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PHOSPHORUS(III) OXIDE: THE REACTION OF TETRAPHOSPHORUS HEXAOXIDE WITH GROUP VIB METAL CARBONYLS

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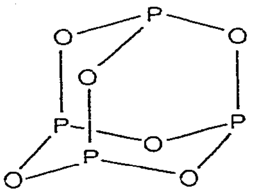
Summary

The monosubstituted Group VIB metal carbonyl derivatives of phosphorus(III) oxide, P_4O_6, have been prepared and characterized by mass spectrometry, and IR and ^{31}P NMR spectroscopy. The ^{31}P NMR chemical shift of the uncoordinated phosphorus(III) atoms in the P_4O_6 cage is found to be a measure of the extent of interaction between the coordinated phosphorus atom and the Lewis acid metal carbonyl site. The P_4O_6 cage appears to be a strong π acceptor ligand.

Introduction

Phosphorus(III) oxide was first reported in 1890 by Thorpe and Tutton [1,2], and since that time relatively little work has been done with the compound. The compound P_4O_6 is a structural derivative of the tetrahedral P_4 cage of elemental yellow phosphorus, where the six edges of the tetrahedron are occupied by oxygen atoms [3]. Each phosphorus atom has a lone pair of electrons which should be available for donation to a Lewis acid site such as metal carbonyls. Recent work demonstrated the ability of P_4O_6 to sequentially coordinate up to four $Ni(CO)_3$ moities [4], as well as the boron Lewis acid B_2H_6 [5]. Thus P_4O_6 may be classified as a non-chelating tetradentate ligand. In investigating the reaction of P_4O_6 with $Fe_2(CO)_9$, it was found that the reaction could be stopped at monosubstitution by carefully controlling the stoichiometry [6]. In this paper we describe the use of P_4O_6 as a monodentate ligand in reactions with the Group VIB metal carbonyls.



Experimental

All solvents used were reagent grade and were purified by distillation from CaH_2 and were stored over CaH_2. Tetraphosphorus hexaoxide was obtained by the controlled combustion of white phosphorus [7]. Metal carbonyls (Pressure Chemical) were sublimed before use. Molybdenum hexacarbonyl was also obtained as a gift from Climax Molybdenum Company. A Perkin—Elmer 457 grating spectrophotometer was used for IR measurements, and mass spectra were recorded on a Varian-Mat 311. NMR spectra were recorded using a Varian Model XL-100-15 nuclear magnetic resonance spectrometer with chemical shifts reported relative to an external 50% solution of P_4O_6 in benzene-d_6. Negative chemical shifts are downfield from this external reference. Photochemical reactions were carried out by using a 100-watt medium-pressure Hanovia lamp irradiating through Pyrex reaction vessels.

Preparation of $(CO)_5Cr(P_4O_6)$; photochemical reaction

$Cr(CO)_6$ (1 g, 4.5 mmol) was dissolved in 50 ml of degassed tetrahydrofuran (THF). To this, under a nitrogen blanket, was added 0.46 ml (4.0 mmol) of P_4O_6, and the resulting solution was irradiated from the underside of the flask for 2 h. The THF was removed by vapor transfer, and the resultant white residue was transferred in a drybox into a sublimator. The crude material was sublimed (50°C/10^{-5} Torr) for 3 h to remove any excess $Cr(CO)_6$. The unsublimed material was transferred to an all glass filtering system, and, using inert atmosphere techniques, was washed 3 times with 30 ml portions of cyclohexane, and the undissolved material was discarded. The cyclohexane was removed under vacuum, yielding 0.8 g (45% yield) of $(CO)_5Cr(P_4O_6)$.

Preparation of $(CO)_5Mo(P_4O_6)$; photochemical reaction

The same procedure was used as for the preparation of $(CO)_5Cr(P_4O_6)$, with removal of $Mo(CO)_6$ at 50°C/10^{-5} Torr for 5 h and recrystallization from cyclohexane.

Preparation of $(CO)_5Mo(P_4O_6)$; thermal reaction

$Mo(CO)_6$ (10 g, 37.9 mmol) was added to a 3-necked round bottom flask containing 150 ml of degassed methylcyclohexane. To the solution was added, under nitrogen, 3.5 ml (34.0 mmol) of P_4O_6, and the solution was heated at reflux for 4.5 h. After cooling, the reaction mixture was filtered in an all glass filtering system. The solvent was removed by vapor transfer, leaving a white solid, which was purified in the same manner as the residue from the photochemical reaction, yielding approximately 10 g of $(CO)_5Mo(P_4O_6)$.

