The Potential Constants of Phosphorus Trihalide and Phosphoryl Halides

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The Raman and infrared spectra of phosphorus trihalides and phosphoryl halides in the solid, liquid and vapor phases have previously been obtained.[1a,1b] The normal vibrations of PCl_3 and PBr_3 have been calculated on the basis of the general quadratic potential function derived by Howard and Wilson.[2] Using the mean square amplitudes of vibration obtained from gaseous electron diffraction experiments, together with the normal vibration frequencies, Iwasaki and Hedberg attempted to get a reasonable set of potential constants of the general quadratic function where the interaction terms between bond stretching and angle deformation are included.[3] On the other hand, no detailed studies of the potential constants of phosphoryl halides have yet been tried.

It is necessary to undertake a theoretical treatment of the experimental data on the vibrational spectra of phosphorus compounds in order to obtain reasonable potential constants which are transferable among phosphorus compounds.

At first the normal vibrations of pyramidal-type molecules, such as PCl_3 and PBr_3, were calculated by means of a modified Urey-Bradley force field (UBFF), and then phosphoryl halides, $OPCl_3$ and $OPBr_3$ were calculated by

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[1] a) PF_3: H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952); M. L. Delwaulle and F. François, ibid., **46**, 87 (1949).

PCl_3: M. L. Delwaulle, *Compt. rend.*, **224**, 389 (1947); M. L. Lorenzell and K. D. Moler, ibid., **248**, 1980 (1959); M. L. Lorenzell, ibid., **252**, 3219 (1961).

PBr_3: M. L. Delwaulle and F. François, *J. Phys. Radium*, **7**, 15, 53 (1946).

b) OPF_3: M. L. Delwaulle and F. François, *Compt. rend.*, **226**, 895 (1948); **222**, 550, 1173 (1946); *J. Chim. Phys.*, **46**, 87 (1949); H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

$OPCl_3$: M. L. Delwaulle and F. François, *Compt. rend.*, **220**, 817 (1945); *J. Phys. Radium*, **7**, 15, 53 (1946).

$OPBr_3$: M. L. Delwaulle and F. François, *Bull. soc. chim. France*, **13**, 206 (1946); *J. Chim. Phys.*, **45**, 50 (1948).

[2] J. B. Howard and E. B. Wilson, ibid., **2**, 630 (1934); H. S. Gutowsky and A. D. Liehr, ibid., **20**, 1652 (1952); V. Lorenzell and K. D. Moler, *Compt. rend.*, **248**, 1980 (1959); V. Lorenzell, ibid., **252**, 3219 (1961); P. W. Davis and R. A. Oetjen, *J. Mol. Spectry.*, **2**, 253 (1958).

[3] M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 594 (1962).

means of a Urey-Bradley-Shimanouchi force field (UBSFF). It was found that there exists a relationship between the potential constants of the PCl_3, PBr_3, $OPCl_3$ and $OPBr_3$ compounds and the constants for the mixed halogen phosphorus compounds, PCl_2Br, $PClBr_2$, $OPCl_2\cdot Br$ and $OPClBr_2$.

Normal Coordinate Treatment and Results

The Calculation of the Potential Constants of PCl_3 and PBr_3.—The Raman spectra of PCl_3 and PBr_3 reported by Delwaulle were used for the calculation of the potential constants in the present study. PCl_3 and PBr_3 have the pyramidal-type structure with C_{3V} symmetry.

