

157. The Infrared Absorption Spectra of Normal and ¹⁸O-Labelled Triphenylarsine Oxide.

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The spectra of normal and *ca.* 90 atom % triphenylarsine [¹⁸O]oxide have been measured in the 3700—420 cm.⁻¹ region, for chloroform, bromoform, and acetonitrile solutions, and assignment of the observed bands made. The As=¹⁶O band at 880 cm.⁻¹ appears to be the only one which is shifted in the case of the labelled oxide, and the observed shift (40 cm.⁻¹) is in agreement with that expected from theory (41 cm.⁻¹). The relative integrated absorption intensity of the As=¹⁸O band is only 82% of that for the As=¹⁶O band, while the expected value is as high as 91%.

THE effect of substitution by oxygen-18 on the infrared absorption of various X=O compounds (X = C, P, N, or S) has recently been studied.¹ As a result it seemed interesting to measure the spectra of the series Ph₃X=O (X = P, As, Sb, or Bi) in order to find out whether the X=O stretching frequency approaches that of a diatomic X=O molecule with increase of the atomic weight of X, as expected. The synthesis of *ca.* 90 atom % triphenylarsine [¹⁸O]oxide and 25 atom % triphenylstibine [¹⁸O]oxide was therefore carried out. Attempts to synthesize triphenylbismuth oxide were unsuccessful.

The infrared bands observed in the 3700—420 cm.⁻¹ region for solutions of triphenylarsine oxide in chloroform, bromoform, and acetonitrile are reported in Table 1. The appreciable absorption at *ca.* 3300 cm.⁻¹ for both the normal and the labelled compound

TABLE 1.

The observed absorption bands of normal and labelled triphenylarsine oxide.*

Material	Solvent	Concn. (g./l.)	Cell thickness (mm.)	Bands (optical densities in parentheses)
Normal †	CHCl ₃	20	1	3260(0.49), 2965, ~2500(0.14), 1960(0.09), 1887(0.11), ~1815(0.11), ~1765(0.11), 1630(0.22), 1584(0.18), 1481(0.29), 1434(0.31), 1334(0.12), 1309(0.21), ~1260, 1086(0.43), 999(0.19), ~880(≥1)
Labelled †	CHCl ₃	20	0.5	3300(sh; 0.18), 2965(0.6), ~2500(0.07), 1960(0.03), 1887(0.03), ~1815(0.05), ~1765(0.03), ~1630(0.07), 1584(0.05), 1484(0.19), 1437, 1334, 1309(0.12), ~1260(0.15), 1086, 999, 880(0.11), ~840(~1)
Normal ‡	CHBr ₃	28	0.2	738(0.87)
Labelled ‡	CHBr ₃	16	0.2	738(0.42)
Normal §	MeCN	16	0.2	693(0.21), 512(0.03), 479(0.18), 460 (0.08)
Labelled §	MeCN	23	0.2	693(0.33), 512(0.10), 479(0.28), 461 (shoulder)
Normal ¶	CHCl ₃	20	0.2	880(0.52)
Labelled ¶	CHCl ₃	38	0.2	840(0.70)

* The optical densities quoted are of relative numerical significance only for bands of the same spectrum with the same solvent. Uncertainties in the nominal cell-lengths may cause differences of up to 30% in the intensities of analogous bands in different spectra. † Measured in the 3700—830 cm.⁻¹ region only. ‡ Measured only between 830 and 720 cm.⁻¹. § Measured in the 720—420 cm.⁻¹ region. ¶ Measured only in the 900—800 cm.⁻¹ region.

seems to be due to traces of water tenaciously held by them in spite of drastic drying; most of this absorption remained after reheating the dried sample of the normal compound above 105° for 2 hours. However, a Karl Fischer determination showed that the final water content of the sample was only about 1% (0.2 mole/mole).

