

^{34}S , ^{36}S , and ^{18}O Isotope Effects on ^{31}P Chemical Shifts in Thiophosphate Anhydrides

C. Roeske,[†] P. Paneth,^{*†} M. H. O'Leary,[†] and W. Reimschuessel[§]

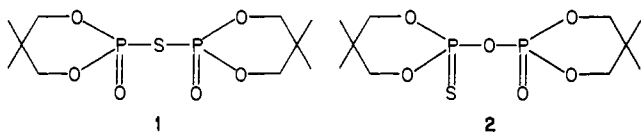
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Institute of Applied Radiation Chemistry, Technical University (Politechnika) of Lodz, 90-924 Lodz, Poland. Received July 19, 1984

Abstract: ^{34}S , ^{36}S , and ^{18}O isotope effects on ^{31}P chemical shifts were measured for the isomeric thiophosphate anhydrides bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulfide (**1**) and *P*-oxo-*P'*-thionobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) oxide (**2**). The doubly bonded S in **2** gave isotopic shifts of 0.0097 and 0.018 ppm upfield of $\text{P}=\text{S}$ for ^{34}S and ^{36}S , respectively. The singly bonded S in **1** gave a smaller isotopic shift, the exact value being obscured by the line widths. ^{18}O in the nonbridging position in **1** gave an isotopic shift of 0.0455 ppm. ^{18}O in the bridging position in **2** gave an isotopic shift of 0.019 ppm. These observations confirm the expectation that ^{36}S effects should be twice as large as the corresponding ^{34}S effects.

Isotope effects on chemical shifts in NMR spectra have been studied with increasing frequency over the past few years.¹ The ^{18}O isotope effect on ^{31}P chemical shifts is probably the best known example, having been used extensively in studying positional isotope exchange, bond cleavage sites, kinetic behavior of intermediates, and the stereochemistry of phosphate-transfer reactions.^{2,3} Since thiophosphoroorganic compounds have attained increasing attention among chemists and especially biochemists, the S isotope effect on ^{31}P chemical shifts is an interesting augmentation to the present body of knowledge.

^{34}S isotope-induced shifts have previously been reported for ^{13}C and ^{19}F NMR spectra (0.009 ppm for doubly bonded C=S and 0.05 ppm^{4,5} for singly bonded F—S, respectively). We wish to report the first observation of ^{34}S and ^{36}S isotope effects on ^{31}P NMR spectra. To the best of our knowledge, this is also the first measurement of a ^{36}S isotope effect on any NMR spectrum and the first comparison of isotope shifts for three different isotopes of the same element.

Measurements were performed on the following two isomeric compounds:



^{34}S , ^{36}S , and ^{18}O in the thiophosphate anhydrides examined all led to upfield shifts of the ^{31}P peaks compared to compounds containing ^{32}S and ^{16}O . The magnitude of the isotope effects increased from ^{34}S to ^{36}S (vs. ^{32}S) to ^{18}O (vs. ^{16}O) and also increased with bond order.

Experimental Section

Synthesis of Labeled Compounds. ^{18}O was substituted at the non-bridging position in **1** and at the bridging, exocyclic position in **2**. Bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulfide (**1**) substituted with ^{34}S and ^{36}S was synthesized⁶ by using elemental sulfur (Texnabexport USSR) containing 20 atom % ^{34}S and 80 atom % ^{36}S . The compound containing a natural abundance S was labeled with ^{18}O by using^{6,7} 95 atom % ^{18}O H_2O . ^{34}S - and ^{36}S -labeled *P*-oxo-*P'*-thionobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) oxide (**2**) was obtained by the quantitative isomerization⁸ of isotopically modified **1**. Compound **2** containing a natural abundance S was synthesized by a known method.⁹ **2** with an ^{18}O label only in the bridging position was obtained in the same way, starting with 40 atom % ^{18}O H_2O . ^{31}P NMR spectra were measured

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

isotope	compound	
	1	2
^{34}S vs. ^{32}S		0.0097 ppm (P=S)
^{34}S vs. ^{36}S	(0.004 ppm) ^a (P—S)	0.0087 ppm (P=S)
^{36}S vs. ^{32}S		0.0184 ppm (P=S)
^{18}O vs. ^{16}O	0.0455 ppm (P=O)	0.019 ppm (P—O)

^a The line width prevents an accurate measurement of the isotopic shift. See Figure 3.

for the isotopically labeled compounds both before and after mixing with natural abundance material.

