The Molecular Structure of Trimethylphosphine Oxide

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Electron diffraction methods were used to find the molecular structure of trimethylphosphine oxide $(CH_3)_3PO$ in the gaseous phase. The most important distances within the molecule are the $P-O$ and the $P-C$ distances, which were found to be 1.48 Å and 1.81 Å, respectively; the angles $C-P-C$ and $C-P-O$ are 106.0° and 112.3°.

Several authors have published results from investigations carried out on phosphine oxides and different acceptor molecules. These results have mainly been obtained from infra-red and Raman-spectroscopic methods. By measuring the variations of the $P-O$ stretching frequency in the addition compounds one observed shifts to lower frequencies compared with the free phosphine oxide. This variation indicates that oxygen is the donor atom in these compounds.[1,2] A shift in the $P-O$ stretching frequency has also been observed in the free phosphine oxides if the substituents on the phosphorus atoms are changed.[3,4] Lately, Lindqvist et al.[5] have carried out a series of investigations on addition compounds between phosphine oxides and various metal halides. These works include structure determinations by X-ray methods, infra-red investigations and thermochemical studies. On the basis of the above it was considered to be of interest to determine the $P-O$ bond distance in the free trimethylphosphine oxide with as great accuracy as possible.

Trimethylphosphine oxide was prepared from $POCl_3$ by means of a Grignard reagent. The product forms highly hygroscopic, white, needle-shaped crystals. These were recrystallized by sublimation. The melting point was found to be 140°C. The electron diffraction apparatus used for the experiments was that of the University of Oslo, Department of Physical Chemistry. Trimethylphosphine oxide was sublimed in the instrument at a nozzle temperature of 105—110°C. Exposures were made at two different distances between the point of scattering and the photographic plate, 477.62 mm and 192.02 mm. Microphotometer recordings of the photographic plates were read off at intervals of $s = 1/4$ Å^{-1}, and the intensity curve treated as described elsewhere.[6] The experimental and theoretical intensity curves are given in Fig. 1.

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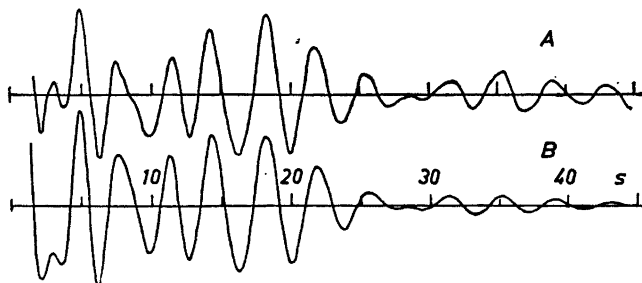
Fig. 1. Intensity curves. A) Experimental. B) Theoretical.

RESULTS AND DISCUSSION

In the radial distribution curve the peaks representing the distances $C-H$, $P-O$, and $P-C$ are well resolved. In Fig. 2 the experimental and theoretical radial distribution curves are reproduced. The difference between the two distances $C-O$ and $C-C$ is relatively small, and the two peaks representing these distances in the radial distribution curve do overlap. The sum of the two peaks can be seen in Fig. 2 as the one broad peak with maximum at about 2.8 Å. The two distances, and also the two angles $C-P-C$ and $C-P-O$ are coupled together, so that we can choose only one of these four values as the variable. The $C-O$ distance was here chosen as the variable. A series of theoretical radial distribution curves with varying $C-O$ distances and the corresponding distance $C-C$ and angles $C-P-O$ and $C-P-C$ were com-