The bands at about 1960, 1887, 1815, and 1765 cm.⁻¹ are due to the monosubstituted phenyl rings, although their relative intensities are a little different from those of the usual pattern.² The fact that the aromatic 1630 cm.⁻¹ band appears for triphenylarsine oxide

¹ (a) Halmann and Pinchas, *J.*, 1958, 1703; (b) 1958, 3264; (c) 1960, 1246; (d) Pinchas, Samuel, and Weiss-Brodsky, *J.*, 1961, 1688, 2666; (e) 1961, 2382; (f) 1961, 3063; (g) 1962, 3968; (h) 1963, 1128.

² See, e.g., Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 90.

above the usual range³ of 1600 ± 5 cm.⁻¹ seems analogous to the behaviour for nitrobenzene, ascribed to the electronegativity of the nitro-group.³ That the intensity of the 1584 cm.⁻¹ band is almost equal to that of the 1630 cm.⁻¹ band is interesting since it is usually assumed that the intensity of the 1580 cm.⁻¹ band is comparable to that at 1600 cm.⁻¹ only in conjugated rings.⁴ However, the ultraviolet absorption of triphenylarsine oxide proves the absence of such conjugation here by showing the same spectrum as benzene itself [λ_{max} in propan-2-ol] 2580 (ϵ 206), 2640 (250), and 2700 Å (210)]. In triphenylphosphine oxide also the conjugation between the phenyl rings and the P=O group is only very limited.^{1b,5} It seems therefore that the intensity of the 1580 cm.⁻¹ band is more the effect of a double bond adjacent to the phenyl ring than the result of its conjugation with it.

The bands at about 1481 and 1434 cm.⁻¹ are analogous to the bands for heavily mono-substituted benzenes at about 1480 and 1446 cm.⁻¹ reported by Katritzky and Lagowski⁶ and assigned by them to A_1 and B_1 C-C stretching, respectively. The 1086 and 999 cm.⁻¹ bands appear to be related to those reported by them⁶ at about 1073 and 996 cm.⁻¹, and assigned to a B_1 in-plane C-H bending and an A_1 ring vibration, respectively. The strong band at 880 cm.⁻¹ in the normal spectrum, which loses almost all its intensity in the spectrum of the labelled compound, is clearly due to the stretching of the As=O group. A Nujol mull of normal triphenylarsine oxide is also reported⁷ to absorb at 880 cm.⁻¹.

The strong 738 cm.⁻¹ band appears also in the spectrum of triphenylarsine (at 736 cm.⁻¹) and was assigned there to the out-of-plane C_{Ar} -H bending vibration.⁸ The 693 cm.⁻¹ absorption must be assigned to a C-C-C deformation (ν_8 according to the notation of Herzberg⁹) since this vibration is known to absorb in the 688—693 cm.⁻¹ region in Ph_nX compounds where X belongs to the fifth group of the Periodic Table.¹⁰ Triphenylarsine also absorbs near 695 cm.⁻¹, although it seems to have been wrongly assigned.⁸

The band at 512 cm.⁻¹ is probably due to the C_{Ar} -AsO stretching since the analogous C-P stretching seems to be in the 650—710 cm.⁻¹ region.¹¹ On the assumption that the force constants of these bonds are approximately the same and that Hooke's equation holds, one gets for their expected frequency ratio:

$$\begin{aligned} \nu(\text{C-As})/\nu(\text{C-P}) &= [\mu(\text{C-P})/\mu(\text{C-As})]^{\frac{1}{2}} \\ &= [(31 \times 12)(91 + 12)/(31 + 12)(91 \times 12)]^{\frac{1}{2}} = 0.90 \end{aligned}$$

this rough calculation thus gives for the C-AsO stretching vibration the region near 600 cm.⁻¹.

Finally, the doublet at 479m and 460w cm.⁻¹ can be assigned to an out-of-plane C_{Ar} -AsO bending mode (Herzberg's⁹ ν_{19}), split into two components in Ph_3R molecules;¹² this bending gives rise to a doublet at 490s and ~432w cm.⁻¹ for triphenylphosphine, and a band at 460 cm.⁻¹ for triphenylstibine.¹²

As expected, the spectrum of the labelled triphenylarsine oxide is, within experimental error, the same as the normal spectrum, except for the As=O bands. The observed isotopic shift of 40 cm.⁻¹ can be compared with the value of 41 cm.⁻¹ calculated for the diatomic

³ Ref. 2, p. 71.

