where κ is the volume susceptibility, μ_0, the Bohr magneton, n, the electron density, and h, Planck's constant.

After the corrections for the diamagnetism of O^{2-} and Os^{4+} according to Selwood,[10] one calculates $\chi_M = 172 \times 10^{-6}$ cgsu. Assuming a rutile structure for OsO_2 with $a_0 = 4.51$ Å and $c_0 = 3.19$ Å,[5] a value of $\kappa = 8.6 \times 10^{-6}$ cgsu cm^{-3} is calculated. Using this value of κ and as a first approximation taking $m^* = m_0$ in the Landau term for the collective electron diamagnetism, we obtain the calculated value of $n = 2.03 \times 10^{26}$ cm^{-3}, an absurd result. A value of $m^*/m_0 > 8$ is required to bring n into the range defined by the Hall effect results. Such a large value of m^*/m_0 is more characteristic of narrow-band carriers, as are encountered in the transition metals themselves,[11] than of nearly free carriers.

Goodenough[12] has suggested that, in transition metal oxides with the rutile structure, conduction bands can be formed from direct overlap of t_{2g} orbitals on adjacent metal atoms along the c axis, giving rise to a metallic conductivity in a d band only along the c axis, and/or from overlap of t_{2g} orbitals on the metal with oxygen p–π orbitals, giving rise to a nearly isotropic conductivity in a π^* band. In this scheme the metal d band would contain 2 electrons/OsO_2 unit while the π^* band would have a capacity of 4 electrons/OsO_2 unit. These two bands are expected to lie close in energy and may overlap. Three situations can be imagined: (1) the top of the π^* band lies below the bottom of the d band; (2) the top of the d band lies below the bottom of the π^* band; (3) the two bands overlap appreciably.

The first of these possibilities can be ruled out as OsO_2 has exactly 4 valence electrons/OsO_2 unit and these would just fill the π^* band and give rise to nonmetallic behavior. Possibilities (2) and (3) are compatible with the observed metallic behavior. In case (2) the d band would be filled and the π^* half-filled, whereas in case (3) the 4 electrons would inhabit a composite band with total capacity of 6 electrons/OsO_2 unit. The carrier densities predicted by these two models are also consistent with the Hall data and the narrow band picture as case (2) predicts $n = 6 \times 10^{22}$ cm^{-3}, $\mu = 2.5$ cm^2 V^{-1} sec^{-1}, and case (3) predicts $n = 1.2 \times 10^{23}$ cm^{-3}, $\mu = 1.5$ cm^2 V^{-1} sec^{-1}.

In summary, we submit that the available, albeit scant, data on OsO_2 can be consistently rationalized on the basis of a wholly collective electron approach such as that suggested by Goodenough and involving the concepts of narrow bands and high density of states which are quite commonly encountered in the transition metals and their compounds.

Acknowledgment.—J. E. G. acknowledges support by the USAEC. We also wish to thank Dr. Ronald Goldner, Mr. Harvey Serreze, and Mr. John Heaton of the Tufts University Materials Science Laboratory for considerable assistance in making the transport measurements.

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[10] P. W. Selwood, "Magnetochemistry, 2nd ed, Interscience Publishers, New York, N. Y., 1956, p 78.

[11] C. Kittel, "Introduction to Solid State Physics," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1953, p 259.

[12] J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).

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Mass Spectra of Hexachlorotriphosphonitrile and Octachlorotetraphosphonitrile

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Until recently no electron-impact studies of phosphorus–nitrogen polymers had been reported. Our results complement the mass spectral study of the bromophosphonitriles[1] and fluorophosphonitriles[2] and add important details to the abbreviated summary of spectral data for chlorophosphonitrile oligomers.[3] Together these studies provide a comprehensive description of the behavior of phosphonitriles to electron impact.

