TABLE II

AMIDE–AMMONIA COMPOUNDS

Probable formula	Stability range (% of NH₃)	Transition temp. to amide, °C.	Eutectic temp. with NH₃, °C.	M.p., °C. (by-extr.)
NH₃·HCONH₂[3]	53.5–71	−75.5	..ᵃ	−75
NH₃·CH₃CONH₂[2]	68–92	−32	−82	−25
NH₃·HCONHCH₃ (metastable)	...	..	−102	−96
NH₃·HCONHCH₃ (stable)	61–74	−82	−96	−75
NH₃·HCON(CH₃)₂	52–67	−87.5	−94	−87

ᵃ A second addition compound, 2NH₃·HCONH₂, undergoes transition to the 1:1 compound and solution at −92°; its eutectic temperature with ammonia is −96°.

it appears highly probable that each of them consists of amide and ammonia in equimolecular ratio. The NMF–ammonia compound occurs in two modifications, one of which appeared here only as a metastable phase. Stability and melting point data are shown in Table II, in which the 1:1 compounds of acetamide and formamide with ammonia, reported in previous papers,[2,3] are included for comparison.

Discussion

Since the amide–formic acid compounds of Table I are relatively stable at their melting points and since they are all formally analogous to ammonium formate, the names by which they are designated in the table appear to be appropriate. It is significant that the sharpness of the maxima in the equilibrium curves,

and the steepness of these curves in the region where formic acid is solid phase, both increase in the order formamide <NMF<DMF. This variation indicates increasing extent of compound formation in solution in the same order, corresponding to the known increase in basicity of the amides with successive introduction of N-methyl groups. It may be noted that according to the above criteria, acetamide, although it differs little from formamide in basicity, closely resembles its isomer NMF with respect to extent of compound formation with formic acid.

In the amide–ammonia systems, the order of increasingly extensive compound formation in solution, as indicated by the same criteria, is reversed, increasing in the order DMF<NMF<acetamide<formamide. In this case, however, the nature of the addition compounds is by no means obvious. The suggestion in an earlier paper from this Laboratory[3] that the 1:1 formamide–ammonia compound, by analogy with the sodium salts of formamide, might be regarded as an ammonium aquo-ammono formate of the formula HCONHNH₄, loses much of its plausibility in view of the fact that a similar compound with ammonia is formed not only by NMF but even by DMF, in which there is no hydrogen available for proton donation to ammonia. Because of the general similarity of the equilibrium curves in all the amide–ammonia systems considered, it appears preferable to suppose, in line with an alternative suggestion made in the paper just mentioned, that compound formation in these systems may result from the sharing of the electron pair of the ammonia molecule with the electron-deficient carbon atom of the carbonyl group of the amide.

Calculated Bond Characters in Phosphoryl Compounds

BY E. L. WAGNER

The bond characters of a series of symmetrically substituted phosphoryl molecules, Y₃PO, have been calculated using the internally consistent LCAO–MO method previously developed for the π-electrons of such systems, but also taking into account the varying polarities of the YP and OP σ-bonds and the changing hybridization of the π-bonding orbital of the central phosphorus atom. The resulting PO bond characters are directly related to the electronegativities of the substituent Y-groups. The calculated PO π-bond orders correlate well with the experimental bond vibrational frequencies and the charge distributions are consistent with the observed dipole moments and other properties of the molecules.

In many phosphoryl molecules. Y₃PO, the PO bond stretching frequencies and bond lengths, the YPY angles, and the relative YP bond distances, all seem to vary considerably as the Y-group is varied, indicating significant changes in the PO bond characters. It has been shown[1] that there is a correspondence between the phosphoryl frequency and the electronegativity of the substituent groups, as seen in Table I, but the quantitative nature of these bonds apparently has not been discussed. Since bond character of the type involved in the phosphoryl group can be calculated by the internally consistent molecular orbital method previously developed for such systems,[2] it is possible to deduce the effects of changing the substituents Y on the PO bond in the different Y₃PO molecules.