Preparation of $(CO)_5W(P_4O_6)$; photochemical reaction

The same procedure was used as in the preparation of $(CO)_5Cr(P_4O_6)$. The residue was heated at 75°C for 12 h to remove $W(CO)_6$, with approximately a 35% yield of $(CO)_5W(P_4O_6)$ being produced following recrystallization from cyclohexane.

Results and discussion

As part of an extensive study of the ligative properties of phosphorus cage compounds, particularly P_4O_6, we recently reported the results of a study of the reaction of P_4O_6 with iron carbonyls [6]. The results of that investigation indicated the desirability of obtaining some ^{31}P NMR comparison data on the products of P_4O_6 with other metal carbonyl systems. The Group VIB metal carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, offered an ideal series for NMR studies, since none of the metals have a nuclear quadrupole that would result in line broadening with possible concommitant loss of fine structure.

The formation of the air-sensitive monosubstitution products $(CO)_5M(P_4O_6)$, where M = Cr, Mo, and W, was confirmed by mass spectrometry, IR and ^{31}P NMR spectroscopy.

The mass spectral data are summarized in Table 1. In all cases there was a parent ion peak, in addition to peaks corresponding to successive loss of CO, $(CO)_nM(P_4O_6)$, $n = 5$—0. In addition to expected ion fragments, also present were peaks of relatively low intensity (<20%) corresponding to metal atom ions with attached fragments of the phosphorus—oxygen cage, such as $M(P_3O_4)$. This is not surprising considering the fragmentation of the P_4O_6 cage itself [7].

The IR data for the compounds (Table 2) were that expected for monosubstitution at the metal center, showing four bands in the carbonyl region [8] together with four bands in the P—O region [7]. In cyclohexane solvent the P—O bands were generally broad and poorly resolved, whereas in CS_2 solvent these peaks were better resolved. The carbonyl stretching frequencies increased going down the Group, qualitatively indicating a decrease in the π^* carbonyl orbital population. This is expected due to a decrease in the phosphorus 3*d* orbital overlap with the larger, more diffuse 4*d* and 5*d* orbitals on molybdenum and tungsten, respectively.

Monodentate phosphorus coordination of the P_4O_6 cage should produce a ^{31}P NMR spectrum of a coupled doublet (relative area 3) and quartet (relative area 1), assuming that there are no other nuclear spins within the molecule. As expected, this was the observed ^{31}P NMR pattern for the molecules $(CO)_5M(P_4O_6)$, M = Cr, Mo, and W (Table 3). Of particular interest is the chemical shifts, of which there are now two types: the coordinated phosphorus(IV) atom:

TABLE 1

MASS SPECTRAL DATA OF GROUP VIB METAL CARBONYL DERIVATIVES [a]

Ion^{+} [b]	Cr	Mo	W
$(CO)_5MP_4O_6$	35.4	19.2	16.2
$(CO)_4MP_4O_6$	5.7	16.1	19.1
$(CO)_3MP_4O_6$	12.8	22.0	15.7
$(CO)_2MP_4O_6$	34.0	20.2	20.6
$COMP_4O_6$	85.7	41.9	10.1
MP_4O_6	93.9	56.1	65.2
MP_3O_4	23.4	13.2	21.0
P_4O_6	99.3	98.4	100

[a] Reported as % ion intensity. [b] Based on isotopic peaks ^{52}Cr, ^{98}Mo, and ^{184}W.

TABLE 2

INFRARED DATA OF GROUP VIB METAL CARBONYL DERIVATIVES

Compound	ν(CO) [a]	ν(PO) [b]
$(CO)_5CrP_4O_6$	2090m, 2062m, 1991vs, 1961s	947m, 922s, 900(sh), 891s
$(CO)_5MoP_4O_6$	2090m, 2070m, 1995vs, 1965s	945m, 922s, 900(sh), 889s
$(CO)_5WP_4O_6$	2101m, 2071m, 1996vs, 1969s	945s, 923s, 900s, 885s

[a] C_6H_{12} solution, KBr plates. [b] CS_2 solution.

