

Table I. ^{31}P NMR Parameters for the $\text{RP}[\text{P}(\text{O})(\text{OR}')_2]_2$ Compounds^a

Compd	Chem shifts, ppm			
	RP<	(RO) ₂ P- (O)-	$J_{1,2}$, Hz	$J_{2,3}$, Hz
$\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$	+63.4	-29.7	160.9	163.6
$\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$	+61.4	-27.1	157.2	160.5
$\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$	+87.3	-34.1	175.0	178.0
$\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$	+84.8	-31.4	170.5	173.1

^a The chemical shifts and coupling constants are taken from the calculated spectra which best fit the observed ones. $J_{1,2}$ and $J_{2,3}$ refer to the calculated P-P coupling constants in $\text{P}_2(\text{O})-\text{P}_2-\text{P}_3(\text{O})$. Presumably $J_{1,2}$ equals $J_{2,3}$.

Fourier-transform accessories. The spectra were recorded both in the Fourier-transform and continuous-wave modes. Broad-band proton noise decoupling was employed and the chemical shifts were referenced to 85% H_3PO_4 . Analysis of the spectra was carried out on the Nicolet 1080 minicomputer using the programs ITRCL1 and ITRCL2. In this study, it was possible to fit the experimental spectra using the iterative approach developed by Castellano and Bothner-By.⁸

Dichloromethylphosphine was obtained from Edgewood Arsenal and dichlorophenylphosphine was purchased from Orgmet, Inc., Hampstead, N.H. Trimethyl phosphite, triethyl phosphite, dimethyl phosphite, and diethyl phosphite were procured from Aldrich, Inc., Milwaukee, Wis. All of these reagents were distilled prior to use. Triethylamine obtained from J. T. Baker Chemical Co. was distilled over NaOH. Anhydrous ether from Mallinckrodt Chemical Works was dried over metallic sodium prior to use. All operations were performed in the absence of air and moisture.

All the compounds examined in this study were prepared by using methods reported previously.^{1,3} Thus, $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$ was made either from $\text{C}_6\text{H}_5\text{PCl}_2$ and $\text{P}(\text{OCH}_3)_3$ or from $\text{C}_6\text{H}_5\text{PCl}_2$ and $(\text{CH}_3\text{O})_2\text{POH}$ in the presence of triethylamine. $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$ was prepared from CH_3PCl_2 and $\text{P}(\text{OCH}_3)_3$ or from CH_3PCl_2 and $(\text{CH}_3\text{O})_2\text{POH}$ in the presence of triethylamine. Since $(\text{CH}_3\text{O})_2\text{PONa}$ is an insoluble solid in ether, its reaction with CH_3PCl_2 or $\text{C}_6\text{H}_5\text{PCl}_2$ in this solvent gave an intractable yellow precipitate and essentially no soluble products. To circumvent this, $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$ and $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$ were made by treating $\text{C}_6\text{H}_5\text{PCl}_2$ or CH_3PCl_2 , respectively, with $(\text{C}_2\text{H}_5\text{O})_2\text{PONa}$ in Et_2O . $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$ and $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$ were also obtained by the methods used for $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$. All operations were performed at room temperature or below. Typically, after the removal of either NaCl or $(\text{C}_2\text{H}_5)_3\text{NHCl}$ by filtration from the reaction mixture, the solvent was volatilized under vacuum and the resulting product was examined by ^{31}P NMR.