We have applied this MO method to a series of symmetrically substituted phosphoryl compounds taking into account the varying polarity of the σ-bonds, the changing hybridization of the π-bonding orbital

of the central P-atom, and the different degree of π-bonding involved in each compound. The method predicts appreciable participation of the P-atom d-orbitals in the π-bonding such that the total order of the PO bonds varies from a nearly pure coördinate single bond in (CH₃)₃PO to almost a triple bond in F₃PO. The charge distributions vary in the series in such a way that the calculated dipole moment completely reverses direction. The calculated π-bond orders of the PO bond give a good correlation with the PO bond stretching frequencies or force constants when a reasonable set of β(dπ) values is chosen, indicating that our calculated bond strengths, based on bond orders, at least vary in a consistent manner.

Now if we consider only symmetrically substituted molecules of symmetry C₃ᵥ, the "group" orbitals of the three Y-atoms which enter into the σ-bonding with phosphorus can be represented by (σa₁) and (σe), the corresponding P-atom hybrid orbitals which combine with these are the (3s3pz)-hybrid represented by (3ra₁) and the (3pₑ3dₑ)-hybrid represented by (3r′e). The other components of these P-atom hybrids, (3ta₁)

(1) J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, J. Am. Chem. Soc., 76, 5185 (1954); L. W. Daasch and D. C. Smith, Anal. Chem., 23, 853 (1951).

(2) E. L. Wagner, J. Chem. Phys., 37, 751 (1962).

PO STRETCHING FREQUENCIES IN Y₃PO MOLECULES

Compound	Group electro-negativity[1]	PO stretching frequency, cm.$^{-1}$	Estimated PO force constants (md/A)
F_3PO	4.0	1404–1395	11.4
F_2ClPO	(3.67)$_{av}$	1358	10.8
F_2BrPO	(3.6)$_{av}$	1350	10.7
FCl_2PO	(3.33)$_{av}$	1331	10.4
$FClBrPO$	(3.27)$_{av}$	1319	10.3
FBr_2PO	(3.2)$_{av}$	1303	10.0
$(C_6H_5O)_3PO$	3.2	1311–1299	10.1
$(CH_3C_6H_4O)_3PO$	3.0	1307–1299	10.0
Cl_3PO	3.0	1295–1290	9.9
$(p\text{-}NO_2C_6H_4CH_2O)_3PO$	3.0	1278	9.7
Cl_2BrPO	(2.93)$_{av}$	1285	9.8
$(CH_3O)_3PO$	2.9	1274	9.6
$ClBr_2PO$	(2.87)$_{av}$	1275	9.6
Br_3PO	2.8	1266–1260	9.5
$(c\text{-}C_6H_{11})_3PO$	2.6	1218	8.8
$(C_6H_5)_3PO$	2.4	1202–1190	8.5
$(ClC_6H_4)_3PO$	2.2	1180	8.3
$(CH_3)_3PO$	2.0	1176–1170	8.2

and (3Xe), form the σ- and π-bonds, respectively, with the O-atom. In terms of the resulting MO's, the electronic structure of Y_3PO then may be described qualitatively as

$$(ta_1)^2(ra_1)^2(r'e)^4(\bar{\sigma}a_1)^2(Xe)^4$$

The letters t, r, r', $\bar{\sigma}$ and X simply serve to identify a particular orbital and have no other meaning. The other symbols designate the symmetries of the orbitals which result from the over-all molecular symmetry.

In this proposed electronic structure, $(ta_1)^2$ represents the PO σ-bonding orbital whose most general LCAO form is

$$\Psi(ta_1) = c_P{}^t\Phi_P(3ta_1) + c_O{}^t\Phi_O(\sigma a_1),$$

$(ra_1)^2$ and $(r'e)^4$ represent the three YP σ-bonding orbitals

$$\Psi(ra_1) = c_P{}^r\Phi_P(3ra_1) + c_Y{}^r\Phi_Y(\sigma a_1)$$
$$\Psi(r'e) = c_{P'}{}^r\Phi_P(3r'e) + c_{Y'}{}^r\Phi_Y(\sigma e),$$

