

so a comparison of metrical parameters in these two complexes is not complicated by solid-state effects. The theoretical studies examined $M(R_1)(R_2)(PH_3)_2$ complexes, $M = Pd, Pt$; $R_1, R_2 = H, CH_3$.

These theoretical and experimental studies were completed simultaneously and independently (Table I). Of particular interest are the differences in bond lengths, $\Delta_C = (Pt-C) - (Pd-C)$ and $\Delta_P = (Pt-P) - (Pd-P)$, which are of opposite sign.⁸ Figure 1 illustrates the inner coordination sphere in these complexes and presents pertinent bond distances and angles. Coordination about the central metal in both complexes is essentially square-planar with a very slight tetrahedral distortion. Chemically equivalent bond distances in both structures agree within the estimated standard deviations. Average distances are tabulated in Table I. No structures of comparable accuracy have been reported that permit a reliable estimate of Δ_C ; there are a few structures where Δ_P has been determined to about the same level of significance [e.g., $M[P(Ph)(t-Bu)_2]_2$, $Pt-P = 2.252$ (1), $Pd-P = 2.285$ (2) Å, $\Delta_P = -0.033$ (2) Å].⁹

One would expect that the opposite sign found for Δ_P and Δ_C is connected with some change in the electronic character of the wavefunctions for Pd vs. Pt. This could be considered consistent with the general trend in the literature that "hard" or σ -bonding ligands, such as alkyls and halides, tend to show longer bonds to third-row transition metals than to their second-row analogues, whereas the opposite is true for "soft" or π -bonding ligands, such as phosphines. We will now use the wavefunctions from theory to analyze more precisely the origin of geometric changes from Pd to Pt.

In fact, detailed comparisons of the electronic structure for Pd-C vs. Pt-C bonds do not provide an explanation of the short Pd-C bond length relative to Pt-C. Thus, calculations on $M(CH_3)_2$ yield $Pt-C = 1.97$ Å vs. $Pd-C = 1.96$ Å and $C-Pt-C = 98^\circ$ vs. $C-Pd-C = 92^\circ$, which can be compared with 2.06 Å, 2.02 Å, 89°, and 81° calculated for $M(CH_3)_2(PH_3)_2$. All four complexes involve M-C bonds that are essentially covalent with one electron in a C sp^3 orbital and the other in an M spd hybrid. [$Pt(CH_3)_2(PH_3)_2$ $Pt = s^{0.23}p^{0.10}d^{0.49}C^{0.17}$ and $CH_3 = (sp)^{-0.03}d^{0.13}C^{0.18}p^{0.71}$; $Pd(CH_3)_2(PH_3)_2$ $Pd = s^{0.17}p^{0.07}d^{0.49}C^{0.24}$ and $CH_3 = (sp)^{-0.02}d^{0.15}C^{0.18}p^{0.68}$; $Pt(CH_3)_2$ $Pt = s^{0.27}p^{0.01}d^{0.62}C^{0.10}$ and $CH_3 = (sp)^{0.00}d^{0.15}C^{0.14}p^{0.70}$; $Pd(CH_3)_2$ $Pd = s^{0.16}p^{0.03}d^{0.55}C^{0.24}$ and $CH_3 = (sp)^{0.01}d^{0.20}C^{0.28}p^{0.52}$.] The effective electronic configuration on the metal is d^9s^1 , affording two singly occupied orbitals (one s, one d) that are hybridized to form two sd hybrids suitable for bonding the two methyl groups. The M orbital of Pd has less sp character (0.24 Pd vs. 0.33 Pt) and concomitantly more charge transfer to the CH_3 (0.24 Pd vs. 0.17 Pt). Such a difference is not surprising since Pt prefers the d^9s^1 atomic configuration, whereas Pd prefers d^{10} . Unfortunately these differences do not account for our mystery. The $M(CH_3)_2$ bonds have nearly the same bond distances but similar differences in hybrid character. Analysis of Mulliken populations for the Pd and Pt complexes shows less M sp character on Pd (by 0.40 e) for $M(CH_3)_2(PH_3)_2$, but the same comparison for $M(CH_3)_2$ shows a similar decrease (by 0.37 e).

