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The Homologues of Nitrosyl and Thionitrosyl Halides. Triatomic 18e Molecules Containing N, P, As, or Sb in the Central Position in Comparison to Related Isoelectronic Compounds

MICHAEL BINNEWIES*

Institut für Anorganische und Analytische Chemie der Universität Freiburg, Albertstrasse 21, D-7800 Freiburg, West Germany

HANSGEORG SCHNÖCKEL

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2, West Germany

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Contents

I. Introduction

In this paper we review molecules of the nitrosyl halide type containing the elements P, As, and Sb in the central position. These compounds are compared to the nitrosyl halides as well as to other isoelectronic molecules.

Most chemists are familiar with some members of the small family of triatomic molecules of main-group elements containing 18 electrons in the valence shell. The dihalides of the elements C, Si, Ge, Sn, and Pb have been well-known for many years. All of them have been observed in the gas phase at high temperatures. In the solid state, however, only GeX_2, SnX_2, and PbX_2 (X = halogen) are isolable. Upon quenching SiF_2 vapor, a metastable $(SiF_2)_x$ polymer is formed. At room temperature the half-life of SiF_2 is 150 s.[1] In contrast, the species CF_2 is a short-lived molecule, with a half-life of 1 s.[1] The thermodynamically favored reactions of these two compounds (as examples for other dihalides of carbon and silicon) are disproportionation into the element and the tetrahalide or polymerization.

This consideration shows the well-known trend in stability of main group element compounds in low valence states.

Isoelectronic neighbors of CF_2 in the periodic system are ONF and O_3.[2] The only compound in this row of molecules (FCF, ONF, OOO) that is thermodynamically stable at room temperature is ONF. Its standard heat of formation is −65.7 kJ/mol.[3] It may be interesting that nitrosyl fluoride is the only exothermic nitrosyl halide (ΔH°_{298} = −65.7 kJ/mol[3]). ONCl (ΔH°_{298} = 51.7 kJ/mol[3]) and ONBr (ΔH°_{298} = 82.1 kJ/mol[3]) are metastable compounds; ONI is unknown. Considering the trend in stability of the group IV compounds mentioned above, one would expect an increase in stability of OEX compounds (E = element of group V) with increasing atomic weight of the central atom E. Surprisingly, no molecular compounds of this type containing the heavier homologues of nitrogen as the central atom were known up to 1983. In the following years the formation of several molecules of this type has been described (O=E—X and S=E—X, E = P, As Sb).[4-17]

In contrast to the nitrosyl halides, in the analogous sulfur–halogen–nitrogen system compounds with sulfur in the central position are lower in energy than those with nitrogen. The chemistry of these thiazyl halides has been described in several reviews[18-20] (they are not considered in this paper). Transition-metal complexes of NSX have been prepared.[21,25,26]

The combination of three group VI elements leads also to isoelectronic species. From this type of molecular compound, O_3 was mentioned above. It is metastable (ΔH_{298} = 142.7 kJ/mol[3]) at room temperature. The molecules S_3, Se_3, and Te_3 are not known in the solid state but they are well-known in the vapors of these elements mainly at higher temperatures.[22]

Thermodynamically stable examples of such types of 18e molecules are the dioxides of sulfur, selenium, and tellurium. It should be noted that solid SeO_2 forms infinite chains containing alternating selenium and oxygen atoms.[1] The vapor of SeO_2 consists of monomeric and dimeric OSeO molecules.[1] The structure of solid TeO_2 is more complicated than that of SeO_2. In the vapor above $TeO_{2,s,l}$ the existence of OTeO molecules and oligomers $(OTeO)_{2-4}$ has been proved.[23]

In contrast, SSO is indeed an isolable compound, which is stable with respect to the elements (ΔH°_{298} = −56.5 kJ/mol[3]) but unstable with respect to formation of sulfur and sulfur dioxide.

In this paper we discuss the molecules mentioned above in comparison to isoelectronic neighbors in the periodic system. The formation, thermodynamic stability, vibrational spectra, chemical bonding (from an

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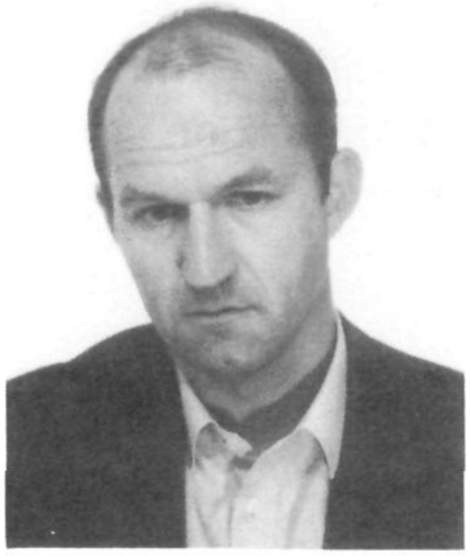

Professor Dr. Michael Binnewies was born 1947 in Hagen, Germany. He studied chemistry at the University of Münster and received his doctoral degree in 1973 under the supervision of Professor Dr. Harald Schäfer with a thesis about complex gaseous metal halides. In the following years he worked on the thermodynamics of solid–gas reactions and studied high-temperature molecules using mass spectrometric techniques. He was appointed professor in 1987 at the University of Freiburg.

Hansgeorg Schnöckel studied chemistry at the University of Münster, where he received his Diplom-Chemiker degree in 1967 under the supervision of Professor Dr. H. J. Becher. In 1970 he obtained his doctoral degree with a thesis about spectroscopy of boron-containing molecules. In the following years he worked on reactive high-temperature molecules, which were studied by IR spectroscopy in solid noble gases. In 1980 he completed his Habilitation in inorganic chemistry. His principal research interests include reactive intermediates (matrix isolation and bonding) and preparative cryochemistry. In 1987 he became apl. professor at the University of Münster. Starting in autumn 1989 he will continue his work at the University of Munich.

experimental and theoretical point of view), and some chemical reactions of these compounds will be discussed in detail.

II. Formation of O=E—X and S=E—X Molecules (E = P, As, Sb)

All molecules of this type are known only in the gas phase at high temperatures but not in the condensed state as a solid or a liquid. This fact means that these molecules can only be detected and characterized by special experimental methods as described in section III.

Solid compounds of this composition such as BiOCl form typical ionic lattices in which molecules no longer are present. These compounds will not be considered here. OBiCl molecules are not known.