Results and Discussion. Since the structures of the phosphorus compounds resulting from the reactions of $\text{C}_6\text{H}_5\text{PCl}_2$ with either $\text{P}(\text{OCH}_3)_3$ or $\text{P}(\text{OC}_2\text{H}_5)_3$ are known¹ to be molecules of the type $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OR}')_2]_2$ with P-P bonds, we first examined the derivatives of $\text{C}_6\text{H}_5\text{PCl}_2$ obtained via reactions 3 and 4 using the corresponding dialkyl phosphites. Our results show that all the three preparative methods, i.e. eq 2-4, result in the same type of products, namely, $\text{RP}[\text{P}(\text{O})(\text{OR}')_2]_2$. Also, we have obtained the same compound, $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$, either from CH_3PCl_2 and $\text{P}(\text{OCH}_3)_3$ or from CH_3PCl_2 and $(\text{CH}_3\text{O})_2\text{POH}$ in the presence of triethylamine. Furthermore, the compound obtained from CH_3PCl_2 and $\text{NaOP}(\text{OC}_2\text{H}_5)_2$ exhibited a ^{31}P NMR pattern very similar to that of $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$ showing that it too has the structure $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$. It should be pointed out that the crude products resulting from CH_3PCl_2 and $\text{NaOP}(\text{OC}_2\text{H}_5)_2$ as well as from CH_3PCl_2 and $(\text{CH}_3\text{O})_2\text{POH}$ in the presence of triethylamine showed several unidentified minor peaks in their NMR spectra. However, these peaks, presumably attributable to impurities appeared in the "phosphate region" of the spectrum, i.e., above -50 ppm, and hence are not assignable to any compounds with the structure $\text{RP}[\text{P}(\text{O})(\text{OR}')_2]_2$.

It has been suggested² previously that a reasonable mechanism for the formation of P-P bonded compounds from a chlorophosphine and a trialkyl phosphite might involve an onium intermediate proceeding via an Arbusov-type rearrangement. A similar mechanism may well be operating in reactions 3 and 4 to give P-P bonded compounds.

The ^{31}P NMR spectra of these triphosphine derivatives exhibit some interesting features. The $^{31}\text{P}\{\text{H}\}$ spectra of $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$ and $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$ were reported¹ by Fluck and Binder as exhibiting a triplet in the positive region of the spectrum ($\text{C}_6\text{H}_5\text{P}<$ moiety) and a doublet in the negative region ($(\text{R}'\text{O})_2\text{P}(\text{O})->$ moiety). Although this is roughly true, under optimum conditions of resolution it can be seen that all the $\text{RP}[\text{P}(\text{O})(\text{OR}')_2]_2$ compounds reported in this study show an AXX' NMR pattern so that the center peak of the triplet really consists of a close-lying doublet. The pertinent NMR data on these compounds are given in Table I.

It is interesting to note that these spectra to some extent resemble the spectrum of the tripolyphosphate anion.⁹ In the latter case, under optimum experimental conditions, the center resonance of the tripoly middle-group triplet is also seen to be composed of two closely spaced transitions.

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Registry No. $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$, 17052-31-2; $\text{C}_6\text{H}_5\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$, 17052-29-8; $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OCH}_3)_2]_2$, 59389-80-9; $\text{CH}_3\text{P}[\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2]_2$, 59389-81-0; ^{31}P , 7723-14-0.

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Direct Injection Chemical Ionization Mass Spectrometry. Mechanism of Aquation of (Dimethylformamide)pentaamminecobalt(III) and (Dimethyl sulfoxide)pentaamminecobalt(III) in Oxygen-18-Labeled Water

AIC60014N

Sir:

The use of isotopically labeled compounds is an extremely useful, powerful, and general method of studying mechanisms of chemical reactions since the method often furnishes information which can be obtained in no other way and since

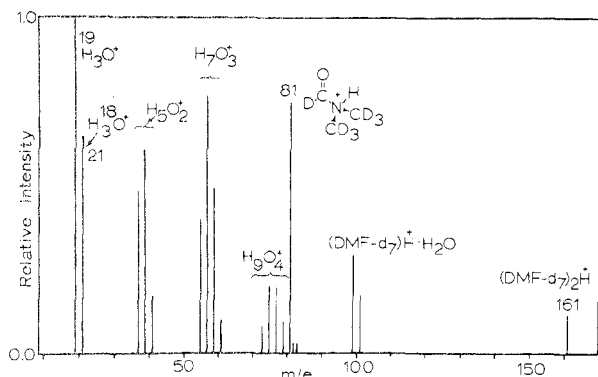


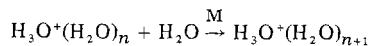
Figure 1. Water chemical ionization spectrum obtained by injecting 20 μl of $\text{Co}(\text{NH}_3)_5(\text{DMF-}d_7)^{3+}$ reaction mixture into the mass spectrometer operated at 130 $^\circ\text{C}$. Only the 39.2% water- ^{18}O and dimethylformamide- d_7 are sufficiently volatile to reach the ion source.

