[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

An Investigation of the Molecular Structure of Phosphorus Oxytrichloride by Electron Diffraction[1]

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The molecular structure of phosphorus oxytrichloride has been reinvestigated by electron diffraction using the visual correlation procedure. The following structural parameters were obtained: P–Cl = $1.99_5 \pm 0.02$ Å., P–O = 1.45 ± 0.05 Å. and $\angle$ClPCl = $103.5 \pm 1°$. These values are significantly different from those obtained in an earlier investigation but are in excellent agreement with a recent microwave determination.

Introduction

An early electron diffraction investigation[2] of the molecular structure of $POCl_3$ gave P–Cl = 2.02 ± 0.03 Å., $\angle$ClPCl = $106 \pm 1°$ with the P–O distance assumed to be 1.58 Å. A recent microwave study[3] produced the following parameters: P–Cl = 1.99 ± 0.02 Å., $\angle$ClPCl = $103.6 \pm 2°$ and P–O = 1.45 ± 0.03 Å. The discrepancy between these results suggested a reinvestigation of the molecular parameters of $POCl_3$ by electron diffraction.

Experimental

The sample of $POCl_3$ was prepared by numerous distillations of the commercial product. The middle cut of the last fractionation was chosen for photographing and the purity was estimated at better than 99%.

A series of photographs was obtained using the method described by Brockway.[4] Several exposures were made on each of several Kodak 33 plates using a camera distance of 107.8 mm. and an electron wave length of 0.05938 Å. (as determined from transmission patterns of zinc oxide). Measurements of three of the best plates by three independent observers led to the q_0 values listed in Table I and the visual curve shown in Fig. 1.

TABLE I

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR $POCl_3$

Max.	Min.	q_{obs}	B_5 q/q_0	C_8 q/q_0
1		15.13	(0.938)	(0.934)
	2	18.38	(0.964)	(0.958)
2		21.68	(0.991)	(0.991)
	3	25.35	(0.999)	(1.000)
3		28.42	(0.993)	(0.989)
	4	30.55	(0.967)	(0.945)
4		33.99	(0.982)	(0.975)
	5	37.76	0.991	0.987
5		41.62	0.998	1.010
	6	48.39	1.004	1.000
6		52.99	0.993	0.988
	7	56.23	1.005	0.996
7		58.90	....	(1.007)
	8	61.33	....	(0.987)
8		64.14	0.991	0.994
	9	67.86	0.998	0.996
9		71.41	1.005	1.001
	10	74.38	1.019	1.013
10		77.40	1.010	1.001
	11	81.35	0.981	0.983
11		83.22	1.006	1.005
	12	87.84	0.997	0.996
12		91.34	1.000	.997
	13	95.05	0.995	.993
13		97.66	0.997	.991
	14	100.31	(0.995)	(.992)
14		102.25	(1.011)	(1.009)
		Av.	0.999	0.997
		Av. dev.	0.007	0.007

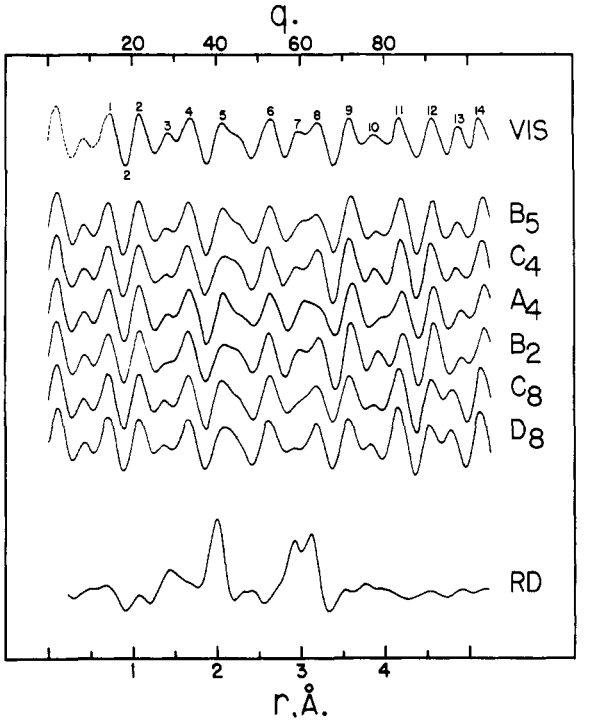

Fig. 1.—Intensity and radial distribution curves for $POCl_3$.

Correlation Procedure

Theoretical intensity curves were calculated according to the equation

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \sin \frac{\pi}{10} q r_{ij}$$

using the punched card method.[5] Assuming C_{3v} symmetry, the P–Cl distance was fixed at 2.00 Å. and the remaining parameters (P–O distance and $\angle$ClPCl) were varied. The range of parameters covered is shown in Fig. 2; the dotted line encloses the parameter field of acceptable models. Of these, the curves for models B_5 and C_4 are shown in Fig. 1.

(1) From the M.S. Thesis of G. R. Badgley, Purdue University, 1951–1953.

(2) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

(3) Q. Williams, J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).

(4) L. O. Brockway, *Revs. Mod. Phys.*, **8**, 231 (1936).