NMR Measurements. The ^{34}S , ^{36}S , and ^{18}O isotope effects on ^{31}P NMR signals were measured by using a JEOL FX-200 spectrometer with a 10-mm probe. Protons were broad-band decoupled by using 30% of the full power to avoid heating the samples. Thirty-two or 40 scans were collected. Samples were prepared by dissolving 20 mg of **1** or **2** in 0.4 mL of CDCl_3 (99.8 atom % D containing 1% Me_4Si from Stohler Isotope Chemicals). Thin-walled sample tubes (5-mm) were used with a capillary insert containing 85% H_3PO_4 for a reference when necessary. ^{31}P chemical shifts were determined by using a sweep width of 8000 Hz, a 60° pulse angle with a pulse delay of 100 ms, and 8K data points. The isotope effects on the chemical shifts were determined by using a sweep width of 160 Hz and a 80° pulse angle with a pulse delay of 100 ms. The 4K data points were extended to 8K by zero-filling. No line-broadening factor was used.

Mass Spectrometry. Electron impact mass spectra of labeled material were run on Finnigan 4000 with quadrupole and Kratos MS 80 mass spectrometers. The energy of the bombarding electrons was 20 or 70 eV for the Finnigan MS and 30 eV for the Kratos MS. The acceleration voltages were 2 kV for the Finnigan MS and 3 kV for the Kratos MS. Samples were introduced with the aid of a direct probe. Isotopic composition was measured on the basis of intensities of the parent peaks M (330), M + 2 (332), and M + 4 (334). Typical spectra for both compounds are shown in Figure 1.

Results

The ^{31}P NMR spectrum of compound **1** shows a single signal 7.0 ppm downfield from H_3PO_4 . The spectrum of compound **2** has a pair of doublets at 44.8 ppm (P=S) and -21.8 ppm (P=O).

- (1) Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 4609-4614.
- (2) Cohn, M. *Ann. Rev. Biophys. Bioeng.* **1982**, *11*, 23 and references cited therein.
- (3) Linde, S. A.; Jakobsen, H. J. *J. Magn. Reson.* **1975**, *17*, 411.
- (4) Rodmar, S.; Rodmar, B.; Sharma, M. K.; Granowitz, S.; Christiansen, H.; Rosen, V. *Acta. Chem. Scand.* **1968**, *22*, 907.
- (5) Gillespie, R.; Quail, J. W. *J. Chem. Phys.* **1963**, *39*, 2555.
- (6) Kaminski, R. Ph.D. Thesis, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, 1978.
- (7) Michalski, J.; Mikolajczyk, M.; Mlotkowska, B.; Zwierzak, A. *Angew. Chem.* **1967**, *79*, 1069.
- (8) Michalski, J.; Reimschuessel, W.; Kaminski, R. *Usp. Khim.* **1978**, *47*, 1528.
- (9) Michalski, J.; Skowronska, A. *J. Chem. Soc. C* **1970**, 703.

[†] University of Wisconsin.

^{*} On leave from the Institute of Applied Radiation Chemistry.

[§] Institute of Applied Radiation Chemistry.

