

changes in the electron-nuclear attractions (ΔNA) and nuclear-nuclear repulsions (ΔNR). Thus a ΔE_i term for each occupied MO, ϕ_i , is given approximately as $\Delta E_i = \langle \phi_i^0 | \Delta NA | \phi_i^0 \rangle + \langle \phi_i^0 | \Delta NA | \Delta \tilde{\phi}_i \rangle$. The corresponding *exact* expression from the IHFT,^{14,17} is $\Delta E^{IHFT} = \langle \psi^0 | \Delta NA | \psi^0 \rangle + \langle \psi^0 | \Delta NA | \Delta \tilde{\psi} \rangle + \Delta NR$, where $\Delta \tilde{\psi} = (\psi/\eta) - \psi^0$, and ψ^0 and ψ are the *exact* N -electron wavefunctions for the undistorted and distorted geometries. Here, $\eta = \langle \psi^0 | \psi \rangle$, $\Delta \tilde{\phi}_i = (\phi_i/\eta_i) - \phi_i^0$ and $\eta_i = \langle \phi_i^0 | \phi_i \rangle$. Then $\Delta E = \Delta E^{IHFT} \approx \sum_i^N \Delta E_i + \Delta NR$. If we let $\Delta H \approx SH' + (S^2/2)H''$ and $\Delta \tilde{\phi}_i \approx S\phi_i'$, then this becomes the usual first- and second-order perturbation-theory formulas based on MO wavefunctions.¹²

Now, the ΔE_i s can be physically *understood* in terms of the Hellmann-Feynman force acting along the path between the two confirmations (of ψ^0 and ψ), via the two components given above. The first component ($\langle \phi_i^0 | \Delta NA | \phi_i^0 \rangle$) gives the energy change for motion of the nuclei, relative to ϕ_i^0 , with no change in ψ_{SCF}^0 . This should be a conceptual component of the thinking of chemists. The term $\langle \phi_i^0 | \Delta NA | \Delta \tilde{\phi}_i \rangle$ gives the modification of the first term due to relaxation of ϕ_i^0 (to ϕ_i) which arises from the *mixing* of the *occupied* MOs with the *unoccupied* MOs (ϕ_k^0 , $k > N$). This is also an important conceptual component in the thinking of chemists, giving rise to the Woodward-Hoffmann HOMO-LUMO "frontier MO" mixing ideas.¹⁵ (Only occupied and unoccupied MOs of *like* symmetry, along the "reaction coordinate", can "mix" to form the new MOs, ϕ_i .) Although the $\langle \psi^0 | \Delta NA | \psi^0 \rangle$ term is nearly always positive it can contain some very negative $\langle \phi_i^0 | \Delta NA | \phi_i^0 \rangle$ components. For example for the "spontaneous bending" of linear H₂O, planar NH₃ and planar CH₄, $\langle 1\pi_z | \Delta NA | 1\pi_z \rangle \approx \lambda \langle 1\pi_z | \bar{H}'' | 1\pi_z \rangle$ is *very negative* ($1\pi_z \rightarrow 3a_1$) and more than accounts for the molecular energy lowering ΔE_{SCF} .¹⁴ (Here $\Delta NA = \Delta \bar{H} = \Delta H - \Delta NR \approx SH' + \lambda \bar{H}''$, $\lambda = S^2/2$.) It is the major component of $\Delta E(3a_1)$ of the Walsh-Mulliken diagram. BeH₂ and BH₃, for which the $1\pi_z$ MO is unoccupied, do not spontaneously bend from linear and planar, respectively.

The $\langle 3a_1^0 | \Delta NA | 4a_1^0 \rangle$ term ($\langle 1\pi_z | \Delta NA | 3\sigma_g^* \rangle$) for linear H₂O) is very small, so HOMO-LUMO mixing is not of much importance to the "allowed" spontaneous bending of linear H₂O and planar NH₃ and CH₄. Frontier MO ideas are *not always* the total explanation for an "allowed" or "forbidden" nuclear arrangement.¹⁵

Here again, within the context of the Hellmann-Feynman theorem or second-order perturbation theory, we *could* say that

H₂O, NH₃, and CH₄ have "bent" equilibrium structures *because* of the $\langle 1\pi_z | \Delta NA | 1\pi_z \rangle$ term.¹⁷ However, this is only one of the many important effects determining the equilibrium structures. We see that every supposedly general *simple* idea of the explanation of molecular geometries and "allowed" nuclear rearrangements is "doomed to failure" in some situations, because many very strong effects determine potential energy surfaces. Perhaps there is some simple general idea, yet to be discovered, which will do this, but it will not be found without careful examination of *all* the important effects such as we have begun here.

Both the high barrier for H₂O and low barrier for NH₃ are "HOMO-LUMO symmetry-allowed" inversion barriers. Because of *three* interproton repulsions in NH₃, ΔNR is very large and nearly destroys an otherwise high inversion barrier. We believe that the quite different behavior of ($E - ER$) in the figures for H₂O and NH₃ is closely related to these very different ΔNR s. Again we see the tremendous complexity of *understanding* the energy surfaces of even these very simple molecules.

Note that ($E_{SCF} - EA$) gives fairly good geometries but too small bond angles and much too high inversion barriers. This corresponds to *distinguishable* electrons occupying orthogonal SCF LMOs. Certainly without the orthogonality (i.e., linear independence) of the MOs the electrons would all tend to "collapse" into a somewhat expanded inner shell on the O atom. Thus antisymmetry does have a great deal of importance to the structure of all atoms and molecules. However, it is not *the* dominating influence for the *angular* structures of H₂O and NH₃. The classical repulsion of the MO charge clouds (CER), nuclear repulsions, electronic kinetic energies, etc., are also of critical importance. Although $\Delta E^{IHFT} \approx \Delta E_{SCF}$ is sensitive to errors in ψ_{SCF} (to first order),¹⁷ we have found it to be reliable for small distortions (e.g., bending of H₂O and NH₃) and highly visualizable in its MO components.¹⁴ ΔE^{IHFT} seems to provide a good beginning toward a *correct* understanding of energy surfaces. Because of the difficulty of accurate quantum calculations for large molecules and activated complexes, this understanding is badly needed. Although the Woodward-Hoffmann HOMO-LUMO terms must be augmented by the $\langle \phi_i^0 | \Delta NA | \phi_i^0 \rangle$ terms for a complete understanding of MO correlation diagrams, the widespread success of the former shows the power of this approach.

Registry No. H₂O, 7732-18-5; NH₃, 7664-41-7.

Molecular PO₂Cl: Matrix IR Investigations and ab Initio SCF Calculations^{1a}

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Contribution from the Institut für Physikalische Chemie und Elektrochemie, Lehrstuhl für Theoretische Chemie, Universität Karlsruhe, 7500 Karlsruhe, FRG, and Anorganisch-Chemisches Institut der Universität Münster, 4400 Münster, FRG. Received June 18, 1985

Abstract: PO₂Cl produced by a photochemical reaction between O₃ and POCl in solid Ar has been studied by IR spectroscopy. The same species is formed in a high-temperature reaction between POCl₃, O₂, and Ag. IR spectra including ¹⁶O/¹⁸O and ³⁵Cl/³⁷Cl shifts show that the OPO angle is about 135° and that the PCl bond is unexpectedly strong ($f(\text{PCl}) = 3.7$ mdyn Å⁻¹). These results are confirmed by ab initio SCF calculations. Bonding in PO₂Cl is compared with that of similar molecules.