The following five types of reaction may lead to O=E—X or S=E—X molecules:

(1) Reduction of phosphoryl halides and thiophosphoryl halides with elementary silver

$$E(O)X_{3,g} + Ag_{s,l} = O{=}E{-}X_g + 2AgX_g$$

Examples are the formation of OPCl (from $P(O)Cl_3$) (T = 1100 K),[4,5] OPBr (from $P(O)Br_3$) (T = 1000 K),[11] OPF (from $P(O)FBr_2$) (T = 1300 K),[12] SPCl (from $P(S)Cl_3$) (T = 1100 K),[6,7] and SPF (from $P(S)FBr_2$) (T = 800 K).[13,14]

(2) Reaction of EX_3/O_2 mixtures with elementary silver

$$EX_{3,g} + \tfrac{1}{2}O_{2,g} + 2Ag_{s,l} = O{=}E{-}X_g + 2AgX_g$$

Examples are the formation of OAsCl (from $AsCl_3/O_2$) (T = 1300 K),[8,9] OSbCl (from $SbCl_3/O_2$) (T = 1300 K),[8,9] and OPBr (from PBr_3/O_2) (T = 1100 K).[11]

(3) Thermolysis of $E(S)X_3$

$$E(S)X_3 = S{=}E{-}X + X_2$$

An example is the formation of SPBr (from $P(S)Br_3$) (T = 500 K).[13,15]

(4) Partial hydrolysis of EX_3 with small amounts of water

$$EX_3 + H_2O = O{=}E{-}X + 2HX$$

Examples are the formation of OPCl (from PCl_3) (T = 700 K)[17] and OPBr (from PBr_3) (T = 700 K).[17]

(5) Thermolysis of $ROPCl_2$ (R = $CH_2{=}CHCH_2$)

$$ROPCl_2 = O{=}P{-}Cl + CH_2{=}CHCH_2Cl$$

An example is the formation of OPCl (from allyl-$OPCl_2$) (T = 1150 K).[16]

The following remarks on the different ways of formation of these 18e molecules are given.

(1) The reaction of phosphoryl halides with silver at temperatures of ca. 1000 K is the simplest and also the best way to form these compounds. All of the reactions mentioned above are strongly endothermic (some hundred kJ/mol), but the entropy term is about +360 J/K mol.[5] Therefore, the position of equilibrium is shifted to the right side with increasing temperature and decreasing pressure. The unusual reducing agent has been chosen for the reduction of phosphoryl halides for a simple reason: silver removes only the halogen but not the oxygen from the starting compound because it forms a stable halide but not a stable oxide. Attempts to use metals like Al or Mg for the reduction have failed; the metal oxides and PCl_3 are formed.[24] When $P(O)F_3$ was used as the initial compound, OPF could not be observed[12] because of the very high thermodynamic stability of $P(O)F_3$. $P(O)FBr_2$, a starting compound with two "weak" P–Br bonds leads, however, to O=P—F in high concentrations. For the thiophosphoryl halides the anticipated side reaction forming Ag_2S and PX_3 has been observed.[6,7,10] This is caused by the higher stability of Ag_2S compared to Ag_2O.

(2) Arsenic and antimony form no stable oxotrihalides. Therefore mixtures of $AsCl_3/O_2$ have been chosen as starting compounds. These reactions are also strongly endothermic.[8]

(3) The thermodynamic stability of $P(Y)X_3$ (Y = element of group VI) decreases with increasing atomic weight of X and Y. In the case of $P(S)Br_3$, the reducing agent silver is not necessary for the formation of S=P—Br. Thermolysis of $P(S)Br_3$ at temperatures somewhat above room temperature leads to the formation of S=P—Br.[13]

(4) Upon reaction of small amounts of water with PCl_3 and PBr_3 at 700 K, O=P—Cl and O=P—Br are formed. This could be confirmed by matrix isolation spectroscopy.[17]

(5) The formation of O=P—Cl by thermolysis of allyl dichlorophosphite at 1150 K has been demonstrated.[16] Several side reactions occur. Reactions of this type are not suitable for obtaining higher concentrations of O=E—X molecules.

III. Investigational Methods

The triatomic molecules considered in this paper have been investigated by special experimental and theoretical methods. The methods are (A) mass spectroscopy in combination with Knudsen cell measurements, (B) photoelectron spectroscopy, (C) matrix isolation of the molecules and vibrational spectroscopy, and (D) quantum chemical calculations.

A. Mass Spectroscopy

The Knudsen effusion method is one of the classical methods for determining vapor pressures and thermodynamic data for solid–gas (or liquid–gas) equilibria. The applicability of this method was enlarged by combining Knudsen cell evaporation with mass spectroscopic detection of the species leaving the Knudsen cell. In this manner it became possible to detect species in low concentrations and to derive their thermodynamic data. Because many readers will not be familiar with this method, a brief description is presented.

A molecular beam consisting of two or more species leaves the effusion orifice of the Knudsen cell. The beam enters the ion source of the mass spectrometer and the molecules are ionized by electron impact. Usually fragmentation of each species in the beam occurs on ionization. The sum of intensities of the fragment ions related to the partial pressure of their parent molecule in the Knudsen cell is given by eq 1 (the assignment of the observed ions to their molecular precursors is sometimes difficult). In eq 1 P_i = partial

$$P_i = f\frac{\sum I_i T}{\sigma_i S_i} \tag{1}$$

pressure of i, $\sum I_i$ = sum of all ion intensities formed by ionization and fragmentation of i, T = equilibrium temperature (K), σ_i = ionization cross section of i, S_i = electron efficiency at the conversion dynode of the multiplier (if used), and f = calibration factor. The partial pressures of all species involved in a given chemical reaction lead to the equilibrium constant of the reaction. From these values thermodynamic data can be derived in the usual way (second law or third law). Figure 1 shows a typical assembly to study high-temperature reactions by this method, used to characterize the compounds discussed here. The same furnace assembly has been used in matrix isolation experiments (cf. section III.C).

