Table I. Distribution of L_3O^+ Ions in Equilibrium with $D_2O/H_2O/HOD$ Mixtures at 25 °C

mixture 1: $X_{H_2O(l)}{}^a = 0.498$; $X_{H_2O(g)}{}^b = 0.268$; $X_{HOD(g)} = 0.493$; $X_{D_2O(g)} = 0.239$			mixture 2: $X_{H_2O(l)} = 0.493$; $X_{H_2O(g)} = 0.263$; $X_{DOH(g)} = 0.495$; $X_{D_2O(g)} = 0.243$		
species	mass	ion fraction	species	mass	ion fraction
H_3O^+	19	$0.20_9 \pm 0.02_5$	H_3O^+	19	$0.18_7 \pm 0.01_7$
DH_2O^+	20	$0.38_1 \pm 0.01_0$	DH_2O^+	20	$0.38_4 \pm 0.00_4$
D_2HO^+	21	$0.30_7 \pm 0.01_7$	D_2HO^+	21	$0.32_0 \pm 0.00_9$
D_3O^+	22	$0.09_6 \pm 0.01_1$	D_3O^+	22	$0.11_4 \pm 0.02_0$

[a] Directly from weights of $D_2O(l)$; $H_2O(l)$. [b] Calculated from $X_{H_2O(l)}$.

HDO(g), and D_2O(g) in the vapor above this liquid mixture were calculated from data given in the literature.[12] The inlet system of the ion cyclotron resonance (ICR) spectrometer was conditioned by repeatedly exposing the system to this vapor and then pumping the inlet system out. This was continued (4 h) until the D to H ratio in the mass spectrum of the mixture was constant. The neutral partial pressures of H_2O, HOD, and D_2O calculated from the L_2O^+ peak intensities agreed within 5% of those calculated from liquid vapor equilibrium data. At a partial pressure of L_2O of 1×10^{-6} torr at 25 °C in an ICR cell, with the instrument operating in the trapped ion mode,[13] all primary L_2O^+ ions produced at 70 eV rapidly lead to production of L_3O^+, eq 2. This

$$L_2O^+ + L_2O \rightarrow L_3O^+ + LO \qquad (2)$$

is followed by fast proton–deuteron exchange between L_3O^+ and L_2O to yield an equilibrium distribution of L_3O^+ ions. The distributions obtained from two different mixtures of H_2O(l) and D_2O(l), made up and run 10 months apart, are given in Table I.

At least 12 equilibrium constants involving single hydrogen ion transfers can be calculated from the values of ion and neutral concentration in Table I. All except three of these contain redundant information. Three reactions, eq 3–5, are chosen as

$$H_3O^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + DH_2O^+(g) \qquad (3)$$

$$DH_2O^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + D_2HO^+(g) \qquad (4)$$

$$D_2HO^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + D_3O^+(g) \qquad (5)$$

representative. Equilibrium constants obtained are $K_3 = 2.07 \pm 0.25$, $K_4 = 0.85 \pm 0.05$, and $K_5 = 0.35–0.04$. The predominate factors in determining these equilibrium constants are the statistical factors of 3, 1, and $^1/_3$, respectively.[14]

The common reference for isotope effects is *liquid* water. Fractionation factors for the sequential replacement of H with D on the hydronium ion can be calculated by multiplying the equilibrium constants for reactions 3–5 by the fractionation factor for gaseous water of 0.93, eq 6, and dividing by the statistical

$${}^1/_2H_2O(g) + {}^1/_2D_2O(l) \rightleftharpoons {}^1/_2D_2O(g) + {}^1/_2H_2O(l) \qquad (6)$$

factors. Values obtained are $\phi_3 = 0.64 \pm 0.08$, $\phi_4 = 0.79 \pm 0.05$, and $\phi_5 = 0.97 \pm 0.11$. The variation of ϕ with successive deuteration indicates that D_2HO^+ and DH_2O^+ are less stable than would be expected on the basis of D_3O^+, H_3O^+ stabilities and the rule of the geometric mean.[15] These results indicate that replacement of hydrogen by deuterium in lyonium ions is an endothermic process, a consequence of the difference in zero point energies of the lyonium ions and isotopic water molecules.