As a potential function, the following modified UBFF was used:

$$
\begin{aligned}
V= & \sum K'_{i0}\Delta r_{i0}+1/2\sum K_{i0}(\Delta r_{i0})^2 \\
& +\sum H'_{i0j}(r_{i0}r_{j0})^{1/2}\Delta\phi_{i0j}+1/2\sum H_{i0j}r_{i0}r_{j0}\cdot \\
& (\Delta\phi_{i0j})^2+\sum F'_{ij}\Delta q_{ij}+1/2\sum F_{ij}(\Delta q_{ij})^2 \\
& +\sum k_{ij}(\Delta r_{i0})(\Delta r_{j0}) \\
& +\sum h_{ijk}(r_{i0}r_{j0})^{1/2}(r_{j0}r_{k0})^{1/2}(\Delta\phi_{i0j})(\Delta\phi_{j0k})
\end{aligned}
\tag{1}
$$

where K, H and F are the potential constants for bond stretching, angle deformation and interaction between non-bonded atoms respectively; k and h are the interaction terms between two bond-stretching coordinates and between two angle-deformation coordinates respectively. The following symmetry coordinates were used:

$$S_1(A_1)=3^{-1/2}(\Delta r_{01}+\Delta r_{02}+\Delta r_{03})$$

$$S_2(A_1)=3^{-1/2}(\Delta\phi_{102}+\Delta\phi_{203}+\Delta\phi_{301})$$

$$S_3(E)=2^{-1/2}(\Delta r_{02}-\Delta r_{03})$$

$$S_4(E)=2^{-1/2}(\Delta\phi_{301}-\Delta\phi_{102})$$

$$S_3^*(E)=6^{-1/2}(2\Delta r_{01}-\Delta r_{02}-\Delta r_{03})$$

$$S_4^*(E)=6^{-1/2}(2\Delta\phi_{203}-\Delta\phi_{301}-\Delta\phi_{102})$$

The secular equation, $|GF-E\lambda|=0$, is set up according to Wilson's method.[4]

An IBM model 7090 digital computer was used for the numerical computations involved in the normal coordinate treatment.

In the calculations using the simple UBFF, where k and h are assumed to be zero and F' is $-F/10$, the stretching, K_{AS}, and deformation, H_{AS}, potential constants of PCl_3 (and PBr_3) against F were determined from the two frequencies observed at 510 cm^{-1} and 257 cm^{-1} (380 cm^{-1} and 162 cm^{-1}) belonging to the A_1 species; also K_{ES} and H_{ES} were determined from the 480 cm^{-1} and 190 cm^{-1} (400 cm^{-1} and 116 cm^{-1}) belonging to the E species. A convenient representation of the relationship among the potential constants is obtained by plotting K and H against F in Figs. 1 and 2.

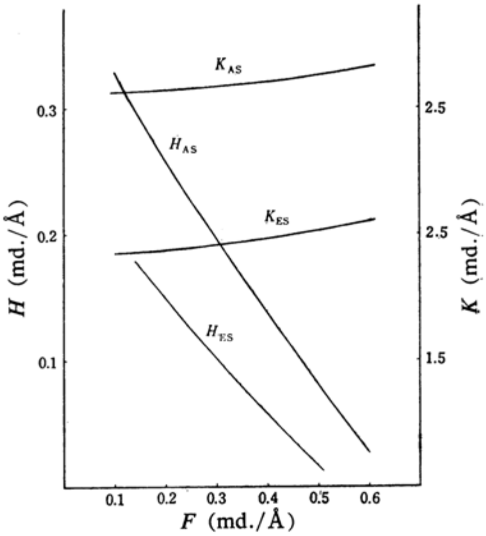

Fig. 1. The correlation of potential constants for PCl_3.

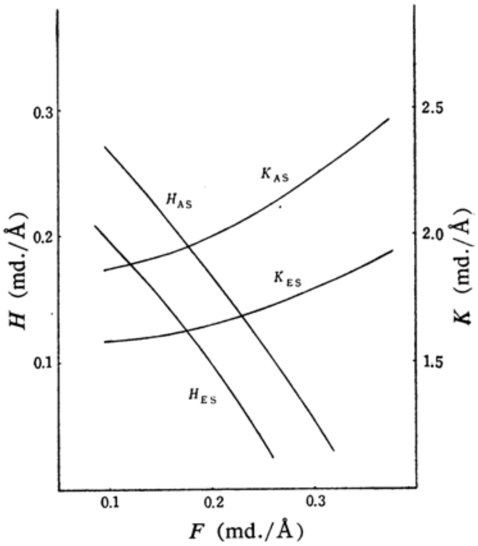

Fig. 2. The correlation of potential constants for PBr_3.