Because of the large increase in relativistic effects from Pd to Pt, the valence s electrons on Pt are greatly stabilized with respect to valence d electrons, leading to a d^9s^1 ground state for Pt (with d^{10} higher by 11.0 kcal/mol),¹⁰ whereas Pd has a d^{10} ground state (with d^9s^1 higher by 21.9 kcal/mol).¹⁰ Similarly, the electron affinity¹¹ of Pt(d^{10}) is 2 eV greater than for Pd(d^{10}). Since Pt d^{10} is a far better Lewis acid than Pd d^{10} , it is not surprising that Pt(PH_3)₂ has a much shorter bond distance than Pd(PH_3)₂. (From

theory $Pt-P = 2.32$ Å vs. $Pd-P = 2.41$ Å for linear complexes.) Addition of the two methyl groups forces the phosphines together (calculated $P-Pt-P = 101^\circ$, $P-Pd-P = 98^\circ$) and promotes the metal from d^{10} toward d^9s^1 . Both these effects tend to increase the M-P distance, but the Pt-P remains 0.04 Å smaller. Comparing $M(CH_3)_2$ and $M(CH_3)_2(PH_3)_2$, we find that the Pt- CH_3 bond distance increases by 0.09 Å, while the Pd- CH_3 bond distance increases by only 0.06 Å. The smaller increase for Pd can be understood in terms of the smaller PH_3-CH_3 interactions that result from the longer Pd- PH_3 bond distance. This explanation that steric effects dominate the differences in Δ_C between Pd and Pt is consistent with the fact that the respective $P \cdots C(Me)$ distances in the two compounds are essentially equal [3.038 (6) and 3.197 (7) Å for Pt and 3.022 (3) and 3.189 (3) Å for Pd]. Additional structural studies of comparable accuracy would be valuable in ascertaining the generality of this explanation in terms of both electronic and steric effects.

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On the Freeness of the Metaphosphate Anion in Aqueous Solution

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The mechanism of hydrolysis of phosphate monoesters remains uncertain in spite of intensive study in a number of laboratories.¹ On the basis of pH-rate profiles, the involvement of a hypothetical metaphosphate ion in the aqueous solvolysis of these compounds was first proposed 3 decades ago by Westheimer² and by Bunton.³ Bunton^{4a} and Kirby^{4b} further supported this mechanism with studies on the hydrolysis of substituted phenyl phosphates at a number of pH values. Subsequent medium and product studies uncovered evidence of free metaphosphate ion in aprotic media,⁵ and its direct observation in the gas phase by negative ion mass spectrometry was reported shortly thereafter.⁶

Recent investigations, on the other hand, have tended to emphasize that these reactions cannot generate a completely free metaphosphate ion intermediate, at least not in protic media. The hydrolysis of esters chiral at phosphorus by ¹⁶O, ¹⁷O, and ¹⁸O substitution proceeded with inversion of configuration.⁷ Transfer of a phosphoryl residue from a pyridinium^{8a} or quinolinium^{8b}

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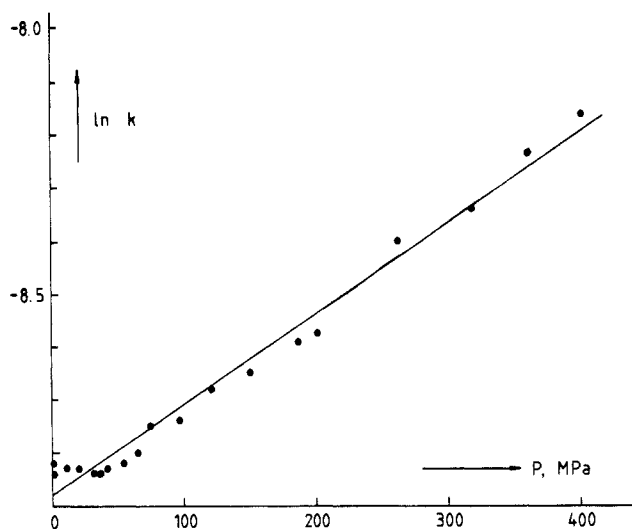


Figure 1. Pseudo-first-order rate constants as a function of pressure (1 MPa = 10 bar) for the hydrolysis of 2,4-dinitrophenyl phosphate at pH 12 (43.2 °C).

phosphonate to a substituted pyridine was found to be kinetically second-order and furthermore the second-order rate constants were not quite independent of the pK_a of the attacking pyridine.