$(\bar{\sigma}a_1)^2$ represents the lone-pair electrons on the oxygen atom, and the normalized PO π-bonding MO is given by

$$\Psi(Xe) = \sin\theta\,\Phi_P(3Xe) + \cos\theta\,\Phi_O(\pi e).$$

The P-atom hybrid orbitals involved in these bonds are delineated by

$$\Phi_P(3ta_1) = \sin\zeta\,\Phi_P(3sa_1) + \cos\zeta\,\Phi_P(3p_za_1)$$
$$\Phi_P(3ra_1) = \cos\zeta\,\Phi_P(3sa_1) - \sin\zeta\,\Phi_P(3p_za_1)$$

and by

$$\Phi_P(3Xe) = \cos\gamma\,\Phi_P(3pe) + \sin\gamma\,\Phi_P(3de)$$
$$\Phi_P(3r'e) = \sin\gamma\,\Phi_P(3pe) - \cos\gamma\,\Phi_P(3de),$$

where ζ and γ are the hybridization parameters. Only when $\zeta = \pi/4$ and $\gamma = \pi/2$ will the σ-bond skeleton be tetrahedral. As ζ becomes greater than $\pi/4$, or when γ becomes less than $\pi/2$, the strength of the PO bond increases, the strongest PO π-bond resulting when $\gamma = \gamma^0 = \arctan\beta^d(PO)/\beta^p(PO)$. However, in general, γ will not be this small since the YP bonds also want to be as strong as possible. These processes for strengthening the over-all PO bond all tend to decrease the YPY angle, although steric factors favor the tetrahedral arrangement.

In applying our MO method to the π-electrons in these systems,[2] we need consider only a single π-bonding MO, $\Psi(Xe)$. Then the π-electron energy per electron can be written as

$$E_\pi = \sin^2\theta\,\alpha_P + \cos^2\theta\,\alpha_O + 2\sin\theta\cos\theta\,\beta_{PO},$$

where $\alpha_i = \int\Phi_i H\Phi_i\,dv$ and $\beta_{PO} = \int\Phi_P H\Phi_O\,dv$ are the usual two-center Coulomb and exchange integrals,

respectively. An ordinary variation treatment, taking into account the dependence of α_i on θ, gives

$$\left[\alpha_P + \tfrac{1}{2}\tan\theta\,(d\alpha_P/d\theta)\right] - \left[\alpha_O - \tfrac{1}{2}\cot\theta\,(d\alpha_O/d\theta)\right] +$$
$$(\cot\theta - \tan\theta)\beta_{PO} = 0$$

In order to use this equation, we assume with Mulliken[3] that the α's are proportional to the valence state electronegativities, χ_i, that is

$$\alpha_i = (\alpha_k{}^0/\chi_k{}^0)\,\chi_i,$$

where $\alpha_k{}^0/\chi_k{}^0$ is the ratio of the Coulomb integral to the electronegativity of a "k" atom in some reference state (generally the carbon atom in benzene). We further assume that the valence state electronegativity is proportional to the charge on the atom in the molecule[4] according to the relation

$$\chi_i = \chi_i{}^0 + \delta_i\,Q_i,$$

where $\chi_i{}^0$ is the tabulated electronegativity of the ith atom, Q_i the net charge on this atom, and δ_i the change in electronegativity per unit charge. Then we find that

$$\alpha_P = (\alpha_k{}^0/\chi_k{}^0)[\chi_P{}^0 + \delta_P Z_P - \delta_P\,n^e\sin^2\theta]$$

and

$$\alpha_O = (\alpha_k{}^0/\chi_k{}^0)[\chi_O{}^0 + \delta_O Z_O - \delta_O\,n^e\cos^2\theta],$$

where here Z_i is the total (variable) formal positive charge on the ith atom exclusive of the π-electrons, and n^e the total number of π-electrons in the degenerate MO of symmetry e. It has been shown[2] that a degenerate orbital such as this can be treated as pairs of equivalent two-electron orbitals by replacing n^e by $(^1/_2 n^e + 1)$, so that from the above relations we find that the basic equation for our MO method in this case takes the form

$$(\chi_P{}^0 - \chi_O{}^0) + (\delta_P Z_P - \delta_O Z_O) - (^1/_2 n^e + 1)(\delta_P - \delta_O) +$$
$$(^1/_2 n^e + 1)(\delta_P + \delta_O)\cos 2\theta + 2(\chi_k/\alpha_k{}^0)\beta_{PO}\cot 2\theta = 0.$$

Solution of this equation for θ in any particular instance gives the coefficients in the π-bonding MO, $\Psi(Xe)$, and from these the bond characters can be obtained.

