that Z is the atomic number minus the number of inner-shell electrons. In calculating $n/2$ we used $Z = 2$ for Hg_2^{2+}, assigning the 5d electrons to the "inner shell." The same procedure was followed by Long and Plane in calculating bond orders for tetrahalomercury(II) complexes.[24] On the other hand, it is quite possible that d electrons participate in the Hg–Hg bond, but if all ten d electrons are subtracted from the inner shell giving $Z = 12$, then the calculated bond order is 2.4.

For the Bi(III), Pb(II), and Tl(I) complexes Z was taken to be 5, 4, and 3, respectively, assigning five d electrons, but not six s electrons, to the inner shell, by analogy with Hg(I). For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ Z was taken to be 7 considering that all the d electrons are involved in either metal–metal or metal–ligand bonds. It is evident that counting electrons in this way is rather an arbitrary procedure and constitutes a limitation on the usefulness of the Long and Plane equation. It may be that for evaluation of relative metal–metal bond orders, the parameter $\bar{\alpha}_u'/r^3$ is preferable to $n/2$.

There is also the possibility that $\bar{\alpha}_u'$ depends somewhat on the shapes of the bonding orbitals. Chantry and Plane[9] suggested that increasing s-orbital contribution to carbon–carbon single bonds decreases the associated bond polarizability derivative, and rationalized the low $\bar{\alpha}'_{\mathrm{C-C}}$ of CH_3CN relative to that of CH_3CH_3 on this basis. Possibly the low value of $n/2$ found here for Hg_2^{2+} might also be a reflection of the s character of the Hg–Hg bonding orbital. On the other hand it should be pointed out in the case of H_2, where s-orbital involvement in the bonding is surely maximal, the $\bar{\alpha}'_{\mathrm{H-H}}$ calculated with the Long and Plane equation is within 25% of the experimental value.[24]

The polarizability derivatives for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are puzzling. For these two molecules the internuclear distances are nearly the same, as are the electronic structures and electronegativities, so that the metal–metal bond polarizability derivatives should be directly comparable. They are clearly in the wrong order considering that the Mn–Mn bond is expected to be substantially weaker than the Re–Re bond on the basis of electron impact measurements[26] and force constant determinations.[22] Conceivably we are dealing with a breakdown in the assumption of the Wolkenstein theory that bond polarizability derivatives are independent of the stretching of other bonds. Breakdown of this assumption has previously been suggested for highly delocalized systems.[9]

In summary, we conclude that measured Raman intensities can be used to give order of magnitude estimates of metal–metal interaction and that the method is quite sensitive. On the other hand it appears that current theory is not yet adequate to place the determination of metal–metal bond orders on a quantitative basis.

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(26) H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 2836 (1967).

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Kinetics and Mechanism of the Base-Catalyzed Exchange of Hydrogen on Hypophosphite Anion[1]

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The kinetics of the exchange of the phosphorus-bonded hydrogens in the hypophosphite anion has been studied in basic solutions, using proton nmr to follow the reaction. The exchange of $H_2PO_2^-$ follows the rate law rate $= k_{PH}(OD^-)(H_2PO_2^-)$ in D_2O and the analogous expression for $D_2PO_2^-$ in H_2O, with $k_{PH} = (3.6 \pm 0.4) \times 10^{-3}\ M^{-1}\ \mathrm{min}^{-1}$ and $k_{PD} = (1.15 \pm 0.05) \times 10^{-3}\ M^{-1}\ \mathrm{min}^{-1}$, both at 25°. A mechanism invoking base-assisted removal of the hydrogen from hypophosphite appears to be consistent with all of the kinetic data and with the equilibrium isotopic distribution in 50:50 atom % H–D mixed solvent.