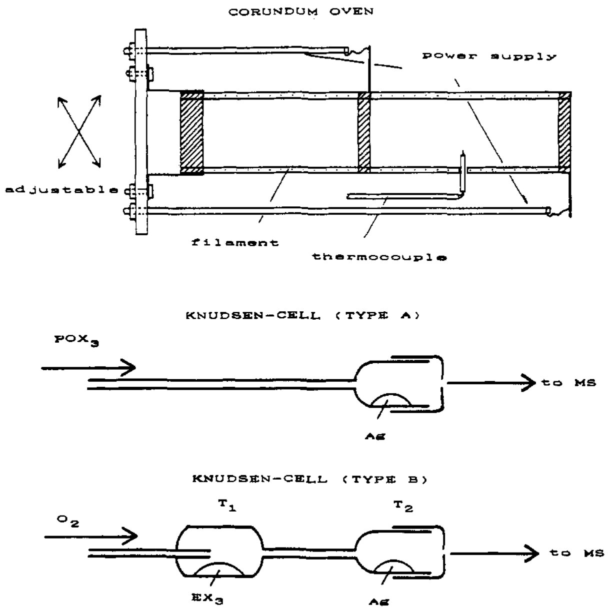

Figure 1.

B. Photoelectron Spectroscopy

Photoelectron (PE) spectroscopy is an important method for the characterization of gaseous compounds, especially short-lived molecules.[35] However, only two of the molecules under discussion (OPCl and SPCl) have been studied by PE spectroscopy.[10] The experimental procedure has been described.[35] Therefore, no further detailed discussion of this method is given here.

The experimental ionization patterns are in good agreement with the results of quantum chemical calculations.

C. Vibrational Spectroscopy and Normal Coordinate Analysis

The vibrational spectroscopy of small molecules provides information about structure and bonding. For example, for the well-known 18e-molecule SO_2, one can derive the value of the bond angle and infer the presence of SO double bonds from the observation of the three fundamental vibrations and their $^{16}O/^{18}O$ isotopic shifts in the gas-phase IR spectrum alone. Understandably, only gas-phase spectra give information about the molecular structure.

Since the molecules under discussion (e.g., OPCl) are only present at low pressure and at high temperatures, they should preferably be measured under these conditions in order to obtain information about their molecular structure. Because of the well-known problems with high-temperature IR spectroscopy, the matrix isolation technique is a good alternative. In this technique gaseous species are cocondensed with an excess of noble gas (e.g., 1:200 in most of the experiments discussed here) on a cooled surface (about 20 K). In this way the interactions among the species are small, comparable to the situation in the gas phase. Also the interactions with the noble gas atoms are small, as the frequency shifts of the gas-phase values are normally only about 1%.

As several reviews on the matrix isolation of high-temperature species have already been published,[36] we shall not discuss this method in detail. The furnace and

TABLE I. Thermodynamic Data and Ionization Potentials of Triatomic 18e Molecules

molecule	ΔH°_{298}, kJ/mol	ref	$\Delta H^\circ_{\mathrm{at},298}$, kJ/mol	ref	S°_{298}, J/(K·mol)	ref	IP_1, eV	ref
O=N—F	-65.7	3	867.2	3	248.1	3		
O=N—Cl	51.7	3	791.9	3	261.7	3	12.7	75
O=N—Br	82.1	3	752.3	3	273.5	3		
O=P—F	-404.4	12	1064.5	12			12.1	12
O=P—Cl	-215.1	5	919.4	5	275.0	5	11.7	10
O=P—Br	10.8	11	706.0	11	292.9	11	10.6	11
O=As—Cl	-30.8	8	703.0	8			11.1	8
O=Sb—Cl	-0.1	8	632.2	8			10.8	8
S=P—F	-260.8	13	950.6	13			9.6	13
S=P—Cl	-11.9	7	745.9	7	285.9	7	10.0	6
S=P—Br							7.7	13
F—C—F	-182.0	3	1057.0	3	240.8	3	11.7	34
F—Si—F	-587.9	3	1196.8	3	256.6	3	11.3	34
F—Si—Cl			1029.3	77				
Cl—Si—Cl	-168.6	3	861.7	3	281.3	3	10.4	76
Br—Ge—Br	-73.3	31	671.9	31, 3				
I—Sn—I	15.9	32	499.2	32				
O—O—O	142.7	3	605.4	3	238.9	3		
S—S—S	141.5	3	690.0	3	269.5	3	9.9	34
Se—Se—Se	176.3	22	530.3	22	318.7	73		
Te—Te—Te	203.9	33	431.7	33				
O=S=O	-296.8	32	1032.8	32	248.2	3	12.3	24
O=S=S	-56.5	3	860.2	3	267.0	3	10.5	74

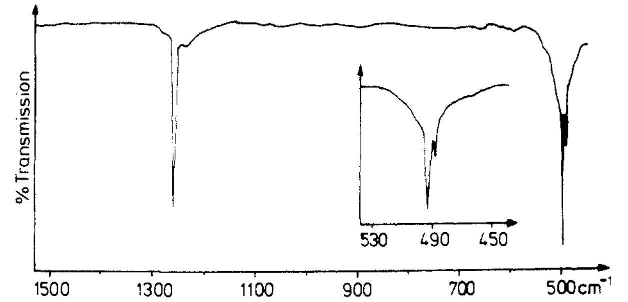

Figure 2. Infrared spectrum of O=P—Cl isolated in solid argon.

the reaction cell for the generation of the analogues of ONX have been described above (section III.A). When the high-temperature gas mixture (e.g., $P(O)Cl_3$, AgCl, and OPCl) leaves the Knudsen cell, it is mixed with an excess of noble gas. Subsequently, this mixture is condensed on a helium-cooled surface separated by about 5 cm from the furnace. The IR spectra as well as the Raman spectra are recorded in a 180° arrangement.

As an example, the data interpretation procedure for the molecule OPCl,[4] the first species in this series, is described.