The above data can be used to calculate a fractionation factor for the gaseous hydronium ion, ϕ_7, eq 7, of 0.79. This is larger

$${}^1/_3H_3O^+(g) + {}^1/_2D_2O(l) \rightleftharpoons {}^1/_3D_3O^+(g) + {}^1/_2H_2O(l) \qquad (7)$$

$$\phi_7 = 0.93(K_3K_4K_5)$$

than the value for the hydrated hydronium ion of 0.69 indicating that the force field of the gaseous hydronium ion is reduced less than that of the hydrated hydronium ion relative to liquid water. This is consistent with the recent spectroscopic observations of vibrational frequencies of gaseous H_3O^+ by Saykally[16] and Oka.[17] For example, the stretching frequencies ν_1 and ν_3 in H_3O^+ are determined to be 3520 and 3630 cm^{-1}, respectively, while those of H_2O are 3657 and 3756 cm^{-1}. It is of interest to note that the stretching frequencies in H_3O^+ are lower than those in H_2O even though the calculated O–H bond dissociation energies in H_3O^+ are larger indicating the importance of spectroscopic data in interpretation of isotope effects for gaseous ions.

The fact that the fractionation factor observed for gaseous H_3O^+ is identical with that in CH_3CN[10] is of considerable interest since it infers that hydrogen bonding from hydronium ion to acetonitrile has a negligible effect on the fractionation factor. Thus it appears that H_3O^+–CH_3CN interactions in acetonitrile solution are sufficiently weak to cause only minor changes in the force fields of H_3O^+ relative to those in the gas phase.

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Phosphorus–Sulfur Bond Order in Phosphorothioate Anions

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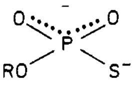
The question of negative charge localization between phosphorus-bonded oxygen and sulfur in aqueous solutions of phosphorothioate anions has long attracted attention in organophosphorus chemistry.[1] Owing to the absence of relevant physical data, uncertainties have often found expression in the use of chrage-delocalized structures. When negative charge was indicated as localized it was placed on oxygen, with sulfur being shown as doubly bonded to phosphorus.[2]

A recent review of available physical data indicates, however, that the structures of *O*-alkyl and *O*,*O*-dialkyl phosphorothioate anions in aqueous solutions should be represented as **1** and **2**, with



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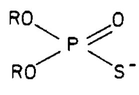

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[†] University of Wisconsin.

[‡] Technical University of Łódź.

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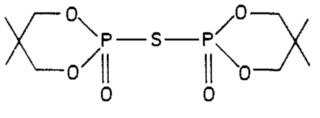
Table I. Isotope Effects on ^{31}P Chemical Shifts

compd	solvent	$\Delta\delta P$ $^{18-16}$O	 $^{36-34}$S	 $^{36-32}$S	 $^{34-32}$S
3^{a}	CD_2Cl_2	0.0455^{b}	0.003^{c}	*d*	*d*
4^{a}	CD_2Cl_2	0.019^{b}	0.009^{b}	0.018^{b}	0.010^{b}
5	D_2O	0.041	*e*	0.0065^{c}	*e*

^{a}3 and 4 were prepared as described earlier.[8] ^{b}Previously reported.[6] ^{c}Figure 1. ^{d}Undetermined. ^{e}Unresolved in aqueous solution.

negative charge preferentially localized on sulfur and P–O bond orders of approximately 1.5 in **1** and 2 in **2**.[3a,b] This conclusion is supported mainly by data in P–O bond orders, specifically P–O stretching frequencies and the ^{18}O-induced perturbation of ^{31}P NMR signals. The magnitude of isotopic perturbation of chemical shifts are known to be correlated with bond order.[4] On this basis data on ^{18}O-enriched compounds indicate that the P–O bond orders in monoester dianions such as **1** are approximately 1.5 for unalkylated oxygens, while for diester monoanions such as **2** they are nearly 2, consistent with the proposed structures with P–S single bonds and charges localized on sulfur. Currently available evidence regarding P–S bond order in phosphorothioate anions is limited to P–S stretching frequencies of $HPSO_3^{2-}$ and PSO_3^{3-}, which are consistent with single bonds.[5]

Recently the observation of ^{34}S- and ^{36}S-induced upfield shifts in ^{31}P NMR signals for **3** and **4** has been reported.[6] Doubly



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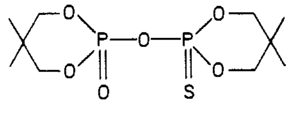

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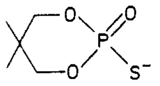
bonded ^{36}S shifted the ^{31}P NMR signal for **4** upfield by 0.008 ppm, whereas singly bonded ^{36}S in **3** shifted the signal upfield by an estimated 0.004 ppm relative to the ^{34}S species, confirming the expected relationship between ^{36}S-induced shifts and P–S bond order.

