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Calculations on Some Phosphate Ions by a Modified CNDO Method

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Calculations are presented of the electronic structures of some phosphate ions, namely, H_3PO_4, $H_2PO_4^-$, $HPO_4^{=}$, $PO_4^{\equiv}$, HPO_3, and PO_3^-. It is shown that the π character of the P–O bonds is marked and the 3*d* orbitals contribute substantially to the bonding. Using the total energy data for the orthophosphate ions, the ratio of the dissociation constants for the ions is calculated and found to be in good agreement with the experimental data.

Introduction

In a previous paper [1] we have discussed the participation of the phosphorus 3*d* orbitals in the P–O bond and the way in which the chemistry of the compounds concerned may be correlated with this. An important class of P–O compounds comprise the oxyacids in which, moreover, there has been speculation as to the mechanism and extent of *d*-orbital participation. It is therefore the purpose of this paper to investigate the potentiality of CNDO-type SCF theory to describe the bonding in orthophosphoric acid, H_3PO_4, and the related conjugate bases $H_2PO_4^-$, $HPO_4^{=}$ and $PO_4^{\equiv}$. Metaphosphoric acid, HPO_3, and its anion PO_3^-, are also considered. From the calculated total energies, qualitative information about equilibrium constants involving the above species can also be obtained.

Phosphoric acid has been studied previously by the NEMO method [5] and the extended Hückel method [2]. The latter authors found that the inclusion of 3*d* orbitals was not strictly necessary to explain many of the properties of the phosphorus-oxygen bond. However, better agreement with *ab initio* calculations, plus a generally more satisfactory account of physical properties may be generated if they are included. A series of calculations, by the extended Hückel method, on simple phosphate ions has also been carried through [6].

Further cogent evidence for the importance of *d* orbital participation comes from the work of Lipscomb and Boyd [3], who performed LCAO MO SCF calculations on PH_3, PO, and PO^-: they found that inclusion of 3*d* orbitals in the basis set improved the total energies significantly and also altered the distribution of electronic charge. These and other authors have also concluded that participation of phosphorus 3*d* orbitals in the phosphate ion, $PO_4^{\equiv}$, would be substantial [3, 9]. In addition, an *ab initio* calculation on the hypothetical ion PO_2^- revealed a 58% contribution by phosphorus 3*d* to the P–O overlap population [4]. It therefore seems reasonable to expect that, in compounds containing the phosphate group, *p*–*d* bonding would be manifest, and experimental data

(e. g., the bond angle in tetrametaphosphate [8] and thermochemical studies of triethylphosphate [7]) have been invoked as evidence for its reality.

Because the previous calculations (cited above) on the phosphate ions were of a non-iterative type, then the charge distribution yielded is likely to be distorted. Hence, a new calculation of the charge distribution seemed to be required. The calculational scheme employed here was essentially the same as that of the previous papers [1, 14a] although "atomic" repulsion integrals were employed. In the light of the previous findings [1], the most appropriate *d* orbital for phosphate ions is clearly the contracted form. Calculations were performed in which the *d* orbitals were neglected or were included in a "diffuse" or "contracted" form [14b]. Of the latter two series, only the results from the contracted orbitals are reported here.

Bond lengths and interbond angles for neutral H_3PO_4 and HPO_3 were abstracted from "Interatomic Distances" [12]. The geometries of the ions related to H_3PO_4 were then generated by stepwise removal of hydrogen from neutral H_3PO_4, leaving the rest of the species unperturbed. For PO_3^-, a planar ion was assumed with a P–O bond length of 1.54 Å.