In Figure 2 the matrix IR spectrum of OPCl is shown. The two stretching vibrations of the triatomic molecule are at 1257.7 $\mathrm{cm^{-1}}$ (ν(PO)) and 489.4 $\mathrm{cm^{-1}}$ (ν(PCl)). The deformation vibration, of much lower intensity, lies at 308.0 $\mathrm{cm^{-1}}$. If the experiment is performed with ^{18}O-enriched samples, each absorption is shifted: 1257.7 → 1211.8 $\mathrm{cm^{-1}}$; 489.4 → 484.7 $\mathrm{cm^{-1}}$; 308.0 → 298.0 $\mathrm{cm^{-1}}$. These data confirm the assignment and the assumption about the sequence of the atoms O–P–Cl. Furthermore, it is possible to limit the bond angle by means of a normal coordinate analysis to a value of 109 ± 5°. This is confirmed by quantum chemical calculations (109 ± 2°), which are discussed later on (section VI). The geometry obtained by quantum chemical methods was the basis for force constant calculations of all molecules under discussion. For OPCl the following data have been obtained (mdyn/Å; deformation constants are normalized to the PO distance): f(PO) = 9.78, f(PO/PCl) = 0.02; f(PCl) = 2.20, f(PO/OPCl) = 0.02; f(OPCl) = 0.53, f(PCl/OPCl) = 0.10. With the help of these force constants, all observed isotopic shifts (^{16}O/^{18}O, ^{35}Cl/^{37}Cl) can be reproduced.

D. Quantum Chemical Calculations

Ab initio SCF calculations were performed for the electronic ground state of the O=P—X and S=P—X molecules (X = F, Cl, Br) by using the Karlsruhe version[37] of the Columbus system of programs.[38-41] The following CGTO basis sets were employed: O, (9,5,1)/[5,3,1], η_d = 1.0; F, (9,5,1)/[5,3,1], η_d = 1.3; P, (11,7,1)/[6,4,1], η_d = 0.4; S, (11,7,1)/[6,4,1], η_d = 0.55; Cl, (11,7,1)/[6,4,1], η_d = 0.65; Br, (14,11,6)/[9,8,2], η_d = 0.26. The parameters of the s and p CGTO basis functions were taken from Huzinaga's tables.[42] 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 1–2 pm. For the Br-containing molecules no relativistic corrections have been taken into account. For the molecules OPF and OPCl calculations were also done including effects of electron correlation by means of single-reference CI(SD) and CPF (coupled pair functional)[43] computations.[44]

In order to visualize electronic structures, population analyses based on occupation numbers have been carried out.[46-48] Within this approach the electronic structures were characterized by atomic net charges Q(A) for atom A and the shared electron number SEN(AB) for the AB bond. The SEN provides a reliable measure of the covalent bond strength.[49]

IV. Thermodynamic Stability

In detail the following triatomic 18e molecules of the nitrosyl halide type have been described: O=N—F, O=P—F, S=P—F; O=N—Cl, O=P—Cl, O=As—Cl, O=Sb—Cl, S=P—Cl; O=N—Br, O=P—Br, S=P—Br. In Table I the thermodynamic data for these and some isoelectronic compounds are listed (heat of formation ΔH°_{298}, heat of atomization $\Delta H^\circ_{\mathrm{at},298}$, entropy S°_{298}, and their first ionization potentials).

TABLE II. Heats of Atomization [(kJ/mol)] of Isoelectronic 18e Molecules

F—C—F 1057.0	O═N—F 867.2	O—O—O 605.4
Cl—Si—Cl 861.7	S═P—Cl 745.9	S—S—S 690.0
Br—Ge—Br 671.9	(Se═As—Br)	Se—Se—Se 530.3
I—Sn—I 499.23	(Te═Sb—I)	Te—Te—Te 431.7
F—Si—F 1196.8	O═P—F 1064.5	O═S═O 1032.8
F—Si—Cl 1029.3	O═P—Cl 919.4	O═S═S 860.2

The heats of formation of molecular compounds are poorly suited for discussion and comparison of thermodynamic stability. In order to compare the standard heats of formation of O═N—Cl and O═P—Cl, one must compare the stability not only of the *compounds* but also of the *elements* in their standard states. The standard states of nitrogen and phosphorus, however, are quite different (gaseous N_2, solid P_4!). Therefore the heats of atomization are much better, comparable values for discussion of thermodynamic stabilities, because here the dissociation of the compound into the *atoms* is considered. The numerical value of the heat of atomization of a molecular compound is equal to the *sum* of all bond energies within the molecule. In the case of molecules containing more than two different atoms, it is impossible to divide exactly the heat of atomization into single values of bond energies. The atomization enthalpies have been derived from the ΔH°_{298} values using literature data[3] (Table I).

Let us first consider the stabilities ($\Delta H^\circ_{\mathrm{at},298}$ in parentheses) within the row of homologous compounds: O═N—Cl (791.9), O═P—Cl (919.4), O═As—Cl (703.0), O═Sb—Cl (632.2). We see a distinct maximum in stability for O═P—Cl. Although at first this seems surprising, there are several other examples of similar trends in main-group chemistry. The best known examples are the dissociation energies of the halogen molecules X_2: F_2 (158.2), Cl_2 (242.7), Br_2 (192.0), I_2 (151.0).[3] This trend is explainable by two familiar effects (e.g., ref 27): (a) repulsion of lone pairs for compounds containing elements of the second row (here O═N—Cl) and (b) support of $p\pi$–$d\pi$ interactions for compounds containing atoms of the third and higher rows (a more detailed discussion of chemical bonding is given in section VI).

The difference in stability between O═N—Cl and O═P—Cl is 127.5 kJ/mol. The difference in stability between O═N—F and O═P—F, however, is somewhat larger (197.3 kJ/mol). Possibly this fact is connected with the extended lone-pair repulsion between nitrogen/oxygen and nitrogen/fluorine. From this very simple point of view, one would expect an extended destabilization of O═N—F compared to O═N—Cl.

It is instructive to survey thermodynamic stabilities for rows of isoelectronic molecules. However, only a few such examples (e.g., NN, CO) are known in inorganic chemistry. The thermodynamic data for the molecules discussed here give several trends in stability within groups of isoelectronic species. In Table II some rows of isoelectronic molecules are listed together with their heats of atomization.

TABLE III. Observed IR Frequencies of the Molecules OPF, OPCl, OPBr, SPF, SPCl, and SPBr in Solid Argon[a]

molecule	ν(OP), ν(SP)	ν(PX)	ν(OPX), ν(SPX)
OPF[b]	1292.2	811.4	416.0
OPCl[c]	1257.7	489.4	308.0
OPBr[d]	1253.0	407.1	253.7
SPF[e]	720.2	791.4	313.6
SPCl[f]	716.1	462.4	229.0
SPBr[g]	712.1	372.1	184.5

[a] Frequencies in cm^{-1}. [b] Reference 12. [c] Reference 4. [d] Reference 11. [e] Reference 14. [f] Reference 7. [g] Reference 15.