and the three, magnetically equivalent, uncoordinated phosphorus(III) atoms. Grim et al., have shown [9] that coordination of a series of metal carbonyls to phosphorus(III) produced a downfield shift of the phosphorus resonance relative to the uncoordinated phosphine or phosphite. While downfield shifts are common for tertiary phosphines, it is not uncommon for coordinated phosphites to be shifted upfield of the free ligand [10]. Thus, with P_4O_6 acting as a monodentate ligand, the coordinated ^{31}P resonance was shifted to —46.0 and —20.2 ppm (relative to P_4O_6) in $(CO)_5Cr(P_4O_6)$ and $(CO)_5Mo(P_4O_6)$, respectively. However, for $(CO)_5W(P_4O_6)$, the coordinated phosphorus atom is shifted upfield +9.7 ppm (Table 3). This observation may be explained by the neighboring anisotropy effect causing by heavy atoms, i.e., tungsten, as has been observed previously [11] in series of Cr, Mo, and W compounds. A similar trend has been noted for the compounds $(CO)_5CrP(OMe)_3$, $(CO)_5MoP(OMe)_3$, and $(CO)_5WP(OMe)_3$ with ^{31}P NMR shifts (relative to free $P(OMe)_3$) of —39, —21, and +4 ppm, respectively [12].

The chemical shift of the three equivalent, uncoordinated phosphorus(III) atoms in a monosubstituted P_4O_6 compound appear to be almost solely dependent upon inductive effects through the P^{IV}—O—P^{III} linkage. Thus the chemical shift of the uncoordinated phosphorus atoms give a direct measure of the interaction of the coordinated phosphorus atom with a Lewis acid. The chemical shift of the phosphorus(III) atoms in the compounds $(CO)_5Cr(P_4O_6)$, $(CO)_5Mo(P_4O_6)$, and $(CO)_5W(P_4O_6)$ was almost independent of the coordinating metal center (Table 3) as the σ donating ability of P_4O_6 should vary little in this homologous series. A greater interaction was observed as monitored by the shift of the phosphorus(III) resonances, between P_4O_6 and the metal carbonyls in $(CO)_3Ni(P_4O_6)$ and $(CO)_4Fe(P_4O_6)$ with shifts of —4.0 [6] and —5.6 ppm [4],

TABLE 3

^{31}P NMR DATA OF GROUP VIB METAL CARBONYL DERIVATIVES

Compound [a]	$\delta_{coord.}$	$\delta_{uncoord.}$	J(P—O—P)
$(CO)_5CrP_4O_6$	—46.0	—2.4	35.5
$(CO)_5MoP_4O_6$	—20.2	—2.5	35.0
$(CO)_5WP_4O_6$	+ 9.7	—2.7	33.0 [b]

[a] C_6H_6 solutions. [b] $J(^{31}P—^{183}W)$ 485.5.

respectively. Substantiating data to support this argument is evidenced by the dramatic shifts produced on the phosphorus(III) atoms when the P_4O_6 coordinates to the very electronegative Group VIA elements, O, S, and Se, with shifts of −20 ppm in $(P_4O_6)O$, −12 ppm in $(P_4O_6)S$, and −11 ppm in $(P_4O_6)Se$ [13].

There is evidence to support the idea that P_4O_6 behaves as a very strong Lewis base only when the cage can also be a strong π electron acceptor. For example, P_4O_6 can act as a tetradentate base towards $Ni(CO)_4$ [4] and $Fe(CO)_5$ [6], but, since the highest observed [5] value of n in the series of compounds $P_4O_6 \cdot nBH_3$ was 3 instead of 4, it appears that the phosphorus cage exhibits only moderate basicity towards B_2H_6 (which cannot behave as a π donor). The argument for P_4O_6 behaving as a strong π acceptor is greatly supported by the coupling constant $J(^{31}P{-}^{183}W)$ in $(CO)_5W(P_4O_6)$. Grim et al. [11] found a linear relationship between $J(^{31}P{-}^{183}W)$ and the E species C—O stretching frequency for a number of complexes of the type $(CO)_5WPR_3$, and they interpreted their relationship in terms of π acceptor ability of the phosphines. They found the best π acceptor phosphine to be $(C_6H_5)_3P$, based on the fact that the complex $(CO)_5$-$WP(C_6H_5)_3$ had the highest C—O stretching frequency (1943 cm^{-1}) and the greatest $J(^{31}P{-}^{183}W)$ (280 Hz). They extended their study to phosphite complexes $(CO)_5WP(OR)_3$, and found the best π acceptor ligand to be $P(OPh)_3$, with a $\nu(CO)$ of 1959 cm^{-1} and a coupling constant of 411 Hz [14]. Assuming at least the qualitative validity [15] of interpretation of the data in terms of π acceptor ability of the ligand, then P_4O_6 is indeed an excellent π acceptor ligand, as indicated by $J(^{31}P{-}^{183}W)$ of 485.5 Hz a C—O stretching frequency of 1996 cm^{-1}.

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