Results and Discussion

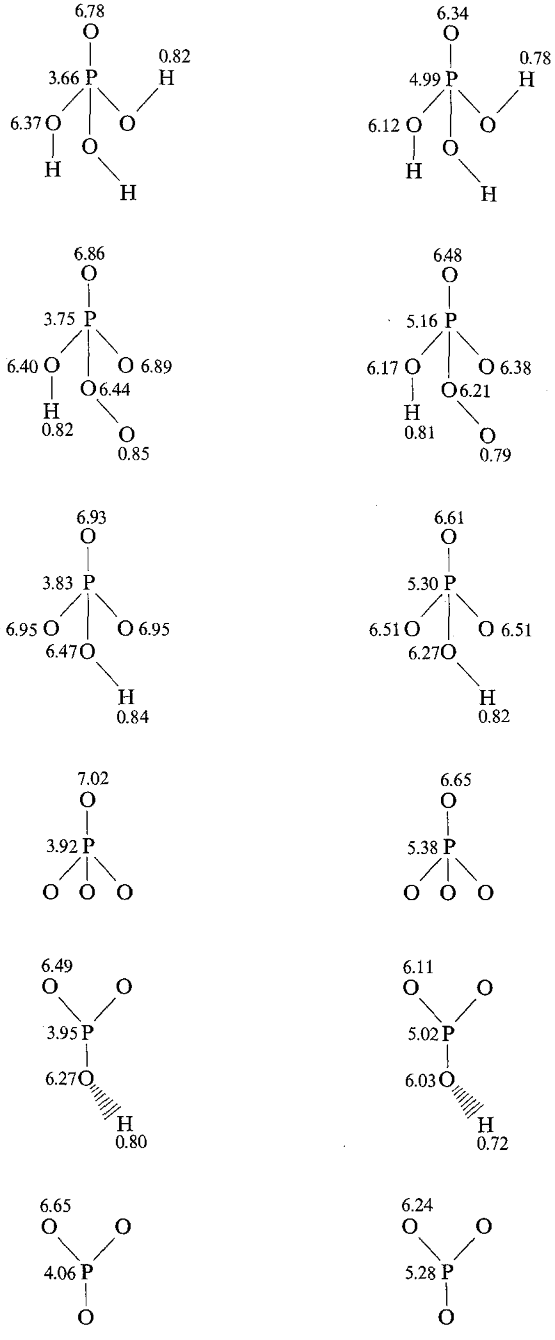
a) *Charge Distribution*

A population analysis performed on each species yielded the charge distributions shown in Fig. 1. Series A are the results from calculations which neglected the 3*d* orbitals whilst for Series B they were included.

The atom charges are substantially evened out and are clearly much more realistic when *d* orbitals are included in the basis set. The total *d* orbital populations are considerable and range from 1.7 to 2.1 electrons in HPO_3 and $PO_4^{\equiv}$ respectively. Similar results have previously been found for other compounds containing P–O bonds [1, 3, 4, 15], although the actual orbital populations were lower. The *d* orbitals become occupied at the expense of the 3*p* orbitals and this seems to be quite general for phosphorus compounds [1, 10, 11, 13].

It is interesting that the *excess* charges on the ionic species are very much concentrated on the oxygen atoms, the hydrogens being quite positive. The phosphorus atom is effectively neutral in H_3PO_4 but increases in negative character over the series H_3PO_4, $H_2PO_4^-$, $HPO_4^=$, $PO_4^{\equiv}$. The same trend occurs in the two species HPO_3, PO_3^-. The trend in charge in the former series is identical to that of Boyd and Lipscomb's calculations [3], although there is a displacement in the absolute values (e.g., the previous authors obtained a charge of +0.27 on the phosphorus atom in H_3PO_4).

These observations are consistent also with those of Lipscomb and Boyd [3, 4] in their study of PO, PO^- and PO_2^-. For the first they found that the phosphorus atom was slightly positive (as we find in H_3PO_4) whilst in PO^- and PO_2^- the phosphorus is substantially negative (in PO_2^- it was calculated that the P atom is negatively charged to the extent of 0.61e). If our charge distributions are combined with those of the *ab initio* work of Lipscomb and Boyd, we find that the negative charge on phosphorus for the singly negative ions decreases



Series A

Series B

Fig. 1. Charge distribution in phosphate ions. – Series A without 3*d* orbitals. Series B with contracted 3*d* orbitals

in the order $PO^- > PO_2^- > PO_3^- > H_2PO_4^-$. In the species studied by Lipscomb and Boyd, a substantial *d*-orbital population was also found in the calculations.