Introduction

The acid-catalyzed exchange of the phosphorus-bonded hydrogens in hypophosphorous acid has been studied by Fratiello and Anderson[4] and by Jenkins and Yost.[5] These studies, particularly the latter, indicated the existence of an intermediate common to the exchange and reduction[6] reactions of H_3PO_2. This active hypophosphorous acid is believed to be an isomeric form of the normal structure of the acid. Studies of the exchange between the phosphorus-bonded pro-

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(4) A. Fratiello and E. W. Anderson, *J. Am. Chem. Soc.*, **85**, 519 (1963).

(5) W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, **11**, 297 (1959).

(6) P. Hayward and D. M. Yost, *J. Am. Chem. Soc.*, **71**, 915 (1949), and previous references cited therein.

tons and solvent in basic solution[5,7] were inconclusive, reportedly due to extensive decomposition of the hypophosphite under these conditions. We have not observed such effects under conditions appropriate to the exchange reaction and have been able to carry out a fairly complete study of the base-catalyzed exchange of the hydrogens bonded to phosphorus in the hypophosphite and deuteriohypophosphite anions.

Experimental Section

Anhydrous NaH_2PO_2 was prepared by heating $NaH_2PO_2 \cdot H_2O$ (Fisher) for ~15 hr at 100° under vacuum. D_2O (99.8% D), NaOD (99% D), and DCl (99% D) were used as supplied by Stohler Isotope Chemicals. Hypophosphorous acid (Fisher purified 50% solution) was purified by the method Jenkins and Jones.[8]

The proton nmr spectrum of the hypophosphite ion is similar to that of pure H_3PO_2, consisting of a doublet caused by phosphorus coupling. In the monodeuterated hypophosphite ion, each component of the doublet is split by the deuterium into a triplet and is shifted upfield by ~1 cps. A spectrum of a mixture of $H_2PO_2^-$ and $HDPO_2^-$ in D_2O at a pH of 8, taken on a Varian Model HA-100 nmr spectrometer, shows that there is an isotope chemical shift of 0.02 ppm as well as a change in the phosphorus–hydrogen coupling constant: $J_{P-H}(H_2PO_2^-) = 515.4$ cps, $J_{P-H}(HDPO_2^-) = 514.7$ cps. An nmr technique similar to that of Fratiello and Anderson[4] was used to follow the exchange reaction.

The kinetic experiments were carried out by mixing known concentrations of reactants (NaH_2PO_2 and NaOD) in D_2O. The reaction was followed by recording the integral of the peak areas of one of the doublet components using a Varian A-60A nmr spectrometer. The property thus followed was the concentration of phosphorus-bonded hydrogens in both species $H_2PO_2^-$ and $HDPO_2^-$. The ionic strength of all solutions was kept constant by the addition of a D_2O solution of $NaNO_3$. The temperature was controlled to ±0.8° by a Varian V-6040 variable-temperature controller. It was found that solutions of NaH_2PO_2 in D_2O did not exchange over very long periods of time (>2 weeks) and these solutions were used as a check on spectrometer drift before and after the kinetic runs.

The reverse exchange reaction

$$NaD_2PO_2 + H_2O \xrightarrow{OH^-} NaHDPO_2 + HDO$$

was studied in a similar fashion by recording the growth of the phosphorus-bonded hydrogen peaks. Deuterated sodium hypophosphite was prepared by exchanging the hydrogens in H_3PO_2 and then neutralizing the acid. A 0.2 *M* solution of H_3PO_2 in D_2O was allowed to exchange for ~48 hr. The water was removed by vacuum evaporation, keeping the temperature low to avoid oxidation to phosphite. The solution was restored to the original volume by addition of D_2O and allowed to exchange for another 24 hr. The solution was then neutralized with NaOD and the water was removed by vacuum evaporation.

