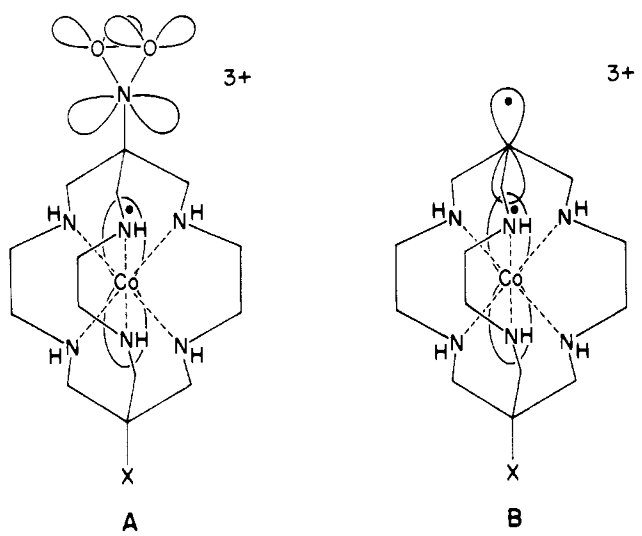
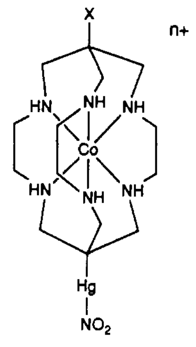


Figure 4. Overlap between the $\pi^*(NO_2)$ orbital and a Co(II) t_2 orbital (A) and between a bridgehead radical p_z orbital and a t_2 orbital of Co(II) (B).



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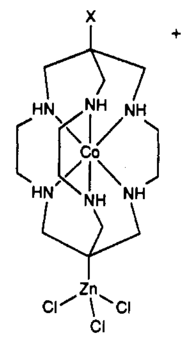

II

organic chemistry, and the intramolecular redox process (4) has been detected during photochemical production of the radical species.[39] The exact role of the electrode in these reductions is uncertain but organomercury complexes of the type shown in I could be intermediates by analogy with the well-characterized and stable zinc species II.[40] Unlike the reduction of the nitro groups, the reduction of radical species via an intramolecular route is expected and observed to be very facile. Such an expectation arises from a consideration of the geometric overlap of orbitals, as considered in Figure 4. The reduction by Co(II) of the bridgehead radical is not concerted because considerable concentrations of the dimer (reaction 7) have been generated by alternative methods.[39] Reactions 4-6 result in a 2-electron reduction of the nitro group while reaction 7 results in a net 1-electron reduction. The competition between these two pathways may explain the variation in electron counts between 1 and 2 electrons for coulometric reductions performed in aprotic solvents. Some of the above facets are currently being investigated further.

Conclusions

By control of reductions it is seen that the products from the reduction of nitro functional groups of cage complexes may be controlled, in part, to give desired products. Further details are needed of work involved in the synthesis of azoxy-bridged cage complexes. It is apparent that the above chemistry leaves open many potential areas of interest.

Acknowledgment. We thank the ANU Microanalytical and NMR Services for the many microanalyses and ^{13}C NMR spectra. We are also indebted to Dr. J. M. Harrowfield for communication of some preliminary results. Finally, P.A.L. is grateful for support from a Queen Elizabeth II Postdoctoral Fellowship during the completion of this research.

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Contribution from the Departments of Chemistry and Physics, University of Oulu, Linnanmaa, SF-90570 Oulu, Finland,
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^{77}Se NMR Spectroscopic Study of Fluxional Selenium Sulfide 1,2,3,4,5-Se_5S_2

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Received November 9, 1989

The ^{77}Se NMR spectrum has been recorded for the fluxional heterocyclic selenium sulfide 1,2,3,4,5-Se_2S_5, which has been prepared from the ^{77}Se-enriched $[Ti(C_5H_5)_2Se_5]$ (enrichment 94%) and from S_2Cl_2. The spectrum shows three second-order multiplets at 1087.1, 1025.0, and 978.9 ppm (relative to Me_2Se) corresponding to a five-spin [AMM′XX′] system. A simulation enables the complete assignment of all transitions to be made and yields the refined values of all ^{77}Se-^{77}Se coupling constants. The number of NMR signals, their coupling pattern, and the values of the spin-spin coupling constants are consistent with the concept of facile pseudorotation in the seven-membered chalcogen-containing ring molecules.