As we have seen, the π-bonding in the PO bond results entirely from the four π-electrons in $\Psi(Xe)$ distributing themselves on the nuclear framework $P^{+Z_P}-O^{+Z_O}$. However, in order to take into account the effect of the σ-bond polarity on the π-electron distribution, we must interpret Z_P as the total formal positive charge on the P-atom resulting from the removal of the single π-electron ($z_P = 1$) plus that due to the polarity of the YP and PO σ-bonds, and Z_O as the formal positive charge on the O-atom resulting from the removal of the three π-electrons ($z_O = 3$) plus that from the reversed polarity of the PO σ-bond. That is

$$Z_P = z_P + 3U_Y + U_O$$
$$Z_O = z_O - U_O$$

where the U-values represent the amount of charge to be apportioned to the atoms as a result of the σ-bond polarity. These U-values will depend upon the electronegativity differences between the Y and P and between the O and P atoms. In lieu of a more satisfactory and convenient approach, we use Pauling's expression[5] for U

$$U_i = 1 - \exp\{-\,^1/_4(\chi_i - \chi_P)^2\}$$

but the electronegativity values must be the valence state electronegativities actually occurring in the molecule, i.e.

$$\chi_P = \chi_P{}^0 + \delta_P Q_P = \chi_P{}^0 + \delta_P(z_P + 3U_Y + U_O - q_P{}^\pi)$$
$$\chi_O = \chi_O{}^0 + \delta_O Q_O = \chi_O{}^0 + \delta_O(z_O - U_O - q_O{}^\pi)$$
$$\chi_Y = \chi_Y{}^0 + \delta_Y Q_Y = \chi_Y{}^0 + \delta_Y(-U_Y)$$

(3) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949).
(4) P. and R. Daudel, *J. Phys. Radium*, **7**, 12 (1946).
(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, p. 98.

TABLE II
BOND CHARACTERS IN R_3PO AS FUNCTIONS OF β AND γ

$\beta(p\pi)$, ev.	$\beta(d\pi)$, ev.	$\gamma = 90°$			$\gamma = 60°$			$\gamma = 45°$		
		U_0	$\pm Q$	P_π	U_0	$\pm Q$	P_π	U_0	$\pm Q$	P_π
−1.0	0	0.13	1.130	0	0.18	0.849	0.553	0.196	0.777	0.866
	−0.5	.182	0.849	0.553	.201	.755	0.997	.218	.679	1.449
	−1.0	.217	0.697	1.345	.22	.676	1.478	.237	.599	2.071
−2.0	0	.13	1.130	0	.217	.697	0.673	.237	.599	1.036
	−0.5	.182	0.849	0.276	.231	.626	0.923	.253	.532	1.360
	−1.0	.217	.697	0.673	.244	.566	1.184	.268	.473	1.693
	−2.0	.263	.494	1.576	.268	.467	1.725	.292	.375	2.378
−3.0	0	.13	1.130	0	.241	.582	0.742	.268	.473	1.129
	−1.0	.217	0.697	0.449	.265	.479	1.101	.292	.375	1.585
	−2.0	.263	0.494	1.051	.286	.397	1.472	.312	.297	2.052

