(VI)], relatively large [H_2O_2], and acidities $\geq$0.0050 M.

The simple rate law summarized in eq 1 is remarkable in view of the corresponding formation kinetics determined for the molybdenum(VI) system over the same acidity range.[3,6] Here the rate law was second order with respect to [H_2O_2] at 0.10 M H^+ but first order at [H^+] $\leq$ ca. 0.005 M. In 0.1 M acid, $HMoO_3^+$ and MoO_3 are the predominant monomeric Mo(VI) species; in 0.005 M acid, MoO_3 is the principal form. The formation rate constants are pH dependent both in the strongly acidic region and in dilute acid, where the order with respect to hydrogen peroxide is second and first, respectively. This feature arises in part from the changing speciation with respect to Mo(VI).

We propose the scheme given in eq 2–4 to account for the rate law observed for the tungsten(VI) system. We have formulated

$$WO_2(OH)_2(H_2O)_2 + H_2O_2 \rightarrow WO_2(O_2)(H_2O)_3 + H_2O \quad \text{slow, } k_2 \quad (2)$$

$$WO_2(O_2)(H_2O)_3 \rightleftarrows WO_2(O_2)(OH)(H_2O)_2^- + H^+ \quad \text{rapid, } K_a > 0.1 \quad (3)$$

$$WO_2(O_2)(OH)(H_2O)_2^- + H_2O_2 \rightarrow WO(O_2)_2(OH)(H_2O)^- + 2H_2O \quad \text{rapid} \quad (4)$$

the neutral W(VI) monomer according to the preference of Tytko, although the exact formulation is not critical, provided it remains as a neutral species over our acidity range. Similarly, the precise formula for the monoperoxo intermediate formed in the first reaction is not important as long as it is largely deprotonated at acidities $\leq$0.10 M, as shown in eq 3. This scheme is consistent with the observed rate law, but we must attempt to justify some of the assumptions that have been made and also to account for the differences seen in the molybdenum(VI) system.

We have proposed[3] that K_a for the monoperoxo complex of Mo(VI) is ca. 0.01. In the acid range where the neutral form is predominant, we suggest that entry of the first peroxo ligand is reversible and entry of the second peroxo ligand is rate determining. Conversely, when the monoperoxo intermediate is largely hydrolyzed, the reaction scheme is analogous to that shown above for W(VI), except for speciation changes of the free Mo(VI) with pH. At pH values near 2 the order with respect to hydrogen peroxide would lie between 1 and 2, as is observed experimentally.

In the case of W(VI) we propose that the formula of monomeric W(VI), presumably $WO_2(OH)_2(H_2O)_2$, does not change from 0.005 to 0.10 M H^+ and that the monoperoxo intermediate is largely deprotonated over the same acidity range as shown in eq 2 and 3. Some experimental support is provided by our spectral data for monomeric W(VI) and the rate expression for the formation of oxohydroxodiperoxotungsten(VI), respectively. If we are correct, then the species we have formulated as $WO_2(OH)_2(H_2O)_2$, $WO_2(O_2)(H_2O)_3$, and $WO(O_2)_2$ are each more acidic than their molybdenum(VI) counterparts. Only in the case of oxodiperoxotungsten(VI) is there direct experimental confirmation of this conclusion.[1,6] Paradoxically, WO_4^{2-} and HWO_4^- are probably more *basic* than MoO_4^{2-} and $HMoO_4^-$.[18]

The first-order rate constant for the formation of oxohydroxodiperoxomolybdenum(VI) is about twice as great as that for the W(VI) analogue in 0.005 M H^+ and in the neutral region. The formation constants[3] are also comparable around pH 7. It appears that the principal differences in the equilibrium and kinetic parameters for these oxo diperoxo complexes are the instability of monomeric tungsten(VI) in acidic solution and the greater acidity of the mono- and diperoxo complexes of tungsten(VI). We have also observed that the activation of peroxide toward reducing agents by the oxo diperoxo complexes of W(VI) and Mo(VI), is similar, though the effect is slightly more pronounced with W(VI).[1,3]

Acknowledgment. This research was supported by the U.S. Army Research Office.