Results

The line spectrum of octachlorotetraphosphonitrile is shown in Figure 1. The relative abundances of ions in the mass spectra of the trimer and the tetramer are recorded in Tables I and II, respectively. The abundances are reported as a percentage of the total ion abundance. The measured intensities of the multiply charged ions were divided by the charge on the ion to provide comparability with the singly charged ions. Several ions not reported earlier[3] have been observed in low abundance.

Discussion

Certain characteristic behaviors of the chlorophosphonitriles to electron impact are evident from the relative abundance data. As noted previously,[3] the $P_nN_nCl_{2n-1}^+$ ion is the most abundant in both spectra. The phosphonitrile ring appears to be cleaved to a very great extent upon electron impact. The P_4N_4 ions in the tetramer spectrum account only for 25.0% of the total ions and the P_3N_3 ions in the trimer spectrum make up 32.4% of the total ions. Fragments which contain the P_3N_2 and P_2N backbone and are presumed to have a linear structure[3] appear to be stable. These fragments make up 19.8% of the total ions both in the tetramer and in the trimer.

The dominance of even-electron ions over odd-electron ions is striking. Of the ions which contain both phosphorus and nitrogen and are present in amounts greater than 0.1% in the trimer, 46.5% are even-electron ions and 17.3% are odd-electron ions. In the tetramer spectrum the figures are 46.8 and 15.1%, respectively. Two correlations are evident when the relative abundances of odd- and even-electron P_3N_3 and P_4N_4 ions of identical stoichiometry are compared. The data in Table III show that the relative abundance of an even-electron ion is always greater than the odd-electron ion of the same stoichiometry except for the

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[1] G. E. Coxon, T. F. Palmer, and D. B. Sowerby, *J. Chem. Soc., A*, 1568 (1967).

[2] C. E. Brion and N. L. Paddock, *ibid., A*, 392 (1968).

[3] C. E. Brion and N. L. Paddock, *ibid., A*, 388 (1968).

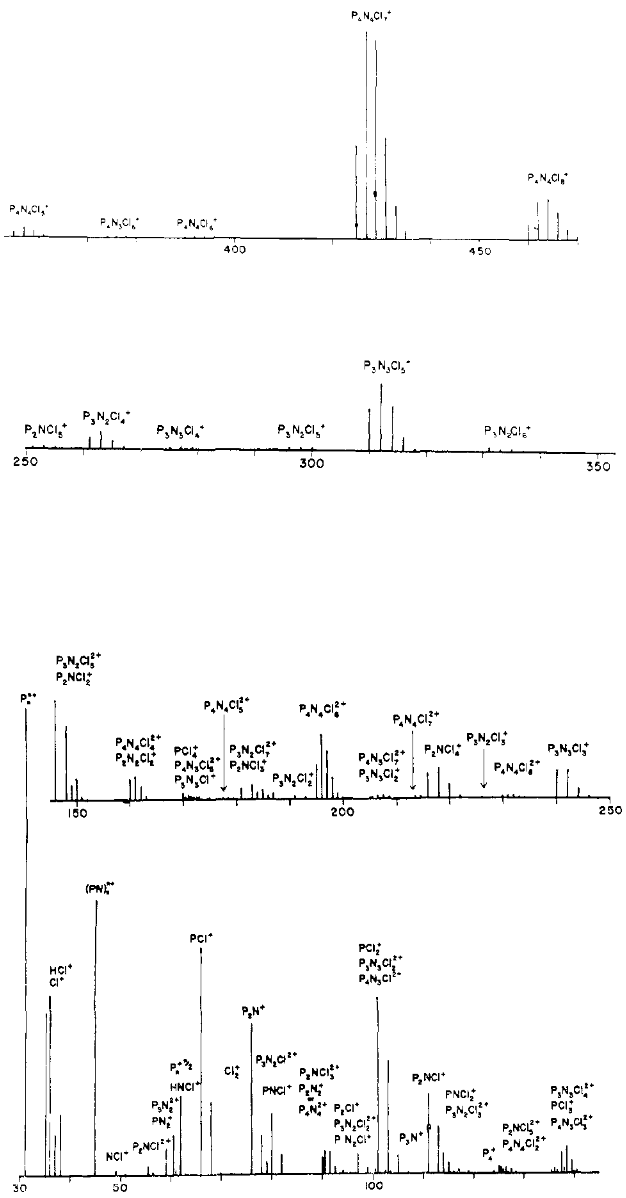

Figure 1.—Mass spectrum of octachlorotetraphosphonitrile.