Results

Essentially two observable reactions occur in the isotopic equilibration of hydrogen and deuterium in mixed hypophosphite–water systems. These are $H_2PO_2^- + (O\text{–}D) \rightleftharpoons HDPO_2^- + (O\text{–}H)$ and $HDPO_2^- + (O\text{–}D) \rightleftharpoons D_2PO_2^- + (O\text{–}H)$, where the symbols (O–D) and (O–H) stand for exchangeable D and H in the solvent system. These are presumably largely the water species H_2O, HDO, and D_2O, but might also include OH^- and OD^-. The rates of exchange between the phosphorus-bonded hydrogens and those in the solvent system are sufficiently slow that any isotopic distribution reactions among the oxygen species may safely be assumed to be at equilibrium at all points in the reaction.

The conditions of the first two series of experiments were $[D_2O] \gg [H_2PO_2^-] \gg [H_2O]$ and $[H_2O] \gg [D_2PO_2^-] \gg [D_2O]$. The reactions being studied under these conditions were for the most part

$$H_2PO_2^- \longrightarrow HDPO_2^- \longrightarrow D_2PO_2^- \qquad (1)$$

and

$$D_2PO_2^- \longrightarrow HDPO_2^- \longrightarrow H_2PO_2^- \qquad (2)$$

The reactions showed first-order kinetics with respect to hypophosphite and deuteriohypophosphite in these studies. The variations of the psuedo-first-order rate constants with catalyst concentration (OH^- or OD^-) established first-order dependence on base as well. Data are summarized for these two reactions in Tables I and II. The rate constants for both reactions were determined at 25, 35, and 45°. The rate law for reaction 1 has the form

$$\text{rate} = k_{PH}[OD^-][H_2PO_2^-] \qquad (3)$$

Table I

Data for the Reaction

$D_2O + H_2PO_2^- \rightleftharpoons H_2O + D_2PO_2$ (D_2O solvent)

Temp, °C	$[H_2PO_2^-]$, *M*	$[OD^-]$, *M*	10^3k_{PH}, M^{-1} min^{-1}
25	1.0	0.75	3.25
25	1.0	0.50	3.68
25	1.0	0.25	3.60
25	1.0	1.0	3.55
25	0.5	1.0	3.22
25	1.0	0.50	2.90
25	1.5	0.5	3.96
25	1.75	0.25	4.24
25	1.9	0.10	4.40
25	1.0	1.0	4.08
25	0.5	1.0	3.41
25	0.25	1.0	3.07
35	1.0	1.0	11.0
35	0.5	1.0	9.5
35	1.0	0.5	10.7
45	1.0	1.0	29.9
45	1.0	0.5	32.6
45	1.2	0.4	25.2

Table II

Data for the Reaction

$H_2O + D_2PO_2^- \overset{OH^-}{\rightleftharpoons} D_2O + H_2PO_2^-$ (H_2O solvent)

Temp, °C	$[D_2PO_2^-]$, *M*	$[OH^-]$, *M*	10^3k_{PD}, M^{-1} min^{-1}
25	0.50	1.0	1.17
25	0.50	1.0	1.12
35	1.01	1.0	4.56
35	1.00	1.0	3.98
45	1.02	1.0	7.60
45	0.66	1.0	8.98

Average deviations among the rate constants for a given temperature were about 10%. All of the rate constants and Arrhenius activation energies are summarized in Table III. In all cases data are for a constant ionic strength $\mu = 2.0$.

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[7] A. I. Brodski and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **85**, 1277 (1952).

[8] W. A. Jenkins and R. T. Jones, *J. Am. Chem. Soc.*, **74**, 1353 (1952).

TABLE III

SUMMARY OF KINETIC PARAMETERS

Temp, °C	Forward[a] (D_2O solvent) 10^3k_{PH}, M^{-1} min^{-1}	Reverse[b] (H_2O solvent) 10^3k_{PD}, M^{-1} min^{-1}
25	3.6 ± 0.4	1.15 ± 0.05
35	10.4 ± 0.6	4.3 ± 0.3
45	29 ± 3	8.3 ± 0.7

[a] $E_a = 18.9 \pm 0.5$ kcal/mol. [b] $E_a = 18.7 \pm 1.5$ kcal/mol.