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Contribution from the Radiation Laboratory,
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Intermediates in the Charge-Transfer and Ligand-Labilization Photoreactions of Molybdenum(V) μ-Oxo Dimers[†]

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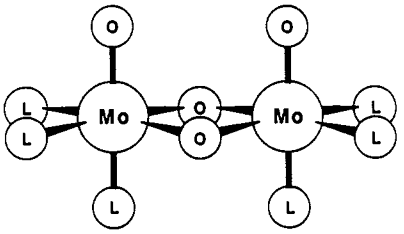
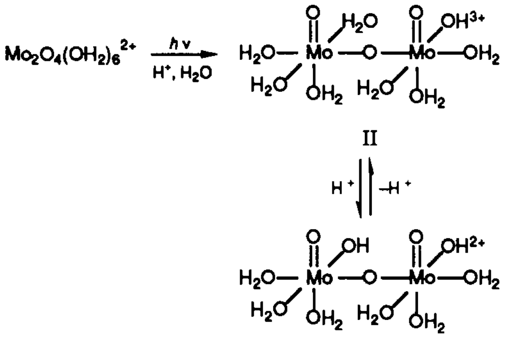
There has been considerable interest in the chemistry of Mo complexes because of its occurrence in biological systems as an essential component of enzymes and its potential applications as a catalyst.[1-7] Recent studies have dealt with the photochemical properties of Mo in its VI, V, IV, III, and II oxidation states, but little is known yet about such properties in molybdenum(V) oxo complexes.[6] In a flash-photochemical study of the (μ-oxo)bis(oxomolybdenum(V)) aquo ion dimer (I),[8] it has been established that photolabilization induces the formation of a single-bridged μ-oxo dimer (II and III in eq 1–3) that experiences dissociative disproportionation into very reactive monomeric Mo(IV) and Mo(VI) species.[9]



I (basic $M_2O_4^{2+}$ core; O = oxygen, L = ligand)



(1)

II

(2)

III

$$\text{II, III} \rightarrow Mo^{IV}O(OH)^+ + Mo^{VI}(OH)_6 + H^+ \quad (3)$$

Such a reactivity suggests that photochemical primary charge-transfer processes leading to the reduction of the metal center and the oxidation of a ligand may have a significant role in the photochemistry of the Mo(V) complexes. These photoprocesses have been investigated in this work by flash photolysis and pulse radiolysis of $Mo_2O_4(OH_2)_6^{2+}$ and $Mo_2O_4Cl_6^{4-}$.

Experimental Section

Photochemical Procedures. The apparatus used for flash photolysis has been described elsewhere.[10] Two FP-8-100C lamps were fired in series at energies adjusted to values between 250 and 40 J/pulse. A lifetime of 30 μs was measured for the flash pulse under these conditions. Hence, points for either kinetic or spectral determinations were collected for times equal to or longer than 50 μs. The wave-form recorder, Biomation 805, was interfaced to a computer, VAX 11/780, for data analyses. Solutions were irradiated at preselected wavelengths, i.e. λ_{exc} > 210 or 240 nm, respectively, by using appropriate cutoff filters. Streams of ultrapure N_2 or ethylene were used for the deaeration of the solutions prior to the irradiations.

Pulse-Radiochemical Procedures. The apparatus and procedures used for pulse radiolysis have been described in previous literature reports.[11,12] The investigated reactions were initiated by oxidizing the Mo(V) complex

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[†] Document No. NDRL-3176 from the Notre Dame Radiation Laboratory.