All the combinations of the K and H potential constants for the A_1 species are incompatible with those of the E species. We could not find any common values for the potential constants of the two symmetry species.

Therefore, we used a modified UBFF in our calculations. The relationship between the potential constants, K and H, of the simple UBFF and those of the modified UBFF may be expressed as follows:

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[4] E. B. Wilson, Jr., ibid., 7, 1047 (1939); 9, 76 (1941).

TABLE I. POTENTIAL CONSTANTS (md./Å) AND MOLECULAR PARAMETERS OF PHOSPHORUS CHLORIDE

	K	H	k	h	F_{calcd}	r, Å	ϕ (degree)
PCl_3	2.182	0.168	0.217	0.036	0.244	2.039	100° 27′
PBr_3	1.870	0.106	0.110	0.021	0.231	2.18	101° 5′
$AsCl_3$*	2.021	0.148	0.182	0.025	0.127	2.16	98° 4′
$SbCl_3$*	1.774	0.164	0.199	0.030	0.032	2.33	99° 5′
$BiCl_3$*	1.186	0.100	0.172	0.025	0.010	2.48	100° 0′

* The potential constants of the Vth group elements were calculated by the same method.

TABLE II. MOLECULAR PARAMETERS OF PHOSPHORYL CHLORIDE AND BROMIDE

	r_{01}	r_{02}	ϕ_{102}	ϕ_{203}
$OPCl_3$	1.45 Å	1.99 Å	115° 16′	103° 6′
$OPBr_3$	1.45 Å	2.18 Å	117°	101°

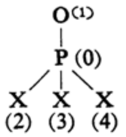

TABLE III. POTENTIAL CONSTANTS OF PHOSPHORYL CHLORIDE AND BROMIDE (md./Å)

	$OPCl_3$			$OPBr_3$	
	Set 1	Set 2		Set 1	Set 2
$K_{P=O}$	9	9.85	$K_{P=O}$	9	9.50
K_{P-Cl}	2.2	2.54	K_{P-Br}	1.9	1.9
$F_{O\cdot\cdot(P)\cdot\cdot Cl}$	0.13	0.25	$F_{O\cdot\cdot(P)\cdot\cdot Cl}$	0.10	0.10
$F_{Cl\cdot\cdot(P)\cdot\cdot Cl}$	0.27	0.27	$F_{Br\cdot\cdot(P)\cdot\cdot Br}$	0.25	0.25
H_{OPCl}	0.2	0.286	H_{OPBr}	0.15	0.28
H_{ClPCl}	0.2	0.12	H_{BrPBr}	0.1	0.1
χ (md. Å)	0.06	0.06	χ (md. Å)	0.04	0.04

$$K=1/3(K_{AS}+2K_{ES}) \qquad k=1/3(K_{AS}-K_{ES})$$
$$H=1/3(H_{AS}+2K_{ES}) \qquad h=1/3(H_{AS}-H_{ES})$$

where K_{AS} and H_{AS}, and K_{ES} and H_{ES} are the stretching and deformation constants obtained from the A_1 and E species respectively, using the simple UBFF. The repulsive potential constants, $F_{Cl\cdot\cdot(P)\cdot\cdot Cl}$ and $F_{Br\cdot\cdot(P)\cdot\cdot Br}$, are estimated from the interatomic forces between Ar··Ar atoms and also from those between Kr··Kr atoms on the basis of the Lennard-Jones potential.5) The potential constants, K, H, k and h, can be calculated from the observed frequencies by using the modified UBFF.

The potential constants and molecular parameters6) are shown in Table I.