^{77}Se NMR spectroscopy is a useful tool for the identification and characterization of individual heterocyclic selenium sulfides, which are generally produced as a complicated mixture of different molecular species (for a recent review, see ref 2). The spectral analysis has been based on the combined information obtained from the ^{77}Se NMR spectra of the samples containing natural-abundance selenium and from those of the ^{77}Se-enriched samples of the same chemical composition.[3,4]

Bis(cyclopentadienyl)titanium sulfides and selenides of the types $[Ti(C_5H_5)_2E_5]$ and $[Ti(C_5H_5)_2(\mu\text{-}E_2)_2Ti(C_5H_5)_2]$ (E = S, Se) have successfully been applied in the preparation of stoichiometrically pure selenium sulfides with ring sizes of six, seven, and eight.[5]

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(1) (a) Department of Chemistry, University of Oulu. (b) Department of Physics, University of Oulu. (c) University of Joensuu.

(2) Laitinen, R. S. *Acta Chem. Scand., Ser. A* **1987**, *41*, 361.

(3) Because of the low natural abundance of the ^{77}Se isotope, the ^{77}Se-^{77}Se coupling effects can only be seen as small satellites that are often lost in the background. Isotope enrichment leads to complete information on the coupling when the enrichment is sufficiently high.

(4) (a) Laitinen, R. S.; Pakkanen, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1381. (b) Laitinen, R. S.; Pakkanen, T. A. *Inorg. Chem.* **1987**, *26*, 2598. (c) Laitinen, R. S.; Pekonen, P.; Hiltunen, Y.; Pakkanen, T. A. *Acta Chem. Scand.* **1989**, *43*, 436.

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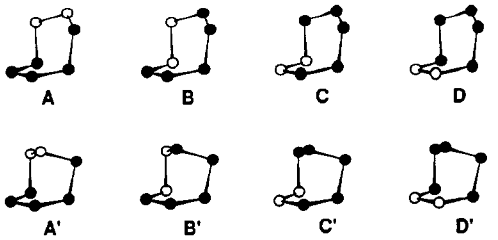

Figure 1. The four isomers of 1,2,3,4,5-Se_5S_2 in chair conformation (top) and boat conformation (bottom).

These products have been characterized by vibrational analysis, and in most cases their natural-abundance ^{77}Se NMR spectra have also been reported.[5-7]

A particularly interesting class of compounds is the seven-membered heterocyclic selenium sulfides Se_nS_{7-n}. These species contain a fragment of four approximately coplanar atoms,[5c,6] like in cycloheptasulfur,[8] resulting in a significant alternation in the bond lengths.[9] The seven-membered chalcogen species are fluxional, undergoing easy pseudorotation as predicted by theoretical considerations[11] and deduced from the observed natural-abundance ^{77}Se NMR spectra of 1,2-Se_2S_5[7a] and 1,2,3,4,5-Se_5S_2.[7b]

We present here an NMR study of ^{77}Se-enriched 1,2,3,4,5-Se_5S_2, since the observation of the ^{77}Se–^{77}Se coupling constants should give more information on the nature of the fluxionality of the heterocyclic Se_nS_{7-n} molecules. Though all the known seven-membered homo- and heterocyclic chalcogen species have the chair conformation, the corresponding boat conformation has also been predicted to be relatively stable.[12] This leads to eight possible isomers of 1,2,3,4,5-Se_5S_2, which are shown in Figure 1. The observed coupling patterns and the values of the ^{77}Se–^{77}Se coupling constants should either verify the rapid mutual interconversion of the different isomers of 1,2,3,4,5-Se_5S_2 as a consequence of the pseudorotation in the molecule or indicate which discrete isomers are present in the solution.

