stated, then, we believe the emitting state is one of the spin–orbit components of $^3A_{2u}$ (A_{1u} or E_u). Assignment of the emission to $^1A_{2u} \rightarrow {}^1A_{1g}$, however, is not entirely out of the question, as a large geometrical distortion in the $^1A_{2u}$ state of $M_2X_8{}^{n-}$ complexes could lead to nonoverlapping emission and absorption systems. The Duschinsky effect[17] could then operate to give an emission band shape that is considerably distorted from that of the corresponding absorption.[18] For the $M_2X_8{}^{n-}$ (M = Re, Mo; X = Cl, Br; n = 2 or 4) compounds, the excited-state distortion most likely would involve an eclipsed (D_{4h}) to noneclipsed (D_{4d}) conformational change. Even if this type of distortion occurs, it apparently does not affect the a_1 vibrational modes to a large extent, as the ground to excited state frequency shifts of a_1(ReRe) and a_1(ReReCl) are small.[13] Additionally, the calculations of Norman and Kolari[4,5] for $Mo_2Cl_8{}^{4-}$ suggest that chloride–chloride attractions contribute to the stabilization of the eclipsed geometry. Thus there is doubt whether the $^1A_{2u}$ state would distort at all from the eclipsed configuration.

The evidence favors assignment of the emission to one of the transitions $A_{1u}(^3A_{2u})$ or $E_u(^3A_{2u}) \rightarrow {}^1A_{1g}$. This interpretation places the singlet–triplet ($^1A_{2u}$–$^3A_{2u}$) separation in the range 1000–3000 cm^{-1}. This range is quite in line with the only documented singlet–triplet splitting in a binuclear Re(III) or Mo(II) compound, which is 1800 cm^{-1} for the $^{3,1}E_g(\delta \rightarrow \pi^*)$ excited states of $Mo_2(O_2CCF_3)_4$.[2] Further elucidation of the nature and position of the low-lying triplet excited states in $M_2X_8{}^{n-}$ complexes will require much additional theoretical and experimental effort.

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Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

^{31}P NMR Study of Some Coordination Complexes of the Phosphorus Cage Molecule Tetraphosphorus Heptaoxide[1]

MICHAEL L. WALKER and JERRY L. MILLS*

The molecule P_4O_7 is a structural derivative of the phosphorus cage molecule P_4O_6, and, as such, can potentially behave as a nonchelating, tridentate ligand. Complexes formed between P_4O_7 and the metal carbonyls $Ni(CO)_4$, $Fe_2(CO)_9$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are characterized by ^{31}P NMR spectroscopy. A two-to-one complex is formed between BF_3 and P_4O_7, while borane and trimethylborane do not react with P_4O_7. A comparison between the ligative properties of P_4O_6 and P_4O_7 is discussed in terms of ^{31}P NMR spectral data.

## Introduction

Earlier we communicated the preparation of P_4O_7, giving
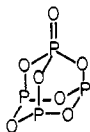
spectroscopic evidence for the compound retaining the adamatane-like structure of P_4O_6, with the addition of an exocyclic oxygen atom to the cage.[2] Since P_4O_6 had been shown to react with $Ni(CO)_4$,[3] iron carbonyls,[4] group 6B metal carbonyls,[5] and diborane,[6] it was expected that P_4O_7 should behave in a similar manner and act as a tridentate, nonchelating ligand. Also of interest was the effect of oxidation of one phosphorus atom of the P_4O_6 cage on the potential Lewis basicity of the other three phosphorus Lewis base

sites. The present paper reports the details of preparation and ^{31}P NMR characterization of several P_4O_7 metal carbonyl complexes, with comparison to the P_4O_6 analogues.