(5) P. A. Schaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

The limits of acceptable shapes for the unresolved pair, maxima seven and eight, are indicated by these curves.

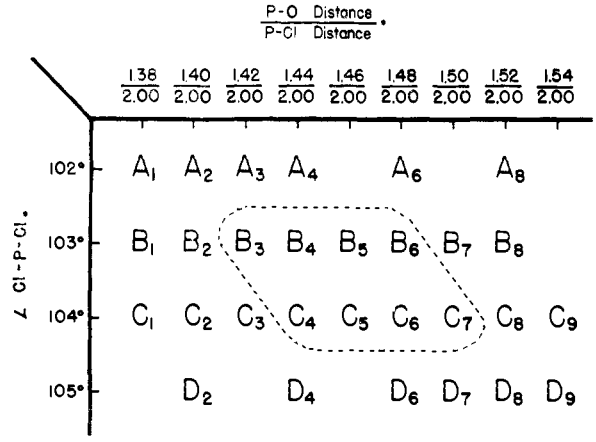

Fig. 2.—Parameters for calculated models of $POCl_3$.

In setting the limits of the acceptable models, the unsatisfactory models of the parameter field were rejected for the following reasons.

Curves for models A_4, A_6 and A_8 were rejected because of the discrepancy in the shape of maxima seven and eight. Curves A_1, A_2 and A_3 are satisfactory as regards these features but are not correct in that the intensity of maximum eleven is much too low, being much lower than in curve A_4. The latter curve is shown in Fig. 1.

The main discrepancy in curve B_2 is also the low intensity of maximum eleven; curve C_3 is better in this respect but the shape of the fifth peak is entirely wrong in this curve. Curve B_7 has maxima seven and eight wrong and maximum ten is virtually absent. In curve C_8 the seventh maximum is almost completely missing and the eleventh maximum is too intense. Of this group, curves B_2 and C_8 are shown in Fig. 1 since they are actually somewhat more nearly acceptable than C_3 and B_7.

Of the 105° models, D_2, D_4 and D_6 give rise to curves with a completely wrong shape for maximum five. D_8 is nearly satisfactory in this respect but has maximum seven too weak, maximum eleven too strong and minimum eleven too deep as compared with minimum ten. Curve D_8 is shown in Fig. 1.

In addition to the above, curves were calculated for a few models in which account was taken of vibrations of the atoms. With reasonable values of vibrational damping factors, no significant changes in the agreement of curves resulted.

The mean q/q_0 values for models B_5 and C_5 are listed in Table I. The values in parentheses are not included in computing the averages because the measurements on these features were not considered to be sufficiently reliable. The average deviation from the mean of the q/q_0 values for all acceptable models was 0.006 or 0.007.

A radial distribution curve[6] was calculated using the function

$$rD(r) = \sum_{q\min}^{q\max} I_{obs}\, e^{-bq^2} \sin\,(\pi/10)qr$$

where $e^{-bq^2} = 0.10$ for $q = 100$. This curve is shown in Fig. 1; its strongest peaks correspond to the values listed opposite RD in Table II.

TABLE II

INTERATOMIC DISTANCES IN $POCl_3$ FROM ACCEPTABLE MODELS

Model	P–O	P–Cl	O–Cl	Cl–Cl	∠Cl–P–Cl
B_3	1.421	2.002	2.913	3.133	103°
B_4	1.440	2.000	2.920	3.130	103°
B_5	1.459	1.998	2.937	3.127	103°
B_6	1.479	1.998	2.947	3.127	103°
C_4	1.437	1.996	2.904	3.144	104°
C_5	1.456	1.994	2.911	3.141	104°
C_6	1.474	1.992	2.928	3.137	104°
C_7	1.492	1.990	2.945	3.134	104°
RD[a]	1.445	1.986	2.916	3.110	

RESULTS OF THIS INVESTIGATION

P–O distance	1.45 ± 0.05 Å.
P–Cl distance	1.99_5 ± 0.02 Å.
O–Cl distance	2.92 ± 0.05 Å.
Cl–Cl distance	3.13 ± 0.03 Å.
Cl–P–Cl angle	103.5 ± 1°

[a] Radial distribution curve.

The values of the interatomic distances listed for the acceptable models in Table II are those obtained by multiplication of the assumed distances by the average of q/q_0 for each model. The final results, based on a model midway between B_5 and C_5, are also listed in Table II.

Discussion

The results of this investigation are in excellent agreement with those given by the microwave determination (see Introduction). The present results are not, however, in agreement with those of the earlier electron diffraction study.[2] A model corresponding to the parameters of the earlier diffraction work gives a curve which is in complete disagreement with the visual curve shown in Fig. 1. In the earlier investigation, the diffraction patterns did not extend to as large scattering angle as the ones obtained here and, in addition, the interpretation of the shapes and intensities of maxima seven and eight were different in the two investigations. The latter fact accounts for the difference in shape parameters observed previously and in this investigation.

Gordy[3] has calculated, for comparison with the observed distances, the length of the P–Cl bond using the Schomaker–Stevenson rule and the length of the P–O bond; only the P–Cl distance is in good agreement with the calculated value and a possible explanation of the decrease in the P–O distance has been suggested.

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(6) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).