The Calculation of the Potential Constants of $OPCl_3$ and $OPBr_3$.—In order to investigate the relationship between the potential constants of phosphoryl halides and phosphorus trihalides, the normal vibrations of $OPCl_3$ and $OPBr_3$ were also calculated on the basis of the UBSFF. For this type of molecule, the internal tension, due to the redundancy among six angles is introduced.7)

The following set of linear combinations of internal coordinates was chosen as the symmetry coordinates:

For the A_1 type:

$$S_1=\Delta r_{01}$$
$$S_2=3^{-1/2}(\Delta r_{02}+\Delta r_{03}+\Delta r_{04})$$
$$S_3=(3A^2+3B^2)^{-1/2}[B(\Delta\phi_{102}+\Delta\phi_{103}+\Delta\phi_{104})-A(\Delta\phi_{304}+\Delta\phi_{402}+\Delta\phi_{203})]$$
$$S_4=(3A^2+3B^2)^{-1/2}[A(\Delta\phi_{102}+\Delta\phi_{103}+\Delta\phi_{104})+B(\Delta\phi_{304}+\Delta\phi_{402}+\Delta\phi_{203})]$$

(S_4 is redundant.)

$$A=2ab(c-1)^2 \quad B=2d(c-1)(a^2-c)$$
$$a=\cos\phi_{102},\quad b=\sin\phi_{102},\quad c=\cos\phi_{203},\quad d=\sin\phi_{203}$$

For the E type:

$$S_5=6^{-1/2}(2\Delta r_{02}-\Delta r_{03}-\Delta r_{04})$$
$$S_6=6^{-1/2}(2\Delta\phi_{102}-\Delta\phi_{103}-\Delta\phi_{104})$$
$$S_7=6^{-1/2}(2\Delta\phi_{304}-\Delta\phi_{402}-\Delta\phi_{203})$$
$$S_5^*=2^{-1/2}(\Delta r_{03}-\Delta r_{04})$$
$$S_6^*=2^{-1/2}(\Delta\phi_{103}-\Delta\phi_{104})$$
$$S_7^*=2^{-1/2}(\Delta\phi_{402}-\Delta\phi_{203})$$

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5) T. Shimanouchi, *Pure Appl. Chem.*, 7, 131 (1963).

6) P. W. Allen and L. E. Sutton, *Acta Cryst.*, 3, 46 (1950).

7) T. Shimanouchi, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 21, 825 (1942).

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES (IN cm^{-1})

a) $OPCl_3$

	ν_{obs}	ν^1_{calcd}	Δ^1	ν^2_{calcd}	Δ^2
A_1 species	1292	1231	− 4.7	1292	0
	486	444	− 8.6	480	−1.2
	268	265	− 1.1	256	−4.5
E species	582	542	− 7.0	587	+0.9
	337	269	−20.0	339	+0.6
	191	218	+14.1	191	0

b) $OPBr_3$

	ν_{obs}	ν^1_{calcd}	Δ^1	ν^2_{calcd}	Δ^2
A_1 species	1260	1225	− 2.8	1259	−0.1
	340	336	− 1.2	342	+0.6
	173	166	− 4.0	176	+1.7
E species	488	446	− 8.6	486	+0.2
	267	217	−18.7	266	−0.4
	118	122	+ 3.4	122	+3.4

Δ: Percent deviation $100(\nu_{calcd}-\nu_{obs})/\nu_{obs}$

The molecular parameters[8)] used in the calculations are given in Table II.

The potential constants of set 1 (Table III) were estimated from those of PX_3. Then the potential constants of set 2 (Table III) were selected to yield a better agreement between the observed and calculated frequencies for $OPCl_3$ and $OPBr_3$, except for $F_{Cl\cdot\cdot(P)\cdot\cdot Cl}$ and $F_{Br\cdot\cdot(P)\cdot\cdot Br}$, which were estimated from the Lennard-Jones potential as in the case of PX_3-type molecules. The calculated frequencies are compared with the observed frequencies in Table IV.