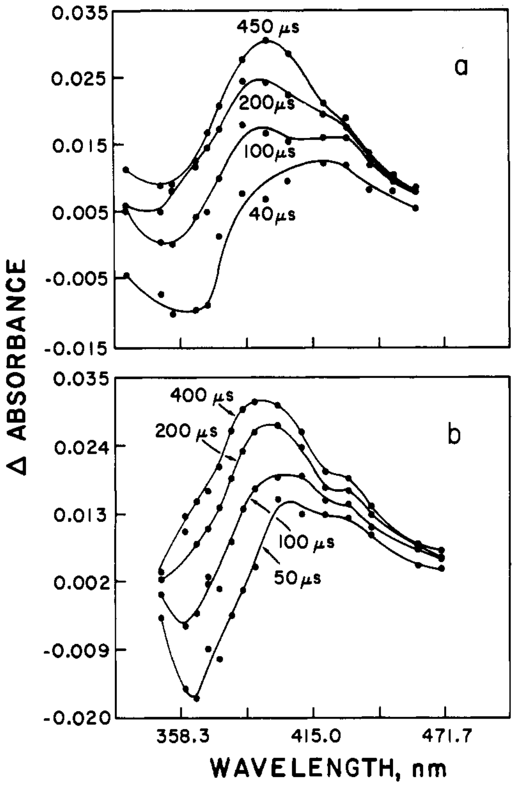

Figure 1. Time-resolved spectral changes recorded in flash irradiations ($\lambda_{exc} > 210$ nm) of 7.5×10^{-5} M $Mo_2O_4(OH_2)_6^{2+}$ in 0.2 M $HClO_4$. Solutions of the complex were deaerated with streams of N_2 (a) or C_2H_4 (b).

with OH radicals in aqueous solutions deaerated with streams of N_2O. In the reduction of the complex with Zn(I), the reaction was initiated by intercepting e⁻(aq) with Zn^{2+} ions and the OH radicals with 0.1 M 2-propanol, respectively, in solutions deaerated with ultrapure N_2. Other procedures have been reported elsewhere in the literature.[11]

Materials. The $(NH_4)_2MoOCl_5$ was available from a previous work,[9] and its purity was verified from its absorption spectrum. Solutions of $Mo_2O_4(OH_2)_6^{2+}$ in 1.0 M $HClO_4$ were prepared from $(NH_4)_2MoOCl_5$ and standardized by literature procedures.[9,13,14] In these solutions, Cl^- was replaced by ClO_4^- by performing an ion exchange over Dowex 50W (Sigma). All the manipulations were carried out under a N_2 atmosphere, and all the liquids were deaerated with streams of N_2. The ionic strength was adjusted to 0.5 M $NaClO_4$ unless explicitly indicated in the text. Other chemicals were reagent grade and were used without further purification.

Results

Flash irradiations ($\lambda_{exc} > 210$ nm) of 7.5×10^{-5} M $Mo_2O_4(OH_2)_6^{2+}$ in deaerated 0.2 M $HClO_4$ bleached the solution's spectrum at wavelengths $\lambda_{ob} < 380$ nm and induced new absorptions with a broad maximum at $\lambda_{max} = 410$ nm (Figure 1a). Further spectral changes were observed in a millisecond–second time domain, i.e. the growth of new maxima with $\lambda_{max} = 400$ and 430 nm, respectively, and changes in the optical density between 340 and 360 nm, which are suggestive of an intense absorption band with $\lambda_{max} < 350$ nm (Figure 1). Observations below 340 nm were precluded by the large absorptions of $Mo_2O_4^{2+}$.

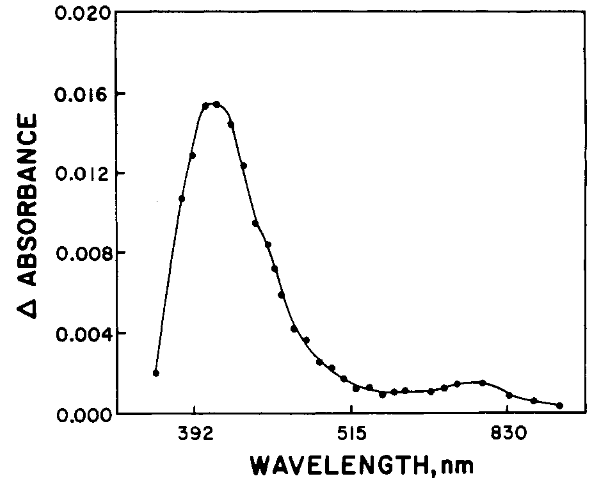

Figure 2. Transient spectrum recorded 100 μs after flash irradiations ($\lambda_{exc} > 210$ nm) of 3.2×10^{-5} M $Mo_2O_4(OH_2)_6^{2+}$ in 0.2 M $HClO_4$. In these measurements, the solutions were deaerated with streams of N_2.