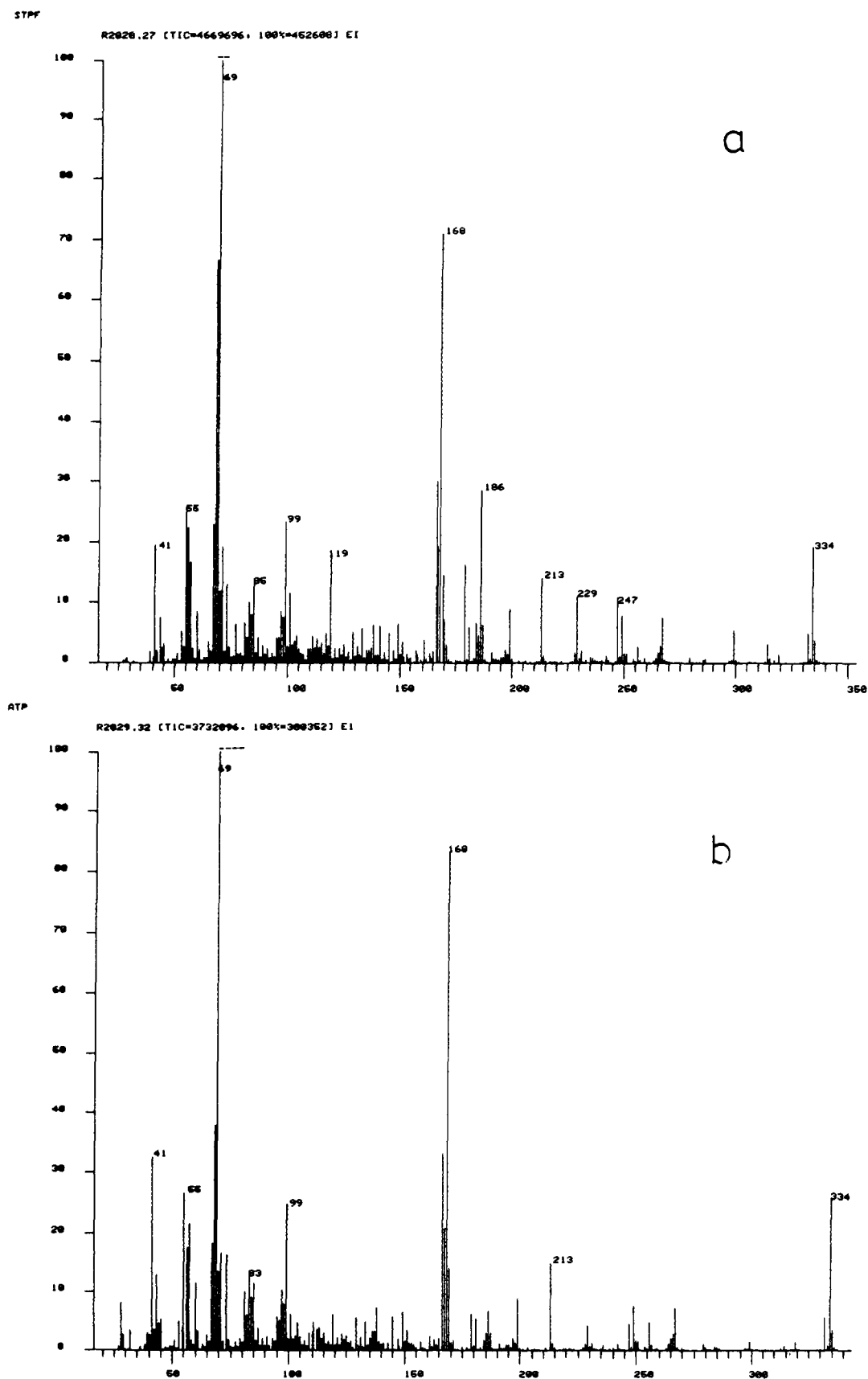


Figure 1. (a) Mass spectrum of $[^{34}\text{S},^{36}\text{S}]\text{-1}$ at 30 eV. (b) Mass spectrum of $[^{34}\text{S},^{36}\text{Si}]\text{-2}$ at 30 eV.

The two-bond phosphorus-phosphorus coupling constant is 33.3 Hz. These values are in good agreement with those previously reported.⁸

Restricted acquisition of the thionophosphate ($\text{P}=\text{S}$) in a mixture of ^{34}S - and ^{36}S -labeled and -unlabeled **2** showed three doublets, one for each isotope (Figure 2). No S isotope effect

was observed on the $\text{P}=\text{O}$ signal in **2**. The S isotope effect on the ^{31}P chemical shift for compound **1** was smaller than in **2**. Unfortunately, the exact value of the isotope effect was obscured by the 0.4-Hz line width. Figure 3 shows the ^{31}P peak of ^{34}S - and ^{36}S -labeled **1**. We attribute the shoulder downfield from the main peak to $[^{34}\text{S}]\text{-1}$.

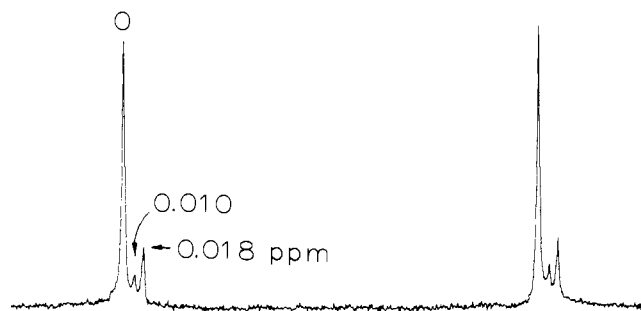


Figure 2. Thionophosphate (P=S) signals of ^{31}P NMR spectra of **2** containing ^{32}S , ^{34}S , and ^{36}S (see text).

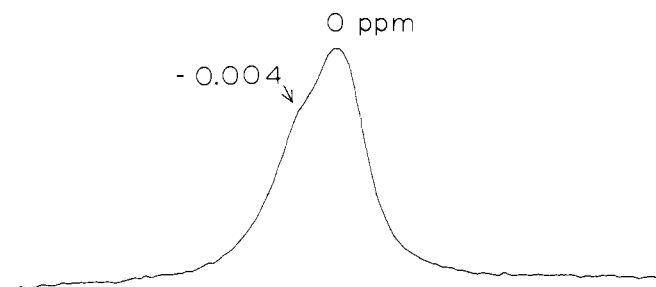


Figure 3. ^{31}P NMR signal of ^{34}S - and ^{36}S -labeled **1** (see text).

