] and triphenylmethylphosphonium iodide,[6] and even approaches that of benzene, itself. The wave length of the highest maximum in the partially resolved bands of triphenylphosphonium chloride is compared with the corresponding wave lengths for triphenylphosphine oxide, triphenylmethylphosphonium chloride, and benzene

	$\log_{10} \epsilon$	λ, mμ
$(C_6H_5)_3PHCl$	3.57	269
$(C_6H_5)_3PO$	3.38	265
$(C_6H_5)_3CH_3PI$	3.70	263
C_6H_5	2.35	255

The data indicate that phosphorus is in a quaternary state when triphenylphosphine is dissolved in concd. hydrochloric acid, with the three phenyl

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(3) H. H. Willard and L. R. Perkins, *Anal. Chem.*, **25**, 1635 (1953).

(4) H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1954).

(5) H. H. Jaffe and L. D. Freedman, THIS JOURNAL, **74**, 1069 (1952).

(6) F. G. Mann, *et al.*, *J. Chem. Soc.*, 1130 (1953).

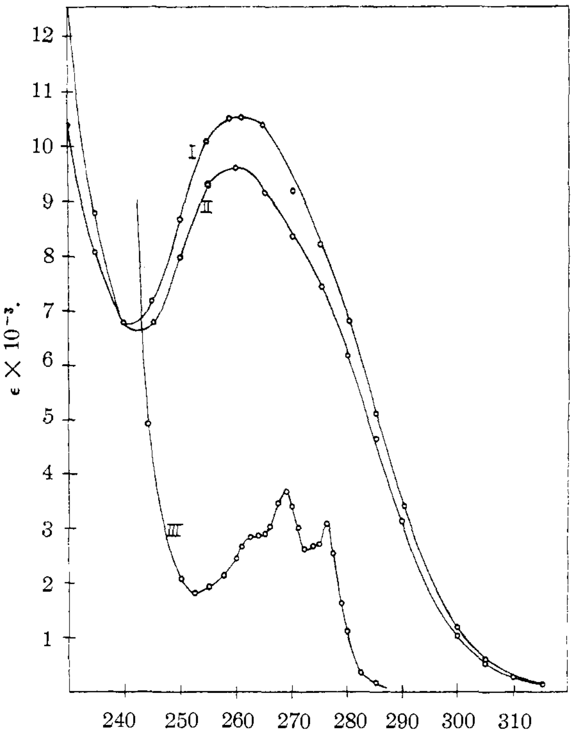

Fig. 1.—λ, mμ.

groups absorbing more independently and in a fashion similar to benzene itself.

The Composition of Triphenylphosphonium Chloride.—The formula $[(C_6H_5)_3PHCl]_3 \cdot HCl$ is compatible with the analytical data. Such a bizarre formulation is not unknown in acid–base complex involving large, weakly basic donors. Berliner and Hann[7] present evidence for representing many hydrofluorides of aromatic amines as complexes of the type B·HF·3HF. The change in chlorine content after evacuation at 10^{-6} mm. and −60° for six hours is only just detectable. It is our opinion that the "fourth" hydrogen chloride is not just loosely held. The substance has a marked odor of hydrogen chloride at room temperature. The dissociation pressure of hydrogen chloride over the solid in the range 0 to 70° is not rigidly reproducible. We are not certain that our data represent true vapor–solid equilibria. The results show a consistent trend, however, agreement being poorest at pressures below 10 mm. The data are best represented by the equation $\log P_{\text{mm}} = 9.66 - 2520/T$. The gradient yields a value of approximately 11 kcal. for the enthalpy of dissociation. Care was taken to ensure that no more than the "fourth molecule" of hydrogen chloride was vaporized in any measurement. Thus we feel that the extra molecule of hydrogen chloride is actually bound by a weak chemical bond.

Properties of Triphenylphosphonium Salts.—The compounds are generally insoluble in nonpolar organic solvents. They appear to undergo marked dissociation when dissolved in polar solvents containing no excess hydrogen halide. Molecular weight determinations in freezing nitrobenzene yielded values below the simple formula in each case.