Some of us have recently detected analogues of NOCl, for example, the high-temperature molecules POCl,² PSCl,³ AsOCl,⁴

(1) (a) Presented in part at Chemie-Dozententagung, 1984, Konstanz, Verlag Chemie; International Matrix Conference, 1985, Fontevraud. (b) Universität Karlsruhe. (c) Universität Münster.

(2) Binnewies, M.; Lakenbrink, M.; Schnöckel, H. Z. Anorg. Allg. Chem. 1983, 497, 7.

etc., and investigated their structures. In addition to such molecules, in which a group Va element has a formal oxidation state of three and a coordination number of two, there is increasing interest in compounds of phosphorus(V) with a coordination

(3) Schnöckel, H.; Lakenbrink, M. Z. Anorg. Allg. Chem. 1983, 507, 70.

(4) Schnöckel, H.; Lakenbrink, M.; Zhengyan, Lin J. Mol. Struct. 1983, 102, 243.

number of three. The first definitively characterized molecule of this type was (Me₃Si)₂N-P[NSiMe₃]₂.⁵ Since then, other similar molecules have been described in which the phosphorus atom forms two double bonds, e.g. ref 6.⁶ In these cases, at least one of the double-bonded atoms possesses other bulky ligands,⁷ which stabilize the molecule toward the thermodynamically favorable polymerization. A molecule with two PO double bonds is expected to polymerize; until now such species have indeed been isolated only as polymers⁸ or postulated as reactive intermediates.⁹

Our aim was to synthesize a species PO₂X from POX and to investigate its structure with the help of matrix isolation techniques. This seemed especially interesting, since PO₂X has the same number of valence electrons as SO₃ and OSiF₂¹⁰ and occupies an intermediate position between them.

We began our investigation with PO₂Cl, which has recently been detected at high temperatures by Binnewies,¹¹ as a product of reaction 1 by means of its mass spectrum. The matrix isolation



of such a high-temperature equilibrium gas promised to be difficult firstly because the concentration of PO₂Cl is very small and secondly because there are many other species present in the vapor.¹²

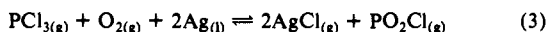
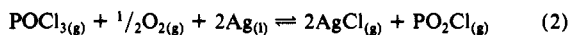
Therefore we synthesized PO₂Cl by photolysis of O₃ in the presence of POCl isolated in a noble gas matrix and have unequivocal evidence for its formation. This result was supported by additional matrix isolation experiments with the high-temperature gas performed in analogy to the mass spectrometric investigations (eq 1).¹¹

In order to gain additional information concerning the electronic and molecular structure, we have furthermore performed ab initio SCF calculations. Here we compare these results with those obtained experimentally.

Technical Details

(a) Preparation and Spectroscopy. PO₂Cl was formed in a matrix photoreaction between POCl² and O₃. The formation of O₃ from O₂ was achieved by means of a static electrical discharge (Tesla coil) in a glass bulb at 77 K. The reaction was monitored by the decrease in pressure. The residual O₂ was pumped off. A suitable concentration of O₃ in the matrix was obtained if the Ar stream was passed over solid O₃ at 84 K. Photolysis was performed in two steps, first as 310 nm and then by a broad-band irradiation (only H₂O filter) for nearly 20 min (Osram HBO 200). Starting with POCl and ¹⁸O₃ we got pure P¹⁶O¹⁸OCl.

We have further succeeded in isolating PO₂Cl as a high-temperature molecule in solid Ar. It was then generated in the high-temperature reactions (2) and (3).¹¹ For this purpose, mixtures (1:5 to 1:10) of



POCl₃/O₂ or PCl₃/O₂ were passed over heated silver at a temperature of 1300 K. The high-temperature equilibrium mixture was condensed with an excess of Ar (1:200 to 1:500) on a helium-cooled Cu surface (ca.

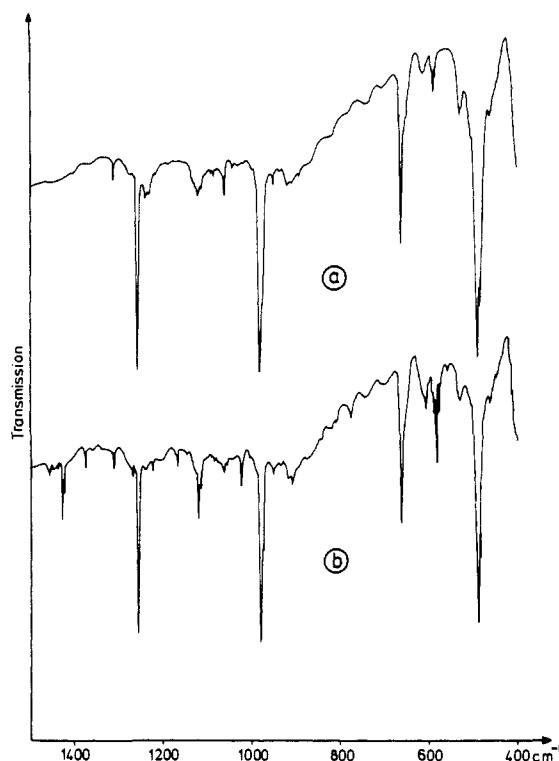


Figure 1. (a) Infrared spectrum of the high-temperature species POCl (POCl₃/Ag) condensed with ¹⁸O₃ in an Ar matrix. (b) Infrared spectrum of the sample after photolysis by a high-pressure mercury lamp for 15 min (310 nm and H₂O filter).

15 K). The conditions were similar to those described for the mass spectrometric investigation of PO₂Cl.^{11,13}

P¹⁸O₂Cl was obtained in the same way by starting with ¹⁸O₂ and P¹⁸OCl₃.¹⁴ However, it was experimentally simpler to pass a mixture of PCl₃/¹⁸O₂ or P¹⁶OCl₃/¹⁸O₂ over heated silver. We generally worked with an Ar matrix. The deposition rates varied between 5 and 10 mmol h⁻¹. Further technical details of the low-temperature apparatus have been described elsewhere.¹⁵

IR absorption spectra have been recorded with a reflection unit including the cold Cu surface covered with the matrix. Two spectrometers have been used: (a) PO₂Cl generated at high temperatures has been detected with a PE 225; (b) PO₂Cl formed in a matrix reaction between O₃ and POCl has been measured with a Bruker IFS 113v FIR instrument.

(b) Details of Computations. Ab initio SCF computations were performed for the electronic ground state of PO₂Cl by using the Karlsruhe version¹⁶ of the Columbus system of programs.^{17,18} A gradient program¹⁹ was used for the geometry optimization.

The following CGTO basis was used: P(11,7,1)/[6,4,1], η(d) = 0.4; O(9,5,1)/[5,3,1], η(d) = 1.0; Cl(11,7,1)/[6,4,1], η(d) = 0.65. The parameters of s and p CGTO basis functions were taken from Huzinaga's tables.²⁰ The basis is of DZP quality, or better, which on the SCF level usually gives geometric structure constants with errors of about 1–2° or pm.

The electronic structure was visualized by means of a population analysis based on occupation numbers.^{21–23} Within this approach the

(5) Niecke, E.; Flick, W. *Angew. Chem.* **1974**, *86*, 126. Pohl, S.; Niecke, E.; Krebs, B. *Angew. Chem.* **1975**, *87*, 284.

(6) Van der Knaap, T. A.; Bickelhaupt, F. *Phosphorus Sulfur* **1983**, *18*, 47. Niecke, E.; Rüger, R.; Lysek, M.; Schöller, W. W. *Phosphorus Sulfur* **1983**, *18*, 35. Appel, R.; Peters, J.; Westerhaus, A. *Angew. Chem.* **1982**, *94*, 76. Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem.* **1983**, *95*, 1008.