parent ion. Secondly, an even-electron ion is always more abundant than the odd-electron ions that have one more or one less chlorine atom. A similar pattern exists in the chlorophosphonitrile trimer spectrum and the bromophosphonitrile spectra,[1] but no notice was taken of it.

A theoretical explanation was sought to account for this behavior. We have assumed that the thermodynamic stability of a gaseous ion is the dominant factor in determining its abundance. Actually, the rates of formation and dissociation of an ion would have to be included in a detailed theoretical model. Since the kinetic effects are impossible to evaluate even qualitatively, they necessarily have been omitted.

Theoretical treatments of bonding in phosphonitriles have been published.[4-6] To a first approximation, the σ bonds in the ring may be regarded as bonds formed by the overlap of sp^3 hybrid orbitals of the phosphorus atoms with the sp^2 orbitals of the nitrogens. Although there is some disagreement as to which d orbitals are used in the ring π system, there is agreement that delocalization of bonds occurs through d_π–p_π molecular orbitals.

TABLE I

RELATIVE ABUNDANCES OF IONS IN THE MASS SPECTRUM OF HEXACHLOROTRIPHOSPHONITRILE[a]

	n							
Charge	0	1	2	3	4	5	6	Total
$P_3N_3Cl_n$								
+1	...	0.5*	0.1	2.0*	0.4	21.1*	4.2	28.3
+2	...	...	0.2*	0.1	3.6*	0.2	0.1*	4.1
$P_3N_2Cl_n$								
+1	tr	tr	0.1*	tr	0.3*	...	...	0.4
+2	0.8	1.0*	tr	1.1*	...	1.0*	...	3.9
$P_2N_2Cl_n$								
+1	...	0.2*	0.3	0.5*	tr	...	...	1.0
+2	...	...	...	...	...	...	...	...
P_2NCl_n								
+1	3.1*	3.1	5.7*	0.7	0.8*	tr	...	13.3
+2	...	0.4*	tr	1.3*	...	0.4*	...	2.1
PN_2Cl_n								
+1	0.8*	0.2	...	...	...	...	...	1.0
+2	...	...	...	...	...	...	...	...
$PNCl_n$								
+1	6.9	2.3*	0.5	...	...	...	...	9.6
+2	...	0.1	...	...	...	...	...	0.1
PCl_n								
+1	8.5*	8.2	8.6*	0.3	0.2*	...	...	25.8
+2	...	tr	...	...	...	...	...	...

[a] Other species present: Cl^+, 3.6; HCl^+, 4.7; NCl^+, 0.1; P_2^+, 0.8; Cl_2^+, 0.1; P_2Cl^+, 0.9; $P_2Cl_2^+$, 0.1; and $P_2Cl_3^+$, 0.1. An asterisk designates an even-electron ion.

The reasonable expectation that the strength of a bond is determined significantly by overlap of hybridized atomic orbitals and that the magnitude of the overlap integral reflects this contribution to bond strength has been treated theoretically for bonds between two like atoms.[7] Calculations showed that the σ-bond overlap integral of an sp^2 hybrid is greater than that of an sp^3 hybrid. If the elimination of a chlorine atom from the odd-electron parent ion $P_3N_3Cl_6\cdot^+$ to give the even-electron $P_3N_3Cl_5^+$ ion is accompanied by rehybridization from sp^3 to sp^2 of the phosphorus atomic orbitals of the PCl group, the σ bonding of the phosphorus to the neighboring nitrogen atoms will be increased. In addition, the phosphorus atom to which the single chlorine is attached now has a 3p$_z$ orbital available for p_π–p_π bonding to nitrogen.