Compound	Concn., wt. %	Mol. wt. Found	Mol. wt. Theory
$(C_6H_5)_3P \cdot 1.33HCl$	0.50	195	311
$(C_6H_5)_3PHSbCl_4$	1.05	340	527
	0.57	270	
$(C_6H_5)_3PHFeCl_4$	0.65	180	460
	0.028	160	

It is not clear whether ionization or dissociation is the more important factor in yielding such results.

The dissociation pressures of hydrogen halide over $(C_6H_5)_3PHFeBr_4$, $[(C_6H_5)_3PH]_2SnCl_6$ and $([C H_5)_3PH]_2SnBr_6$ are much lower than the corresponding figures for the hydrochloride. They were also much less informative, inasmuch as they were scarcely reproducible. It is doubtful whether a true equilibrium measurement was obtained, approaching either from a low or a high temperature. In addition, other reactions become important at higher temperatures. In the case of the bromostannate compound, tin(IV) bromide can be seen condensing on the walls of the apparatus. Iron(III) bromide decomposes easily into bromine and iron(II) bromide, the bromine being accepted by the triphenylphosphine.

Infrared Spectra.—The absorption spectrum of triphenylphosphonium tetrachloroferrate is shown in Fig. 2 from 1300 to 625 cm.$^{-1}$. It is typical of the other triphenylphosphonium salts.[8] The only significant feature observed between 5000 and 1300 cm.$^{-1}$ is a barely detectable band at 2400–2300

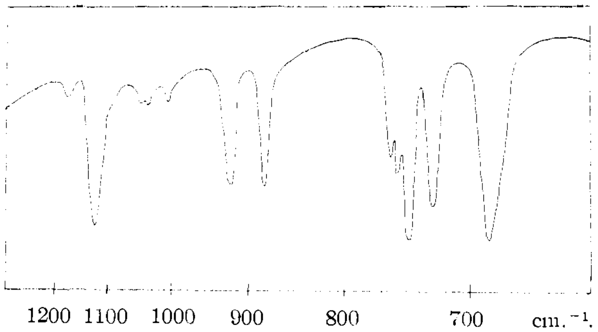

Fig. 2a.—$(C_6H_5)_3PHFeCl_4$.

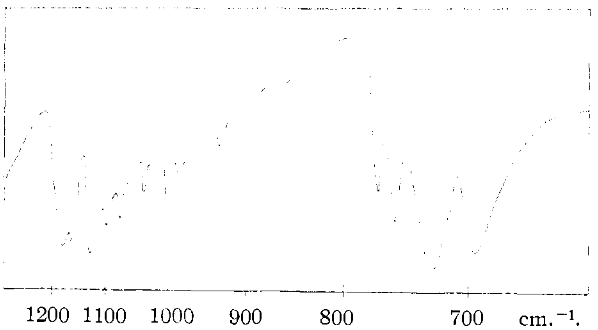

Fig. 2b.—$(C_6H_5)_3PO$.

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[7] J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, **32**, 1142 (1928).

[8] Absorption spectra of the other triphenylphosphonium salts reported in this paper have been deposited as Document number 5420 with 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 in advance by check or money order payable to Chief, Photoduplication Service.

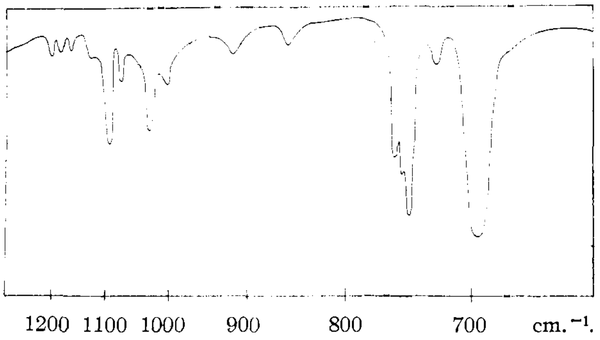

Fig 2c.—$(C_6H_5)_3P$.