The Potential Constants of Mixed Halides of Phosphorus Compounds: PCl_2Br, $PClBr_2$, $OPCl_2Br$ and $OPClBr_2$.—Delwaulle and others[9)] have shown that the mixing of PCl_3 and PBr_3 yields PCl_2Br and $PClBr_2$.

The normal vibrations of PCl_2Br and $PClBr_2$ were calculated. The values of the stretching-potential constants, K_{PCl} and K_{PBr}, were transferred from those of PCl_3 and PBr_3, while those of the deformation constant, H_{ClPBr}, and the repulsive constant, $F_{Cl\cdot\cdot(P)\cdot\cdot Br}$, for PCl_2Br and $PClBr_2$ were assumed to be the harmonic mean of those for PCl_3 and PBr_3 as follows:

$$k_{ij}=2\,[k_{ii}k_{jj}/(k_{ii}+k_{jj})]$$

The derivation of the values of the $[h]$ constants, for example, $h_{ClPBr\cdot BrPBr}$ may be shown as follows:

$$h_{ClPBr\cdot BrPBr}=2\,[h_{ClPBr}\cdot h_{BrPBr}/(k_{ClPBr}+h_{BrPBr})]$$

where

$$h_{ClPBr}=2\,[h_{ClPCl}\cdot h_{BrPBr}/(h_{ClPCl}+h_{BrPBr})].$$

Those potential constants of PCl_2Br and $PClBr_2$ are shown in Table V. The arithmetic mean was taken for the value of molecular parameters. Table VI compares the observed and calculated frequencies for PCl_2Br and $PClBr_2$.

The normal vibrations of $OPCl_2Br$ and $OPClBr_2$ were calculated by the same method as was used for PCl_2Br and $PClBr_2$.

TABLE V. POTENTIAL CONSTANTS OF MIXED HALOGEN COMPOUNDS (md./Å)

PCl_2Br		$PClBr_2$	
K_{P-Cl}	2.182	K_{P-Cl}	2.182
K_{P-Br}	1.870	K_{P-Br}	1.870
H_{ClPBr}	0.130	H_{ClPBr}	0.130
H_{ClPCl}	0.168	H_{BrPBr}	0.106
$F_{Cl\cdot\cdot(P)\cdot\cdot Cl}$	0.244	$F_{Br\cdot\cdot(P)\cdot\cdot Br}$	0.231
$F_{Cl\cdot\cdot(P)\cdot\cdot Br}$	0.237	$F_{Cl\cdot\cdot(P)\cdot\cdot Br}$	0.237
$k_{PCl\cdot PBr}$	0.146	$k_{PCl\cdot PBr}$	0.146
$k_{PCl\cdot PCl}$	0.217	$k_{PBr\cdot PBr}$	0.110
$h_{ClPBr\cdot BrPBr}$	0.023	$h_{ClPBr\cdot BrPBr}$	0.023
$h_{ClPCl\cdot ClPBr}$	0.031	$h_{ClPCl\cdot ClPBr}$	0.031
$h_{ClPBr\cdot ClPBr}$	0.026	$h_{ClPBr\cdot ClPBr}$	0.026
$OPCl_2Br$		$OPClBr_2$	
$K_{P=O}$	9.72	$K_{P=O}$	9.77
K_{P-Cl}	2.54	K_{P-Cl}	2.54
K_{P-Br}	1.90	K_{P-Br}	1.90
$F_{O\cdot\cdot(P)\cdot\cdot Cl}$	0.25	$F_{O\cdot\cdot(P)\cdot\cdot Cl}$	0.25
$F_{O\cdot\cdot(P)\cdot\cdot Br}$	0.10	$F_{O\cdot\cdot(P)\cdot\cdot Br}$	0.10
$F_{Cl\cdot\cdot(P)\cdot\cdot Cl}$	0.27	$F_{Br\cdot\cdot(P)\cdot\cdot Br}$	0.25
$F_{Cl\cdot\cdot(P)\cdot\cdot Br}$	0.26	$F_{Cl\cdot\cdot(P)\cdot\cdot Br}$	0.26
H_{OPCl}	0.286	H_{OPCl}	0.286
H_{OPBr}	0.28	H_{OPBr}	0.28
H_{ClPCl}	0.12	H_{BrPBr}	0.10
H_{ClPBr}	0.11	H_{ClPBr}	0.11
χ(md. Å)	0.06	χ(md. Å)	0.04