It is expected that the sum of bond energies in these molecules should decrease with increasing interatomic distance (FCF···ISnI, ONF···(TeSbI)). It is evident that ozone is an exception to this general rule. Extrapolating the values in the row TeTeTe, SeSeSe, SSS..., one would expect for OOO a heat of atomization of about 750–800 kJ/mol. The measured value of 605.4 kJ/mol, however, is significantly lower. This is due to a special situation in chemical bonding for this molecule, which will not be discussed here.

Consideration of the values in the horizontal rows shows us two remarkable facts: (a) The stability increases from right to left, according to an increasing ionic part in chemical bonding. (b) The stabilities of the compounds in the middle column are approximately the average of those of the isoelectronic neighbors on the left and right side.

This shows that an interpolation or extrapolation of the heats of atomization in rows of isoelectronic molecules is a good way to get information about the thermodynamic stabilities of unknown compounds or unknown values of known compounds.

The discussion given above makes no prediction about the *chemical* stability of these molecules. Up to now we have only considered sums of bond energies. From these values no predictions about possible consecutive reactions such as polymerization, oligomerization, or disproportionation are possible. The chemical reactivity of a compound cannot be given by a numerical value. To make predictions about the chemical behavior of compounds, "chemical intuition" is indispensable.

V. Results from Spectroscopy of the Matrix-Isolated Species

In the manner described above (sections III.A and III.C), the high-temperature molecules OPBr and OPF have been generated and isolated in solid argon. The measured frequencies are listed in Table III. With the help of additional $^{16}O/^{18}O$ isotopic shifts[50] and on the grounds of geometry obtained by quantum chemical computations (section VI), force constants have been calculated (Table IV). These data and especially their sequence are expected: The diagonal force constants decrease from OPF to OPCl to OPBr. On the whole this is also true for the interaction constants. However, small deviations of these constants usually do not have any physical meaning.

The molecule SPCl was the first species to be investigated in the group of analogous sulfides.[7] In contrast to OPCl, the sequence of atoms in SPCl was not immediately evident; for the similar NSF[18–20] species,

TABLE IV. Force Constants of the Molecules OPF, OPCl, OPBr, SPF, SPCl, and SPBr[a]

molecule	F_{11} (P=O) (P=S)	F_{12}	F_{13}	F_{22} (P—X)	F_{23}	F_{33} (OPX) (SPX)
OPF[b]	10.30	0.1	0.2	4.7	0.1	0.62
OPCl[c]	9.78	0.02	0.0	2.2	0.0	0.53
OPBr[d]	9.71	0.0	0.0	1.8	0.02	0.46
SPF[e]	4.87	0.35	0.05	4.3	0.1	0.35
SPCl[f]	4.65	0.2	0.05	2.1	0.0	0.30
SPBr[g]	4.64	0.05	0.1	1.9	0.1	0.28

[a] Force constants in mdyn/Å. [b] Reference 12. [c] Reference 4. [d] Reference 11. [e] Reference 14. [f] Reference 7. [g] Reference 15.

TABLE V. Observed and Calculated Relative Intensities of the Stretching Frequencies of the Molecules OPF and SPF (PSF)[a,b]

	OP/PF (OPF)	SP/PF (SPF)	PS/SF (PSF)
exptl	0.7	0.21	
calcd (SCF)	0.4	*b*	*b*
calcd (MNDO)	0.52	0.13	0.65

[a] Reference 41. [b] Reference 51.

there was an intensive discussion during the 1960s about the stability of the isomers NSF and SNF, finally decided in favor of NSF. However, the bonding of SPCl and of the other SPX species is different. This is illustrated by the matrix IR spectra of ^{34}S-enriched samples. For ^{32}SPCl the following frequencies have been measured (cm^{-1}): ν(PS) = 716.1; ν(PCl) = 462.4; δ(SPCl) = 229.0. Upon ^{34}S substitution ν(PS) is shifted to 705.9 cm^{-1}. No shift was observed for the PCl vibration. Therefore, an arrangement PSCl could be excluded. In this latter isomer sulfur would be involved in all vibrations, and consequently the three frequencies should exhibit a detectable shift. A value of 110° for the SPCl bond angle, first concluded from the spectra, was confirmed by quantum chemical calculations (section VI). On the basis of this geometry the force constants listed in Table IV have been obtained.

For SPF and SPBr as well only the isomers with phosphorus in the central position have been observed. This was concluded from the ^{32}S/^{34}S shift of the IR absorptions[14,15] and from a comparison between calculated and observed intensities of these absorptions (Table V). All frequencies of the molecules SPF and SPBr are listed in Table III. The deformation vibration δ(SPBr) could not directly be detected. Its value was concluded from the first overtone, which is enhanced by a Fermi interaction with ν(PBr).

On the basis of these frequencies and with the help of the geometry resulting from quantum chemical calculations, force constants have been obtained. These are listed in Table IV.

These sulfides show similarities to the oxides: As expected, the diagonal force constants decrease in the direction SPF → SPCl → SPBr.

In summary, for all of OPX and SPX species the structure (sequence of the atoms) and bond angle can be deduced from the IR spectra. The force constants calculated from the observed vibrational frequencies show that in these molecules PO or PS double bonds and PX single bonds are present.

When the high-temperature molecule OAsCl is isolated in solid Ar, the following IR absorptions are measured (cm^{-1}): ν(AsO) = 984.4; ν(AsCl) = 378.7.[9] The ^{18}O isotopomer shows absorptions at 938.4 and 371.6. With the help of these data and some additional constraints, a value of 105 ± 5° could be deduced for the bond angle. The following force constants are calculated (mdyn/Å): f(AsO) = 7.5; f(AsCl) = 2.0. For the deformation vibration a value of 200 cm^{-1} has been estimated.