Results

Due to the extreme air sensitivity of P_4O_7 and its derivative metal carbonyl adducts, attempts to isolate the compounds in pure form were unsuccessful. The use of ^{31}P NMR allowed the study of reaction mixtures with the identification of the compounds by hyperfine splitting patterns and chemical shift data. In all cases the reaction of metal carbonyls with P_4O_7 followed the general scheme

$$n\text{M(CO)}_m + \text{P}_4\text{O}_7 \rightarrow [\text{M(CO)}_{m-1}]_n(\text{P}_4\text{O}_7) + n\text{CO}$$
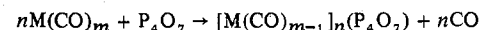
For nickel carbonyl an entirely closed system was used to exclude air and water. Progressive addition of $Ni(CO)_4$ to P_4O_7 from a mole ratio of about 0.7 to 4.0 favored saturative ligation of the P_4O_7 cage, with a mixture of products [Ni-

Table I. ^{31}P NMR Data for Metal Carbonyl Complexes of P_4O_7 in Benzene Solvent

Compd	Spin system	Chemical shift,[a] ppm	Pattern[g]	Coupling constants, Hz
$[Ni(CO)_3](P_4O_7)$[b]	AM_2X	$\delta pIV(\delta_A)$ −33.3	t of d	$J_{pIII-pIV}(J_{AM}) = 30.5$
		$\delta pIII(\delta_M)$ −15.4	d of d	$J_{pIV-pV}(J_{AX}) = 22.5$
		$\delta pV(\delta_X)$ +168.9	d of t	$J_{pIII-pV}(J_{MX}) = 1.5$
$[Ni(CO)_3]_2(P_4O_7)$[b]	A_2MX	$\delta pIV(\delta_A)$ −31.3	d of d	$J_{pIII-pIV}(J_{AM}) = 28.5$
		$\delta pIII(\delta_M)$ −7.8	t of d	$J_{pIV-pV}(J_{AX}) = 26.5$
		$\delta pV(\delta_X)$ +166.7	t of d	$J_{pIII-pV}(J_{MX}) = 5.0$
$[Ni(CO)_3]_2(P_4O_7)$[b]	A_3X	$\delta pIV(\delta_A)$ −27.3	d	$J_{pIV-pV}(J_{AX}) = 31.5$
		$\delta pV(\delta_X)$ +165.4	q	
$[Fe(CO)_4](P_4O_7)$	AM_2X	$\delta pIV(\delta_A)$ −66.0	Overlapping d of t	$J_{pIII-pIV}(J_{AM}) = 26.0$
		$\delta pIII(\delta_M)$ −13.9	d of d	$J_{pIV-pV}(J_{AX}) = 32.5$
		$\delta pV(\delta_X)$ +168.8	d of t	$J_{pIII-pV}(J_{MX}) = 3.0$
$[Fe(CO)_4]_2(P_4O_7)$	A_2MX	$\delta pIV(\delta_A)$ −60.6	d of d	$J_{pIII-pIV}(J_{AM}) = 22.0$
		$\delta pIII(\delta_M)$ +2.2	t of d	$J_{pIV-pV}(J_{AX}) = 39.0$
		$\delta pV(\delta_X)$ +165.2	t of d	$J_{pIII-pV}(J_{MX}) = 9.5$
$[Cr(CO)_5](P_4O_7)$[c]	AM_2X	$\delta pIV(\delta_A)$ −66.0	q[d]	$J_{pIII-pIV}(J_{AM}) = 28.0$
		$\delta pIII(\delta_M)$ −13.1	d of d	$J_{pIV-pV}(J_{AX}) = 28.0$
		$\delta pV(\delta_X)$ +168.7	d of t	$J_{pIII-pV}(J_{MX}) = 2.5$
$[Mo(CO)_5](P_4O_7)$[c]	AM_2X	$\delta pIV(\delta_A)$ −40.4	q[d]	$J_{pIII-pIV}(J_{AM}) = 25.0$
		$\delta pIII(\delta_M)$ −13.4	d of d	$J_{pIV-pV}(J_{AX}) = 25.0$
		$\delta pV(\delta_X)$ +168.6	d of t	$J_{pIII-pV}(J_{MX}) = 2.0$
$[Mo(CO)_5]_2(P_4O_7)$[c]	A_2MX	$\delta pIV(\delta_A)$ −35.2	d of d	$J_{pIII-pIV}(J_{AM}) = 23.0$
		$\delta pIII(\delta_M)$ −0.2	t of d	$J_{pIV-pV}(J_{AX}) = 30.5$
		$\delta pV(\delta_X)$ +166.9	t of d	$J_{pIII-pV}(J_{MX}) = 7.5$
$[W(CO)_5](P_4O_7)$[e]	AB_2X	$\delta pIV(\delta_A)$ −9.4	Complex	$J_{pIII-pIV}(J_{AB}) = 24.6$[f]
		$\delta pIII(\delta_B)$ −12.3	Complex	$J_{pIV-pV}(J_{AX}) = 27.0$[f]
		$\delta pV(\delta_X)$ +168.8	Complex	$J_{pIII-pV}(J_{BX}) = 2.5$[f]