TABLE III
CALCULATED BOND CHARACTERS IN Y_3PO MOLECULES

Compound	$\beta(p\pi)$, ev.	$\beta(d\pi)$, ev.	γ	% d in $\Phi(3Xe)$	PO bond character			Charge on 3Y
					Q_P	Q_O	P_π	
F_3PO	−2.2	−1.2	28° 37′	22.93	+1.332	−0.201	1.983	−1.131
$(C_6H_5O)_3PO$	−2.0	−0.7	53°	63.78	+0.896	− .443	1.356	−0.453
$(CH_3C_6H_4O)_3PO$	−1.9	− .6	59°	73.47	+ .826	− .526	1.188	− .30
Cl_3PO	−1.9	− .6	59°	73.47	+ .826	− .526	1.188	− .30
$(p\text{-}NO_2C_6H_4CH_2O)_3PO$	−1.9	− .6	59°	73.47	+ .826	− .526	1.188	− .30
$(CH_3O)_3PO$	−1.9	− .55	62°	77.96	+ .792	− .561	1.079	− .231
Br_3PO	−1.9	− .5	65°	82.14	+ .766	− .598	0.961	− .168
$(c\text{-}C_6H_{11})_3PO$	−1.8	− .35	72°	90.45	+ .747	− .717	.647	− .03
$(C_6H_5)_3PO$	−1.7	− .2	78°	95.68	+ .842	− .827	.370	− .015
$(ClC_6H_4)_3PO$	−1.7	− .1	84°	98.91	+ .925	− .946	.144	+ .021
$(CH_3)_3PO$	−1.6	0	90°	100	+1.03	−1.132	0	+ .102

where q_i^π is the fractional number of π-electrons ending up on the ith atom.

Using these results the basic equation we must solve to get the LCAO coefficients in the π-bonding MO of Y_3PO molecules takes the form

$$1.800 \cos 2\theta - (1.22/2.84)\, \beta_{PO}^h \cot 2\theta = 1.9333 - (0.8\, U_Y + 0.6\, U_O)$$

Here we have used the values $\alpha_C^0/\beta_{CC}^0 = 4.1$, $\beta_{CC}^0 = -2.84$ ev., and $\chi_C^0 = 2.50$. In this equation, β for the hybrid orbital is given by

$$\beta_{PO}^h = \cos\gamma\,\beta(p\pi) + \sin\gamma\,\beta(d\pi)$$

which has its maximum when $\gamma = \gamma^0 = \arctan \beta^d/\beta^p$. Then our procedure is to solve this basic equation by an iterative method for the appropriate values of γ (which will depend on the nature of the Y-substituents) consistent with the expressions for U, and from these results calculate the bond characters using the atomic charge relations

$$Q_P = Z_P - q_P\pi = Z_P - (2 - 2\cos 2\theta)$$
$$Q_O = Z_O - q_O\pi = Z_O - (2 + 2\cos 2\theta)$$
$$Q_Y = -U_Y$$

and the PO π-bond order expression[2]

$$P_\pi = 2 \sin 2\theta\, \beta^h/\beta^p$$

The justification for this procedure is that from a set of reasonable and self-consistent assumptions good correlations are obtained between calculated and experimental quantities.

In the case where the substituent Y is an idealized alkyl group R, and the RP bonds are strictly homopolar, $Z_P = z_P + U_O$, $Z_O = z_O - U_O$, and we can probably take γ near $\pi/2$ so that $\beta^h = \beta^d$. The coefficients of the π-bonding MO are now obtained by solution of the equation

$$4.1902 \cos 2\theta - \beta^d \cot 2\theta = 4.5006 - 1.3967\, U_O$$

The atomic charges and π-bond orders as functions of β^d and β^p for R_3PO molecules are shown in Table II under the heading $\gamma = 90°$ together with the iterated values of U_O. In the more real situations, γ is always less than $\pi/2$. In such cases the bond characters

depend on the hybridization parameter in $\Phi_p(3Xe)$ in the manner shown in the other columns in Table II.