Experimental Section

Preparation of Li_2Se_x. Selenium powder (50 mg, 0.63 mmol) that was enriched in the ^{77}Se isotope (94% enrichment, Techsnabexport) was mixed with 5 mL of dried and degassed tetrahydrofuran (thf, J. T. Baker Chemicals) and reduced with 1 mL of the 1 M solution of $LiBHEt_3$ in thf ("Super-hydride", Aldrich) in N_2 atmosphere by applying the method described by Gladysz et al.[13]

Preparation of $[Ti(C_5H_5)_2Se_5]$. The synthesis of $[Ti(C_5H_5)_2Se_5]$ was carried out according to the method of Shaver and McCall[14] by adding 5 mL of a thf solution containing 32 mg (0.13 mmol) of $[Ti(C_5H_5)_2Cl_2]$ (Fluka Chemie AG) to the Li_2Se_x mixture with subsequent refluxing. The solvent was evaporated, and the crude product was extracted with 40 mL of methylene chloride (E. Merck GmbH). After workup, 57.2 mg of $[Ti(C_5H_5)_2Se_5]$ was obtained (79% yield). The enriched product was characterized with ^{77}Se NMR spectroscopy.[15]

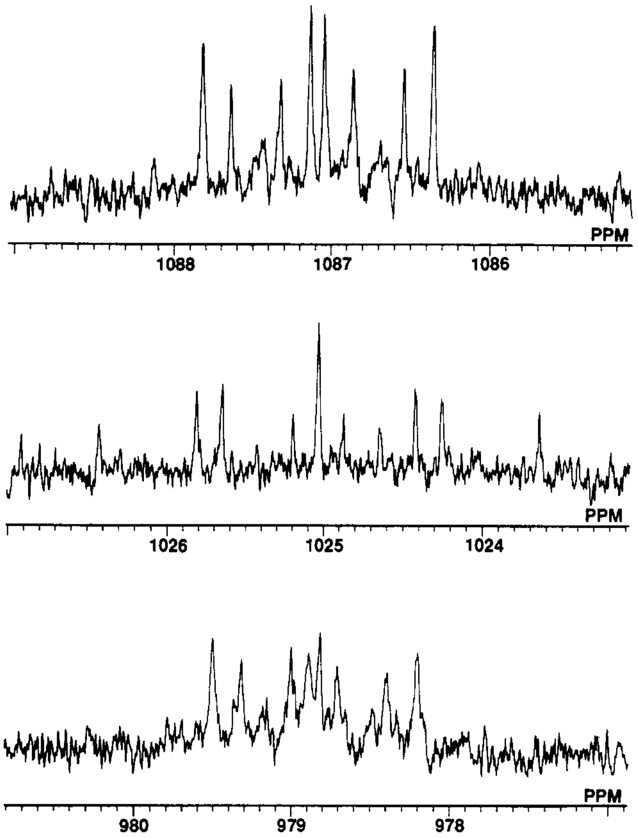

Figure 2. ^{77}Se NMR spectrum of 1,2,3,4,5-Se_5S_2 enriched in the ^{77}Se isotope (enrichment 94%). The signal at 1087.1 ppm is due to the selenium atoms Se(4) and Se(5), that at 1025.0 ppm is due to Se(1), and that at 978.9 ppm is due to Se(2) and Se(3). (For the numbering of selenium atoms, see Figure 3.) The trends in the chemical shift are in agreement with those deduced earlier for the heterocyclic Se_nS_{8-n} species.[4b]

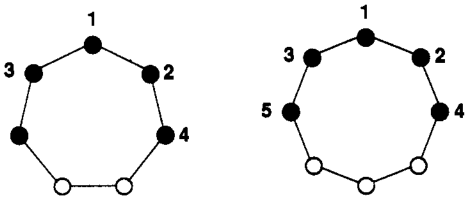

Figure 3. Five-spin [AMM'XX'] system in 1,2,3,4,5-Se_5S_2 and 1,2,3,4,5-Se_5S_3, indicating the numbering of selenium atoms.