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

9) M. L. Delwaulle and M. Bridoux, *Compt. rend.*, 248, 1342 (1959); M. L. Delwaulle and G. Schilling, ibid., 244, 70 (1957); M. L. Delwaulle and F. François, ibid., 223, 796 (1946).

TABLE VI. OBSERVED AND CALCULATED FREQUENCIES (IN cm^{-1}) OF PHOSPHORUS HALIDES

	PCl_2Br			$PClBr_2$		
	Obs.	Calcd.	Δ	Obs.	Calcd.	Δ
A′ species	510	499	− 2.2	480	488	+ 1.7
	361	398	+10.2	386	396	+ 2.6
	230	231	+ 0.4	197	207	+ 5.1
	166	166	0	153	160	+ 4.6
A″ species	479	409	−14.6	400	404	+ 1.0
	149	156	+ 4.7	123	145	+17.9

TABLE VII. OBSERVED AND CALCULATED FREQUENCIES OF $OPCl_2Br$ AND $OPClBr_2$ (IN $cm.^{-1}$)

	$OPCl_2Br$			$OPClBr_2$		
	Obs.	Calcd.	Δ	Obs.	Calcd.	Δ
A′ species	1285	1285	0	1275	1275	0
	546	543	−0.4	552	567	+2.7
	432	424	−1.9	391	398	+1.8
	285	278	−2.5	291	294	+1.0
	242	235	−2.9	209	210	+0.5
	172	173	+0.5	130	131	+0.8
A″ species	580	587	+1.2	492	489	−0.6
	327	338	+3.3	271	266	−1.8
	161	162	+0.6	157	156	−0.6

The calculated frequencies are compared with those obtained by Delwaulle et al.10) in Table VII.

The agreement between the observed and calculated frequencies is satisfactory. Therefore, it is reasonable to assume the transferability of the potential constants among the compounds.

Discussion

The modified UBFF shown in Eq. 1 may be applied to such pyramidal molecules as PCl_3 and PBr_3, and the UBSFF, to such unsymmetric tetrahedral molecules as $OPCl_3$ and $OPBr_3$. Different force fields were used for the PX_3-type and OPX_3-type molecules in the present paper. However, the potential constants may involve physically significant common values among them.

The repulsion terms between the nonbonded halogen atoms for PCl_3 and PBr_3 are estimated from the interaction forces between atoms, on the basis of the Lennard-Jones potential. The K, H, k and h potential constants are the functions of the repulsion constant, F. On the other hand, the potential constants for $OPCl_3$ and $OPBr_3$ have been selected to produce the best agreement between the observed and calculated frequencies.

It was found that the values of K and H of OPX_3 are nearly the same as those of pyramidal molecules, PX_3. This result shows that there is a correlation between the potential constants of phosphoryl and phosphorus halogenides.

In the case of fluorine compounds, the potential constants are not transferable. A further investigation will be necessary in order to estimate the potential constant of $F \cdots F$ nonbonded repulsion.

The k and h potential constants may rise from the resonance energy because of the interaction between the unpaired electron of the P atom and the electrons existing in the PX bond and on the $\dot{X}PX$ plane.

In the calculation of the normal vibrations of mixed trihalogen phosphorus and phosphoryl compounds as well as of dihalogenide carbonyl, better results were obtained by the use of a harmonic mean than by the use of an arithmetical or geometric mean in the estimation of the potential constants. When the values calculated using the harmonic mean are compared with the values which are selected to produce the best agreement between the observed and calculated frequencies, the difference between the observed and calculated frequencies are of nearly the same order for both cases of phosphoryl halides.