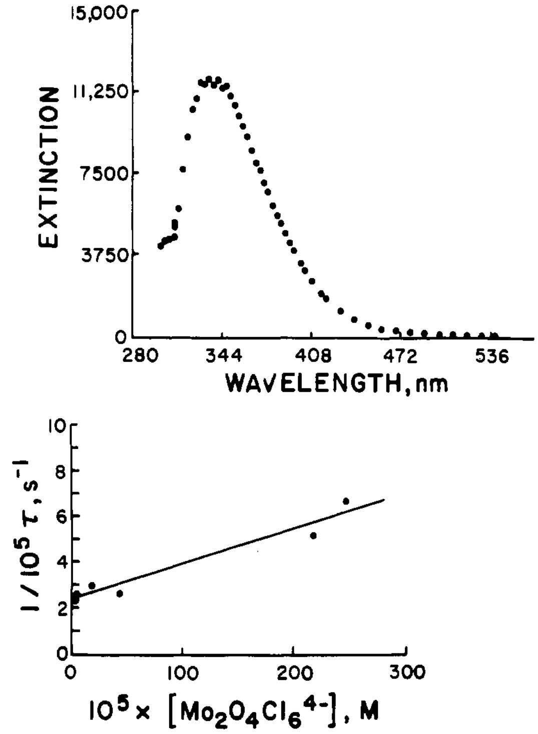

Figure 3. Dependence of the half-life, τ, of the Cl_2^- decay on the Mo(V) concentration in pulse radiolyses of 0.1 M NaCl in 0.01 M $HClO_4$ saturated with N_2O (bottom) and spectrum (top) recorded 10 μs after the pulse-radiolytic irradiation of 1.0 M NaCl in 0.01 M $HClO_4$ containing 9.9×10^{-4} M Mo(V) (top).

Saturation of the $Mo_2O_4(OH_2)_6^{2+}$ solution with ethylene has little effect over the flash-induced spectral changes at wavelengths $\lambda > 350$ nm but modifies the shape of the transient spectra at $\lambda < 350$ nm (Figure 1b). In these conditions the rate of the processes, followed by means of the spectral change, obeys a first-order rate law with $k = 2.4 \times 10^4$ s^{-1}.

Irradiations of $Mo_2O_4(OH_2)_6^{2+}$ in solutions having the same composition described above at $\lambda_{exc} > 240$ nm diminish the intensity of the spectral transformation without a change in the shape of the transient spectra, as is expected for a smaller conversion to products than in irradiations covering shorter wavelengths. The spectrum recorded 100 μs after the flash shows an absorption maximum, $\lambda_{max} = 770$ nm, that is characteristic of the $Mo^{IV}Mo^{V}$

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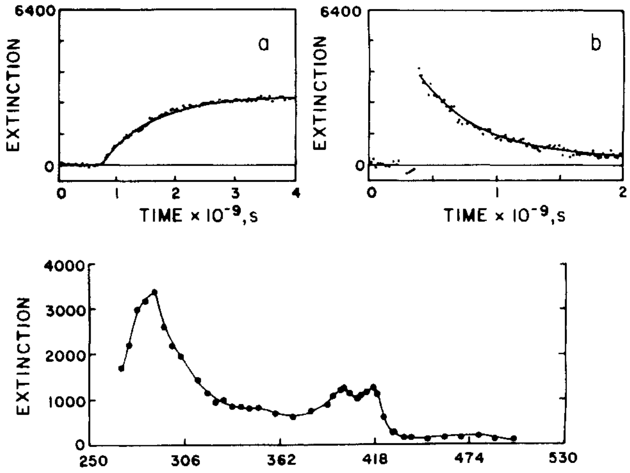