[a] Relative to P_4O_6 using P_4O_7 as an internal standard (doublet, −19.9 ppm; quartet, +173.0 ppm). Upfield shifts are reported as positive. [b] Toluene solution at −16 °C. [c] Obtained with time-averaging computer. [d] Overlapping doublet of triplets to give apparent quartet. [e] J_{W-P} was not observed due to limited solubility of the complex and the second-order spectrum. [f] Obtained by use of computer simulation (see text). [g] Key: d = doublet, t = triplet, q = quartet.

$(CO)_3]_n(P_4O_7)$, $n = 1$–3, being found in all cases; the reaction stoichiometry largely controlled the product distribution. Because of compound decomposition and the fact that the spectral resolution was insufficient to make peak integrations meaningful, formation constants were not calculated; however, qualitatively the degree of substitution on the P_4O_7 cage was approximately statistical. A reaction temperature of about 0 °C was the best compromise between reactivity and thermal decomposition.

In the iron carbonyl system, the use of the reactive intermediate generated by the reaction of $Fe_2(CO)_9$ with an ether solvent was employed.[7] Tetrahydrofuran was found to polymerize at high concentrations of diiron enneacarbonyl; glyme (1,2-dimethoxyethane) was found to be a satisfactory substitute. At small ratios of $Fe_2(CO)_9$ to P_4O_7, the preponderant product was $[Fe(CO)_4](P_4O_7)$. By increasing the ratio of $Fe_2(CO)_9$ to P_4O_7, it was found that more $[Fe(CO)_4]_2(P_4O_7)$ was formed at the expense of P_4O_7 and $[Fe(CO)_4](P_4O_7)$. Due to either reactivity or solubility limitations, the addition of a third $Fe(CO)_4$ moiety to the P_4O_7 cage was not observed. (Some weak resonances were observed in the ^{31}P NMR spectrum in the P–Fe region, but they could not absolutely be assigned to $[Fe(CO)_4]_3(P_4O_7)$.) At high iron ratios of 5 to 1 or greater at 60 °C, no phosphorus NMR resonances were observed.

The use of the reactive intermediate $M(CO)_5THF$[8] was found to be the only practical method of introducing $M(CO)_5$ units onto the P_4O_7 cage. In general the reaction of the group 6B metal carbonyls with P_4O_7 offered low yields.

Tensimetric titrations of P_4O_7 with BF_3 showed a sharp break after the second equivalence point, indicating a strong two to one complex, $(BF_3)_2(P_4O_7)$, being formed at −78 °C. The tensimetric titration indicated the possibility of a weak complex formed with the third equivalent of BF_3. With the Lewis acids B_2H_6 and BMe_3, tensimetric titrations indicated no complexation with P_4O_7.