(7) This is only valid if O, C, or N atoms are double bonded to P. But heavy atoms like S are able to form more than one double bond to P: Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem.* **1983**, *95*, 1008. Appel, R.; Gaitzsch, E.; Knoch, F. *Angew. Chem.* **1985**, *97*, 574. Borrmann, H.; Binnewies, M. *Chemie-Dozententagung*; Verlag Chemie: Weinheim/Bergstr., Germany, 1985. Roesky, H. W.; Ahlrichs, R.; Brode, S. *Angew. Chem.* **1986**, *98*, 97.

(8) Wannagat, U.; Rademachers, J. Z. *Anorg. Allg. Chem.* **1957**, *289*, 66. Dehnicke, K. *Chem. Ber.* **1964**, *97*, 3358.

(9) Caminade, A. M.; Khatib, F. E.; König, M. *Phosphorus Sulfur* **1983**, *18*, 97.

(10) Schnöckel, H. J. *Mol. Struct.* **1980**, *65*, 115.

(11) Binnewies, M. Z. *Anorg. Allg. Chem.* **1983**, *507*, 77.

(12) POCl, POCl₃, P₄O₁₀, AgCl, and some species, which have not been identified so far (Table I).

(13) An important difference, however, is the density of the molecular beam, which, for matrix experiments, requires only about 10% of that required for the measurement of a mass spectrum. Furthermore we used an Al₂O₃—instead of a SiO₂—Knudsen cell to avoid formation of P₄O₁₀.

(14) P¹⁸OCl₃ is formed by a reaction of ¹⁸O₂ and PCl₃ in a sealed glass ampule, heated to 200 °C for several hours.

(15) Becher, H. J.; Schnöckel, H.; Willner, H. Z. *Phys. Chem. (Wiesbaden)* **1974**, *92*, 33. Schnöckel, H.; Göcke, H. J.; Elspeter, R. Z. *Anorg. Allg. Chem.* **1982**, *494*, 78.

(16) Ahlrichs, R.; Böhm, H. J.; Erhardt, C.; Scharf, P.; Schiffer, H.; Lischka, H.; Schindler, M. *J. Comput. Chem.* **1985**, *6*, 200.

(17) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. Rys, J.; Dupuis, M.; King, H. F. *J. Comput. Chem.* **1983**, *4*, 154.

(18) Pitzer, R. M. *J. Chem. Phys.* **1973**, *58*, 3111.

(19) Schaefer, H. F.; Pitzer, R. M. private communication.

(20) Huzinaga, S. *Approximate Atomic Functions*. Technical Report 1971; University Alberta, Canada.

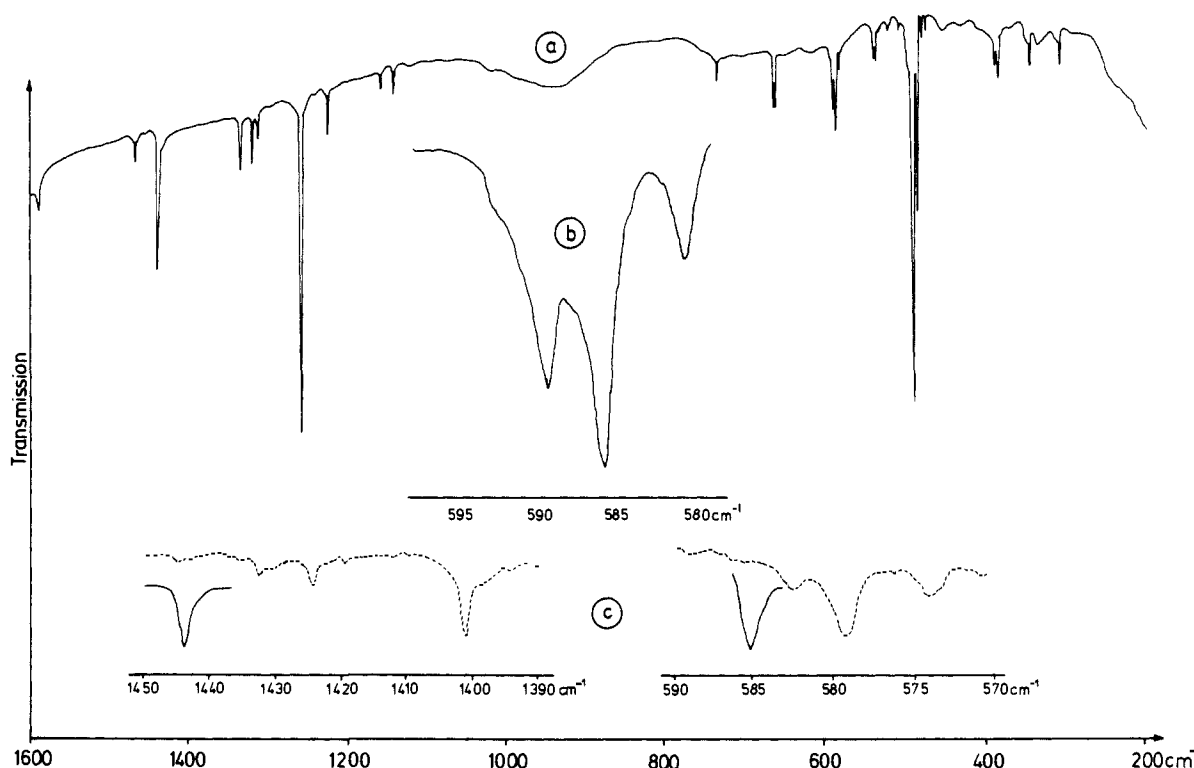


Figure 2. (a) Infrared spectrum of the high-temperature (1300 K) equilibrium gas mixture ($\text{POCl}_3/^{16}\text{O}_2/\text{Ag}$) deposited in an Ar matrix. (b) Expanded scale for POCl vibration of PO_2Cl . (c) Expanded scale for experiments with ^{18}O -enriched samples.

electronic structure is characterized by atomic net charges $Q(A)$ for atom A and the shared electron number $\text{SEN}(AB)$ for the AB bond.²⁴

Results

(1) IR Spectrum after Cocondensation of POCl with O_3 followed by Photolysis. Figure 1a shows the spectrum after cocondensation of POCl (formed by a high-temperature reaction of POCl_3 with Ag) with $^{18}\text{O}_3$ in an excess of Ar.²⁵ In addition to the strong absorptions of POCl (1258, 491 cm^{-1}) and $^{18}\text{O}_3$ (982, 663 cm^{-1}),²⁶ one observes bands of only very low intensity.²⁷ Two of them have to be assigned to POCl_3 (1313, 590 cm^{-1}). In the low-frequency region (450–150 cm^{-1}), which is not shown here, the observed absorptions are also very weak (less than 5% of the strong bands).²⁸

After photolysis (310 nm) for 15 min, the spectrum has changed dramatically (Figure 1b). The intensity of the POCl and O_3 bands

has obviously diminished. At the same time three new bands of medium intensity appear (1429, 1122, and 583 cm^{-1}), apart from some very weak absorptions.²⁹

These three absorptions belong to the same species since they have the same relative intensity under different conditions. The two absorptions with the highest energy further show the same structure.³⁰ Such a site splitting is often observed when molecules are formed in matrix reactions.^{10,31} Annealing the matrix causes similar changes of structure for both bands: the low-frequency component becomes stronger, whereas the other one is diminished.³²

The three observed new bands are in the expected region for the stretching vibrations of a PO_2Cl molecule. This is confirmed by experiments with POCl and $^{16}\text{O}_3$, for which the observed frequencies are listed in Table I. In addition to isotopic splitting, the relative intensity of the PO absorptions confirms the assignment to a PO_2Cl molecule. For $\text{P}^{16}\text{O}^{18}\text{OCl}$ $I(1429)/I(1122)$ is nearly one, whereas for $\text{P}^{16}\text{O}_2\text{Cl}$ $I(1449)/I(1147)$ is about three. This is expected since the symmetric PO_2 vibration should be relatively more intense for the $\text{P}^{16}\text{O}^{18}\text{OCl}$ isotopic species.³³

In the low-frequency region (down to 150 cm^{-1}), there are only absorptions of low intensity. None of the very small bands could be assigned to a PO_2Cl molecule.