Figure 4. Transient spectrum recorded 10 μs after the pulse radiolysis of 7.5 × 10^{-5} M $Mo_2O_4(OH_2)_6^{2+}$ in 0.01 M $HClO_4$ saturated with N_2O.[23] The insert shows (a) the growth and (b) the disappearance of the 290-nm optical density when $HO^\bullet$ radicals are reacted with $Mo_2O_4(OH_2)_6^{2+}$.

dimers (Figure 2).[15] Such spectrum can be considered, therefore, a superposition of the $Mo^{IV}Mo^V$ spectrum and one already reported for a photogenerated molybdenum(V) single-bridged μ-oxo dimer.[9]

The possibility of ligand photooxidation has also been investigated in 1.0 M NaCl acidic, $[H^+] = 0.1$ M, solutions, where the dimeric Mo(V) ions $Mo_2O_4Cl_6^{4-}$ and $Mo_2O_3Cl_8^{4-}$ are expected to be the most abundant species.[8] Flash irradiations ($\lambda_{exc} > 240$ nm) induce transient spectra similar to the one described above (Figure 1a) but with an additional absorption band, $\lambda_{max} = 350$ nm. Such a band can be assigned to Cl_2^-, a radical anion that can in principle oxidize excess $Mo_2O_4Cl_6^{4-}$ and $Mo_2O_3Cl_8^{4-}$. This assignment was verified by pulse radiolysis where the reaction between Cl_2^- and $Mo_2O_4Cl_6^{4-}$ was investigated as a function of the Mo(V) dimer concentration (Figure 3).[16] A rate constant, $k = (1.5 \pm 0.5) \times 10^8$ M^{-1} s^{-1}, was calculated from the slope in the plot of the rate constant for pseudo-first-order kinetics vs the $Mo_2O_4Cl_6^{4-}$ concentration. In pulse radiolysis of 1.4 × 10^{-4} M $Mo_2O_4(OH_2)_6^{2+}$ containing 1.4 × 10^{-3} M Cl^-, the Cl_2^- radical decays by parallel paths, i.e. attack on the dimer and radical disproportionation, respectively, and the transient spectra exhibited some minor differences compared with the Cl_2^- spectrum. Such observations suggest that absorption of light by Cl_2^- makes the major contribution to the transient spectra, a proposition supported by the magnitude of the extinction coefficients reported for the radical, for known Mo^VMo^{VI} complexes, and for the product in the oxidation of $Mo_2O_4(OH_2)_6^{2+}$ with OH radicals (Figure 4).[8,17] In the pulse-radiolysis experiments of Figure 4, a second-order rate constant, $k = (2.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, was calculated from the rate constants, for the product formation under pseudo-first-order kinetics. The product of the oxidation with OH radicals decays via a process with a first-order kinetics, $k = (2.9 \pm 0.3) \times 10^3$ s^{-1}. These reaction kinetics investigated by pulse radiolysis are, therefore, in accord with our flash-photolysis measurements reported above.

Discussion

Transient spectra recorded in near-UV flash photolyses of $Mo_2O_4(OH_2)_6^{2+}$ or $Mo_2O_4Cl_6^{4-}$ in aqueous acidic solutions reflect the formation of species related to the photoinduced opening of one μ-oxo bridge (eq 1) and a photoreduction of the complex to $Mo^{IV}Mo^V$ dimers. Moreover, the effects of scavengers, e.g. Cl^-, C_2H_4, and alcohols, on such transient spectra suggest that the photoreduction of the complex induces a simultaneous oxidation of the coordinated ligand, i.e. H_2O or Cl^-, a process leading to the respective formation of the OH or Cl radicals, which behave as strong oxidants. In these regards, it is possible to represent the photoreduction of the bis(μ-oxo) molybdenum(V) dimers as charge-transfer processes (eq 4, 5). The mono(μ-oxo) dimer, $Mo_2O_3Cl_8^{4-}$, is expected to undergo similar photoprocesses.