The catalysis of the exchange reaction is not limited to hydroxide ion. A comparison between the exchange carried out at pH 11 in the presence of a high phosphate ion concentration and the same reaction with only NaOH present at pH 11 showed that phosphate did also catalyze the exchange. The specific rate constant was smaller for phosphate ion than for hydroxide. Quantitative studies were not pursued, but the reaction apparently is subject to general base catalysis.

Attempts were also made to determine the value of the equilibrium ratio $(HDPO_2^-)/(H_2PO_2^-)$ in 50:50 atom % H–D solvent mixtures by allowing basic solutions of hypophosphite to equilibrate with the solvent. (No detectable decomposition occurred over the duration of these experiments, which lasted up to several days.) The determinations were made using one component of the triplet peak of the proton in $HDPO_2^-$ as a measure of its concentration and the strong central peak as the sum of $H_2PO_2^-$ and $HDPO_2^-$ contributions.

Owing to the small peak separations and relatively low signal-to-noise ratio, the results were not very precise, yielding a value of 1.1 ± 0.2 at both 25 and 45°. A kinetic study of the approach to equilibrium in a mixed-solvent system was also made, the results of which are discussed below.

Discussion

Previous studies of reaction mechanisms involving hypophosphorous acid[4–6] have fairly conclusively established the existence of an "active" form of the acid, postulated[5] to be an isomeric form of $H_2PO(OH)$ containing triply connected phosphorus, $HP(OH)_2$. This is the species believed directly involved in the observed exchange and oxidation behavior of hypophosphorous acid and is probably derived from the ionization of a phosphorus-bonded proton in the protonated acid $H_2P(OH)_2^+$.[9] As there is no pathway for exchange except those involving acid catalysis, water is clearly not a sufficiently strong base to remove very weakly acidic P–H protons in the free acid itself, but the acidity is increased sufficiently by protonation of the additional oxygen atom to allow the formation of a small amount of $HP(OH)_2$ to occur. Reactions of P–H protons in other systems show very similar behavior.[10,11] A mechanism based upon analogous behavior of the P–H bonds in the presence of much stronger bases than water appears to be consistent with the present observations on the base-catalyzed exchange of the hydrogens on the hypophosphite anion.

The rate-determining step in reaction 1 is, as shown above, first order in hypophosphite and in base. By analogy with the acid results, we believe it to correspond to the removal of a hydrogen from the hypophosphite anion to form a triply connected phosphorus dianion, HPO_2^{2-}, *viz.*, $H_2PO_2^- + OD^- \rightarrow HPO_2^{2-} + HDO$. This reactive species then will pick up an additional hydrogen or deuterium atom from the solvent in a rapid step: $HPO_2^{2-} + D_2O \rightarrow HDPO_2^- + OD^-$. If this view is correct, the rate to which eq 3 refers is actually the rate of production of the reactive intermediate. The observed rate of exchange would then also depend upon the atom fraction of deuterium, X_D, in the solvent system and the relative ease of breaking O–H and O–D bonds.

The complete sequence of reactions which we postulate for the isotopic equilibration of hypophosphite with H_2O–D_2O is shown in Figure 1. We have assumed that the rate constant for scission of a P–H or P–D bond remains constant regardless of whether the other hydrogen atom is a proton or a deuteron. Using this assumption the probability of forming the species HPO_2^{2-} from $H_2PO_2^-$ should be twice the probability of forming the species DPO_2^{2-} from $HDPO_2^-$. The first step of reaction 1 is then characterized by a pseudo-first-order rate constant $2k_{PH}(OD^-)$. Remembering the fact that our analytical method, peak intensities in the nmr spectra, responds to both $H_2PO_2^-$ and $HDPO_2^-$ concentrations, it is fairly straightforward to demonstrate that a direct plot of log (intensity) *vs.* time for reaction 1 leads to a straight line of slope $k_{PH}(OD^-)/2.303$; thus the rate constants reported in Tables I–III are those characteristic of the breaking of a single P–H (or P–D) bond and not of the total rate of formation of the intermediates from the hypophosphite species.