Bell et al.11) have shown that there is a linear correlation between the phosphoryl-absorption wavelength in phosphoryl halides

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10) V. W. Kuchen, H. Ecke and H. G. Beckers, *Z. anorg. u. allgem. Chem.*, **313**, 138 (1961); M. L. Delwaulle and F. François, *J. Chim. Phys.*, **46**, 87 (1949); M. L. Delwaulle and F. François, *Compt. rend.*, **220**, 817 (1945); **222**, 550, 1173, 1391 (1946); **224**, 389 (1947); **226**, 895 (1948).

11) J. V. Bell, J. Heisler, H. Tannenbaum and T. Goldensen, *J. Am. Chem. Soc.*, **76**, 5185 (1954).

and the sum of the Pauling electronegativity constants of the halogens. In our present investigation, it was found that a linear correlation is obtained by plotting the phosphoryl potential constants in phosphoryl halides against the sum of the Pauling electronegativity, as is shown in Fig. 3. The value of the phosphoryl-stretching constant rises higher as the sum of the Pauling electronegativity increases. The effects of various substituents upon the P=O-stretching constant in many types of phosphoryl compounds may be due to an induced polarization. It may be interpreted that in the P-oxide the electronic structure can be represented as resonance hybrids: $R_3P^+-O^- \leftrightarrow R_3P=O$.

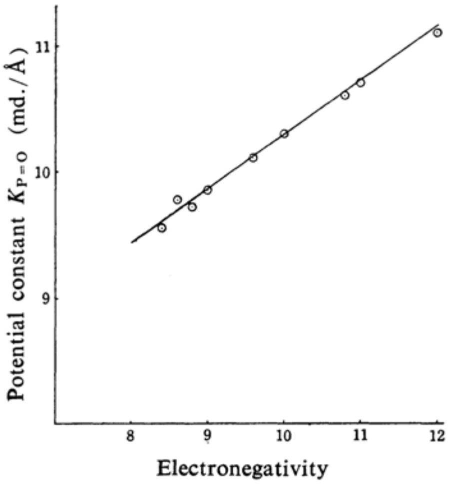

Fig. 3. The correlation between the P=O stretching constant and the sum of electronegativity.

	Sum of electro-negativity	Potential constant
$OPBr_3$	8.4	9.5
$OPClBr_2$	8.6	9.77
$OPCl_2Br$	8.8	9.72
$OPCl_3$	9.0	9.85
$OPFBr_2$	9.6	10.10
$OPFCl_2$	10.0	10.30
OPF_2Br	10.8	10.60
OPF_2Cl	11.0	10.70
OPF_3	12.0	11.10

Summary

It is important to calculate the potential constants of phosphorus compounds systematically in order to determine physically meaningful potential constants.

First the normal vibrations of such pyramidal-type molecules as PCl_3 and PBr_3 have been calculated by the use of a Urey-Bradley force field as supplemented by the interaction terms between two bond-stretching coordinates and between two angle-deformation coordinates, and then such phosphoryl halogenides as $OPCl_3$ and $OPBr_3$ have been calculated by the use of a Urey-Bradley-Shimanouchi force field.

The repulsion terms between nonbonded halogen atoms have been estimated from the interaction forces between inert atoms based on the Lennard-Jones formula.

The force fields used for the PX_3-type and OPX_3-type molecules in the present paper are different. However, it has been found that a relationship exists between the potential constants of such compounds as PCl_3, PBr_3, $OPCl_3$ and $OPBr_3$, and those for mixed halogen phosphorus compounds, such as PCl_2Br, $PClBr_2$, $OPCl_2Br$ and $OPClBr_2$.

The additional potential terms used for the PX_3 type may arise from the resonance energy because of the interaction between the unpaired electrons of the P atom and the electrons existing in the PX bond and on the XPX plane.

In our present investigation, a linear correlation has been found to exist between the phosphoryl potential constants in phosphoryl halides and the sum of the Pauling electronegativity constants of the halogens.

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