$$Mo_2O_4(OH_2)_6^{2+} \xrightarrow{h\nu} {}^*Mo_2O_4(OH_2)_6^{2+} \xrightarrow[H_2O]{} Mo^VO_2(OH_2)_3Mo^{IV}O_2(OH_2)_3^+ + H^+ + HO^\bullet \quad (4)$$

$$Mo_2O_4Cl_6^{4-} \xrightarrow{h\nu} {}^*Mo_2O_4Cl_6^{4-} \xrightarrow[H_2O]{} Mo^VCl_3Mo^{IV}O_2(OH_2)Cl_2^{4-} + Cl^\bullet \quad (5)$$

The photogenerated OH or Cl radicals can enter into their characteristic reactions of dimerization and disproportionation (eq 6–9) in addition to reactions with $Mo_2O_4(OH_2)_6^{2+}$.[18]

$$HO + HO \rightarrow H_2O_2 \quad (6)$$

$$Cl + Cl \rightarrow Cl_2 \quad (7)$$

$$Cl + Cl^- \rightleftarrows Cl_2^- \quad (8)$$

$$Cl_2^- + Cl_2^- \rightarrow 2Cl^- + Cl_2 \quad (9)$$

The time-resolved spectra observed in the attack of $Mo_2O_4(OH_2)_6^{2+}$ by OH or Cl_2^- radicals is the one expected for a mixed-valence Mo^VMo^{VI} dimer, and the oxidation reaction can be written, in general terms, as eq 10,[8,12] where X = Cl (n = 6) or H_2O (n = 0), O = OH or Cl_2^-, and R = H_2O or 2 Cl^-.

$$Mo_2O_4X_6^{2-n} + O \rightarrow Mo_2O_4X_6^{3-n} + R \quad (10)$$

In the competition between reactions (eq 4–10), the relevance of the Mo(V) oxidation (eq 10) in the reaction mechanism is determined by the respective values of the rate constants and concentrations.[18,19] In these regards, the concentrations of the Mo complexes used in our work made such attack observable in flash photolysis. When primary photogenerated radicals, i.e. OH and Cl, are rapidly trapped with ethylene, the time-resolved spectral transformations cannot be assigned to reactions of excess Mo(V) dimer with secondary radicals and must be associated with the formation of the single-bridged μ-oxo dimer. Literature reports about the structural properties of related single-bridged Mo(V) dimers strongly suggest that the observed transformation with a specific reaction rate constant, $k = 2.4 \times 10^4$ s^{-1}, can be the cis–trans isomerization, yielding the equilibrium mixture appropriate for room temperature solutions (eq 11).[8]

$$cis\text{-}Mo_2O_3(OH_2)_8^{2+} \rightarrow trans\text{-}Mo_2O_3(OH_2)_8^{2+} \quad (11)$$

$$k = 2.4 \times 10^4 \text{ s}^{-1}$$

The dual photoreactivity, ligand photooxidation, and ligand photolabilization exhibited by these Mo(V) dimers are probably a consequence of the different excited states that are populated by irradiation in the in UV region. Indeed, the low-lying excited states associated with absorption bands having a $\lambda_{max} > 250$ nm have been assigned as ligand field states, i.e. states whose only difference with the ground state is in the populations of Mo-centered orbitals.[20–22] There are, however, intense absorptions in the spectra of the Mo(V) dimers at wavelengths shorter than 250 nm that must be related with charge-transfer transitions. The

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[16] In these experiments, we have verified that C-centered radicals derived by hydrogen abstraction from various alcohols, i.e. ethanol, 2-propanol, or 2-methyl-2-propanol, do not react with the Mo(V) dimer. A similar behavior has been reported elsewhere in the literature.[15]

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[19] The disappearance of the mixed-valence dimers $Mo^{IV}Mo^V$ and Mo^V-Mo^{VI} via respective reactions with first-order kinetics is probably a consequence of their dissociations in monomeric species. Such species can undergo polymerization and/or reaction with the solvent.