(2) IR Spectrum of the Product Formed in the High-Temperature Reaction between POCl_3 , O_2 , and Ag. When a mixture of POCl_3/O_2 (1:3) is passed over heated Ag and condensed with an

(21) Davidson, E. R. *J. Chem. Phys.* **1967**, *46*, 3320. Roby, K. R. *Molec. Phys.* **1974**, *27*, 81.

(22) Heinzmann, R.; Ahlrichs, R. *Theor. Chim. Acta* **1976**, *42*, 33.

(23) Erhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231.

(24) The SEN provides a reliable measure of the covalent bond strength. In order to give the idea of typical values found for the SEN, we list some representative cases: strong σ -bonds (C—C, C—H) 1.4; double bonds (C=C) 2.2; triple bonds (C≡C, N≡N) 3.3. A reduced SEN is found for polar bonds such as in NaF (SEN = 0.3) and for weak bonds such as for Cl_2 (SEN = 0.9) or F_2 (SEN = 0.6).

(25) When POCl was prepared by the passage of a mixture of PCl_3 and O_2 over heated Ag, we observed the formation of PO_2Cl by the matrix reaction with O_3 only in very high dilution, since the matrix "exploded" at higher concentrations. This reaction with its marked concentration dependence appears to be photochemically induced, probably by the spectrometer source (similar effects have also been observed by us in the study of matrix reactions of SiO^{10}). Therefore, starting with $^{18}\text{O}_3$ and POCl_3 , we obtained only the isotopomer $\text{P}^{16}\text{O}^{18}\text{OCl}$. Pure $\text{P}^{18}\text{O}_2\text{Cl}$ has been observed in low concentrations in high-temperature experiments (text).

(26) The deformation vibration of $^{18}\text{O}_3$ is superimposed by that of CO_2 .

(27) See Table I. Such weak features are necessarily difficult to assign.

(28) Besides the hitherto unobserved $^{35}\text{Cl}/^{37}\text{Cl}$ shift of the POCl deformation mode (Table I), one further sees very weak bands of $(\text{AgCl})_n$, $n = 1-3$, including some $^{35}\text{Cl}/^{37}\text{Cl}$. In addition to the feature reported previously (Martin, T. P.; Schaper, H. *J. Chem. Phys.* **1980**, *73*, 3541), the following absorptions have been observed: 156.9 (155.2) and 254.6 (251.4) cm^{-1} for $(\text{AgCl})_2$; 323.5 (320.9) cm^{-1} for $(\text{AgCl})_3$ (^{37}Cl isotopomers in parentheses).

(29) Their relatively large half-width suggests that they do not belong to well-isolated species.

(30) The site splitting is not of comparable size for the absorption at 583 cm^{-1} . In earlier experiments with OAlX species, we found analogous results for high- and low-frequency modes (Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 267).

(31) Schnöckel, H. *Z. Anorg. Allg. Chem.* **1980**, *460*, 37.

(32) This shows that the 1443- cm^{-1} absorption corresponds to the more stable "site". This observation is also in agreement with the high-temperature experiments (Table I).

(33) This is confirmed by rough intensity calculations in which coupling with other vibrations has been neglected. Such calculations predict the intensity ratio $I_{\nu(\text{as})}/I_{\nu(\text{s})}$ to grow by a factor of 1.3 going from $\text{P}^{16}\text{O}^{18}\text{OCl}$ to $\text{P}^{16}\text{O}_2\text{Cl}$ (Burdett, J. K.; Poliakov, M.; Turner, J. J.; Dubost, H. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1).

Table I. Frequencies (cm⁻¹) of Absorptions Observed in the Infrared Spectrum of Ar Matrices: (1, 2) Containing POCl and O₃ after 310-nm Irradiation; (3) of a High-Temperature Equilibrium Mixture (1300 K) Starting with POCl₃, O₂, and Ag^a

1, P ¹⁶ OCl + ¹⁶ O ₃	2, P ¹⁶ OCl + ¹⁸ O ₃	3, POCl ₃ /O ₂ /Ag (1300 K)	identity
		1473 (w) ^b	
1460 (w) ^b	1458 (w) ^b		
1448.3 (m) }	1429.0 (m) }	1443 (m) ^c	P ¹⁶ O ₂ Cl; site
1443.5 (w) }	1424.2 (w) }		P ¹⁶ O ¹⁸ OCl; site
	1375 (w)	1333 (w)	
1375 (w)		1333 (w)	
		1318 (w)	
1312 (w)	1312 (w)	1312 (vw)	POCl ₃
1271 (w)	1270 (w)		
1258.3 (s)	1258.3 (s)	1258 (s)	POCl
	1225 (w)	1225 (w)	?SiO
1175 (w)			
1169 (w)	1169 (w)		
		1157 (w)	
1149 (sh) }			P ¹⁶ O ₂ Cl; 2 sites
1147.5 (w) }			
1144.5 (w) }		1143 (w) ^e	
	1121.9 (m) }		P ¹⁶ O ¹⁸ OCl; 2 sites
	1119.5 (w) }		
	1116.6 (w) ^d }		
1039.9 (vs)			O ₃
	1025 (w)		
	982.1 (vs) }		¹⁸ O ₃
981 (vw)	976.8 (m) ^f }		
	952 (vw)		
909 (vw)	909 (vw)		
826 (vw)			
807 (vw)	775 (w)		
		735 (w)	
704.4 (s)			O ₃
662 (m)	663.4 (s)	662 (w)	CO ₂ ^h
	656 (nw)		
607 (w)	607 (w)		
	590 (w)	590 (w)	POCl ₃
586.3 (m)		586 (m)	P ¹⁶ O ₂ ³⁵ Cl
	582.9 (m)		P ¹⁶ O ¹⁸ O ³⁵ Cl
581.4 (w)		581 (w)	P ¹⁶ O ₂ ³⁷ Cl
	578.1 (w)		P ¹⁶ O ¹⁸ O ³⁷ Cl
491.3 (m)	491.3 (vs)	491 (vs)	POCl
486.5 (m)	486.5 (s)	487 (m)	PO ³⁷ Cl
344.5 (w)		345 (w)	Ag ³⁵ Cl
337.2 (w)	absorp. <400 cm ⁻¹		Ag ³⁷ Cl
308.3 (w)		308 (w)	PO ³⁵ Cl
305.7 (w)			PO ³⁷ Cl