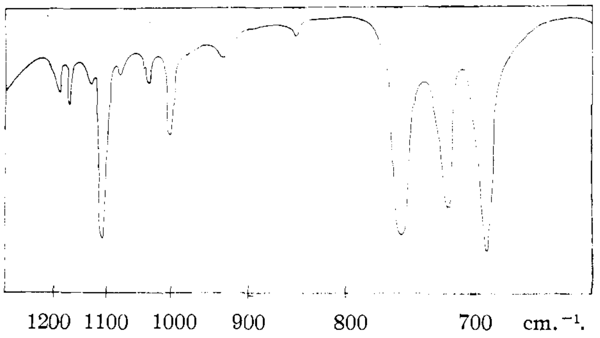

Fig. 2d.—$[(C_6H_5)_3P]_2HgCl_2$.

cm.$^{-1}$, which is probably the P–H absorption. The spectra of triphenylphosphine, triphenylphosphine oxide and bis-triphenylphosphinemercury(II)chloride[9,10] are included in Fig. 2.

All of the proposed triphenylphosphonium compounds show a very strong band at 1120–1118 cm.$^{-1}$. The band in question is almost lost in the perchlorate case due to the intense absorption of the perchlorate ion itself near this frequency. $(C_6H_5)_3P$, $(C_6H_5)_3PO$ and $[(C_6H_5)_3P]_2HgCl_2$ do not show such a single very strong band at 1120 cm.$^{-1}$, although they do show some structure in the region 1300–1000 cm.$^{-1}$. Triphenylphosphine oxide has two strong bands in this region, the one at 1175 cm.$^{-1}$ having been proposed as due to P–O stretching.[11] Triphenylphosphine has no very strong bands in this region. The $HgCl_2$ adduct possesses one strong band in this region, but it is at 1108 cm.$^{-1}$, whereas all of the maxima of the triphenylphosphonium salts lie clearly at 1120–1118 cm.$^{-1}$.

A further similarity among the spectra of the phosphonium salts is the presence of moderate to strong bands in the 940–820 cm.$^{-1}$ region. The non-phosphonium type compounds show no moderate or strong bands here. This latter region is the only region in which marked differences among the phosphonium salts are observed. It appears that the differences may be related to the weight of the anion. The maxima for both bands in each of six cases are

Anion	Frequency, cm.$^{-1}$	
Cl^-	937	918
ClO_4^-	928	897
I^-	930	880
$FeCl_4^-$	920	880
$SbCl_4^-$	905	874
$SnCl_6^{--}$	890	870

The spectrum of triphenylphosphine shows two strong bands, one at 742 cm.$^{-1}$ and the other at 695 cm.$^{-1}$, which are characteristic of a monosubstituted benzene ring. The weak band at 724 cm.$^{-1}$ probably is due to Nujol. In agreement with previous observations it is found that the strong, lower frequency band is little affected by changes in the substituent group on the benzene ring.[12] Thus changes at the phosphorus atom have no effect on this band. However, there is observed along with the 742 cm.$^{-1}$ band another strong band at about 720 cm.$^{-1}$ whenever the phosphorus atom achieves a four-coördinate state. In some cases the band near 742 cm.$^{-1}$ is partially resolved into a triplet (notably in the iodide) and the 720 cm.$^{-1}$ band totally or partially into a doublet.

The characteristic spectrum of a triphenylphosphonium salt appears to be a lone intense band at 1120–1118 cm.$^{-1}$ and two moderately strong bands between 940 and 870 cm.$^{-1}$, which vary with the anion. A strong band also appears at about 720 cm.$^{-1}$, in common with all triphenylphosphine compounds where the phosphorus atom is functioning as a donor.

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(9) Kolitowska, *Roczniki Chem.*, **8**, 568 (1928).

(10) R. Kh. Friedlina, *et al.*, *Bull. Acad. Sci. URSS Classe Sci. Chim.*, 146 (1945).

(11) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(12) M. Margoshes and V. A. Fassel, *Spectrochem. Acta*, **7**, 14 (1955).