

**157. The Infrared Absorption Spectra of Normal and <sup>18</sup>O-Labelled Triphenylarsine Oxide.**

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The spectra of normal and *ca.* 90 atom % triphenylarsine [<sup>18</sup>O]oxide have been measured in the 3700—420 cm.<sup>-1</sup> region, for chloroform, bromoform, and acetonitrile solutions, and assignment of the observed bands made. The As=<sup>16</sup>O band at 880 cm.<sup>-1</sup> appears to be the only one which is shifted in the case of the labelled oxide, and the observed shift (40 cm.<sup>-1</sup>) is in agreement with that expected from theory (41 cm.<sup>-1</sup>). The relative integrated absorption intensity of the As=<sup>18</sup>O band is only 82% of that for the As=<sup>16</sup>O 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.<sup>1</sup> As a result it seemed interesting to measure the spectra of the series Ph<sub>3</sub>X=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 [<sup>18</sup>O]oxide and 25 atom % triphenylstibine [<sup>18</sup>O]oxide was therefore carried out. Attempts to synthesize triphenylbismuth oxide were unsuccessful.

The infrared bands observed in the 3700—420 cm.<sup>-1</sup> region for solutions of triphenylarsine oxide in chloroform, bromoform, and acetonitrile are reported in Table 1. The appreciable absorption at *ca.* 3300 cm.<sup>-1</sup> 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 <sub>3</sub>	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 <sub>3</sub>	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 <sub>3</sub>	28	0.2	738(0.87)
Labelled ‡	CHBr <sub>3</sub>	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 <sub>3</sub>	20	0.2	880(0.52)
Labelled ¶	CHCl <sub>3</sub>	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.<sup>-1</sup> region only. ‡ Measured only between 830 and 720 cm.<sup>-1</sup>. § Measured in the 720—420 cm.<sup>-1</sup> region. ¶ Measured only in the 900—800 cm.<sup>-1</sup> 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.<sup>-1</sup> are due to the monosubstituted phenyl rings, although their relative intensities are a little different from those of the usual pattern.<sup>2</sup> The fact that the aromatic 1630 cm.<sup>-1</sup> band appears for triphenylarsine oxide

<sup>1</sup> (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.

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

above the usual range<sup>3</sup> of  $1600 \pm 5 \text{ cm.}^{-1}$  seems analogous to the behaviour for nitrobenzene, ascribed to the electronegativity of the nitro-group.<sup>3</sup> That the intensity of the  $1584 \text{ cm.}^{-1}$  band is almost equal to that of the  $1630 \text{ cm.}^{-1}$  band is interesting since it is usually assumed that the intensity of the  $1580 \text{ cm.}^{-1}$  band is comparable to that at  $1600 \text{ cm.}^{-1}$  only in conjugated rings.<sup>4</sup> However, the ultraviolet absorption of triphenylarsine oxide proves the absence of such conjugation here by showing the same spectrum as benzene itself [ $\lambda_{\text{max.}}$  in propan-2-ol]  $2580 (\epsilon 206)$ ,  $2640 (250)$ , and  $2700 \text{ \AA} (210)$ . In triphenylphosphine oxide also the conjugation between the phenyl rings and the P=O group is only very limited.<sup>1b,5</sup> It seems therefore that the intensity of the  $1580 \text{ cm.}^{-1}$  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  $1434 \text{ cm.}^{-1}$  are analogous to the bands for heavily mono-substituted benzenes at about  $1480$  and  $1446 \text{ cm.}^{-1}$  reported by Katritzky and Lagowski<sup>6</sup> and assigned by them to  $A_1$  and  $B_1$  C-C stretching, respectively. The  $1086$  and  $999 \text{ cm.}^{-1}$  bands appear to be related to those reported by them<sup>6</sup> at about  $1073$  and  $996 \text{ cm.}^{-1}$ , and assigned to a  $B_1$  in-plane C-H bending and an  $A_1$  ring vibration, respectively. The strong band at  $880 \text{ cm.}^{-1}$  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 reported<sup>7</sup> to absorb at  $880 \text{ cm.}^{-1}$ .