At equilibrium the concentrations of all species in the system are constant and according to the mechanism of Figure 1, the following equations must be satisfied

$$2k_{PH}(B)(H_2PO_2^-) = k_{OH}X_H(HPO_2^{2-})$$

$$k_{PD}(B)(HDPO_2^-) = k_{OD}X_D(HPO_2^{2-})$$

where (B) is the total base concentration, $(OH^-) + (OD^-)$. For a 50:50 atom % H–D solvent system, we have then for the $(HDPO_2^-)/(H_2PO_2^-)$ equilibrium ratio

$$\frac{(HDPO_2^-)}{(H_2PO_2^-)} = \frac{2k_{PH}k_{OD}}{k_{PD}k_{OH}} \qquad (4)$$

Implicit in the discussion thus far has been the assumption that k_{PH} (or k_{PD}) is a constant, regardless of whether the base involved in the reaction is OH^- or OD^-. The consequences of both this assumption and the alternate extreme assumption that the maximum effect of the greater base strength of OD^- is operative through the Brønsted catalysis law will be examined. The two assumptions lead to somewhat

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(9) T. E. Haas and H. D. Gillman, *Inorg. Chem.*, **7**, 2051 (1968).

(10) B. Silver and Z. Luz, *J. Am. Chem. Soc.*, **84**, 1091 (1962).

(11) R. B. Martin, *ibid.*, **81**, 1574 (1959).

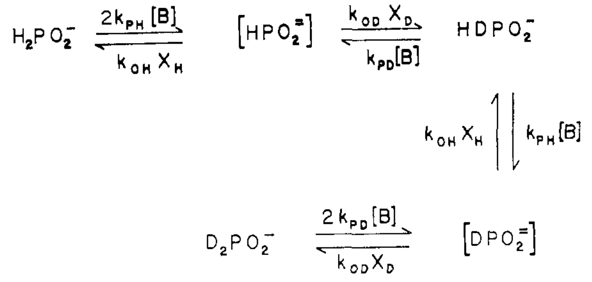

Figure 1.—Proposed exchange mechanism.

different interpretations of the details of the mechanism but are equally consistent with the overall operation of the sequence of reactions shown in Figure 1. It is not possible to distinguish between these two alternatives solely on the basis of the present exchange reaction data.

If the effect of the difference in base strength between hydroxide ion and deuterioxide ion is negligible, then the ratio of k_{PH}/k_{PD} is directly available from the ratios of the rate constants given in Table III. An approximate value of the equilibrium $(HDPO_2^-)/(H_2PO_2^-)$ ratio is also available, and from eq 4 we can calculate that the value of k_{OH}/k_{OD} is approximately 5–6.

If the differences between the rate constants for the hydrogen and deuterium bond breaking are attributed solely to zero-point energy differences, one can apply the equation given by Wiberg[12]

$$\frac{k_H}{k_D} = \exp[(h\nu_H - h\nu_D)/2RT] \qquad (5)$$

Using this relationship with the frequencies $\nu(OH)$ $\sim$3600 cm^{-1}, $\nu(OD)$ $\sim$2400 cm^{-1}, $\nu(PH)$ $\sim$2400 cm^{-1}, and $\nu(PD)$ $\sim$1700 cm^{-1}, the ratio at 45° of k_{PH}/k_{PD} is predicted to be $\sim$5, and the ratio k_{OH}/k_{OD} would be $\sim$9. Experimentally these numbers are approximately 3 and 5, respectively. As Wiberg points out, an observed isotope effect less than that calculated by this method may be interpreted as indicating the presence of bond formation involving the hydrogen, simultaneously with the bond breaking, although other interpretations of such results are also possible.[13] In the present instance it would seem reasonable that the proton transfer from P to O, or *vice versa*, could indeed occur *via* a three-center mechanism.