When Y is a strongly electronegative group, the Y–P bonds will tend to form polarities whose bond dipole moments oppose that in the PO bond and thereby further increase the formal positive charge on the P-atom. As a result of this polarity the Y–P σ-bonding MO $\Psi(r'e)$ will be prepared to cede some of its 3p-character to the P–O π-bonding MO $\Psi(Xe)$, and consequently strengthen the PO π-bonding by letting γ approach the optimum value γ^0. At the same time the increased formal positive charge associated with the P-atom will further strengthen the π-bonding by increasing the magnitude of $\beta^d(PO)$ as well as by decreasing the electronegativity difference between the P and O atoms. In the limit, which is probably attained with F_3PO, we may take $\gamma = \gamma^0$. Then by comparison with other compounds,[6] we choose $\beta^d(PO) = -1.2$ ev., and from overlap considerations we take $\beta^p(PO) = -2.2$ ev., so that $\gamma^0 = 28°37'$ and $\beta^h(PO) = -2.5$ ev. The basic equation we must solve to get the π-electron distribution in F_3PO then becomes

$$1.6694 \cos 2\theta + \cot 2\theta = 1.7931 - 0.9274(0.8U_F + 0.6U_O)$$

The iterated electronegativity differences between the F and P and between the O and P atoms give $U_F = 0.377$ and $U_O = 0.211$ as the charges "transferred" to the P-atom by the FP and OP σ-bonds. These result in a π-bond order for the PO bond of 1.983 and a net charge distribution representable by the structure

$$-1.131\quad +1.332\quad -0.201$$
$$F_3\!\equiv\!P\!\equiv\!O$$
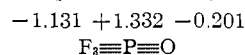
This structure predicts a resultant dipole moment of 1.35 D. in the direction of the F-atoms assuming tetrahedral FPF angles. Using FPF angles of 106.5° gives a calculated dipole moment of 1.735 D., exactly equal to the experimental value.[7] At the other extreme, in the case of $(CH_3)_3PO$, very probably $\gamma = 90°$ and $\beta^d = 0$. These assumptions result in a PO π-bond order of zero, and give for the σ-bond charge transfers to

(6) W. Moffitt, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950).
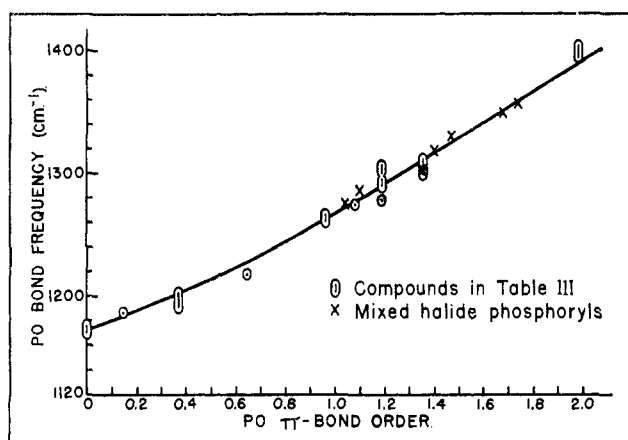
(7) S. J. Senatore, *Phys. Rev.*, **78**, 293 (1950).

Fig. 1.—Correlation between PO bond orders and stretching frequencies in Y₃PO molecules.

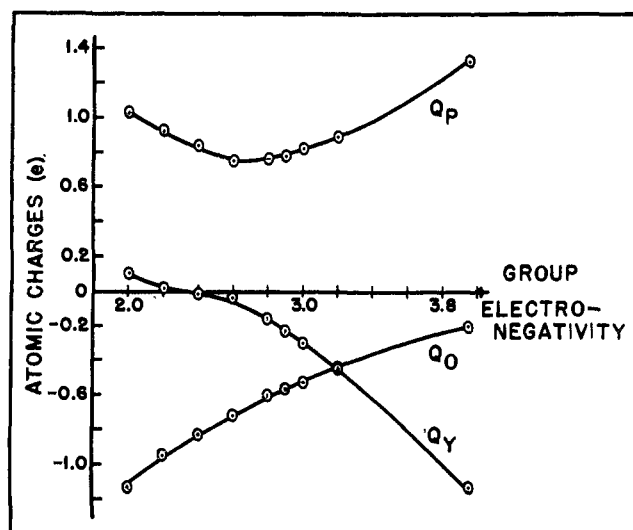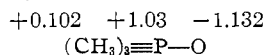Fig. 2.—Variation of atomic charge with group electronegativity of Y-substituent in Y₃PO molecules.

the phosphorus atom $U_O = 0.132$ and $U_Y = -0.034$, so that the bonding and net charge distribution in the molecule can be represented by the structure

$$+0.102 \quad +1.03 \quad -1.132$$
$$(CH_3)_3{\equiv}P{-}O$$

The dipole moment here would be of the order of 8.5 D. in the opposite direction if we neglect any CH₃-group moments.