^a 1 and 2 are measured with a Bruker FTIR 113v and 3 with a PE 225 spectrometer. ^b Most of the weak and very weak absorptions are not assigned so far. ^c N₂ matrix: 1448 cm⁻¹. ^d This feature has been used for measuring the isotopic shift (27.9 cm⁻¹) because it is sharper than the other (probably superimposed) absorptions. ^e N₂ matrix: 1145 cm⁻¹. ^f This shoulder has to probably be assigned to a POCl₃-O₃ complex, as its intensity is reduced to 60% after irradiation. In experiment 1 the shoulder of the corresponding band (1039.9 cm⁻¹) is not as pronounced as in this case, but it is also reduced by irradiation. The corresponding deformation mode (704.4 cm⁻¹) is of much lower intensity (in experiment 2 it is superimposed by the CO₂ bending mode: 663.4 cm⁻¹), and therefore the absorption of the POCl₃-O₃ is not observed in this region. ^g Features identical with those in experiment 1. For lower frequencies, see ref 28. ^h In experiment 2 the concentration of CO₂ is higher than in the other experiments, and therefore aggregates broaden this absorption.

excess of Ar, one obtains the spectrum illustrated in Figure 2. Besides the two most prominent absorptions of POCl (1258, 491 cm⁻¹), there are some other bands of low-to-medium intensity. The strongest absorptions occur at 1443 and 586 cm⁻¹. According to our discussion above, they have to be attributed to PO₂Cl.³⁴

As some POCl₃ is also present in the vapor (1313, 590 cm⁻¹), its strong PCl vibration almost coincides with that of PO₂Cl (586 cm⁻¹). Therefore, this region of the spectrum is shown with ordinate and abscissa expansion (Figure 2b).

Weaker bands at 1473, 1333, 1318, and 1157 cm⁻¹ are tentatively assigned to hydrolysis products.³⁵ Above 1000 cm⁻¹ there remain only two bands: 1225 cm⁻¹, possibly due to SiO, and 1143 cm⁻¹. The latter band has to be attributed to PO₂Cl in agreement with the results of subsection 1.³⁶

In the low-energy part of the spectrum, only absorptions at 308 (POCl), 345 (AgCl), and 662 cm⁻¹ (CO₂) could be assigned.

Only small amounts of P¹⁸O₂Cl have been deposited since the ¹⁸O₂ consumption for this preparation is very large.³⁷ Therefore, only two intense absorptions of P¹⁸O₂Cl could definitely be assigned:³⁸ 1401 and 579 cm⁻¹. Because of the inevitable ¹⁶O/¹⁸O exchange with the furnace material, the corresponding vibrations of the P¹⁶O¹⁸OCl isotopomer can be seen with low intensity at 1424 and 583 cm⁻¹. This is demonstrated in Figure 2c. These frequencies are also in agreement with our former results.

(3) **Summary of the Spectra.** In the preceding sections, we have described how two independent methods, one a matrix reaction, the other a high-temperature synthesis, lead to the same product. ¹⁸O substitution and naturally occurring ³⁵Cl and ³⁷Cl show this product to have two equivalent oxygen atoms together with a lone chlorine atom. Hence, the mass spectroscopic investigations¹¹ and the results obtain by matrix isolation show that this can only be the molecule PO₂Cl.

(4) **Force Constant Calculation.** A planar PO₂Cl molecule should exhibit six vibrations (C_{2v}: 3A₁ + 2B₁ + 1B₂), but only the three stretching vibrations were observed. Although further information can be obtained from the ¹⁶O/¹⁸O shifts of these vibrations and from the ³⁵Cl/³⁷Cl shift of ν(PCl), the potential function of the GVFF is nevertheless underdetermined. By assuming plausible frequencies for the two remaining deformation modes,³⁹ we have endeavored to obtain a meaningful set of force constants. Calculations on P¹⁶O¹⁸OCl can be performed with the same symmetry force constants as for the more symmetrical PO₂Cl, provided the original (C_{2v}) symmetry coordinates are transformed accordingly.⁴⁰

B₁ Symmetry. This representation includes the PO₂ stretching vibration ν_{as}(PO₂) at 1448 cm⁻¹ and the rocking mode ρ(PO₂). The ¹⁶O/¹⁸O shift of ν_{as} is 42.45 cm⁻¹.⁴¹

Extensive calculations, which are not discussed here, in which different values for the rocking frequency (range 250–450 cm⁻¹) and values for a limited range of F[ν_{as}(PO₂)/ρ(PO₂)] are employed show that the OPO angle lies between 130° and 140°.⁴²

(34) The highest frequency observed so far for a PO stretching mode is 1443 cm⁻¹. The differences between the measured absorptions and the results discussed above are caused by different sites and the presence of different species in the two experiments (see ref 32).

(35) Their intensity increases when small amounts of H₂O are passed through the reaction cell. A more extensive study of such hydrolysis products is under way.

(36) Despite the fact that the intensity of the 1143-cm⁻¹ absorption does not exactly parallel that of the 1443-cm⁻¹ band in every experiment.

(37) In addition to the preparation of P¹⁸OCl₃, much ¹⁸O₃ is consumed as its concentration has to be 5–10 times higher than that of P¹⁸OCl₃ in the high-temperature equilibrium.

(38) A very weak absorption at 1093 cm⁻¹ probably belongs to this molecule as well.

(39) The two in-plane deformation modes are estimated to be at 290 (B₁) and 450 cm⁻¹ (A₁). This is in agreement with extensive force constant calculations (v.i.). The out-of-plane motion (B₂) is not discussed here; its frequency should be nearly 400 cm⁻¹.

(40) The 5 A' modes in P¹⁶O¹⁸OCl (C_v symmetry) can be calculated with the elements of the G and F matrices (15 elements, respectively). With linear combinations for the symmetry coordinates like those in the more symmetrical PO₂Cl (C_{2v}), six elements of the F matrix and four of the G matrix will be zero (as in the C_{2v} case). Only two G elements will have small values, e.g. G[ν(PO₂)_{sym}/ν(PO₂)_{asym}] = 0.5(1/m¹⁶O - 1/m¹⁸O).

(41) The corresponding isotopic shift of P¹⁶O₂Cl/P¹⁶O¹⁸OCl is 19.3 cm⁻¹ (1448.3–1429.0 cm⁻¹). After a correction for anharmonicity (Becher, H. J. *Fortschritte der chemischen Forschung*; Springer: Berlin, 1968; Vol. 10), the shift increases to 42.9 cm⁻¹ for P¹⁸O₂Cl (or 19.5 cm⁻¹ for P¹⁶O¹⁸OCl). Only such corrected values can be used for any strict comparison with the results of a normal coordinate analysis.

Table II. Calculated Force Constants and Isotopic Shifts (A_1)^a

$\delta(\text{PO}_2)$, cm^{-1}	$\nu(\text{PO}_2)$, $\text{mdyn } \text{Å}^{-1}$		$\nu(\text{PCl})$, $\text{mdyn } \text{Å}^{-1}$		$\delta(\text{PO}_2)$, $\text{mdyn } \text{Å}^{-1}$		$\Delta\nu(^{16}\text{O}_2/^{16}\text{O}^{18}\text{O})$, cm^{-1}			$\Delta\nu(^{35}\text{Cl}/^{37}\text{Cl})$, cm^{-1}		
	F_{11}	F_{12}	F_{13}	F_{22}	F_{23}	F_{33}	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
350	10.44	0.0	0.0	3.93	-0.3	0.28	28.24	2.12	7.01	0.12	7.82	1.39
400	10.41	0.0	0.0	3.80	-0.3	0.37	28.06	2.50	8.01	0.11	6.76	2.33
400	10.43	0.0	0.0	4.05	-0.4	0.36	28.20	2.10	8.23	0.12	7.86	1.57
400	10.48	0.0	0.05	3.78	-0.3	0.37	28.30	2.44	7.96	0.11	6.70	2.37
400	10.44	0.05	0.0	3.79	-0.3	0.37	28.19	2.44	8.01	0.10	6.75	2.34
450	10.40	0.0	0.0	3.88	-0.4	0.47	27.98	2.75	8.93	0.10	6.19	3.06
450	10.39	0.0	0.0	3.68	-0.35	0.49	27.92	3.43	8.43	0.10	5.08	3.92
450	10.38	0.0	0.0	3.30	-0.30	0.53	27.89	5.20	7.10	0.08	3.00	5.54
450	10.46	0.0	0.05	3.66	-0.35	0.49	28.18	3.40	8.36	0.09	4.97	4.01
450	10.42	0.05	0.0	3.67	-0.35	0.49	28.05	3.38	8.42	0.08	5.06	3.95
450	10.49	0.05	0.05	3.64	-0.35	0.49	28.31	3.35	8.35	0.08	4.95	4.03