⁴ Ref. 2, p. 72.

⁵ Yaffe and Freedman, *J. Amer. Chem. Soc.*, 1952, **74**, 1069; *J. Chem. Phys.*, 1954, **22**, 1430; see also, Rao, Ramachandran, Iah, Somasekhara, and Rajakumar, *Nature*, 1959, **183**, 1475.

⁶ Katritzky and Lagowski, *J.*, 1958, 4155.

⁷ Goodgame and Cotton, *J.*, 1961, 3735.

⁸ Margoshes and Fassel, *Spectrochim. Acta*, 1955, **7**, 14; Rao, Ramachandran, and Balasubramanian, *Canad. J. Chem.*, 1961, **39**, 171.

⁹ Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, 1945, p. 363.

¹⁰ Young, Servais, Currie, and Hunter, *J. Amer. Chem. Soc.*, 1948, **70**, 3758.

¹¹ Jones and Sandorfy in "Chemical Applications of Spectroscopy," Interscience, New York, 1956, p. 551.

¹² Harrah, Ryan, and Tamborsky, *Spectrochim. Acta*, 1962, **18**, 21.

AsO molecule according to Hooke's law; this excellent agreement demonstrates the "pure" of the 880 or 840 cm^{-1} vibration as a group-frequency.

The results of the intensity measurements on the $\text{As}^{=16}\text{O}$ and $\text{As}^{=18}\text{O}$ bands are given in Table 2. The integrated absorption was estimated by multiplying the apparent molecular extinction coefficient by the respective apparent half-width. Quantitative measurements were made on at least two independent solutions; the results in Table 2 are thus supported by more than one set of measurements. The same cell was used in all cases and each measurement was made at least twice, the mean value being taken.

TABLE 2.

The absorption intensity of the triphenylarsine oxide isotopic $\text{As}=\text{O}$ bands.

	Concn. (g./l. in CHCl_3)	ν_{max} (cm^{-1})	Optical density	Mol. extinction coeff. (l. mole $^{-1}$ cm^{-1})	Half- width (cm^{-1})	Integrated absorption (l. mole $^{-1}$ cm^{-2})
Normal	19.85	880	0.519	421 \pm 10	24.5	10,300 \pm 300
Labelled	35.45	840	0.75	373 \pm 10 *	22.5	8400 \pm 300

* Corrected for the lower effective concentration of the labelled compound.

The integrated absorption intensity of the $\text{As}^{=18}\text{O}$ band is seen to be 18% less than that of the $\text{As}^{=16}\text{O}$ band. Theoretically, however, one would expect that (since the 880 or 840 cm^{-1} absorption is a "pure" band and no other bands are affected by the ^{18}O -labelling) the following equation should hold: $^{13} I_{16}/\nu_{16}^2 = I_{18}/\nu_{18}^2$, where I_n is the integrated intensity of the AsO stretching band of $\text{Ph}_3\text{As}^{=n}\text{O}$, and ν_n is its frequency. Insertion of the measured values of ν_n into this equation gives for I_{18}/I_{16} a calculated value of 91% instead of the observed value of 82%. This is analogous to the case of triphenylphosphine oxides^{1b} where the observed difference (for carbon tetrachloride or carbon disulphide solutions) in integrated intensity was about 15% while the calculated one was only about 5%. Similar results were also obtained for monomeric benzoic acid,^{1e} methyl benzoate,^{1e} benzophenone,^{1a} and dicyclohexylurea,^{1h} while a number of other compounds show^{1d,f,g,h} an increase in the intensity of the $\text{X}=\text{O}$ stretching band on labelling with oxygen-18.