Alkaline hydrolysis of either **3** or **4** produces **5**,[7] shown with



5

single-bonded S and double-bonded O. The ^{18}O- and ^{36}S-induced isotopic perturbations of ^{31}P NMR signals for compound **5** support the structure shown in preference to one with double-bonded S and single-bonded O.

The isotope shifts are summarized in Table I. The ^{18}O-induced perturbation of the ^{31}P NMR chemical shift of 0.041 ppm for **5** corresponds to a P–O bond order of nearly 2, on the basis of the perturbation of 0.021 ppm for single-bonded O.[3a,b] On this basis we would expect that the P–S bond order should be close to unity. This is supported by the observed perturbation of ^{31}P NMR signals by isotopic sulfur. Measurements of the previously unresolved $^{36-34}$S isotope shift of 0.003 ppm for compound **3** from the derivative spectrum in Figure 1a enable us to estimate the expected isotopic shift for the $^{36-32}$S with sulfur singly bonded to phosphorus. The expected shift is about 0.006 ppm, or twice the value for $^{36-34}$S. The value for doubly bonded sulfur is 0.018 ppm in agreement with the earlier result.[6] Therefore, the upfield shift of 0.0065 ppm observed for anion **5** (Figure 1b) indicates that P–S bond order is near 1, and the negative charge is largely localized on the sulfur atom.