Alternatively, we can recognize the greater base strength of the deuterioxide ion as compared to hydroxide and attempt to estimate its effect. In mixed H_2O–D_2O solvent systems OH^- is favored with respect to OD^- by the equilibrium[14]

$$2OD^- + H_2O \rightleftharpoons 2OH^- + D_2O \qquad K = 3.21$$

and OD^- is the stronger base by a factor of 1.8 $(=3.21^{1/2})$. If the Brønsted catalysis law holds, eq 4 is still valid, but the experimental values of k_{PH} from Table III are larger than they would be in a medium where the base was OH^-, by a factor of not more than 1.8. These considerations lead to "corrected" values for k_{PH}/k_{PD} and k_{OH}/k_{OD} of $\sim$1.8 and $\sim$4, respectively. These values may be interpreted as above and simply imply an increased importance of the bond formation process in the transition state.

From the present data it is not possible to make a clear-cut decision about the details of the reaction mechanism. (The same problem still exists for the acid-catalyzed reactions, as well.[4,10]) Data on reactions other than the exchange reaction, which would yield an identical product in either H_2O or D_2O mixed solvent, would be most helpful. We tend to feel that the importance of the greater basicity of OD^- is at best not large, by virtue of the success of the following analysis of the data on the approach to equilibrium in a mixed-solvent system. As a means of testing our mechanism, taking k_{PH} and k_{PD} as identical for both OH^- and OD^- catalysis, we have attempted to see whether, using rate constants *within the limits defined in Table III* and the approximate k_{OH}/k_{OD} derived from the equilibrium constant measurements, we could fit the kinetic data on the approach of $H_2PO_2^-$ to equilibrium in a 50:50 atom % mixture of water and heavy water. We should simultaneously fit the observed $(HDPO_2^-)/(H_2PO_2^-)$ ratio, of course. A computer program was written to calculate the concentrations of all three hypophosphite species as a function of time for varying initial conditions. Figure 2 shows a plot of the concentrations of the three species as equilibrium is approached starting from 100% $H_2PO_2^-$. On the same graph we plot the function $2[H_2PO_2^-]$ + $[HDPO_2^-]$, renormalized to arbitrary nmr intensity units of 100 at zero time. The experimental values are indicated by the vertical bars, and the agreement is very satisfying. Thus it would appear that all of the present data are consistent with the exchange mechanism as given in Figure 1.

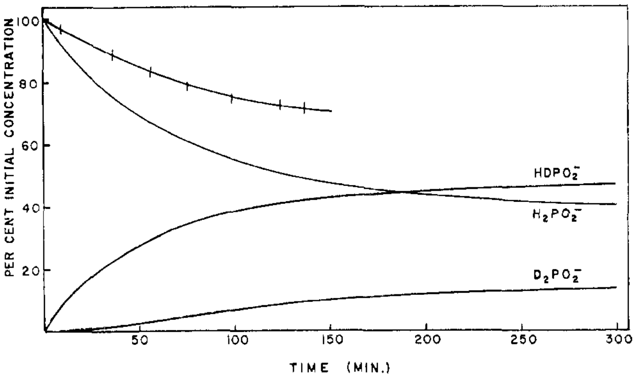

Figure 2.—Calculated concentrations of hypophosphite species *vs.* time and comparison with experimental results for exchange in mixed solvent ($X_D = 0.5$). The unlabeled curve is $2[H_2PO_2^-]$ + $[HDPO_2^-]$, normalized to 100 at $t = 0$. The vertical bars represent experimental nmr total intensity data also normalized to 100 at $t = 0$.

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[12] K. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

[13] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 3890 (1961).

[14] C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).