The strong  $738 \text{ cm.}^{-1}$  band appears also in the spectrum of triphenylarsine (at  $736 \text{ cm.}^{-1}$ ) and was assigned there to the out-of-plane  $C_{\text{Ar}}\text{-H}$  bending vibration.<sup>8</sup> The  $693 \text{ cm.}^{-1}$  absorption must be assigned to a C-C-C deformation ( $\nu_8$  according to the notation of Herzberg<sup>9</sup>) since this vibration is known to absorb in the  $688\text{--}693 \text{ cm.}^{-1}$  region in  $\text{Ph}_n\text{X}$  compounds where X belongs to the fifth group of the Periodic Table.<sup>10</sup> Triphenylarsine also absorbs near  $695 \text{ cm.}^{-1}$ , although it seems to have been wrongly assigned.<sup>8</sup>

The band at  $512 \text{ cm.}^{-1}$  is probably due to the  $C_{\text{Ar}}\text{-AsO}$  stretching since the analogous C-P stretching seems to be in the  $650\text{--}710 \text{ cm.}^{-1}$  region.<sup>11</sup> 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  $600 \text{ cm.}^{-1}$ .

Finally, the doublet at  $479\text{m}$  and  $460\text{w} \text{ cm.}^{-1}$  can be assigned to an out-of-plane  $C_{\text{Ar}}\text{-AsO}$  bending mode (Herzberg's<sup>9</sup>  $\nu_{19}$ ), split into two components in  $\text{Ph}_3\text{R}$  molecules;<sup>12</sup> this bending gives rise to a doublet at  $490\text{s}$  and  $\sim 432\text{w} \text{ cm.}^{-1}$  for triphenylphosphine, and a band at  $460 \text{ cm.}^{-1}$  for triphenylstibine.<sup>12</sup>

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  $40 \text{ cm.}^{-1}$  can be compared with the value of  $41 \text{ cm.}^{-1}$  calculated for the diatomic

<sup>3</sup> Ref. 2, p. 71.

<sup>4</sup> Ref. 2, p. 72.

<sup>5</sup> 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.

<sup>6</sup> Katritzky and Lagowski, *J.*, 1958, 4155.

<sup>7</sup> Goodgame and Cotton, *J.*, 1961, 3735.

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

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

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

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

<sup>12</sup> 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  $\text{cm}^{-1}$  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 $\text{CHCl}_3$ )	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	Optical density	Mol. extinction coeff. (l. mole $^{-1}$ $\text{cm}^{-1}$ )	Half- width ( $\text{cm}^{-1}$ )	Integrated absorption (l. mole $^{-1}$ $\text{cm}^{-2}$ )
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  $\text{cm}^{-1}$  absorption is a "pure" band and no other bands are affected by the  $^{18}\text{O}$ -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  $\nu_n$  is its frequency. Insertion of the measured values of  $\nu_n$  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<sup>1b</sup> 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,<sup>1e</sup> methyl benzoate,<sup>1e</sup> benzophenone,<sup>1a</sup> and dicyclohexylurea,<sup>1h</sup> while a number of other compounds show<sup>1d,f,g,h</sup> 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  $\text{cm}^{-1}$  region, where the  $\text{Sb}=\text{O}$  group is expected to absorb (on the basis of the 880  $\text{cm}^{-1}$   $\text{As}=\text{O}$  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  $\text{cm}^{-1}$ , are almost unaffected by  $^{18}\text{O}$ -labelling (739, 725, and 694  $\text{cm}^{-1}$  for a 25 atom %  $^{18}\text{O}$  content) and can be assigned to the out-of-plane  $\text{C}_{\text{Ar}}-\text{H}$  bending split in the solid state<sup>7</sup> (739 and 725  $\text{cm}^{-1}$ ) and the  $\text{C}-\text{C}-\text{C}$  ( $\nu_8$ ) deformation (693  $\text{cm}^{-1}$ ), respectively, by analogy with the case of triphenylarsine oxide (738 and 693  $\text{cm}^{-1}$ ).

## 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.,<sup>14</sup> 190—191°).

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

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

<sup>14</sup> 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 analysis<sup>15</sup> 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  $90 \pm 2$  atom % of oxygen-18.

*Triphenylstibine* [<sup>18</sup>O] *Oxide*.—Triphenylstibine dichloride (Eastman) (1 g.) was boiled with an excess of <sup>18</sup>O-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 analysis<sup>15</sup> 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. C<sub>18</sub>H<sub>15</sub>OSb requires C, 58.6, H, 4.1%),  $\lambda_{\max}$ . (in Pr<sup>i</sup>OH) 224, 257, 263, and 270 m $\mu$  ( $\epsilon$  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).

We thank Mr. J. Goldberg for technical assistance, Mrs. I. Wasserman for the isotopic analyses, and Mrs. S. Rogozinsky for a Karl Fischer water determination. This investigation was supported in part by a grant from the U.S. Public Health Service.

THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL. [Received, March 29th, 1963.]

<sup>15</sup> Samuel, J., 1960, 1318.

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