Although a long-lived free intermediate is thus ruled out, there is at present no convincing proof for or against the fleeting existence of a metaphosphate ion which remains paired with the leaving group until it is captured. Even investigators who observed a metaphosphate transfer between polymer moieties were unable to give assurance that the reaction occurred without the intervention of a carrier.⁹

The volume change on going from a reactant to an intermediate is informative with regards to the competition between bond making and bond breaking processes.¹⁰ The former is obviously associated with shrinkage and the latter with expansion. Typically the magnitudes of these changes may amount to 20 cm³/mol (these values are calculated from the effect of hydrostatic pressure on the rates). For S_N2 displacement reactions in water both features contribute, but bond formation always dominates leading to activation volumes of -5 to -10 cm³/mol. The expansions deduced from pressure-induced rate retardations have generally exceeded +10 cm³/mol; for instance, the formation of CCl₂ in the base-promoted hydrolysis of chloroform has a ΔV^\ddagger of +16 cm³/mol.

In view of these effects we felt an investigation of the rate of hydrolysis of 2,4-dinitrophenyl phosphate dianion as a function of pressure would yield information on the mechanisms of these reactions. This compound has been extensively investigated and these studies have produced evidence which supports^{4,11} and disfavors^{7a,b} a metaphosphate ion intermediate. The liberation of 2,4-dinitrophenoxide from the phosphate dianion was found to be accelerated by pressure (Figure 1) with $\Delta V^\ddagger = -4.8$ cm³/mol. There is no way to reconcile this result with a free metaphosphate ion since simple bond cleavage should in this case have led to substantial charge delocalization which would have further magnified the expansion normally expected. The curvature often seen in such plots may screen the incursion of a small contribution from a second mechanism, however, there will then be a curvature in the Arrhenius plot. An examination of the temperature dependence of the rate, as shown in Figure 2, yielded a plot that was accurately linear over the whole range. This essentially rules out a significant contribution from a second mechanism.

We conclude that this reaction occurs by a nucleophilic attack by water at the phosphorus with loss of phenoxide ion. We must point out emphatically that these experiments have no bearing

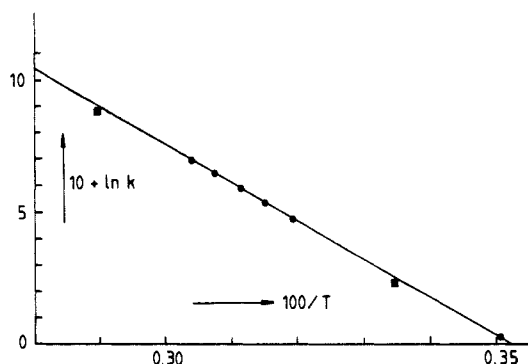


Figure 2. Arrhenius plot for the hydrolysis at atmospheric pressure. Square symbols represent data from the literature.^{4a}

on the mechanism of the reaction in aprotic media.¹² The ion pairing that inevitably accompanies the use of nonaqueous solutions makes it impossible to depend on similar evidence in these media. Since the metaphosphate ion clearly has an independent existence in the gas phase but presumably not in water, there may be liquid media of intermediate internal pressure and/or nucleophilicity in which it may survive however briefly.

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Supplementary Material Available: Rate data as a function of pressure and temperature (2 pages). Ordering information is given on any current masthead page.

(12) Indeed, subsequent to the submission of this paper, evidence was published providing strong stereochemical support for a dissociative mechanism for the reaction of phenyl phosphate with *tert*-butyl alcohol in acetonitrile (Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6126). Further support for this mechanism was also reported for a P¹,P¹-disubstituted pyrophosphate in dichloromethane (Cullis, P. M.; Rous, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 6721).

Evidence for the Formation of a CoFe₃S₄ Cluster in *Desulfovibrio gigas* Ferredoxin II

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Using EPR and Mössbauer spectroscopy we have shown previously¹ that *Desulfovibrio gigas* ferredoxin II (Fd II) contains a 3Fe cluster. EXAFS studies² and chemical analyses³ have suggested that this cluster has a cubane Fe₃S₄ core stoichiometry.

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