The ratio of ^{34}S to ^{36}S in compound **2** was determined both from peak heights (0.29:1) in the NMR spectrum (Figure 2) and from molecular peaks in the mass spectrum (0.25:1). The ^{18}O isotopic shifts (Table I) match previously published values for doubly and

singly bonded ^{18}O in phosphates.²

Discussion

Despite a large number of experiments involving isotope effects on chemical shifts in NMR spectra,¹ this is the first report of a sulfur isotope effect on a ^{31}P chemical shift and, to our knowledge, the first time the effects of three different isotopes have been compared. Based on the ^{18}O isotope effect on ^{31}P chemical shifts in phosphates,¹¹ we expected the sulfur isotopes in thiophosphates to shift the ^{31}P signal upfield. As anticipated,^{10,11} the observed upfield shift increased with mass and bond order and decreased with distance.

The isotope shift also increases by roughly a factor of 2 as the mass is increased from 34 to 36 (vs. 32), as predicted.¹⁰ Both the ^{18}O and S isotope shifts approximately double as the bond order changes from 1 to 2. While there are not enough examples in this case to show whether other factors are involved (e.g., geometry of the molecule), the increase in isotopic shift with bond order has been predicted for diatomic and triatomic molecules¹⁰ and verified experimentally for larger molecules.¹

The observation that the ^{18}O isotopic shifts on thiophosphates is larger than on phosphates¹¹ suggests that the P-O bond order is slightly greater in thiophosphates. The slightly smaller bond order would make the isotopic shift smaller. It would be interesting to see if calculations bear out this decrease in bond order from P-O to P-S.

Registry No. **1**, 16956-55-1; **2**, 15762-04-6.

(10) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983-4988.

(11) Tsai, M.-D. In "Phosphorus-31 NMR: Principles and Applications"; Gorenstein, D. G., Ed.; Academic Press: New York, 1984; pp 175-197.

Communications to the Editor

Novel 16-Electron Organometallic Complexes of Molybdenum and Tungsten: $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})(\text{alkyl})_2^1$

Peter Legzdins,* Steven J. Rettig, and Luis Sánchez

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Y6

Bruce E. Bursten* and Michael G. Gatter

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received October 11, 1984

The familiar 18-valence-electron rule can often be used to rationalize the stability and reactivity of transition-metal organometallic complexes.² It is particularly applicable to compounds possessing monomeric "three-legged piano stool" molecular structures such as $(\eta^n\text{-C}_n\text{H}_n)\text{M}(\text{L})(\text{L}')(\text{L}'')$ where M is a metal from group 6, 7, 8, 9, or 10 and some of the ligands, L, are good π -acceptors (e.g. CO or NO).³ We now wish to report the first, thermally stable examples of a class of such molecules that do

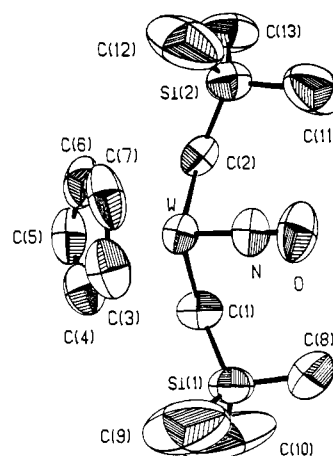


Figure 1. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (\AA) and angles (deg) are W-N = 1.757 (8), W-C(1) = 2.103 (9), W-C(2) = 2.108 (9), W-C(C₅H₅, av) = 2.373 (10), N-O = 1.226 (10), Si-C(CH₂, av) = 1.840 (11), N-W-C(1) = 97.7 (4), N-W-C(2) = 95.7 (4), C(1)-W-C(2) = 109.6 (4), W-N-O = 169.5 (6), W-C(1)-Si(1) = 125.5 (5), W-C(2)-Si(2) = 127.1 (5).

not conform to the rule by virtue of the fact that their lowest unoccupied molecular orbitals (LUMOs) are nonbonding in character. Specifically, we wish to describe the syntheses, characterization, and remarkable properties of the new 16-electron complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (**1**), $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{CH}_2\text{CMe}_3)_2$ (**2**), and $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ (**3**).

(1) Organometallic Nitrosyl Chemistry. 23. For part 22, see: Legzdins, P.; Nurse, C. R. *Inorg. Chem.*, in press.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; Chapters 25-30.

(3) Jolly, W. L. "Modern Inorganic Chemistry"; McGraw-Hill: New York, 1984; Chapter 16.