Discussion

The addition of an exocyclic oxygen atom to the P_4O_6 cage

has a distinct effect on the ability of the other phosphorus atoms in P_4O_7 to behave as Lewis base sites. Tensimetric titrations of P_4O_7 with B_2H_6 at ambient temperature indicated no absorption, whereas P_4O_6 will react with B_2H_6 giving as an insoluble species $(P_4O_6)(BH_3)_2$.[6a] In contrast, P_4O_6 will not form a stable complex with BF_3[6a] but slowly decomposes, whereas P_4O_7 will accommodate up to 2 equiv of BF_3 per P_4O_7 cage. In the Pearson sense,[9] BH_3 is a softer acid than BF_3, and P_4O_6 is a softer base than P_4O_7. The resultant ability of P_4O_7 to coordinate with the hard acid BF_3 is attributed to the inductive effect of the exocyclic oxygen atom oxidizing the phosphorus^{III} to phosphorus^V, which in turn withdraws electron density from the remaining phosphorus^{III} atoms through the P^V–O–P^{III} linkage. (In the remainder of the paper, the phosphorus atoms will be designated as either P^{III}, P^{IV}, or P^V. Phosphorus^{III} refers to trivalent, tricoordinate phosphorus atoms (M in Figure 1); phosphorus^{IV} refers to the tetravalent phosphorus atoms bonded as Lewis bases to metal carbonyls or boron Lewis acids (A in Figure 1); phosphorus^V refers to the unique P=O phosphorus atom in the cage (X in Figure 1). The phosphorus^{III} resonance occurs at −20 ppm (relative to P_4O_6) in P_4O_7;[2] bearing in mind the problems inherent in such chemical shift arguments, this shift is at least qualitatively in accord with reduced, less polarizable electron density at the phosphorus^{III} site.[10]

When P_4O_7 was monocoordinated to a metal carbonyl, the expected first-order ^{31}P NMR spectral pattern was observed, i.e., an AM_2X spin system (Table I and Figure 1). The only second-order spectrum noted was that of $[W(CO)_5](P_4O_7)$, where $J_{P^{IV}-P^{III}}/\Delta\delta = 0.22$, which was therefore a complex AB_2X spin system. The chemical shift, as well as the peak multiplicities, was diagnostic of the type of phosphorus atom in the cage. Upon complexation, three distinct phosphorus resonances were found: the phosphorus^{IV} resonances occurred at low fields, the uncomplexed phosphorus^{III} resonances at very near 0 ppm, and the phosphorus^V resonances at high field (165–170 ppm).

It has been previously reported[4] that when P_4O_6 is poly-
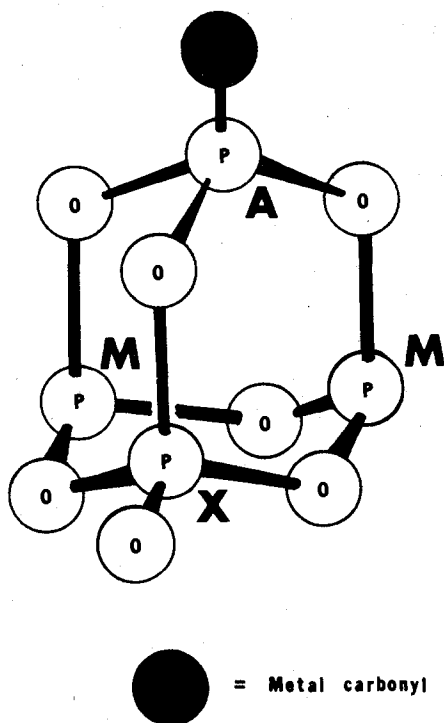
= Metal carbonyl

Figure 1. Proposed structure for a metal carbonyl-P_4O_7 complex. The labels A, M, and X on the phosphorus atoms correspond to the NMR spin system designations in Table I.

substituted by metal carbonyls, the internal coordination chemical shift δ^* (defined as the difference in the ^{31}P NMR chemical shift of the coordinated and the uncoordinated phosphorus atoms in the cage) is inversely proportional to the number of metal carbonyl moieties coordinated to the cage. This was interpreted as indicating that progressive coordination of metal carbonyl units affected the cage in an equivalent manner and that the effect was simply additive. A similar effect was not found in P_4O_7 derivatives. The only clearly established trend in the P_4O_7 series is the small downfield shift of the $P^V=O$ group upon progressive substitution on the cage.