Preparation of 1,2,3,4,5-Se_5S_2. 1,2,3,4,5-Se_5S_2 was prepared by dissolving the ^{77}Se-enriched $[Ti(C_5H_5)_2Se_5]$ in 5 mL of carbon disulfide (E. Merck GmbH) and adding 1 mL of 0.1 M disulfur dichloride (Fluka Chemie AG). The details of the synthesis have been described previously.[5c]

NMR Spectroscopy. The ^{77}Se NMR spectrum of 1,2,3,4,5-Se_5S_2 was recorded with a Jeol JNM-GX400 spectrometer operating at 76.33 MHz. The spectral width was 135.21 kHz, and the resolution, 0.27 Hz/data point. The pulse width was 9.0 μs corresponding to a nuclide tip angle of 45°, and the pulse delay, 2.4 s. The accumulation contained 5000 transients. D_2O was used as an external ^2H lock, and the saturated aqueous solution of SeO_2, as an external reference. The chemical shifts (ppm) are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. The simulation of the spectrum was carried out with the program MAOCON.[16]

Calculations. The dependence of the ^{77}Se–^{77}Se coupling on the conformation and on the location of the SeSe bonds in the seven-membered

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(8) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F.; Reinhardt, R. *Z. Naturforsch.* **1980**, *35B* 1378.

(9) The alternation of the bond lengths and bond orders in S_7 has been explained[10] in terms of the mutual p-lone-pair repulsion of the two central sulfur atoms in the planar S_4 fragment and of the hyperconjugational interaction between these same lone pairs and the empty σ^* orbitals of the bonds connecting the fragment to the rest of the molecule.

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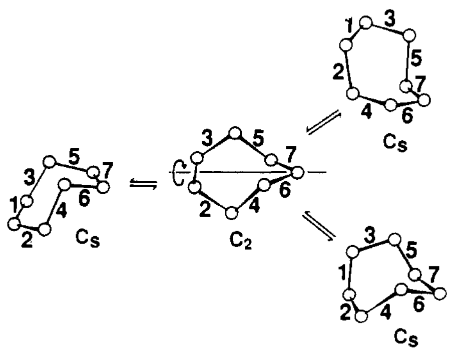
Table I. ^{77}Se–^{77}Se Coupling Constants of 1,2,3,4,5-Se_5S_2 and 1,2,3,4,5-Se_5S_3 (in Hz)

J_{SeSe}[a]	1,2,3,4,5-Se_5S_2	1,2,3,4,5-Se_5S_3[b]	J_{SeSe}[a]	1,2,3,4,5-Se_5S_2	1,2,3,4,5-Se_5S_3[b]
$^1J_{12}$, $^1J_{13}$	−47	−23	$^2J_{23}$	95	108
$^1J_{24}$, $^1J_{35}$	−65	−40	$^3J_{25}$, $^3J_{34}$	10	5
$^2J_{14}$, $^2J_{15}$	59	110	$^4J_{45}$	0	−3

[a] For the numbering of atoms, see Figure 3. [b] Reference 4b.

Scheme I



ring molecule Se_5S_2 was studied by computing the reduced spin–spin coupling constants $^1K_{SeSe}$ and $^2K_{SeSe}$,[17] which were obtained from the relativistically parametrized extended Hückel calculations (the program REX).[18] While this simple method does not reproduce the absolute values of the observed coupling constants, it is found suitable for the semiquantitative comparison of the relative magnitudes within a series of analogous compounds. Since our goal was to inspect the trends in the coupling constants through the seven-membered ring molecule, the calculations were only performed for the chair and boat conformations of cycloheptaselenium. Se_7 is a suitable model compound, since it contains SeSe bonds in all possible chemical environments of the seven-membered ring molecule. It was further assumed that since the bond order varies significantly throughout the molecule, the actual location of the SeSe bonds has a stronger effect on the ^{77}Se–^{77}Se coupling in different isomers of 1,2,3,4,5-Se_5S_2 than the existence of a single SS bond.[19] The rationale in the construction of the internal coordinates of the Se_nS_{7-n} molecules has been described earlier.[6]

Results and Discussion

The NMR spectrum of the ^{77}Se-enriched 1,2,3,4,5-Se_5S_2 is shown in Figure 2. It is composed of three signals at 1087.1, 1025.0, and 978.9 ppm with the intensity ratio of 2:1:2, respectively, in agreement with the chemical shifts reported previously from the natural-abundance NMR spectrum of the product.[7b] The trends in the chemical shift of the three signals are in good agreement with those deduced earlier for the heterocyclic Se_nS_{8-n} species (the assignment of the signals is also indicated in Figure 2).