TABLE VI. Computed Properties of OPF, OPCl, OPBr, SPF, SPCl, SPBr, PSF, PSCl, and PSBr Obtained by SCF, Cl(SD) and CPF Methods(a)

molecule (XPY)	method[b]	R_e(XP)	R_e(PY)	∠XPY	μ	E[c]
OPF	SCF[d]	143.8	157.6	108.7	2.5	-515.090586
	SCF	142.6	154.9	109.9	2.5	-515.124194
	CI(SD)	144.0	155.9	109.7	2.2	-515.649893
	CPF	145.6	157.6	110.0	1.8	-515.718082
OPCl	SCF[d]	143.7	206.6	109.0	2.5	-875.068811
	SCF	142.9	205.5	109.2	2.3	-875.097088
	Cl(SD)	144.6	203.9	109.7	2.0	-875.575115
	CPF	146.4	204.9	109.8	1.6	-875.648424
OPBr	SCF[d]	144.8	227.7	109.0	2.4	-2987.944509
SPF	SCF[d]	188.0	159.4	108.4	1.4	-837.696720
SPCl	SCF[d]	188.5	207.2	109.6	1.3	-1197.682437
SPBr	SCF[d]	188.9	228.3	109.5	1.3	-3310.562107
PSF	SCF[d]	189.1	164.1	110.8	2.0	-837.601478
PSCl	SCF[d]	190.1	214.2	113.1	2.3	-1197.609657
PSBr	SCF[d]	188.9	238.2	114.1	3.0	-3310.496678

[a] Distances in pm, dipole moment μ in D, total energy in au. [b] Method of computation and basis set used as described in the text. [c] At the given geometry. [d] "Small" CGTo basis: O, F, [6,3,1]; P, S, Cl, [7,4,1]; Br, [9,8,2].

The value of the AsO force constant indicates an AsO double bond. For As(O)Cl$_3$ this constant has the same value.[53]

VI. Ab Initio Calculations

A. Results

There are no experimental results from electron diffraction or microwave spectroscopy that allow the accurate determination of the geometrical structure of the molecules under discussion. Thus, in this section we present structural data obtained by quantum chemical calculations. In Table VI we have collected computed results for the geometrical structure of O=P—X and S=P—X molecules obtained by different methods: SCF, CI(SD), and CPF for O=P—F, and O=P—Cl; SCF for all other molecules.[10,12,30,40,41,54,55]

The discussion of bonding trends for related molecules is only reasonable if one compares results performed on the same level. Therefore the following discussion includes only results from SCF calculations with small basis sets. These data are listed in Table VI. The following trend can be seen: The PO and PS bond lengths slightly increase going from the fluorides to the bromides. This can be expected as a consequence of the decrease in electronegativity of the halogens. The same is valid for the phosphorus–halogen bond going from the O=P—X to the S=P—X species. On the other hand, the bond angle of all these molecules is nearly constant. The size of these angles is in the range of comparable valence isoelectronic molecules like SSO (118.1°), SO$_2$ (119.5°), NSF (101.6°), ONF (109.9°), CF$_2$ (104.9°), and O$_3$ (117.8°).[56]

Table VII shows the corresponding bond length of some other phosphorus-containing molecules of the type P(O)X$_3$, P(S)X$_3$, and PX$_3$. The PX bond length in-

TABLE VII. Experimentally Determined Distances and Stretching Force Constants[a] of the Molecules $P(O)F_3$, $P(O)Cl_3$, $P(O)Br_3$, $P(S)F_3$, $P(S)Cl_3$, $P(S)Br_3$, PF_3, PCl_3, and PBr_3

molecule	d(O=P) d(S=P)	d(PX)	f(O=P) f(S=P)	f(PX)
$P(O)F_3$	143.7^{b}	152.2^{b}	11.0^{i}	6.3^{i}
$P(O)Cl_3$	144.9^{c}	199.3^{c}	10.5^{j}	3.03^{j}
$P(O)Br_3$	145^{d}	217^{d}	9.74^{k}	
$P(S)F_3$	185^{e}	154^{e}	5.62^{l}	5.95^{l}
$P(S)Cl_3$	188.5^{c}	201.1^{c}	5.05^{l}	2.66^{l}
$P(S)Br_3$	189^{d}	219^{d}		2.6^{k}
PF_3		156^{f}		5.4^{m}
PCl_3		204^{g}		2.5^{l}
PBr_3		222^{h}		1.8^{k}

[a] Distances in pm; force constants in mdyn/Å. [b] Reference 57. [c] Reference 58. [d] Reference 59. [e] Reference 60. [f] Reference 61. [g] Reference 62. [h] Reference 63. [i] Reference 64. [j] Reference 65. [k] Reference 66. [l] Reference 67. [m] Reference 68.

creases in the sequence $P(O)X_3 \rightarrow PX_3 \rightarrow OPX$.

There is another important result obtained by means of these calculations. The values of the total energy show that for molecules containing phosphorus and sulfur, the isomer with phosphorus in the central position is the most stable one. Their following isomerization energies were calculated on the SCF level: SPF → PSF, +250 kJ/mol; SPCl → PSCl, +191 kJ/mol; SPBr → PSBr, +172 kJ/mol. These results are in accord with analysis of the IR spectra presented in section V.

In most of the molecules under discussion there is a strong mixture of AOs in nearly all MOs. Only for OPF the situation should be simple enough to allow an interpretation of MOs.[12] Nevertheless, some main aspects shall be mentioned.

Generally the highest MO is the lone pair (a′) at the central atom. The second MO is of a″ symmetry; it must be attributed to states in which the double bond is primarily involved. Only for OPCl does this MO exhibit predominant Cl contributions.[10] These results parallel those of PE spectroscopy.[10]

The electronic structure of the molecules under discussion has also been studied by means of ab initio SCF calculations. The SEN's and charges based on SCF geometries of OPX and SPX molecules are collected in Table VIII. With the help of these values, it is possible to understand bonding in these species, since they reflect in a condensed way most of the results of the calculations. Since the SEN is a measure of covalent contributions, it is in accordance with chemical intuition: There are OP and SP double bonds and PX single bonds. Inspection of the charges demonstrates that both bonds are strengthened by ionic contributions.

No quantum chemical calculations have been performed on the molecule OAsCl.

B. Discussion of Bonding

Although one might compare the OPX molecules with the well-known ONX species, the bonding seems to be quite different for the two groups: ONX molecules are known under normal conditions, while OPX molecules are only present under special conditions, such as high temperatures and low pressures.