What effect a change from $2p_\pi$–$3d_\pi$ bonding to $2p_\pi$–$3p_\pi$ bonding would have on the strength of the P–N bond is not readily assessed. The overlap integral for $2p_\pi(N)$–$3p_\pi(P)$ bonding is 0.178[8] as compared to 0.139

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(4) M. J. S. Dewar, E. A. C. Lucken, and M. A. W. Whitehead, *J. Chem. Soc.*, 2423 (1960).

(5) (a) D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962); (b) D. P. Craig and N. L. Paddock, *Nature*, **181**, 1052 (1958).

(6) D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.*, 4682 (1965).

(7) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, pp 208–211.

(8) Calculations were made from Table XXI of R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949). The data in Table XXI are for $S(2p\pi, 3p\pi)$ and not $S(2p\pi, 2p\pi)$ as indicated.

TABLE II

RELATIVE ABUNDANCES OF IONS IN THE MASS SPECTRUM OF OCTACHLOROTETRAPHOSPHONITRILE[a]

Charge	n									Total
	0	1	2	3	4	5	6	7	8	
					$P_4N_4Cl_n$					
+1	...	...	...	tr*	...	0.6*	0.1	15.3*	3.4	19.4
+2	...	...	0.2*	...	1.2*	tr	3.9*	0.1	0.2*	5.6
					$P_4N_3Cl_n$					
+1	...	...	...	...	...	...	tr*	...	...	tr
+2	...	0.1*	...	0.1*	...	0.1*	...	0.2*	...	0.6
					$P_3N_3Cl_n$					
+1	tr	0.2*	tr	1.5*	0.2	3.5*	...	...	...	5.5
+2	...	...	0.1*	tr	1.4*	...	...	...	...	1.6
					$P_3N_2Cl_n$					
+1	...	tr	0.1*	tr	0.8*	0.1	0.2*	...	...	1.3
+2	0.9	1.2*	tr	1.1*	tr	0.8*	...	0.5*	...	4.6
					$P_2N_2Cl_n$					
+1	0.4	tr*	0.1	...	...	...	...	...	...	0.5
+2	...	...	...	...	...	...	...	...	...	...
					P_2NCl_n					
+1	3.5*	2.4	3.9*	0.6	1.6*	0.1	...	...	...	12.1
+2	...	0.3*	...	1.2*	...	0.4*	...	...	...	1.9
					PN_2Cl_n					
+1	0.6*	0.1	...	...	...	...	...	...	...	0.7
+2	...	...	...	...	...	...	...	...	...	...
					$PNCl_n$					
+1	6.4	1.9*	0.2	...	...	...	...	...	...	8.5
+2	...	...	...	...	...	...	...	...	...	...
					PCl_n					
+1	10.8*	7.0	7.2*	0.3	0.2*	...	...	...	...	25.4
+2	...	...	...	...	...	...	...	...	...	...

[a] Other species present: HCl^+, 5.5; NCl^+, 0.2; Cl_2^+, 0.1; P_2^+, 1.8; P_2Cl^+, 0.6; $NHCl^+$, 0.1; Cl^+, 3.8; and trace amounts of $P_2Cl_2^+$, P_3N^+, P_4^+, $P_2Cl_3^+$, and $P_4N_4Cl_5^{3+}$. An asterisk designates an even-electron ion.