so many isotopes are available. However, the cost of isotopically labeled compounds is often very high so that it is desirable to use small samples to conserve material. Furthermore, rather lengthy, laborious laboratory techniques must frequently be employed to prepare samples for isotopic abundance measurements together with corrections for fractionation effects or induced exchanges involved in sample preparation. More often than not in the past, it has not been possible to attain the twin goals of small samples and experimental convenience in a given technique and we cite only two examples of hundreds to illustrate the point. For a full understanding of the mechanism of substitution reactions of transition metal complex ions it is important to determine whether the metal-ligand bond breaks or whether an intraligand bond breaks; examples of both types of bond fission are known. The metal-oxygen bond was found¹ to be broken in the alkaline hydrolysis of $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ by precipitating $[\text{Co}(\text{NH}_3)_5\text{OH}_2]\text{Br}_3$, thoroughly drying to eliminate uncoordinated water, pyrolyzing to release the coordinated water, collecting the water, equilibrating with CO_2 , and analyzing for the $^{16}\text{O}:^{18}\text{O}$ ratio in the CO_2 . One metal-oxygen bond and one intraligand oxygen-carbon bond was found² to be broken in the alkaline hydrolysis of $\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)^+$ by precipitating $\text{Ag}_2\text{C}_2\text{O}_4$, thoroughly drying, and pyrolyzing completely to release CO_2 which could be analyzed for the $^{16}\text{O}:^{18}\text{O}$ ratio.

Here we report results of bond-breaking studies in similar substitution reactions which are accomplished with a much greater economy of time and sample material using a new technique in which the aqueous reaction mixture is injected directly into a chemical ionization mass spectrometer.^{3,4} This method avoids the many time- and energy-consuming steps involved in the conversion of coordinated or bulk-solvent water or reaction product to gaseous CO_2 . Previously used mass spectrometric methods of determining isotopic content require that the sample be essentially pure and converted to CO_2 for ^{18}O analysis. The new method requires only that the kinetically important isotopically labeled species be volatile or, if no volatile component is involved, that volatile compounds can be prepared by suitable treatment of the reaction products.

In a typical experiment, 4 μl of a freshly prepared solution of 0.22 M (dimethylformamide- d_7)pentaamminecobalt(III) perchlorate and 0.10 M perchloric acid was added to 40 μl of 40 atom % water- ^{18}O in an ampule made from an 8-cm length of 6-mm Pyrex glass tubing. The ampule was sealed and placed in a water bath at 45 $^\circ\text{C}$ for 72 h, i.e., 10 times the half-life for the aquation reaction under these conditions. The spectrum shown in Figure 1 was obtained by injecting 20 μl of this reaction mixture into the batch inlet of a Du Pont

21-490 mass spectrometer modified for chemical ionization studies.⁴ The net oxygen-18 content of the solvent was 39.2%, determined most conveniently in this case from the ratio of the $\text{H}_3^{18}\text{O}^+$ ion peak at m/e 21 to the $\text{H}_3^{16}\text{O}^+$ ion peak at m/e 19. The reaction



accounts for the groups of intense peaks at m/e 37, 39, and 41 corresponding to H_5O_2^+ , m/e 55, 57, 59, and 61 corresponding to H_7O_3^+ , and m/e 73, 75, 77, and 79 corresponding to H_9O_4^+ . The large peak at m/e 81 is primarily protonated DMF- d_7 ($\text{C}_3\text{D}_7\text{HNO}^+$) although there is a 2% contribution from $\text{H}_9^{18}\text{O}_4^+$. The protonated DMF- d_7 readily clusters with a water molecule producing the pair of peaks at m/e 99 and 101. Because the use of 20 mM solutions for direct injection produced DMF- d_7 concentrations in the ion source somewhat higher than normally required, the protonated DMF- d_7 ion can also react with neutral DMF- d_7 to form the proton-bound dimer ion at m/e 161, $(\text{DMF-}d_7)_2\text{H}^+$. The ratio of the peaks at m/e 163 and 161 places an upper limit of 0.8% on the ^{18}O content of the DMF- d_7 and therefore shows that at least 98% of the aquation reaction occurred by $\text{Co}^{\text{III}}\text{-O}$ bond cleavage. If account is taken of a small background signal at m/e 83, the ratio of m/e 83 to m/e 81 gives a similar but less precise result.