TABLE VIII. Results Obtained by Population Analysis[a] for the Molecules OPF, OPCl, OPBr, SPF, SPCl, SPBr, PSF, PSCl, and PSBr

XPY XSY	SEN(XP) SEN(XS)	SEN(PY) SEN(SY)	Q(X)	Q(P) Q(S)	Q(Y)
OPF	1.962	0.805	−0.486	0.904	−0.418
OPCl	1.963	0.842	−0.469	0.778	−0.310
OPBr	2.009	0.781	−0.428	0.774	−0.346
SPF	1.841	0.861	−0.283	0.674	−0.391
SPCl	1.865	0.926	−0.230	0.481	−0.251
SPBr	1.946	0.877	−0.170	0.451	−0.282
PSF	1.826	0.639	−0.059	0.518	−0.459
PSCl	1.807	0.700	0.006	0.273	−0.279
PSBr	1.983	0.603	0.008	0.325	−0.333

[a] Roby population analysis; cf. section III.D.

In contrast to OPX molecules, there is obviously a missing propensity to oligomerize among ONX species; e.g., $(OPX)_2$ molecules have been observed. The reason for this different behavior is the well-known stability of multiple bonds if only elements of the second period are involved in bonding. On the other hand, elements of higher periods prefer single bonds.[27] In comparison to monomeric OPX species, oligomeric molecules are favored since the coordination number of P increases during oligomerization. A quantitative measure of the stability of monomeric in comparison to oligomeric species is the enthalpy of dimerization. By means of these values, which can be obtained by quantum chemical methods, different bonding in ONX and OPX molecules could be visualized. Though ONX in comparison to OPX species are more stable with respect to oligomerization, they are less stable with respect to their thermal decomposition to the atoms. This follows from the atomization enthalpies: e.g., OPCl, 919 kJ/mol; ONCl, 791 kJ/mol.

The whole situation is even more complicated when the bond distance and force constant are considered. These parameters characterize a bond near the equilibrium distance, while at large distances a bond is better described by the bond energy. These difficulties in characterizing bonds are anticipated, since a bond can only be completely described by the potential function and not by a single parameter. Therefore it is not surprising that with respect to distance (pm) and force constant (mdyn/Å), bond strength in ONCl is higher than in OPCl, though the sum of bond energies is higher in OPCl: ONCl, f(NO) = 14.1, f(NCl) = 2.2,[69] d(NO) = 114, d(NCl) = 197;[70] OPCl, f(PO) = 9.8 f(PCl) = 2.2, d(PO) = 146, d(PCl) = 205.

While there are nearly no similarities between ONX and OPX species, there are interesting correlations among some isoelectronic species. A comparison is particularly interesting for OPF as it is isoelectronic with the well-known species SiF_2 and SO_2. The list of structural data presented in Table X shows that OPF, with respect to its bonding, is intermediate between SiF_2 and SO_2. Therefore structural data as well as the thermodynamic stability of OPF can be interpolated from corresponding values of these "neighbor" molecules.

These given considerations of bond strength and stability should demonstrate that these concepts can be used in a different manner. Thus, the following discussion is limited to the comparison of force constants and bond length of P-containing molecules.

PO and PS Bonds

The trends within OPX and SPX molecules are first considered. The valence bond force constants of the

TABLE IX. Results Obtained by Population Analysis[a] for the Molecules $P(O)F_3$, $P(O)Cl_3$, $P(O)Br_3$, $P(S)F_3$, PF_3, and PCl_3[b,c]

molecule	SEN(OP) SEN(SP)	SEN(PX)	Q(O) Q(S)	Q(P)	Q(X)
$P(O)F_3$	1.645	0.837	-0.704	1.828	-0.378
$P(O)Cl_3$	1.526	0.950	-0.696	1.221	-0.151
$P(O)Br_3$	1.604	0.925	-0.683	1.328	-0.215
$P(S)F_3$	1.546	0.820	-0.481	1.607	-0.379
PF_3		0.975		1.010	-0.337
PCl_3		1.030		0.508	-0.169

[a] Cf. section III.D. [b] On the grounds of the experimentally determined geometry. [c] Reference 41.

TABLE X. Structural Parameters of the Isoelectronic Molecules SiF_2, OPF, and SO_2[a]

parameter	SiF_2	O=P—F	SO_2
$\Delta H^\circ_{at,289}$, kJ/mol	1114.6	1064.5	1032.8
bond distance, pm	159	145, 157	143
bond angle, deg	101	110	119
stretching-bending force constant, mdyn/Å	0.44	0.57	0.82

[a] Reference 12.

P=O and P=S bonds determined from the vibrational frequencies show the expected trend. The increasing electronegativity in the direction Br → Cl → F is accompanied by an increasing contraction of the orbitals at phosphorus and consequently with a significant strengthening of the P=O or P=S bonds. This is also confirmed by inspection of the atomization energies determined experimentally: the P=O bond in OPF is the strongest in all molecules under discussion.[71]

This simple model of bonding is also in line with an increase of P=O and P=S force constants in the $P(O)X_3$ and $P(S)X_3$ molecules going from the bromides to the fluorides (Table VIII).

In the following text bonding in OPX and SPX molecules will also be discussed with respect to the results of population analysis (Table VIII). The OPX molecules are normal valent species with polar PO double bonds, which is visualized by the SEN's of about 2 and the charges on the P and O atoms (Table VIII). In $P(O)X_3$ (Table IX) and PO_2X[30,54] the SEN(PO) varies between 1.5 and 1.6, which indicates a less pronounced double-bond character than in OPX. On the other hand, charges on P and O increase going from OPX to $P(O)X_3$, which indicates a higher stabilization of the PO bonds in $P(O)X_3$ and also in PO_2X species by ionic contributions.

Within the group of OPX species, the covalent bond strength of the PO bond increases with respect to the SEN's going from OPF to OPBr. This enhancement of covalent bond strength is in contrast to the trend of the force constants (Table IV). Obviously, force constants will be significantly enhanced by the higher ionic stabilization of the PO bond in OPF in comparison with OPBr.

Nearly the same arguments are valid for the PS double bonds. As expected, these bonds are less polar and the covalent contributions are comparable to those in PO double bonds.

To sum up, one can say that P=O and P=S bonds in these molecules are polar unprotected double bonds and that reactivity (e.g., concerning dimerization) of these species is mainly caused by these bonds. The most stable species with respect to dimerization should be SPBr, since here the double bond has the highest SEN and the lowest polarity. Thus, preparative work on this molecule promises to be most successful. On the other hand, OPF should exhibit the highest reactivity.

PX Bonds

As expected, PX bonds in OPX and SPX molecules are polar single bonds. With respect to SEN values their covalent bond strength is very similar (Table VIII).