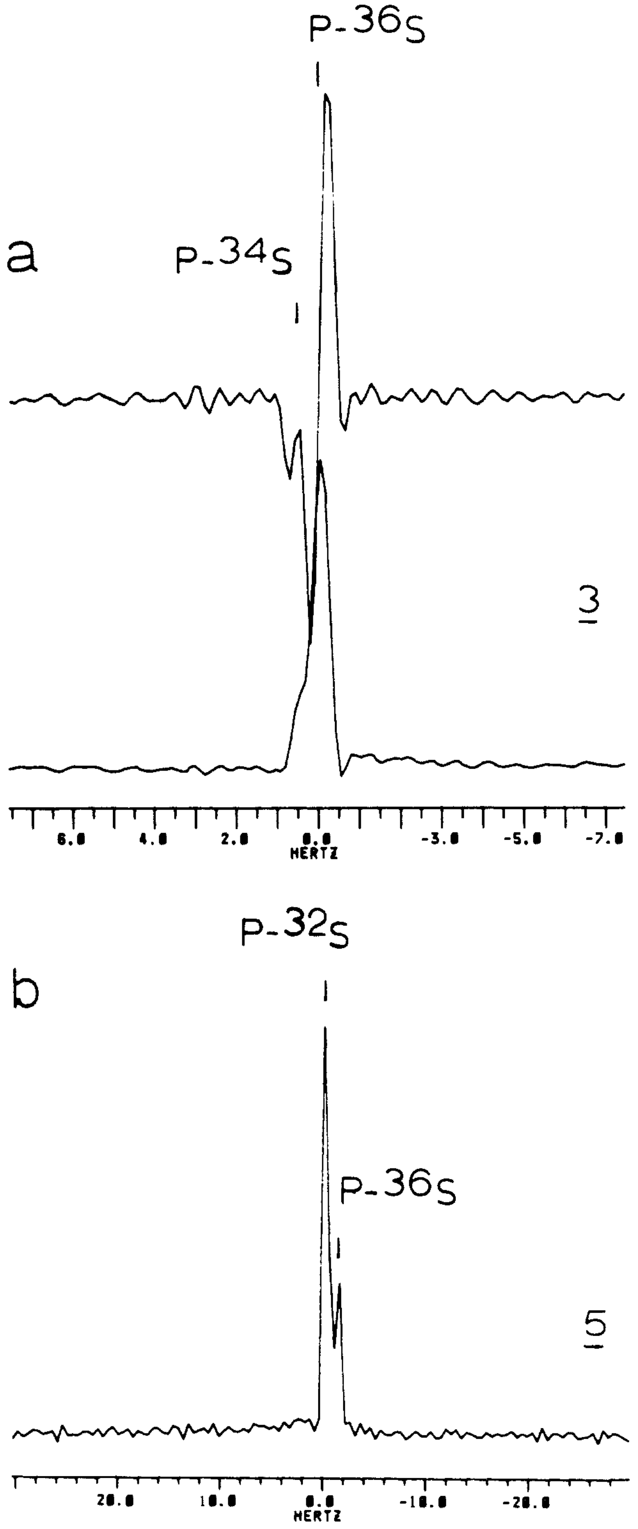


Figure 1. ^{31}P NMR signals perturbed by sulfur isotopes of compounds (a) **3** and (b) **5**. Each sample contained approximately 20 mg of material. **5** was dissolved in D_2O and the pH adjusted to 9 with NaOD; no buffer was used. Spectra were obtained on Bruker AM 500 operating at 202.5 MHz with a tip angle of 20° and a repetition rate of 2 s. The FID was multiplied by a Lorentz to Gaussian conversion with Lorentzian line narrowing of 0.6 Hz and Gaussian broadening of 0.4 Hz and then zero-filled to give 0.1-Hz digital resolution. Spectrum of **3** was obtained after 400 scans and spectrum of **5** required 36 scans.

The $^{36-34}$S-isotope shift values for **3** and **4** given in Table I do not appear to be strictly proportional to expected bond orders.

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This may be explained by experimental errors in measuring very small values. In any case the $^{36-32}S$ value for **5** is compatible only with the values for singly bonded S in the model compounds.

Acknowledgment. We thank Dr. Bruce Adams for his assistance and helpful discussions. Supported in part by Grant No. GM30480 from the National Institute of General Medical Sciences.

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Facile Stereospecific Synthesis of a Dihydroxyindenoindene Unit from an Alkyne and CO via Samarium-Mediated CO and CH Activation[1]

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We have recently reported that the low-valent samarium complex $(C_5Me_5)_2Sm(THF)_2$ (I)[3] has the capacity to assemble three CO molecules into a dimetal-substituted ketenecarboxylate unit in $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$.[4] This remarkable transformation, in which one CO loses its oxygen as it is homologated, suggests that considerable reactivity is available in the samarium/CO reaction system. We were interested in utilizing this reactivity to functionalize hydrocarbon substrates with CO and we report here the results of a reaction with an alkyne substrate.

Complex I reacts with $C_6H_5C{\equiv}CC_6H_5$ to form a compound identified as $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ (II) by elemental and chemical analysis.[5] II may have an enediyl structure: $[(C_5Me_5)_2Sm](C_6H_5)C{=}C(C_6H_5)[Sm(C_5Me_5)_2]$.[6] The black II (141 mg, 0.14 mmol) reacts with CO at 90 psi over a 1-day period in 20 mL of hexane in a 3-oz Fischer-Porter aerosol reaction vessel to form a brown-red solution from which yellow-orange crystals (III, 105 mg) are obtained. III was isolated by filtration in a glovebox and characterized by complexometric metal analysis and ^1H NMR and IR spectroscopy.[7]

These data did not specify the identity of III and an X-ray structural determination was carried out.[9] The diffraction data identified III as $[(C_5Me_5)_2Sm]_2(O_2C_{16}H_{10})$, which has the structure shown in Figure 1. The ^1H NMR spectrum of the solution from which III was obtained showed that III was the major product of the reaction giving an overall yield of 70%.[10]

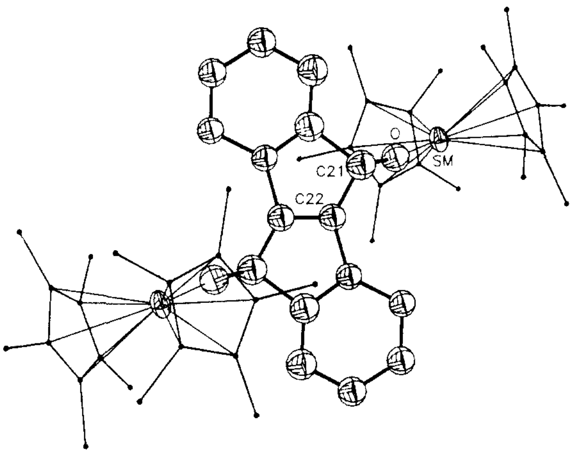
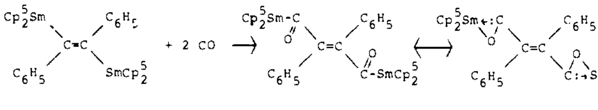


Figure 1. ORTEP plot of the molecular structure of $[(C_5Me_5)_2Sm]_2O_2C_{16}H_{10}$ with C_5Me_5 carbon atoms represented as dots for clarity. Sm′ is above the plane of the dihydroxyindenoindene ligand; Sm is below. Selected bond distances (Å) and angles include: Sm-C(ring) av, 2.70 (3); Sm-O, 2.08 (2); (ring centroid)-Sm-(ring centroid), 139.85°; Sm-O-C21, 173 (2)°; C21-O, 1.43 (4); C(22)-C(22)′, 1.25 (5); C(21)-C(22), 1.46 (4).