^aThis calculation was based on $\nu_1 = 1145 \text{ cm}^{-1}$, $\nu_2 = 586 \text{ cm}^{-1}$, $\nu_3 = 450 \text{ cm}^{-1}$ (estimated, cf., text). The following isotopic shifts (cm^{-1}) have been observed (corrections in parentheses): $\Delta\nu(\text{PCl})(^{35}\text{Cl}/^{37}\text{Cl}) = 4.82$ (4.9); $\Delta\nu(\text{PCl})(^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}) = 3.38$ (3.4); $\Delta\nu(\text{PO}_2)(^{16}\text{O}/^{16}\text{O}^{18}\text{O}) = 27.9$ (28.2). This force field is also in accordance with $\Delta\nu(\text{PCl})(^{16}\text{O}_2/^{18}\text{O}_2) = 6.7 \text{ cm}^{-1}$ from $\text{P}^{18}\text{O}_2\text{Cl}$ generated in high-temperature vapors. Force constants are normalized for $r(\text{PO})$.

Since this result is compatible with the SCF calculations (v.i.), the following treatment is based on the geometry obtained from such calculations, i.e.: $r(\text{PO}) = 144.1 \text{ pm}$, $r(\text{PCl}) = 198.6 \text{ pm}$, $\angle(\text{OPO}) = 135^\circ$. From this geometry and reasonable limits for $F[\nu_{\text{as}}(\text{PO}_2)/\rho(\text{PO}_2)]$ between 0.0 and 0.05 $\text{mdyn } \text{Å}^{-1}$,⁴³ it is possible to fit the measured value of $\nu_{\text{as}}(\text{PO}_2)$ and its $^{16}\text{O}/^{18}\text{O}$ shift to the calculated values if we further assume a frequency for the rocking vibration of 290 cm^{-1} . To summarize, we obtain the following symmetry force constants ($\text{mdyn } \text{Å}^{-1}$):⁴⁶ $F[\nu_{\text{as}}(\text{PO}_2)] = 10.35 \pm 0.05$, $F[\rho(\text{PO}_2)] = 0.37$ (cf. text), $F[\nu_{\text{as}}(\text{PO}_2)/\rho(\text{PO}_2)] = 0.025 \pm 0.025$.

A₁ Symmetry. In this representation one has two stretching modes and one deformation mode: $\nu_s(\text{PO}_2)$, $\nu(\text{PCl})$, and $\delta(\text{PO}_2)$. The symmetric PO vibration at 1143 cm^{-1} (Table I) is in the expected region but of low intensity.³³ Most remarkable is the high value for the $\nu(\text{PCl})$ frequency (586 cm^{-1}). This was the first evidence for an unusually strong PCl bond.^{47,48}

Taking values between 300 and 500 cm^{-1} for the unobserved deformation mode, we have carried out a series of force constant calculations, a selection of which is given in Table II. This shows the following tendency: as the value of $F[\nu(\text{PCl})/\delta(\text{PO}_2)]$ becomes more negative, the value of $F[\nu(\text{PCl})]$ increases; simultaneously, one isotopic shift ($^{16}\text{O}/^{18}\text{O}$) decreases while the $^{35}\text{Cl}/^{37}\text{Cl}$ shift increases. With the aid of these results and the measured shifts (Table I), it is possible to limit the potential function and to obtain plausible frequencies for $\delta(\text{PO}_2)$. As a result this vibration must lie at 450 cm^{-1} , whereas values from -0.34 to $-0.35 \text{ mdyn } \text{Å}^{-1}$ are obtained for $F[\nu(\text{PCl})/\delta(\text{PO}_2)]$.

This then leads to the following force constants ($\text{mdyn } \text{Å}^{-1}$) which are compatible with all observations: $F[\nu_s(\text{PO}_2)] = 10.45$

(42) Investigations of isostructural phosphorus-nitrogen compounds show that an NPN angle of 130 – 140° is typical (see ref 5).

(43) These limits have been deduced from the results of comparable molecules: viz., COCl_2 ,⁴⁴ NO_2Cl ,⁴⁵ and SiOCl_2 ,³¹ where $F[\nu_{\text{as}}(\text{AB}_2)/\rho(\text{AB}_2)]$ has the following values ($\text{mdyn } \text{Å}^{-1}$): 0.293, 0.131, 0.1.

(44) Schnöckel, H. *J. Mol. Struct.* **1975**, *29*, 123.

(45) Müller, A.; Krebs, B.; Fadini, A.; Glemser, O.; Cyvin, S. J.; Brunvoll, J.; Cyvin, N. B.; Elvebredd, I.; Hagen, G.; Vizi, B., *Z. Naturforsch., A* **1968**, *28a*, 1656.

(46) Force constants involving the deformation mode were normalized for the PO distance.

(47) The calculated PCl force constant, as well as the PCl distance obtained by ab initio computations, confirms this first evidence (v.i.).

(48) After extensive force constant calculations, another assignment (viz., $\delta(\text{PO}_2) = 586 \text{ cm}^{-1}$) for this frequency has been discarded. In the case of such an assignment, the value of $\nu(\text{PCl})$ varied between 400 and 500 cm^{-1} . These limits are derived from the value of the PCl force constant of POCl and POCl_3 . But no hint of an absorption in this region has been found, although it should be of medium intensity. On the basis of force constant calculations, the observed $^{35}\text{Cl}/^{37}\text{Cl}$ shift is compatible only with the assignment as a PCl mode. With the alternative assignment $f(\text{PCl})$ would have to be very small to obtain agreement of calculated and measured results (all isotopic shifts of the 586 cm^{-1} band). But this assumption contradicts the quantum chemical results (v.i.). Additionally an assignment to the out-of-plane deformation (B_2) can be discounted on the grounds of the measured $^{16}\text{O}/^{18}\text{O}$ shift.

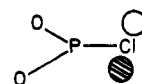
Table III. Population Analysis^{21–23} of POCl , POCl_3 ,^a and PO_2Cl

		POCl	POCl_3	PO_2Cl
at charge	P	0.778	1.221	1.498
	O	-0.469	-0.696	-0.677
	Cl	-0.309	-0.179	-0.151
shared electron no., SEN	PO	1.963	1.526	1.630
	PCl	0.842	0.950	1.022

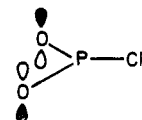
^aResults for POCl_3 are based on the experimentally determined geometry [$r(\text{PO}) = 144.9 \text{ pm}$; $r(\text{PCl}) = 199.3 \text{ pm}$; $\angle\text{ClPCl} = 103^\circ$].