In the ^{77}Se-enriched material all three signals appear as complicated second-order multiplets. The spectrum was simulated as a five-spin [AMM′XX′] system (see Figure 3). The refined ^{77}Se–^{77}Se coupling constants are shown in Table I. With this coupling scheme it was possible to assign all transitions with an excellent fit.

The three multiplets arising from this five-spin [AMM′XX′] system indicate that 1,2,3,4,5-Se_5S_2 is fluxional. If the molecule undergoes no pseudorotation, only the isomers D and D′ (see Figure 1) are consistent with the spectral information, since all other isomers should show five signals in the NMR spectrum. According to the Raman spectroscopic and X-ray crystallographic evidence, the solid-state structure of 1,2,3,4,5-Se_5S_2 shows the chair conformation with A and C as predominant isomers in the lattice.[5c] In view of the low estimated barrier to the pseudorotation[11a] it can be considered unlikely that in solution the molecule assumes a discrete isomeric form that is different from those in the solid state.

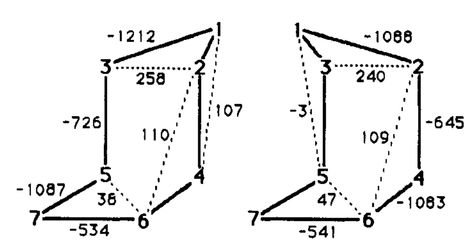
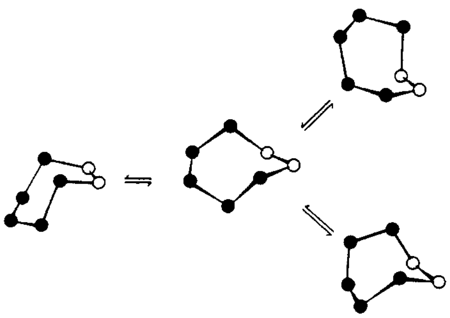


Figure 4. Reduced coupling constants $^1K_{SeSe}$ and $^2K_{SeSe}$ (in N A^{-2} m^{-3}) calculated for the chair and boat conformations of Se_7.

Scheme II



The fluxionality is best described by considering cycloheptasulfur, S_7, (or cycloheptaselenium, Se_7) with the ground-state symmetry of C_s in a chair conformation. The pseudorotation is exemplified by Scheme I. Consider the pseudorotation of 90° about the unique SS bond (bond 7).[20] The subsequent adjustment of all bond lengths to accommodate the changed chemical environment of all sulfur atoms creates a different, but identical, S_7 molecule. An intermediate with C_2 symmetry is obtained upon the pseudorotation of 45°. From this intermediate an alternative pathway can also be conceived. It involves the pseudorotation about bond 1, which is unique in C_2 symmetry. This creates a molecule in boat conformation. Thus, the fluxionality of S_7 produces two series of identical molecules. An ab initio MO study on the energetics of the pseudorotation is currently in progress.

The analogous pseudorotation pathways in the case of 1,2,3,4,5-Se_5S_2 lead to the interconversion between the different isomers as exemplified in Scheme II. Because the isomeric forms A and A′, B and B′, and C and C′ can also exhibit stereoisomerism while the isomers D and D′ cannot, the frequency of occurrence of the six former isomers, as far as NMR results are concerned, is twice to that of the two latter in the cycle of pseudorotation.