It has previously been demonstrated by Gorenstein[11] that the ^{31}P chemical shift for all classes of phosphate esters has a direct relationship to the O–P–O bond angle. The relationship was found to be independent of electronegativity of the pendant organic groups and of the charge of the phosphate esters, except to the extent that they affect the O–P–O bond angle. While Gorenstein made no claim for the applicability of the correlation to other classes of phosphoryl compounds, the extention of the empirical relationship to the chemical shift of the phosphorus^V atom in P_4O_7 is reasonable. Because of the adamantane-like structure of the cage, the O–P–O bond angle of the phosphorus^V in P_4O_7 should be relatively resistant to change upon coordination of the phosphorus^{III} atoms, thus yielding a small range of chemical shifts. The phosphorus^V chemical shift of P_4O_7 coordinated to a single metal carbonyl unit is essentially constant (Table I), irrespective of the metal carbonyl, while di- and tricoordination decreases the shift by a maximum of 4 ppm. For phosphate esters, a change of 4 ppm corresponds to an O–P–O bond angle change of less than 1°.[11]

Interestingly, the chemical shift (Table I) of the phosphorus^{IV} atom in MP_4O_7 complexes (M = Fe, Ni, Cr, Mo, and W carbonyls) can be accurately predicted by comparison to the analogous MP_4O_6 complexes by use of coordination chemical shifts (Table II). Thus the coordination chemical shift, $\Delta\delta$ (the difference between δ of the coordinated phosphorus atom and δ of the free ligand), for a particular MP_4O_6 complex is essentially the same as the coordination chemical

Table II. Constancy of ^{31}P Coordination Chemical Shifts[a] of P_4O_7 Metal Carbonyl Complexes

Metal CO moiety M	Coordination chemical shift	
	For $M(P_4O_6)$	For $M(P_4O_7)$[b]
$Ni(CO)_3$	-13.0^c	-13.3
$Fe(CO)_4$	-48.5^d	-46.0
$Cr(CO)_5$	-46.0^e	-46.0
$Mo(CO)_5$	-20.2^e	-20.4
$W(CO)_5$	$+9.7^e$	$+10.6$

^{a} Coordination chemical shift = (δ of coordinated phosphorus) – (δ of phosphorus^{III} in free ligand). ^{b} The δ for the phosphorus^{III} in the free ligand is -20.0 ppm for the phosphorus^{III} atoms in P_4O_7. ^{c} Reference 3. ^{d} Reference 4. ^{e} Reference 5.

shift for a MP_4O_7 complex (where δ for the free ligand is for the phosphorus^{III} atoms in P_4O_7). This would seem to indicate that the phosphorus^{IV} chemical shift is a direct result of metal carbonyl inductive effects in both P_4O_6 and P_4O_7 complexes.

In all metal carbonyl complexes of P_4O_6, the phosphorus^{III} atoms are shifted downfield relative to P_4O_6.[3-5] However, the phosphorus^{III} atoms in metal carbonyl complexes of P_4O_7 are shifted upfield relative to the phosphorus^{III} atoms in uncomplexed P_4O_7 (δ -19.9 ppm relative to P_4O_6, Table I). The upfield shift of phosphorus^{III} upon metal coordination is unexpected, particularly since it has previously been shown that the chemical shift of the three uncoordinated phosphorus^{III} atoms in a monosubstituted P_4O_6 complex appears to be solely dependent on inductive effects through the P^{IV}–O–P^{III} linkage.[5] Presumably, the effect of the phosphoryl oxygen in P_4O_7 complexes partially negates the inductive effects of the metal carbonyl.

An examination of the phosphorus–oxygen–phosphorus coupling constants in P_4O_7 complexes reveals that, in general, the couplings increase in the order P^{III}–O–P^V < P^{III}–O–P^{IV} < P^{IV}–O–P^V. Assuming that $^2J_{PP}$ is dominated by the Fermi contact term, its magnitude should mirror the partial charge, as related to the substituent electronegativity, of the nuclei involved. A change in the phosphorus coordination number brings about a change in the s electron density in the P–O bonds coincident with small variations in the cage bond angles, which, as noted above, need to be measured to fully interpret the NMR data.

Experimental Section

Materials and Methods. All compound syntheses and manipulations were performed using standard vacuum line and inert atmosphere techniques.[12] Solvents were distilled from CaH_2 or $LiAlH_4$ and stored over CaH_2. Prior to use, solvents were degassed with dry N_2 for at least 5 min. The metal carbonyls $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Fe_2(CO)_9$ were purchased from Pressure Chemical. Before use, the hexacarbonyls were sublimed, and $Fe_2(CO)_9$ was dried in vacuo at 50 °C for 1 h.[7] The compounds $Ni(CO)_4$ and BF_3 were purchased from Matheson Gas Products and used as received. Diborane was prepared[13] according to literature procedures. A Varian Associates NMR spectrometer Model XL-100-15 operating at 40.55 MHz was used in conjunction with a Model 1024 time averaging computer to obtain ^{31}P spectra. Upfield (more shielded) chemical shifts are reported as positive and are relative to external P_4O_6 (50 vol % in C_6D_6). Photochemical reactions were carried out using a 100-W medium-pressure Hanovia lamp in Pyrex reaction vessels.