TABLE III

RELATIVE ABUNDANCE OF ODD- AND EVEN-ELECTRON IONS WITH THE SAME STOICHIOMETRY IN THE MASS SPECTRUM OF $P_4N_4Cl_8$

Even-electron ion	% abundance	Odd-electron ion	% abundance
$P_4N_4Cl_8^{2+}$	0.2	$P_4N_4Cl_8\cdot^+$	3.4
$P_4N_4Cl_7^+$	15.3	$P_4N_4Cl_7\cdot^{2+}$	0.1
$P_4N_4Cl_6^{2+}$	3.9	$P_4N_4Cl_6\cdot^+$	0.1
$P_4N_4Cl_5^+$	0.6	$P_4N_4Cl_5\cdot^{2+}$	tr
$P_4N_4Cl_4^{2+}$	1.2	$P_4N_4Cl_4\cdot^+$	...
$P_4N_4Cl_3^+$	tr	$P_4N_4Cl_3\cdot^{2+}$	...
$P_4N_4Cl_2^{2+}$	0.2	$P_4N_4Cl_2\cdot^+$	...
$P_3N_3Cl_5^+$	3.5	$P_3N_3Cl_5\cdot^{2+}$	...
$P_3N_3Cl_4^{2+}$	1.4	$P_3N_3Cl_4\cdot^+$	0.2
$P_3N_3Cl_3^+$	1.5	$P_3N_3Cl_3\cdot^{2+}$	tr
$P_3N_3Cl_2^{2+}$	0.1	$P_3N_3Cl_2\cdot^+$	tr
$P_3N_3Cl^+$	0.2	$P_3N_3Cl\cdot^{2+}$	...

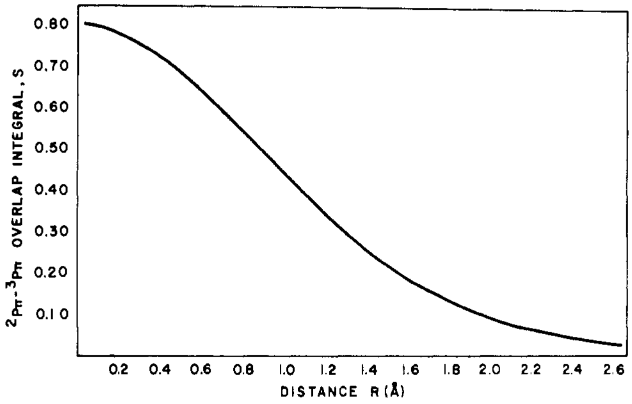

Figure 2.—Nitrogen–phosphorus $2p_\pi$–$3p_\pi$ overlap integrals as a function of interatomic distance.

for $2p_\pi$–$3d_{\pi xz}$ and 0.080 for $2p_\pi$–$3d_{\pi yz}$ ($P_4N_4Cl_8$ with D_{4h} symmetry).[5a] A bond distance of 1.64 Å was used in these calculations. The sum of these overlap integrals for the p_π–d_π bonds is greater than the overlap integral for a $2p_\pi$–$3p_\pi$ bond. However, the apparent loss in π-bond energy in going from p_π–d_π to p_π–p_π bonds need not occur if the bond length is shortened. Craig and Paddock reported that the overlap integral for the $2p_\pi$–$3d_\pi$ bonds would not be significantly different if the bond were shortened from 1.64 to 1.60 Å. Figure 2 shows that the $2p_\pi$–$3p_\pi$ overlap integral increases to 0.190 for a bond distance of 1.60 Å and reaches a value of 0.222 at 1.50 Å. Because the $2p_\pi$–$3p_\pi$ overlap integral increases significantly with decreasing bond distance, it is uncertain what effect the alteration from p_π–d_π to p_π–p_π bonding will have upon ion stability.

To a first approximation, the molecular orbitals[5a] which are formed by the overlap of $d_{x^2-y^2}$ orbitals and d_{xy} orbitals of phosphorus and the sp^2 orbitals of nitrogen containing the lone pair of electrons would be the same for both types of ring bonding described above. Therefore, the overlap integrals associated with these molecular orbitals have been ignored in our bonding model.