The aquation of (dimethyl sulfoxide)pentaamminecobalt(III) perchlorate was carried out in exactly the manner described above except that the reaction required less than 24 h. Again, greater than 98% $\text{Co}^{\text{III}}\text{-O}$ bond breaking occurred. In both systems, a replicate injection was made using the remainder of the reaction mixture to verify that the apparent ^{18}O content of the water was not affected by normal water which might have been adsorbed on the walls of the inlet system. Control experiments using solutions of 20 mM aquopentaamminecobalt(III) perchlorate with either 20 mM DMF- d_7 or DMSO- d_6 in 40% water- ^{18}O in place of the reaction mixtures produced spectra identical with those from the reaction mixtures.

It has been shown⁵ that the experimental data for the aquation of (dimethyl sulfoxide)pentaamminecobalt(III) were best explained by an I_d (or $\text{S}_{\text{N}}1$) substitution mechanism,⁶ rather than a D (or $\text{S}_{\text{N}}1(\text{lim})$) substitution mechanism,⁶ on the central cobalt(III) ion. However, it was not known whether oxygen-cobalt(III) or oxygen-sulfur bond fission occurred, i.e., whether substitution occurred on cobalt(III) or on the S atom of the dimethyl sulfoxide ligand. Since we have found that oxygen-cobalt(III) bond breaking occurred in the aquation reaction we conclude that the aquation has an I_d mechanism. Since we have shown that the aquation of (dimethylformamide)pentaamminecobalt(III) also occurs with oxygen-cobalt(III) bond breaking and since it has been shown elsewhere⁷ that this aquation behaves like the aquation of the dimethyl sulfoxide complex, we conclude that the aquation has an I_d mechanism also.

The technique of direct injection chemical ionization mass spectrometry employed in these two studies gave precise, unambiguous determinations of the point of bond breaking with a great economy of sample and time. The technique is not restricted to the measurement of $^{16}\text{O}:^{18}\text{O}$ ratios or to the use of aqueous solutions but is capable of very wide application to other isotopes, types of reaction, and reaction media wherever the isotopically labeled materials can be volatilized. Most commercially available chemical ionization mass spectrometers can be used without modification for these experiments. Consequently the technique should become a very important tool in the future.

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Registry No. $\text{Co}(\text{NH}_3)_5(\text{DMF})^{3+}$, 31125-61-8; (dimethyl sulfide)pentaamminecobalt(III), 44915-85-7.

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Solvent Exchange at Some Bivalent Metal Ions

AIC60081H

Sir:

Solvent exchange at a metal ion is one of the fundamental reactions of metal ions in solution and often constitutes an important elementary step in a variety of processes taking place in solution, such as substitution reactions, redox reactions, and biochemical reactions involving metal ions or complexes. Solvent exchange at metal ions has been extensively studied and considerable data¹ are now available for making an effort to obtain a general picture of the phenomenon. Caldin and Bennetto² have discussed kinetic parameters of solvent exchange at some bivalent metal ions in relation to structural properties of solvents. They have shown an isokinetic relationship between the enthalpy and entropy of activation and interpreted the results in terms of a structural model for a solvated ion in solution.³ They have also emphasized correlations of fluidity (viscosity/density) and the enthalpy of evaporation with kinetic parameters of solvent exchange.² An account of the Caldin-Bennetto viewpoint has recently been given⁴ and more recently solvent effects on solvent exchange at nickel(II) ion have been discussed.⁵

In this communication a somewhat different approach is put forward: the enthalpy of activation of solvent exchange at some bivalent metal ions is correlated with the solvation enthalpy of metal ion and the enthalpy of evaporation of solvents.

A simple model based on the dissociation (D) mechanism is assumed and the solvent exchange at a metal ion is considered to involve the following four processes: (1) a solvent molecule dissociates from the metal ion; (2) this solvent molecule is incorporated in the bulk solvent; (3) another solvent molecule leaves the bulk solvent; (4) this latter solvent molecule approaches to the metal ion and is accommodated in an available coordination site of the metal ion vacated in process (1).