Preparations. P_4O_7. The procedure used for the preparation of P_4O_7 was as previously described,[2] except for a slight modification in the purification procedure. The purification was performed by sublimation under a high vacuum (10^{-5} Torr) into a cold finger held at -78 °C. The temperature of the bath surrounding the sublimator was raised slowly from ambient temperature to 60 °C over 48 h.

$[Ni(CO)_3]_nP_4O_7$, $n = 1, 2, 3$. The reaction of P_4O_7 with $Ni(CO)_4$ was performed in a reaction vessel constructed from a test tube ended 24/40 glass joint having a total length of 12 cm. Three NMR tubes were attached via a small length of 5-mm tubing to the vessel as near to the ground joint as practical and then the tubes were bent parallel to the reaction vessel, giving the apparatus the appearance of having three "legs". The vessel was carefully dried and placed into a drybox

where, in a typical reaction, 0.346 g (1.47 mmol) of P_4O_7 was transferred into the apparatus. The vessel containing the P_4O_7 was sealed with a stopcock adapter, removed from the drybox, and attached to a vacuum line. Approximately 3 mL of toluene was vapor transferred into the reaction vessel. The solution (ca. 0.49 M in P_4O_7) was frozen at -196 °C, and 1.0 mmol of $Ni(CO)_4$ was condensed into the vessel. The temperature was slowly raised to 0 °C, with concomitant CO evolution. The reaction temperature was maintained at 0 °C for 1.5 h, and then was quenched at -196 °C. The vessel was reevacuated, allowed to warm to -78 °C to degas and again cooled to -196 °C, and reevacuated. The solution was warmed to -78 °C and was then poured into an attached NMR tube that had been precooled to -78 °C. Sufficient solution was poured into the cooled NMR tube to reach a depth of ca. 3 cm. The tube and bulk solution were frozen at -196 °C, and the NMR tube was flame sealed, removed from the reaction vessel, and stored at -196 °C. A ^{31}P NMR spectrum showed a mixture of products, with $[Ni(CO)_3](P_4O_7)$ dominating. The entire process was repeated with the addition of a second millimole of $Ni(CO)_4$ with 1.5 h of reaction at 0 °C. The second NMR tube contained as the primary component $[Ni(CO)_3]_2(P_4O_7)$. Upon addition of a third millimole of $Ni(CO)_4$ and repeating the above process, the ^{31}P NMR spectrum indicated that $[Ni(CO)_3]_3(P_4O_7)$ was the major product. All ^{31}P NMR spectra were recorded at -16 °C to prevent product decomposition with subsequent evolution of CO.

$[Fe(CO)_4]_n(P_4O_7)$, $n = 1, 2$. The reaction between $Fe_2(CO)_9$ and P_4O_7 was carried out in a drybox. To 50 mL of dry glyme was added 1.0 g (2.8 mmol) of $Fe_2(CO)_9$, and 0.7 g (2.9 mmol) of P_4O_7. The mixture was vigorously stirred magnetically for 3 h at 40 °C. A 5-mL aliquot of the solution was removed and the solvent evaporated from it. To the remaining green residue was added 1.0 mL of dry degassed benzene. The major product, as shown by ^{31}P NMR, was $[Fe(CO)_4](P_4O_7)$. To the remaining glyme solution was added another 1.0 g of $Fe_2(CO)_9$, and the solution was stirred for 3 h. After being cooled, the reaction mixture was treated as above; the ^{31}P spectrum showed $[Fe(CO)_4]_2(P_4O_7)$ to be the major product.