References to specific ions in Figure 3 illustrate the manner in which this simple model accounts for relative ion stability in terms of rehybridization of the σ bond and the alteration of the π-molecular orbital. The removal of an electron from a bonding π-molecular orbital of $P_3N_3Cl_6$ reduces the stability of the molecular ion relative to the ground-state molecule. The removal of a second electron from the π system to give $P_3N_3Cl_6^{2+}$ would reduce the stability even further. Bonding stability is achieved by the elimination of a chlorine atom from $P_3N_3Cl_6\cdot^+$ accompanied by a σ-bond rehybridization and some p_π–p_π overlap in the ring to give the even-electron $P_3N_3Cl_5^+$ (Figure 3b). The six electrons in the π system now are paired in bonding molecular orbitals. The removal of a chlorine atom from $P_3N_3Cl_5^+$ to give the odd-electron ion $P_3N_3Cl_4\cdot^+$ (Figure 3c) would be unfavorable on the basis of this model. It would be necessary to place the odd electron into an antibonding π-orbital which would offset any stabilization due to increased p_π–p_π bonding and overlap of phosphorus sp^2 orbitals in the σ system. Removal of an electron from a bonding π molecular orbital of $P_3N_3Cl_5^+$ to give $P_3N_3Cl_5\cdot^{2+}$ would tend to destabilize the resulting ion. Similar reasoning may be applied to the other ions in the tables to account for the patterns of relative abundance.

A brief discussion of ion formation is warranted. Metastable transitions due to halogen elimination were observed and had been noted previously in the chlorophosphonitriles[3] and bromophosphonitriles.[1] A

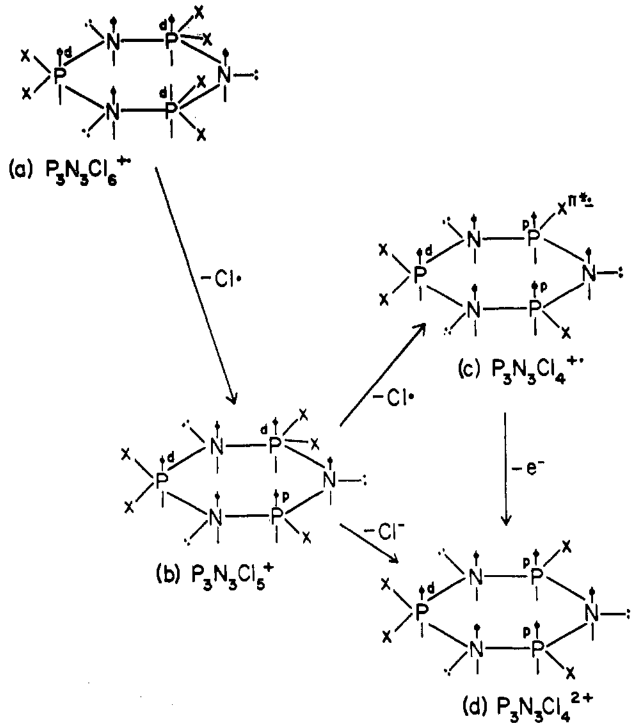

Figure 3.—Electronic configurations of gaseous P_3N_3 ions.

mechanism, previously overlooked, is that of elimination of the chloride ion. The presence of the chloride ion in the negative ion spectra of the trimer and the tetramer supports this mechanism. This ionization path is thought to be particularly important in the formation of the $P_nN_nCl_{2n-1}^{+}$ and $P_nN_nCl_{2m}^{2+}$ ions

$$P_nN_nCl_{2n} + e^- \longrightarrow P_nN_nCl_{2n-1}^{+} + Cl^- + e^-$$

$$P_4N_4Cl_7^{+} \longrightarrow P_4N_4Cl_6^{2+} + Cl^-$$

Metastable transitions in the mass spectra of bromophosphonitriles[1] provide some evidence that the ring contraction can occur by elimination of a PN unit