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[23] Under these experimental conditions $H^\bullet$ does not induce detectable competitive reactions.

availability of excited states that respectively lead to angular (ligand field) and radial (charge transfer) reorganizations of the electronic density with respect to the ground state can justify, therefore, the observed photochemical properties of the Mo(V) dimers.

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Contribution from the Department of Chemistry
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Two Polymorphs of the Diazaphosphole Oxide $C_6H_4(NH)_2P(O)Ph$

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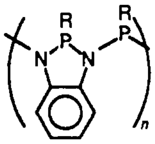
Received May 1, 1989

Our investigations of skeletally stabilized P(III) phosphazane oligomers/polymers (**1**)[1,2] have stimulated studies of P(III) and P(V) 1,3-dihydro-1,3,2-diazaphospholes, especially the *P*-phenyl derivatives **2** (R = Ph) and **3**. Pilgram and Korte[3] claimed the



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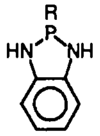

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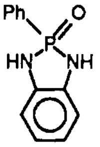

3

preparation of **2** (R = MeC_6H_4) from the 1,2-$(NH_2)_2C_6H_4$/$MeC_6H_4P(OPh)_2$ reaction; however, the characterization was inconclusive. Even the oxide **3** has been only partially characterized.[4,5] We now wish to report recent studies of these systems and the discovery that **3** can be obtained in two polymorphic crystalline forms.

Experimental Section

Apparatus and Materials. ^{31}P and ^{1}H NMR spectra were recorded with a JEOL FX-90Q spectrometer at 36.5 and 90.0 MHz, respectively. ^{31}P and ^{1}H NMR chemical shifts downfield from 85% H_3PO_4 (external) and $(CH_3)_4Si$ (internal) are reported as positive (+δ). IR spectra (4000–400 cm^{-1}) were obtained with a Beckman 4250 grating spectrometer. Mass spectra were obtained at 70 eV with a VG Analytical 7070 EQ-HF spectrometer. Elemental analyses were performed by Huffman Laboratories Inc., Wheatridge, CO. All manipulations were carried out by using standard glovebag techniques under dry N_2.[6]

1,2-$(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene. Et_3N (Baker) was distilled from CaH_2. Toluene (over Na/Pb alloy) and CH_2Cl_2 (over P_4O_{10}) were distilled before use. $PhPCl_2$ (Strem Chemicals) was distilled from CaH_2. $PhP(O)Cl_2$ (Aldrich) was used as obtained. $PhP(OPh)_2$, prepared as described previously,[7] after vacuum distillation contained ca. 3% (m/m) $PhP(O)(OPh)_2$ (by ^{31}P NMR). $[C_6H_4N_2(PPh)_2]_2$ was obtained as described elsewhere.[1]

Table I. Crystal Data, Data Collection Parameters, and Refinement Details for $C_6H_4(NH)_2P(O)Ph$ (**3A** and **3B**)

	3A	**3B**
formula	$C_{12}H_{11}N_2OP$	$C_{12}H_{11}N_2OP$
fw	230.20	230.20
space group	*Pnma*	*Cmca*
a, Å	17.816 (4)	7.679 (2)
b, Å	7.578 (2)	17.127 (3)
c, Å	8.709 (2)	17.210 (4)
V, Å^3	1175.9 (4)	2263.3 (8)
Z	4	8
λ, Å	1.541 78 (Cu Kα)	0.710 69 (Mo Kα)
d_{calc}, g cm^{-3}	1.30	1.35
F(000)	480	960
temp, °C	22–24	22–24
μ, cm^{-1}	19.1	2.15
R	0.036	0.039
R_w	0.051	0.055