For triphenylstibine oxide there is no appreciable band in the 900—740 cm^{-1} region, where the $\text{Sb}=\text{O}$ group is expected to absorb (on the basis of the 880 cm^{-1} $\text{As}=\text{O}$ band and the respective difference in mass). It seems therefore that triphenylstibine oxide does not contain an $\text{Sb}=\text{O}$ group but, as in the case of silica, is instead built of $[\text{Sb}-\text{O}]_x$ units. This would also explain its much lower solubility in chloroform or bromoform as compared with the appreciable solubility of triphenylarsine oxide in these solvents. The strong bands observed for a Nujol mull of triphenylstibine oxide, at 736, 726, and 693 cm^{-1} , are almost unaffected by ^{18}O -labelling (739, 725, and 694 cm^{-1} for a 25 atom % ^{18}O content) and can be assigned to the out-of-plane $\text{C}_{\text{Ar}}-\text{H}$ bending split in the solid state⁷ (739 and 725 cm^{-1}) and the $\text{C}-\text{C}-\text{C}$ (ν_8) deformation (693 cm^{-1}), respectively, by analogy with the case of triphenylarsine oxide (738 and 693 cm^{-1}).

EXPERIMENTAL

Triphenylarsine Oxide.—Commercial triphenylarsine (0.3 g.) was dissolved in benzene (10 ml.), and bromine (0.055 ml.) was added with constant stirring until a brown colour persisted. Sodium hydroxide (0.1 g.) in water (1 ml.) was poured dropwise into the benzene solution and the mixture boiled to remove the benzene. (The mixture was kept basic by additional drops of alkali when necessary.) After almost all the solvent was driven off, the residue was redissolved in benzene, heated until the vapour showed no sign of water, and n-pentane was added. The precipitated triphenylarsine oxide was filtered off and dried for 1 hr. at about 85°; it formed needles (50%), m. p. 190—192° (lit.,¹⁴ 190—191°).

Triphenylarsine [^{18}O]-Oxide.—Water enriched with oxygen-18 (1.5 ml. of 95 atom %) was

¹³ See, e.g., Eggers, Hisatsune, and Van Alten, *J. Phys. Chem.*, 1955, **52**, 1124.

¹⁴ Jensen, *Z. anorg. Chem.*, 1943, **250**, 220.

added under a stream of dry nitrogen to sodium (0.2 g.). A solution of triphenylarsine (1.0 g.) in benzene (20 ml.), which contained bromine (0.18 ml.) distilled over phosphorus pentoxide, was added slowly to the first solution, and the precipitate was filtered off and recrystallized twice from benzene-pentane, m. p. 189–191° (47%). The isotopic analysis¹⁵ showed an oxygen-18 enrichment of 30.7 atom %. This compound (0.35 g.) was sealed with heavy water (95 atom % oxygen-18; 1.0 ml.) in a test-tube and heated at 100–105° for 12 hr. The water was evaporated by high-vacuum distillation during 12 hr. The isotopic analysis showed an enrichment of 90 ± 2 atom % of oxygen-18.

Triphenylstibine [¹⁸O] *Oxide*.—Triphenylstibine dichloride (Eastman) (1 g.) was boiled with an excess of ¹⁸O-enriched water (Weizmann Institute) (10 ml.) for several days. The insoluble precipitate was filtered off, washed until free from chloride, and dried *in vacuo*. Isotopic analysis¹⁵ showed an oxygen-18 enrichment of 25 atom %.

Triphenylstibine Oxide.—This was prepared as for the labelled oxide, using normal water (Found: C, 59.2; H, 4.6. C₁₈H₁₅OSb requires C, 58.6, H, 4.1%), λ_{\max} . (in PrⁱOH) 224, 257, 263, and 270 m μ (ϵ 22,000, 1670, 1800, and 1320).

The infrared measurements were carried out with a Perkin-Elmer model 12C spectrophotometer equipped with a sodium chloride or a potassium bromide prism. The slit-width used for the quantitative studies was about 0.15 mm. (potassium bromide prism).

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¹⁵ Samuel, J., 1960, 1318.