With regard to bond orders involving the phosphorus *d* orbitals, we studied the P–O interactions by orienting each species in C_{3v} symmetry, i.e., with a P–O bond coincident with the C_3 axis; we find that the dominant contributions to the P–O bond are of π type and the sum of these contributions changes in the order: $H_3PO_4 > H_2PO_4^- > HPO_4^{=} > PO_4^{\equiv}$. The σ-type interactions are similar for these species. The π interactions are therefore substantial and are an important factor which must be included in any discussion of the behaviour of phosphate ions or esters.

b) *Molecular and Orbital Energies*

The calculated total energies for all the species, both with and without the *d* orbitals, indicates that there is a stabilising energy gain in each case when *d* orbitals are admixed. This varies between 4.0 and 4.7% of the total energy for the different moieties. The proportional energy gain is thus strikingly similar to that calculated for other compounds containing the P–O bond [1].

The total energies can also be used in an informative way to correlate with the experimental dissociation constants of the ions. Thus, for the dissociation of H_3PO_4 in aqueous solution to its conjugate bases $H_2PO_4^-$, $HPO_4^{=}$, and $PO_4^{\equiv}$, the dissociation constants at 298 K have been determined experimentally [16].

$$\begin{aligned}
H_2O + H_3PO_4 &\rightleftharpoons H_2PO_4^- + H_3O^+ & K_1 &= 0.752 \times 10^{-2}, \\
H_2O + H_2PO_4^- &\rightleftharpoons HPO_4^{=} + H_3O^+ & K_2 &= 0.623 \times 10^{-7}, \\
H_2O + HPO_4^{=} &\rightleftharpoons PO_4^{\equiv} + H_3O^+ & K_3 &= 0.22 \times 10^{-12}.
\end{aligned}$$

These K_a values are the thermodynamic dissociation constants and are affected only by temperature and solvent (which in this case is water itself).

The dissociation constant in each case is related to the standard free energy change by

$$-\Delta G^0 = RT \ln K.$$

Equilibrium constants for the above processes can therefore be correlated with the calculated energies because $-\Delta G^0$ at the absolute zero in each case is related to the change in total electronic energy in the reaction. The latter quantity, ΔE, refers to a reaction between single molecules at the absolute zero and, hence, no thermal effects (vibrational-rotational contributions) or statistical effects bear on the problem. At 0 K, $\Delta H^0 = \Delta G^0$ and we correlate these quantities with the calculated change in total energy, ΔE, from the left- to the right-hand side of the reaction. As stated above, ΔE involves only a change in electronic and coulombic nuclear repulsive energy. The temperature dependence of the right-hand side of the above equation for ΔG^0 can be eliminated if we compare the *ratio* of calculated ΔE values for the three reactions with the ratio of the observed equilibrium constants. In doing this, the reasonable assumption is made that the *ratio* of the three measured equilibrium constants is essentially the same at the absolute zero as at the temperature of measurement (298 K). The standard free energy changes in the reactions were computed by calculating the energy changes on going from left to right in the reactions. This also required separate computations of the total energies of H_2O and H_3O^+.

For the reactions 1, 2, 3 we obtain by calculation $\ln K_1 : \ln K_2 : \ln K_3 = 1 : 2.43 : 4.57$, whilst the experimental ratio is $1 : 3.39 : 5.96$. The agreement is very satisfactory, particularly considering the approximations inherent in such calculations. Since the calculations do reproduce the known acidity order: $H_3PO_4 > H_2PO_4^- > HPO_4^=$, then the method may be a valuable way of obtaining information about the acidity of protons in compounds in general.

The calculations also show an internal consistency in that, in the "mixed" reactions between the ions,

$$H_3PO_4 + HPO_4^= \rightleftharpoons 2H_2PO_4^-$$

and

$$H_2PO_4^- + PO_4^{\equiv} \rightleftharpoons 2HPO_4^= .$$

$-\Delta G^0$ (experimental) is positive left to right and the calculated change in total energy is positive for each reaction in the same way. Hence, despite the known deficiencies of semi-empirical SCF theory, calculated data concerning equilibrium constants agree well with experiment.

When the nature and energy of the highest bonding orbital in neutral H_3PO_4 is examined, it is found that this orbital lies at -7.8 eV and is concentrated mainly on the four oxygen atoms. This is consistent with the known ability of aqueous solutions of orthophosphoric acid to complex with and extract many metal ions.

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