$$P_4N_4Cl_5^{+} + \longrightarrow P_3N_3Cl_5^{+} + PN$$

$$P_4N_4Cl_6^{2+} \longrightarrow P_3N_3Cl_6^{2+} + PN$$

Another reasonable fragmentation mechanism for which there is no evidence at the moment involves ring contraction with the elimination of a $PNCl_2$ fragment

$$P_4N_4Cl_7^{+} \longrightarrow P_3N_3Cl_5^{+} + PNCl_2$$

The presence of $PCl_3\cdot^{+}$, PCl_4^{+}, P_2Cl^{+}, $P_2Cl_2\cdot^{+}$, $P_2Cl_3^{+}$, $P_3N_2Cl_7^{2+}$, $P_2NCl_5\cdot^{+}$, $P_2NCl_5^{2+}$, $P_4\cdot^{+}$, and $P_3N\cdot^{+}$ as 2.2% of the total ions in the $P_4N_4Cl_8$ spectrum indicates bond rearrangement occurs to some extent during fragmentation. It is tempting to suggest that the ions $P_4\cdot^{+}$, $P_3N\cdot^{+}$, and $P_2N_2\cdot^{+}$ represent a series of structurally related ions formed by replacement of the phosphorus atoms with nitrogen atoms in the well-known P_4 tetrahedral molecule.

Experimental Section

The hexachlorotriphosphonitrile and octachlorotetraphosphonitrile were obtained from Hooker and purified by vacuum sublimation at 30–40°. The melting points were 115 and 122°, respectively.

Spectra were obtained on a CEC Model 21-104 single-focusing mass spectrometer. An ionizing voltage of 70 eV was used and the analyzer temperature and pressure were 250 ± 1° and 10^{-6} mm, respectively. Scanning was done electrically at a magnetic current of 4 A. Samples were introduced using a conventional solid inlet system.

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Kinetic Studies of Phosphite Ligand Substitution in *o*-Phenanthroline Complexes of Group VIb Metal Carbonyls

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AND CAROL M. INGEMANSON

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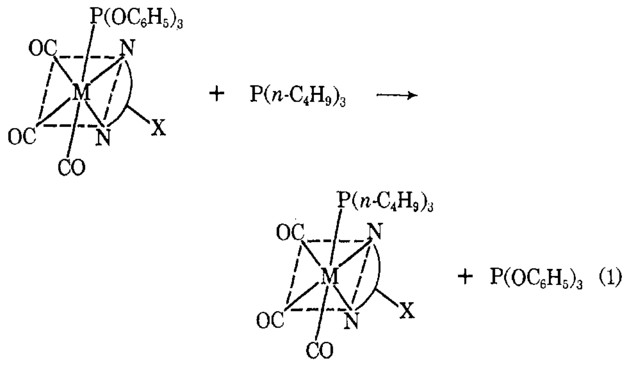
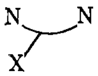
Earlier we reported kinetic studies[1,2] of the substitution reaction

$$M(CO)_4(X\text{-}o\text{-phen}) + L \longrightarrow cis\text{-}M(CO)_3(L)(X\text{-}o\text{-phen}) + CO$$

where M = Cr, Mo, or W, X = a substituted group on *o*-phenanthroline, and L = a phosphine or phosphite. For M = Cr, the kinetic data suggested that the reaction proceeded by only an SN1 mechanism, whereas both SN1 and SN2 paths appeared to operate for the analogous complexes of Mo and W. It was also observed that the rate of CO dissociation (SN1 path) increased as the basicity of X-*o*-phen increased, but the rate of CO displacement by the SN2 mechanism decreased with increasing basicity of the X-*o*-phen. In the present paper, we wish to report the results of a kinetic study of the very similar reactions



where M = Cr, Mo, or W and



is a substituted *o*-phenanthroline. The purpose of this study was to compare the rates and mechanisms of

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[1] R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967).

[2] J. R. Graham and R. J. Angelici, *ibid.*, **6**, 992 (1967).