Since the hybridization parameter γ will depend primarily on the nature of the substituents Y, we can use the two points from F₃PO and (CH₃)₃PO to estimate the γ-values for the other Y₃PO molecules if we assume an approximately linear relationship between γ and the electronegativity of the Y-group.[1] Furthermore, since β^d(PO) depends upon the formal positive charge on the phosphorus atom, we can also correlate β^d with Z_P in the different compounds. The values obtained for γ and β^d in this manner are shown in Table III together with the corresponding β^p(PO) values as estimated from the $(3p\pi, 2p\pi)$ overlap integrals.[8] From these values the pd-hybridization of the Φ(3Xe) orbital on the phosphorus that is involved in the PO π-bonding, the PO bond characters, and the charges on the Y-atoms have all been calculated and also listed in Table III.

(8) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys., 17, 1248 (1949).
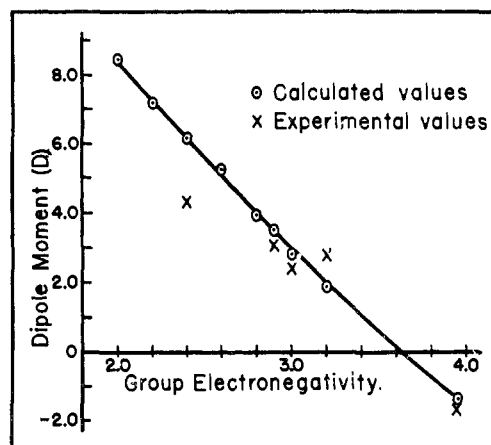

Fig. 3.—Calculated dipole moment *versus* Y-group electronegativity in Y₃PO molecules.

These results are not greatly sensitive in their general trends to our original choice of β^p and β^d in the appropriate ranges expected. They also indicate that the PO bond in these compounds varies from a nearly pure coördinate single bond in (CH₃)₃PO to nearly a triple bond in F₃PO. This additional bonding results from the four π-electrons distributing themselves in the PO π-bonding MO Ψ(Xe). This bonding is greater the more p-character in the P-atom hybrid orbital involved in this π-bond, the greater the formal positive charge on the P-atom, and the smaller the electronegativity difference between the P- and O-atoms. The calculated PO π-bond orders increase regularly in the series of compounds listed and correlate well with the PO bond stretching frequencies, as shown in Fig. 1, and with the PO bond force constants estimated from these frequencies. Points not exactly on the curves can be made to fit by small changes in the starting electronegativities of the appropriate Y-groups.

The net electronic charges on the oxygen atoms and on the three Y-atoms vary monotonically in the series, but the resultant positive charge on the central P-atom goes through a minimum when the electronegativity of the substituent Y-group is about 2.7 on the Pauling scale, as shown in Fig. 2. Thus for nucleophilic reactions involving the charged phosphorus atom, such as hydrolysis reactions, other factors being equal, one would expect greater reactivity with the members at either end of the series than with those in between. Unfortunately, reliable structural data in the form of bond distances and angles are almost completely lacking for these compounds so that dipole moment calculations based on our calculated charge distributions can only be made using estimated bond lengths and assumed bond angles. The values so obtained, assuming tetrahedral angles and neglecting the charge distributions in the Y-groups, are plotted on Fig. 3. From this we would predict large dipole moments in the PO direction for molecules with small Y-group electronegativities which decrease regularly with increasing electronegativity reaching a minimum of zero when the electronegativity of the substituent Y-group is about 3.6, beyond which there is a reversal in direction. Of course, the Y-group moments and the smaller true YPY angles, in certain cases, may greatly affect these calculated values; nevertheless, the meager experimental data available[9] reflect this calculated trend.

(9) J. A. A. Ketelaar, H. R. Gersmann and F. Hartog, Rec. trav. chim., 77, 982 (1958).