Table II. Positional (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $C_6H_4(NH)_2P(O)Ph$ (**3A**)

atom	*x*	*y*	*z*	*U*[a]
P(1)	4586 (1)	2500	9233 (1)	39 (1)
O(1)	5342 (1)	2500	9951 (2)	47 (1)
N(1)	4002 (1)	4075 (3)	9772 (2)	45 (1)
C(1)	4675 (2)	2500	7202 (3)	48 (1)
C(2)	5373 (2)	2500	6524 (4)	77 (22)
C(3)	5428 (3)	2500	4928 (6)	107 (2)
C(4)	4794 (4)	2500	4049 (5)	107 (2)
C(5)	4116 (3)	2500	4706 (5)	101 (2)
C(6)	4043 (2)	2500	6283 (4)	71 (1)
C(7)	3398 (1)	3416 (3)	10638 (2)	45 (1)
C(8)	2855 (1)	4353 (4)	11413 (3)	60 (1)
C(9)	2305 (1)	3401 (4)	12203 (3)	72 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Positional (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $C_6H_4(NH)_2P(O)Ph$ (**3B**)

atom	*x*	*y*	*z*	*U*[a]
P(1)	0	2078 (1)	2042 (1)	41 (7)
O(1)	0	2338 (3)	2865 (3)	50 (2)
N(1)	1550 (5)	2428 (2)	1472 (2)	46 (2)
C(1)	0	1037 (5)	2000 (5)	45 (3)
C(2)	0	620 (6)	2687 (6)	71 (4)
C(3)	0	−200 (7)	2648 (9)	97 (6)
C(4)	0	−578 (7)	1958 (9)	97 (5)
C(5)	0	−168 (7)	1280 (9)	90 (5)
C(6)	0	641 (5)	1294 (5)	63 (4)
C(7)	908 (6)	2943 (3)	913 (3)	40 (2)
C(8)	1820 (8)	3408 (4)	399 (3)	53 (2)
C(9)	894 (8)	3887 (4)	−97 (4)	63 (2)

[a] See footnote *a*, Table II.

$C_6H_4(NH)_2P(O)Ph$ (3). Polymorph 3A. 1,2-$(NH_2)_2C_6H_4$ (17 mmol) and $PhP(OPh)_2$ (17 mmol) were heated in vacuo at 120 °C. After 18 h, ^{31}P NMR spectral resonances occur at δ 157.8 ($PhP(OPh)_2$), 110.5 (**4**), 26.5 (**3**), and 12.8 ($PhP(O)(OPh)_2$) (mol % 69:16:10:5). Upon further heating, the resonance at δ 110.5 (**4**) decreased in intensity. Cooling to 25 °C precipitates **3** from the reaction mixture as **3A** (yield 1.4 g, 33% yield). Attempts to isolate **4** failed.

$PhP(O)Cl_2$ and 1,2-$(NH_2)_2C_6H_4$ were allowed to react in PhBr as described previously.[4] Recrystallization of the product from $CHCl_3$ gave **3A** (mp 278–279 °C; >85% yield, lit.[4] yield 100%). ^{31}P{^{1}H} NMR ($(CD_3)_2SO$): δ 25.5 (s). ^{1}H NMR: δ 9.09 (s). IR (KBr, cm^{-1}): 3182 (s, N—H), 1260 (s, P═O).[5] MS: *m/e* 320 (M^+, $C_{12}H_{11}N_2OP^+$). Anal. Calcd for $C_{12}H_{11}N_2OP$: C, 62.60; H, 4.82; N, 12.17; P, 13.46. Found: C, 62.50; H, 4.94. **3** is only slightly soluble in toluene and CH_2Cl_2 and soluble in Me_2SO.

Polymorph 3B. Crystallization of $[C_6H_4N_2(PPh)_2]_2$, prepared from the 1,2-$(NH_2)_2C_6H_4$/$PhPCl_2$ reaction in toluene,[1] from the toluene reaction solution yields trace quantities of **3** (<1% yield) as **3B** (mp 280–281 °C).

X-ray Analyses. Crystals of **3A** and **3B** were mounted on glass fibers and coated with epoxy resin. Cell parameters were determined on the

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