± 0.05 , $F[\nu_s(\text{PO}_2)/\nu(\text{PCl})] = 0.03 \pm 0.02$, $F[\nu_s(\text{PO}_2)/\delta(\text{PO}_2)] = 0.02 \pm 0.01$, $F[\nu(\text{PCl})] = 3.66 \pm 0.02$, $F[\nu(\text{PCl})/c(\text{PO}_2)] = 0.35$ (cf. text), $F[\delta(\text{PO}_2)] = 0.49$.⁴⁹

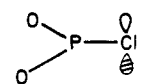
(5) Results of Electronic Structural Computations. First of all we find that PO_2Cl is planar with C_{2v} molecular symmetry. The structural parameters have already been given above (subsection 4). Let us briefly characterize the high-lying MOs since they determine to a large extent the chemical behavior. Starting with the HOMO we got the following IP's according to Koopmann's theorem. $7b_1$: 13.67 eV , in plane, delocalized, dominantly lone pair Cl



$1a_2$: 14.31 eV , π -type nonbonding

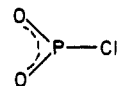


$4b_2$: 14.45 eV , π -type lone pair Cl



$12a_1$: 14.84 eV , σ type, delocalized.

The electronic structure of PO_2Cl is best characterized as



where the dashed line indicates a three-center, four-electron π -system, familiar from the allene anion and often called the

(49) This value corresponds to an estimated frequency of 450 cm^{-1} for $\delta(\text{PO}_2)$.

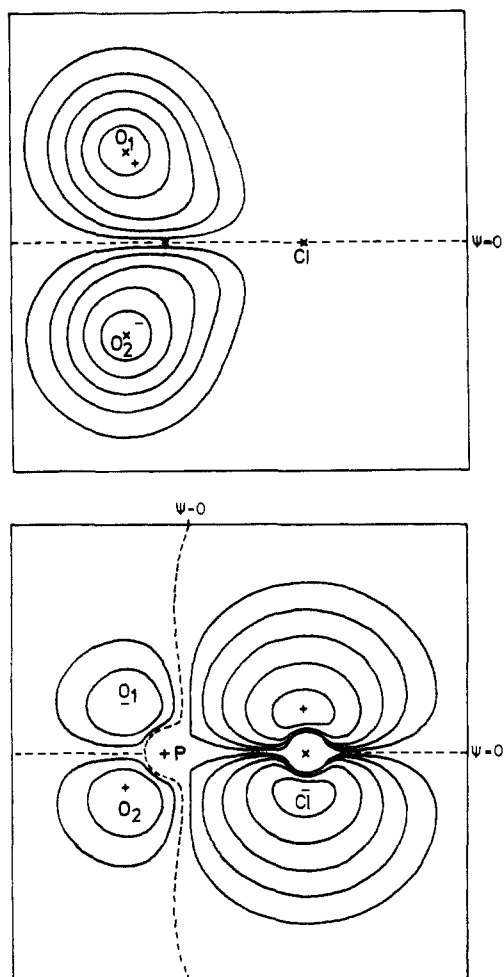
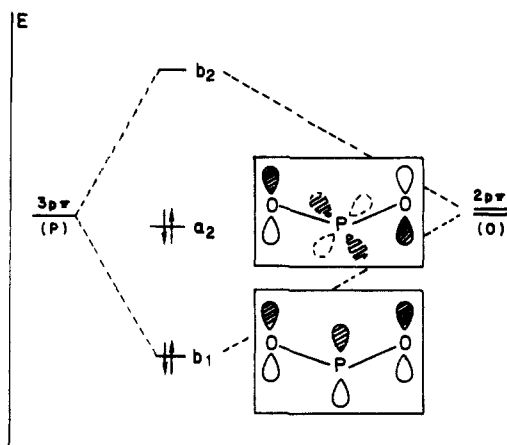


Figure 3. (a, top) Contour diagram of the π -type $1a_2$ MO of PO_2Cl , as discussed in the text. Plotted are the contour lines in a plane 0.8 au above the molecular plane, where the electronic density is (roughly) largest. Plotted values are 0 (dashed), +0.01, +0.025, +0.05, +0.1, +0.2 au. Note the pronounced asymmetry of contour lines with respect to the O_1 - O_2 axis which is mainly caused by phosphorus 3d contributions since 3p(P) AOs do not contribute by symmetry. (b, bottom) Contour lines of the π -type $4b_2$ MO, which is mainly located on Cl. The plane goes through P and Cl and is perpendicular to the molecular plane. Values are plotted as in (a).

Rundle model.⁵⁰ This leads to the following schematic MO diagram for π MOs:



A simple Hückel-type reasoning predicts a π -bond order of ~ 0.7 despite the fact that only one bonding MO, $3b_2$, is occupied. The nonbonding $1a_2$ MO can be stabilized by an admixture of

(50) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112. Discussion of hypervalent molecules by, e.g.: W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262.

phosphorus 3d contributions, which further strengthens the PO bonds. This effect is clearly visible from the contour diagram given in Figure 3a. The $1a_2$ MO is dominantly oxygen 2p (3p AOs of P and Cl cannot contribute by symmetry), and the 3d (P) contribution manifests itself in the pronounced asymmetry with respect to the O-O axis. The Rundle model further predicts a shift of electronic charge from P to O leading to net charges of $Q(O) = -0.5$ and $Q(P) = +1.0$, which is in line with the results of the population analysis discussed further below.

Because of the positive charge on phosphorus, one may wonder about p_π - d_π back-bonding from Cl to P. The contour diagram of the $4b_2$ MO (a π -type lone pair on Cl) shows, in fact, a small but pronounced contribution of the phosphorus 3d AO, cf. Figure 3b.

Discussion

A consistent picture is obtained from the experimental and theoretical results reported in this work. Superimposed on the σ -bond framework there is a four-electron, three-center π -system in the OPO moiety. From this one expects a bond order almost equivalent to a double bond and an accumulation of electrons at oxygen. At first glance the bond angle of 135° may appear somewhat large (as compared to 120° expected for sp^2 hybridization at P), but it is not atypical⁴² since the nonbonded $1a_2$ MO and Coulomb repulsion between O atoms strongly favor the linear structure.

The bonding situation in PO_2Cl is clearly seen from a comparison of its population analysis with that in $POCl$ and $POCl_3$. The results are listed in Table III. We consider mainly the trends across the series $POCl$, $POCl_3$, and PO_2Cl , which, in any case, are more significant than the absolute numbers.

$POCl$ is a normal-valent molecule with a polar PO double bond and a PCl single bond, as indicated by the atomic charges and SEN. As a result of the increased number of electronegative ligands, phosphorus carries a much larger positive charge in $POCl_3$ [$Q(P) = 1.22$] and PO_2Cl [$Q(P) = 1.53$] than in $POCl$ [$Q(P) = 0.78$]. This complicates a comparison between these species. The appreciable charge on P is in line with the Rundle model⁵⁰ for PO_2Cl , as discussed above, and with the idea of a semipolar PO double bond in $POCl_3$. This rationalization is also supported by the SEN of the PO bonds, which, for PO_2Cl and $POCl_3$, indicates covalent contributions stronger than those for a single bond. In both molecules, phosphorus is best considered as a tetravalent P^+ ion, since in each case $Q(P) > 1.0$.