The ^{77}Se–^{77}Se coupling constants of 1,2,3,4,5-Se_5S_2 reflect the pseudorotation shown in Scheme II. It is seen from Table I that while the $^1J_{SeSe}$ coupling constants assume larger values in the seven-membered ring molecule than in the eight-membered 1,2,3,4,5-Se_5S_3 which contains an analogous spin system, their relative magnitudes are observed to be approximately similar in both molecular species. The $^2J_{SeSe}$ coupling constants seem to be somewhat smaller in 1,2,3,4,5-Se_5S_2 than in 1,2,3,4,5-Se_5S_3.

The reduced coupling constants $^1K_{SeSe}$ and $^2K_{SeSe}$ of Se_7 in chair and boat conformations are shown in Figure 4. As expected, the magnitude of $^1K_{SeSe}$ varies significantly depending on the location of the SeSe bonds in the seven-membered ring molecule. The

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(17) The reduced coupling constant is defined as

$$^nK_{ij} = (4\pi^2/h)\gamma_i^{-1}\gamma_j^{-1}(^nJ_{ij}) \quad (n = 1, 2)$$

where γ_i and γ_j are the magnetogyric ratios of the nuclei i and j, h is the Planck constant, and J is the coupling constant.

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(19) This assumption was verified by carrying out control calculations with different isomers of 1,2,3,4,5-Se_5S_2. They resulted in almost identical values of $^1K_{SeSe}$ and $^2K_{SeSe}$ when being compared to the values from corresponding SeSe bond positions in Se_7.

(20) Since the theoretical studies on the barriers to the internal rotation about the SS bond indicate that the mutual p-lone-pair repulsion between the adjacent sulfur atoms is highest when the torsional angle is 0° (see refs 11b and 11c and the references therein), it is plausible that the pseudorotation is initiated at the unique bond 7 in the S_7 molecule.

trends in the ${}^1K_{SeSe}$ coupling constants as compared to those in the observed ${}^1J_{SeSe}$ coupling constants (see Table I) can be used to rule out the existence of the discrete isomers D and D′ in the sample solution as follows:

In isomers D and D′ the atomic positions 6 and 7 (see Figure 4) are occupied by sulfur. It is easily seen that in both isomers D and D′ the ratio ${}^1K_{24}/{}^1K_{12}$ (or symmetry-related ${}^1K_{35}/{}^1K_{13}$) should be significantly smaller than 1.00. In the case of the observed spectrum the corresponding ratio ${}^1J_{24}/{}^1J_{12}$ (or ${}^1J_{35}/{}^1J_{13}$) is clearly over 1.00. The observed trend is approximated by the reduced coupling constants only when the coexistence of different isomers—and their rapid interconversion—is allowed for.

Figure 4 shows a strong dependence of ${}^2K_{14}$ (or ${}^2K_{15}$) on the conformation. In the chair conformation this coupling has a large positive value, while in the boat conformation it is slightly negative. Since the observed coupling over two bonds is smaller in 1,2,3,4,5-Se_5S_2 than in 1,2,3,4,5-Se_5S_3 (see Table I), this seems to indicate that rapid interconversion of isomers with both conformations is taking place in the solution.

Conclusions

The ${}^{77}Se$ NMR spectrum of the fluxional 1,2,3,4,5-Se_5S_2 (94% enrichment with ${}^{77}Se$ isotope) shows three second-order multiplets, which can be assigned in terms of the five-spin [AMM′XX′] system. The simulation of the spectrum yields all ${}^{77}Se-{}^{77}Se$ coupling constants and enables the complete assignment of all transitions. The number of the NMR signals and their coupling pattern are consistent with the concept of facile pseudorotation in the seven-membered chalcogen-containing ring molecules. The fluxionality is further verified by comparison of the trends in the observed ${}^1J_{SeSe}$ and ${}^2J_{SeSe}$ coupling constants to those in reduced coupling constants ${}^1K_{SeSe}$ and ${}^2K_{SeSe}$, which indicate that all possible isomers of 1,2,3,4,5-Se_5S_2 in both chair and boat conformations must rapidly interconvert in solution.

Acknowledgment. The financial support from the Academy of Finland is gratefully acknowledged.