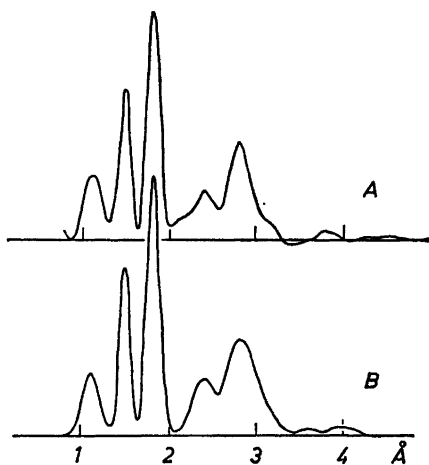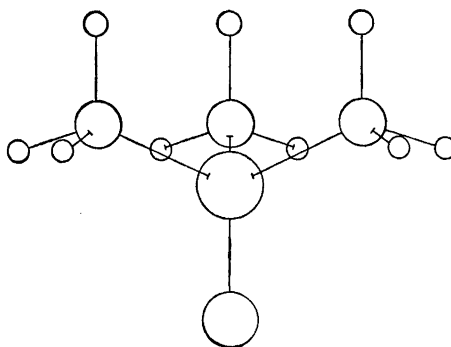*Fig. 2.* Radial distribution curves. A) Experimental. B) Theoretical.

Fig. 3. Model of the molecule $CH_3)_3PO$. The position of the methyl groups shown in the model is the one giving the best agreement between experimental and theoretical curves.

Table 1.

PO	1.47$_9$ Å	CO	: 2.74 Å
CH	1.09$_9$ Å	CC	: 2.90 Å
PC	1.81$_3$ Å	CPO	: 112.$_3$°
PH	2.40 Å	CPC	: 106.$_0$°

pared with the experimental curve in the interval 2—3.5 Å in the radial distribution curve. A value of C—O = 2.74 Å was finally judged to give the best agreement between the experimental and theoretical curve.

The interatomic distances and angles are listed in Table 1. All distances reported in this table are independent of a rotation of the methyl groups. The H—O distance and the H—H and H—C distances between methyl groups are, however, influenced by a methyl group rotation. First a theoretical mean value of the above mentioned distances was calculated, assuming free rotation of the methyl groups. Calculations were also made for a number of different possible fixed positions. The position in which one of the hydrogen atoms is in *trans* position with respect to the oxygen atom was finally chosen, giving the best agreement with the experimental radial distribution curve.

There has been some discussion concerning the nature of the P—O bond. Daasch and Smith [3] have reported a variation in the P—O stretching frequency as the electronegativity of the substituents on the phosphorus atom are changed, from 1170 cm^{-1} in $(CH_3)_3PO$ to 1310 cm^{-1} in $(CH_3O)_2FPO$. As can be seen, the P—O stretching frequency is sensitive to changes in the electron density on the phosphorus atom. This sensitivity can be explained if one assumes a high degree of backbonding in the P—O bond by overlap of filled $p\pi$-orbitals of oxygen with the empty $d\pi$-orbitals of the phosphorus atom. This picture of the P—O bond is confirmed by the results from investigations by Lindqvist *et al.*[5] They have by X-ray methods determined the structures of the addition compounds between $SbCl_5$ and Cl_3PO, and $SbCl_5$ and $(CH_3)_3PO$. In the adduct $Cl_3PO \cdot SbCl_5$ the change in the P—O bonding distance was very small, 1.45 Å in the free donor molecule and 1.46 Å in the addition compound, a difference which probably is within the limits of error, but which the authors claim to be significant. In the other compound $(CH_3)_3PO \cdot SbCl_5$ they found the P—O bonding distance to be 1.61 Å. This is a considerable lengthening compared with that of the free phosphine oxide. The large magnitude of the effect of the substitution of Cl for CH_3 may, as the authors claim, indicate that the polarizability is large for the P—O bond, and that this may be due to the existence of a double bond P=O.

Senatore [7] has determined the structure of F_3PO and reports the P—O distance to be 1.45 Å, the same as in Cl_3PO. Both these distances, and the distance 1.48 Å found in the present investigation are considerably less than the expected single-bond distance (~1.7 Å) and suggests that there is considerable back-bonding.

By means of NMR Haake *et al.*[8] have recently measured the dependence of the ^{13}C—H coupling constants on the electronegativity of attached groups on the phosphorus atom in phosphine oxide. From the measurement of the ^{13}C—H coupling constant for trimethylphosphine oxide in D_2O solution, they

conclude that the phosphorus atom in this compound is nearly neutral, and that the P—O bond is best described as a double bond.

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