A discussion of the PCl bonds in the three molecules is more straightforward, as here one is dealing basically with a single bond in each case. $POCl$ may serve as a standard for a normal PCl bond, as far as the distance and the force constant are concerned; here the SEN and atomic charges correspond to a polar bond. $f(\text{PCl})_h$ mdyn \AA^{-1} : $POCl$,² 2.20; $POCl_3$,⁵¹ 3.03; PO_2Cl , 3.37. $r(\text{PCl})$, pm: $POCl$,² 206.0; $POCl_3$,⁵¹ 199.3; PO_2Cl , 198.6.

There is a drastic increase in the experimentally determined values of $f(\text{PCl})$ in the series $POCl$, $POCl_3$, and PO_2Cl . The unexpectedly strong PCl bond in PO_2Cl is in line with the results of the SCF calculations⁵² and especially of the population analysis: the increase in $f(\text{PCl})$ is paralleled by a corresponding one in the SEN (PCl), Table III.⁵³

The comparison of NO_2Cl with PO_2Cl reveals marked differences in bonding. The following list of XO and XCl force constants in the molecules $POCl$, $NOCl$, PO_2Cl , and NO_2Cl is instructive. $f(\text{XO})$, mdyn \AA^{-1} : $NOCl$,⁵⁴ 15.3; $POCl$,² 9.8;

(51) Filgueira, R. R.; Blom, C. E.; Müller, A. *Spectrochim. Acta, Part A* **1980**, *35A*, 745.

(52) Force constants calculated by ab initio methods show the same trend: $f(\text{PCl})$ mdyn \AA^{-1} : $POCl$, 2.8; PO_2Cl , 4.06. This trend is not accompanied by a pronounced bond shortening.

(53) By extrapolation [$f(\text{PCl})$ in the molecules $POCl$ and $POCl_3$ (obtained experimentally) and SEN in $POCl$, $POCl_3$, and PO_2Cl], $f(\text{PCl})$ in PO_2Cl was found to be a little bit higher than the value of 3.7 mdyn \AA^{-1} observed in this work. This difference may be attributed to ionic contributions in the PCl bond of PO_2Cl (Table III) which reduce the force constant.

(54) Jones, L. H. *Inorganic Vibrational Spectroscopy*; Marcel Dekker: New York, 1971; p 81.

NO_2Cl ,⁵⁵ 10.4; PO_2Cl , 10.4. $f(\text{XCl})$, mdyn \AA^{-1} : NOCl ,⁵⁴ 1.3; POCl ,² 2.2; NO_2Cl ,⁵⁵ 2.4; PO_2Cl , 3.7.

The force constants demonstrate that nitrogen unlike phosphorus, does not form hypervalent compounds.⁵⁶ Therefore, it appears more appropriate to compare PO_2Cl with molecules such as SO_3 , SO_2Cl_2 , FCIO_2 , OSiCl_2 , and the recently characterized ClIO_2 , for which the following XO force constants have been obtained: $f(\text{XO})$ mdyn \AA^{-1} : SO_3 , 10.25;⁵⁷ SO_2Cl_2 , 10.6;⁵⁸ FCIO_2 , 8.8;⁵⁹ SiOCl_2 , 9.0;³¹ ClIO_2 , 6.0.⁶⁰ This list shows that the PO bond in PO_2Cl is relatively strong.⁶¹

(55) Bernitt, D. L. Miller, R. H.; Hisatsune, I. C. *Spectrochim. Acta, Part A* 1967, 23A, 237.

(56) An analogous comparison between the molecules NF_3 , NOF_3 , PF_3 , and POF_3 is present by: W. L. Jolly, *Modern Inorganic Chemistry*; McGraw-Hill: New York, 1985; p 133 ff.

(57) Lovejoy, R. W. *J. Chem. Phys.* 1962, 36, 612.

(58) Hunt, G. R.; Wilson, M. K. *Spectrochim. Acta* 1962, 18, 959.

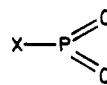
(59) Robiette, A. G. Parent, C. R.; Gerry, M. C. L. *J. Mol. Spectrosc.* 1981, 86, 455.

(60) Hawkins, M.; Andrews, L.; Downs, A. J. Drury, D. J. *J. Am. Chem. Soc.* 1984, 106, 3076.

(61) It is comparable to the strength of SO double bonds, whereas XO double bonds in the fourth and seventh group (Si=O, Cl=O) are significantly weaker.

Conclusions

The structure and bonding of a molecule of the type



are discussed for the first time in this work. Quantum chemical calculations support the experimental findings obtained by vibrational spectroscopy. The most remarkable results for the molecule PO_2Cl , discussed here, are a large OPO bond angle and a strong PCl bond. These results are understandable if we consider electronic structure calculations on molecules like POCl and POCl_3 and if we compare PO_2Cl with other compounds in which phosphorus forms two double bonds.⁶⁷ To get further information on the bonding situation of such species, we will extend our investigation to PO_2Br and PO_2F . The latter will be of particular interest as it is isoelectronic with SO_3 .

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Registry No. PO_2Cl , 12591-02-5; POCl , 21295-50-1; O_3 , 10028-15-6; $^{18}\text{O}_2$, 32767-18-3.

Electronic Excitation and π -Electron Interaction in Borazine

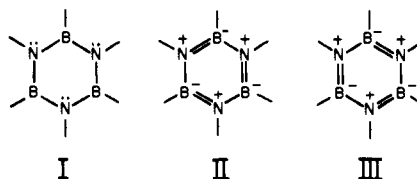
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Abstract: The extent of π -electron interaction in borazine has been investigated by comparing its spectral properties with those of a typical unsaturated molecule, benzene, and benzene's saturated counterpart, cyclohexane. The valence-shell electron energy loss spectrum of borazine is analyzed to reveal the pattern of valence and Rydberg excitations, which is characteristic of a multicenter π -electron chromophore. Though the electronic manifolds of borazine and benzene share a common pattern of Rydberg and valence excitations, the electronic states of borazine do not stand necessarily in a one-to-one relationship with those of benzene. Nonetheless, the magnetic circular dichroism spectra do show that the 7.6-eV band of borazine is closely related to that at 7.0 eV in benzene, both involving doubly degenerate π -electron excitations. In support of the description of borazine as an unsaturated π -electron system, the B 1s and N 1s inner-shell energy loss spectra of borazine are shown to far more closely resemble the C 1s spectrum of benzene than that of cyclohexane. The benzene-like splitting of the π^* MOs of borazine deduced from the inner-shell spectra is abundantly confirmed by the comparisons of the electron transmission spectrum of borazine with those of benzene and cyclohexane. It is concluded that borazine has a planar D_{3h} structure and a delocalized π -electron system much like that of benzene.

Were the borazine molecule $\text{B}_3\text{N}_3\text{H}_6$ represented solely by the valence bond structure I in its ground state, it would exhibit the physical properties characteristic of a saturated system. On the other hand, admitting interaction among the $2p\pi$ orbitals of adjacent B and N atoms leads to structures II and III. Being analogous to the Kekulé structures of benzene, structures II and III of borazine imply unsaturated (aromatic) character in the ground state. Consistent with the π -electron interaction expressed by structures II and III, the B-N distance in borazine (1.44 \AA) is considerably shorter than the 1.57-1.63 \AA which characterize B-N single bonds.¹ The molecule is calculated to have a π -

electron resonance energy² and π -electron delocalization is said to be evident in the NMR spectra.³



In the molecular orbital picture, the $2p\pi$ MOs of borazine cluster into a group of three occupied orbitals in the ground state

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(1) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: London, 1962.

(2) Haddon, R. C. *Pure Appl. Chem.* 1982, 54, 1129.

(3) Hansen, K.; Messer, K. P. *Theor. Chim. Acta* 1967, 9, 17.