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Matrix Infrared Spectra of the Products from Photochemical Reactions of P_4 with O_3 and Decomposition of P_4O_6

Zofia Mielke[†] and Lester Andrews*

Received November 27, 1989

The P_4/O_3 matrix system has been reinvestigated by using dilute P_4 and a wide range of photolysis wavelengths. With red photolysis the major product is terminal P_4O; with ultraviolet photolysis absorptions for oxo-bridged tetrahedral P_4O and cyclic planar P_4O plus a series of oxo-bridged absorptions leading to P_4O_6 and P_4O_7 dominate. Vacuum ultraviolet photolysis and glow discharge of P_4O_6 produced an absorption for P_4O_7 and three absorptions common to the P_4/O_3 photolysis system, which are assigned to oxo-bridged P_4O_5, P_4O_4, and P_4O_3.

Introduction

Recent infrared studies of matrix reactions of oxygen atoms with P_4 led to identification of two isomers of the lowest phosphorus oxide, P_4O. Red photolysis of the P_4--O_3 complex initiated an oxygen atom transfer reaction, which resulted in terminally bonded P_4O as the major product and oxo-bridged tetrahedral P_4O as a minor product.[1] Since these reactions are highly exothermic, further decomposition or rearrangement reactions, which could lead to smaller molecular fragments or isomerizations, must be considered. Addition of two or more oxygen atoms or ozone molecule(s) to the P_4 cage can lead to other stable oxides of general formula P_4O_x (x = 2–6) where the tetrahedral phosphorus cage is maintained and oxygen atoms form oxo-bridged bonds. In the similar phosphorus–sulfur system, six different tetraphosphorus cage compounds of general formula P_4S_x (x = 3–5) have been characterized.[3-6]

Additional studies of prolonged full-arc photolysis of concentrated Ar/O_3 matrices with dilute P_4 have produced a number of new absorptions in addition to those previously observed.[1] Further ozone photolysis studies were combined with three different discharge experiments where discharged Ar/P_4O_6 mixtures, vacuum UV photolysis of P_4O_6, and reaction between discharged P_4 and ozone have generated novel phosphorus oxides. Comparison of these studies provided identification and structural information on the new phosphorus oxides P_4O_5, P_4O_4, and P_4O_3, which are products of the O_3 photochemical reaction with P_4. The results of these studies are presented here.

Experimental Section

The CTI cryogenics Model 22 refrigerator, Perkin-Elmer 983 spectrometer, high-pressure mercury-arc lamp, and vacuum apparatus and techniques for delivering O_3 and P_4 into matrix samples have been described previously.[1] High-resolution spectra were recorded; wavenumber accuracy is ±0.3 cm^{-1}.

Three different types of discharge experiments were done. In the first studies, an Ar/P_4O_6 mixture was codeposited with argon from a separate 6-mm-o.d. quartz tube, and microwave discharge excitation of the argon provided vacuum UV radiation to the condensing sample. In the second set of experiments, the Ar/P_4O_6 mixture was subjected to low-power discharge. Finally, P_4 from a microwave discharge was codeposited with an Ar/O_3 mixture. A coaxial quartz tube[7] was used in the second and third groups of experiments where a P_4 or concentrated Ar/P_4O_6 mixture was passed through a short (1 cm) argon discharge at the end of an open discharge tube about 5 cm from the matrix window.

The P_4O_6 sample prepared by J. L. Mills was free of impurities on the basis of the matrix infrared spectrum.[2]

Results

Three different types of experiments with two precursor systems produced several common P_xO_y species that will be described below.

$P_4 + O_3$. In the first series of experiments, P_4 was evaporated from white phosphorus at 5–10 °C and codeposited with Ar/O_3 = 200/1, 150/1, 100/1, and 75/1 mixtures onto a 12 K window. Accordingly, the O_3/P_4 ratio was varied over a 3-fold range. Weak product bands, which increased later on photolysis, were observed in the deposited sample, presumably owing to source photolysis. The strong ozone fundamental exhibited a satellite complex band

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[†] On leave from Wroclaw University, Wroclaw, Poland.

(1) Andrews, L.; Withnall, R. *J. Am. Chem. Soc.* **1988**, *110*, 5605.
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