The energy for process (1) is assumed to be proportional to the free energy of discharge of the metal ion in the solvent, ΔG_d , which is given by the second term in the modified Born equation:⁶

$$\Delta G_d = -0.5N(ze)^2(r+r')^{-1}\epsilon^{-1} \quad (1)$$

where N denotes Avogadro number, z the charge on the metal

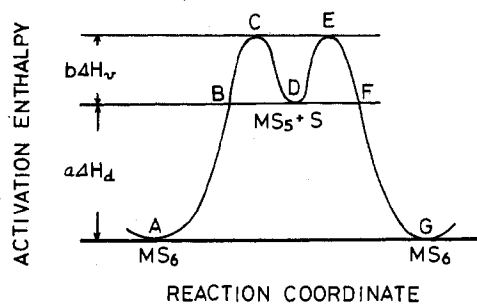


Figure 1. Solvent exchange at a metal ion. M: a metal ion; S: a solvent molecule. Charges are omitted.

ion, e the electronic charge, r the crystal radius of the metal ion, r' the effective increment of radius characteristic of the solvent,^{6,7} and ϵ the bulk dielectric constant of the solvent. From eq 1 we have immediately the corresponding enthalpy change, ΔH_d :

$$\Delta H_d = -0.5N(ze)^2(r+r')^{-1}\epsilon^{-1} [1 + T(r+r')^{-1}\partial(r+r')/\partial T + T\partial \ln \epsilon/\partial T]_p \quad (2)$$

ΔH_d is not an activation parameter but a thermodynamic quantity for the ion-solvent interaction per mole of a metal ion. We assume the activation enthalpy of dissociation of a solvent molecule from a metal ion is proportional to ΔH_d .

Process (2) is thought to be similar to evaporation-condensation; it would require first an energy comparable to the free energy of evaporation, ΔG_v , for the solvent to make a hole in the bulk solvent.² This energy would subsequently be almost compensated in the process of accommodation of the solvent molecule in the hole, a process similar to condensation. During the latter process an energy comparable to ΔG_v would be lost. Process (3) is a reverse process of process (2). Process (4) occurs spontaneously and is assumed to involve a decrease in energy proportional to that given by eq 1.

The enthalpy of activation for the solvent exchange process at a metal ion, ΔH_{ex}^\ddagger , is then expressed as follows:

$$\Delta H_{ex}^\ddagger = a\Delta H_d + b\Delta H_v \quad (3)$$

where a and b are constants. The reaction profile in terms of the activation enthalpy according to the above model is depicted in Figure 1: AB, process (1); BCD, process (2); DEF, process (3); FG, process (4).

Two differentials in eq 2 are now considered: $r^{-1}\partial r/\partial T$ is constant for a given metal ion and would be of the order of 10^{-5} K^{-1} , judging from values of the linear expansion of metals and metal salts.⁸ The value $r'^{-1}\partial r'/\partial T$ is not available; it is expected to vary in parallel with the linear expansion of the solvent. On the other hand we know⁸ that the linear expansion coefficient of most solid organic compounds is around 10^{-4} K^{-1} . Then taking the strong ion-solvent interaction into consideration, $(r+r')^{-1}\partial(r+r')/\partial T$ should be less than 10^{-4} K^{-1} . Therefore at 298 K the term $T(r+r')^{-1}\partial(r+r')/\partial T$ would not exceed 0.03 and its contribution to ΔH_d may be assumed to be unimportant.

The term $T\partial \ln \epsilon/\partial T$ is important in eq 2 as evident from Table I, in which some solvent properties are given. Thus ΔH_d may be approximated as:

$$\Delta H_d = -0.5N(ze)^2(r+r')^{-1}\epsilon^{-1}(1 + T\partial \ln \epsilon/\partial T)_p \quad (4)$$

Data of solvent exchange at some bivalent transition metal ions are summarized in Table II. In making a choice among the available solvent exchange data, we prefer higher and more recent values of the enthalpy of activation obtained from measurements over a wider range of temperature. A trend is obvious in Table II: For the same solvent the activation