Interesting, too, is a comparison of PX bonds in the molecules of the type OPX → PX_3 → $P(O)X_3$. The bond strength increases with increasing oxidation number, which runs parallel to a growing positive charge at phosphorus connected with higher d AO contributions. This correlation is evident in the following scheme (cf. Tables IV and VI–IX):

	O=P—F	PF_3	$P(O)F_3$
Q(P)	+0.9	+1.1	+1.5
f(PF), mdyn/Å	4.7	5.4	6.3
d(PF), pm	157	156	152

Inspection of the series OPCl → $P(O)Cl_3$ → PO_2Cl is also informative. In this sequence the experimentally determined PCl force constants increase from 2.2 to 3.0 to 3.4.[30] This is consistent with the results of population analysis, since the SEN and polarity of the PX bonds also increase (cf. Table IX).

Corresponding to these findings, the positive charge on the phosphorus grows in this series from +0.78 to +1.2 to +1.5.[30] This reduction of electron density at the P atom goes along with a lowering of the empty d AOs combined with better possibilities for $p\pi$–$d\pi$ interactions.[30]

These interactions are more favored for PCl bonds than for PF or PBr bonds as a consequence of the better correspondence of size of the AOs involved. In terms of the SEN, the PCl bond is the strongest of all PX bonds in the series of OPX and SPX molecules.

In summary, the strength of O=P, S=P, and PX bonds in the O=P—X and S=P—X molecules are similar to those in comparable phosphorus-containing compounds.

Conclusion

On the basis of experimental and theoretical results bonding in O=P—X and S=P—X molecules is understandable. Bonding in these molecules is comparable to that of many other phosphorus-containing species and can be related to the bonding of isoelectronic molecules like SiF_2 and SO_2. On the other hand, the O=P—X and S=P—X molecules exhibit marked differences in bonding and structure from the corresponding ONX and NSX species.

VII. Chemical Reactions

All discussed 18e molecules, which contain atoms from three different groups in the periodic system, are highly reactive (except for the nitrosyl halides). It seems to be impossible to prepare them in a condensed state to study their chemical reactions. Some reactions of these compounds are known at their formation conditions (high temperatures, low pressures) and in solid noble gases.

A. Reactions at High Temperatures

The nature of the reactions of coordinatively unsaturated, reactive molecules such as O═P—Cl (which has been studied) with itself and with other compounds is of considerable interest.

An experimental procedure to investigate such high-temperature reactions by mass spectrometry and by matrix IR measurements has been described.[28,29]

Upon cooling the vapor formed by pyrolysis of $CH_2CHCH_2OPCl_2$, which contains O═P—Cl molecules, from 1100 to 400 K, the following compounds have been observed by mass spectrometry: $POCl_3$, PCl_3, P_4O_6, $P_2O_2Cl_2$, $P_3O_3Cl_3$, P_2OCl_4, and $P_4O_5Cl_2$.[16] This indicates the tendency of the unsaturated molecule O═P—Cl to form compounds with coordination numbers higher than 2 for the phosphorus atom. The reaction products show the following overall reactions:

$$6OPCl = P_4O_6 + 2PCl_3$$

$$3OPCl = POCl_3 + \text{lower valent phosphorus compound or } P_4$$

$$2OPCl = P_2O_2Cl_2$$

$$3OPCl = P_3O_3Cl_3$$

$$OPCl + PCl_3 = P_2OCl_4$$

$$5OPCl = P_4O_5Cl_2 + PCl_3$$

One further reaction, the oxidation of OPCl by oxygen to PO_2Cl,[28,30] has been studied in detail. Reaction of OPCl and OPBr with H_2O leads to the monomeric metaphosphoric acid HO—P═O,[29] whereas reaction with CH_3OH leads to the analogous methyl compound $H_3COP{=}O$.[24]

B. Reactions at Low Temperatures

Chemical reactions under matrix conditions provide a suitable method to generate reactive species. For example, $As(O)F_3$ has been obtained by a reaction of AsF_3 with oxygen atoms.[64] A suitable precursor for the generation of oxygen atoms is O_3, since it can be easily photolyzed by ultraviolet radiation.

To obtain some simple molecules of the type PO_2X in which phosphorus has the formal oxidation number V, the following matrix reactions have been performed:

$$OPCl + O_3 \rightarrow PO_2Cl + O_2 \quad [30]$$

$$OPBr + O_3 \rightarrow PO_2Br + O_2 \quad [54]$$

$$SPBr + O_3 \rightarrow POSBr + O_2 \quad [55]$$

The resulting molecules, like PO_2Cl, are very reactive. Thus, they can only be investigated at high temperatures and low pressures (section VII.A) or under the protecting conditions of a low-temperature matrix. After evaporation of the matrix polymeric PO_2Cl is formed.[30,72] Molecular PO_2X species exhibit an unexpected strong PX bond.

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(49) In order to give an idea of typical values found for SEN, we list some representative cases: strong bonds like C–C or C–H (SEN = 1.4); double bonds like C═C (SEN = 2.2); triple bonds like C≡C or N≡N (SEN = 3.3). A reduced SEN is found for polar bonds as in NaF (SEN = 0.3) and for weak bonds such as in Cl_2 (SEN = 0.9) and in F_2 (SEN = 0.6).
(50) The following $^{16}O/^{18}O$ shifts have been observed (cm^{-1}): OPF, $\nu(PO) = 47.0$, $\nu(PF) = 9.8$, $\delta(OPF) = 1.0$;[12] OPCl, cf. section III.C;[4] OPBr, $\nu(PO) = 47.5$, $\nu(PBr) = 2.5$, $\delta(OPBr) = 9.0$.[11]
(51) Quantum chemical computations in which changes of the dipole moment during a normal vibration are obtained have shown that a comparison of calculated and measured intensities of IR absorptions allows a decision between different isomers. By this method the assignment of IR absorptions to the isomer N–S–F instead of S–N–F could be definitely confirmed.[52] With the help of the experimentally determined frequencies and force constants, quantum chemical calculations were performed to obtain relative intensities of the IR absorptions of OPF, which is isoelectronic with NSF. Since extensive SCF computations on OPF give no better results than simple MNDO calculations, the latter method was applied for the species SPF and PSF.[41] This semiempirical method provides a rapid method to see trends of structural parameters, though absolute values for molecules containing atoms from periods higher than 2 do not correspond well with experimental data.
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