The hydrocarbon fragment in $[(C_5Me_5)_2Sm]_2(O_2C_{16}H_{10})$ can be removed by reduction with sodium in THF. Removal of THF from this mixture and extraction with hexane gave 5,10-dihydroindeno[2,1-*a*]indene identified by MS and NMR spectroscopy.[11]

The structure of III indicates that two molecules of CO have been condensed with one molecule of diphenylethyne to form a tetracyclic dihydroindenoindene unit.[12] Hence, the six-membered rings in Figure 1 have C-C distances characteristic of aromatic rings in fused polycyclic hydrocarbon systems[13] and the C22-C22′ connection is formally a double bond.[14] C21 and C21′ have angles consistent with sp^3 hybridization. The hydrogen atoms on these carbon atoms were not located in the X-ray study. C21 and C21′ are substituted in an exclusively trans manner with $OSm(C_5Me_5)_2$ groups.

The formation of III can be rationalized by successive CO insertion and C-H activation steps on the precursor II as shown in eq 1 and 2 ($Cp^5 = C_5Me_5$). CO insertion into lanthanide carbon



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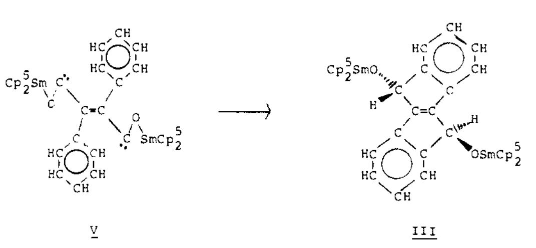

(2)

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(1) Reported in part at the "190th National Meeting of the American Chemical Society," Chicago IL, Sept 1985.

(2) (a) Alfred P. Sloan Research Fellow. (b) University of California—Irvine. (c) University of Alabama.

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(6) ^1H and ^{13}C NMR spectra are consistent with this structure. Hydrolysis gives *trans*-stilbene. A crystallographically characterized azobenzene analogue has this structure.

(7) Anal. Calcd for $[(C_5Me_5)_2Sm]_2O_2C_{16}H_{10}$: Sm, 27.98. Found: Sm, 25.1. ^1H NMR (C_6D_6, 5.58 mM) δ 8.99 (1 H), 1.53 (30 H, C_5Me_5). Resonances attributable to the aryl protons were observed but could not be definitively assigned. The δ 8.99 absorbance is consistent with hydrogen on a carbon bonded to an O-Sm group as previously reported for $\{(C_5Me_5)_2[(C_6H_5)_3PO]Sm\}_2(\mu\text{-}OCH{=}CHO)$.[8] IR (KBr) 2900 s, 2850 s, 1600 m, 1440 s, 1375 m, 1285 s, 1170 vs, 1150 s, 1120 vs, 1020 s, 880 w, 850 vw, 800 vw, 750 sh, 740 s, 680 m.

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(9) The space group is $P2_1/n$ with $a = 15.031$ (6) Å, $b = 9.895$ (6) Å, $c = 17.273$ (5) Å, $\beta = 103.97$ (5)°, and $Z = 2$ for $D_{calcd} = 1.33$. Least-squares refinement on the basis of 1470 observed reflections converged to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.066$. Hydrogen atoms were not included and the carbon atoms were refined with isotropic temperature factors. The thermal motion of the other atoms was dealt with anisotropically.

(10) Additional III is present in the hexane solution along with some diphenylethyne. III can also be isolated as a THF adduct.

(11) ^1H NMR (acetone-d_6) δ 7.560 (d, 2 H), 7.488 (d, 2 H), 7.329 (t, 2 H), 7.205 (t, 2 H), 3.683 (s, 4 H). Mass spectrum calcd for $C_{16}H_{12}$ 204.0939, found 204.0927. Uyehara, T. D.; Honda, T.; Kitahara, Y. *Chem. Lett.* **1977**, *10*, 1233-1236.

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(14) Primed atoms are related to unprimed atoms by a center of inversion which is in the center of the C(22)-C(22)′ bond.