$[M(CO)_5](P_4O_7)$, M = Cr, Mo, W. Into a 50-mL, three-necked round-bottom flask was added under inert atmosphere 20 mL of dry THF, 0.53 g (2.26 mmol) of P_4O_7, and 0.80 g (3.6 mmol) of $Cr(CO)_6$. The solution was stirred until dissolution of the carbonyl and was UV irradiated from the underside of the flask for 2 h. Irradiation was ceased, and the solvent was removed by vapor transfer. The flask was transferred into the drybox, and the residue was treated with 2 mL of dry benzene. The ^{31}P NMR of the benzene solution showed $[Cr(CO)_5](P_4O_7)$. For the preparation of the molybdenum analogue, the above procedure was used with 0.30 g (1.30 mmol) of P_4O_7 and 0.50 g (1.90 mmol) of $Mo(CO)_6$ with 2.5 h of irradiation. The tungsten analogue was prepared using 1.30 mmol of $W(CO)_6$ and

0.90 mmol of P_4O_7, with 3.5 h of irradiation. The reaction of $Mo(CO)_6$ produced some disubstituted product $[Mo(CO)_5]_2(P_4O_7)$, in addition to the monosubstituted product.

Tensimetric Titrations. In a drybox a known quantity (typically 0.1–0.2 mmol) of P_4O_7 was placed in a tensimeter.[14] The tensimeter was transferred to a vacuum line, and ca. 3.0 mL of dry toluene was vapor transferred onto the P_4O_7. The particular Lewis acid (BF_3, BMe_3, and B_2H_6) was then vapor transferred into the tensimeter in increments corresponding to ca. 1:4 mole ratio of the P_4O_7 used. After each addition the solution was rapidly stirred and maintained at -78 °C for 1.5–2 h, to ensure equilibrium conditions, before a pressure reading was taken.

Registry No. $[Ni(CO)_3](P_4O_7)$, 64045-11-0; $[Ni(CO)_3]_2(P_4O_7)$, 64045-10-9; $[Ni(CO_3)]_3(P_4O_7)$, 64045-09-6; $[Fe(CO)_4](P_4O_7)$, 64045-08-5; $[Fe(CO)_4]_2(P_4O_7)$, 64045-07-4; $[Cr(CO)_5](P_4O_7)$, 64045-06-3; $[Mo(CO)_5](P_4O_7)$, 64045-05-2; $[Mo(CO)_5]_2(P_4O_7)$, 64045-04-1; $[W(CO)_5](P_4O_7)$, 64070-32-2; $(BF_3)_2(P_4O_7)$, 64056-83-3; $Ni(CO)_4$, 13463-39-3; $Fe_2(CO)_9$, 15321-51-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

References and Notes

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Contribution from the Departments of Chemistry, Sonoma State College, Rohnert Park, California 94928, and University of Washington, Seattle, Washington 98195

Gas-Phase Ultraviolet and Visible Spectra of Sodium Tetrachloroferrate(III) and of Monomeric and Dimeric Iron(III) Chloride

D. S. RUSTAD and N. W. GREGORY*

Molar absorptivities in the ultraviolet and visible range for $FeCl_3(g)$ at 400–650 °C, $Fe_2Cl_6(g)$ at 200–600 °C, and $NaFeCl_4(g)$ at 450–650 °C have been evaluated; the temperature dependence of the vaporization of $NaFeCl_4$ from a liquid phase in equilibrium with $NaCl(s)$ has also been studied spectrophotometrically. The vapor-phase spectra of these molecules, along with $FeAlCl_6$, are discussed in terms of the different chlorine environments of the iron atoms and are compared with condensed-phase spectra of similar species as reported by other authors.

Introduction

A previous spectrophotometric study[1] of gaseous Fe_2Cl_6 and $FeAlCl_6$ has shown these substances to have similar

* To whom correspondence should be addressed at the University of Washington.

charge-transfer ultraviolet and visible spectra with absorption maxima at 245 and 360 nm. Molar absorptivities of $FeAlCl_6$ are lower, by about one-third at 245 nm and by about one-half at 360 nm, than those of Fe_2Cl_6. The two molecules are expected to have similar structures (fourfold chlorine coordinated metal atoms joined by sharing two of the chlorine