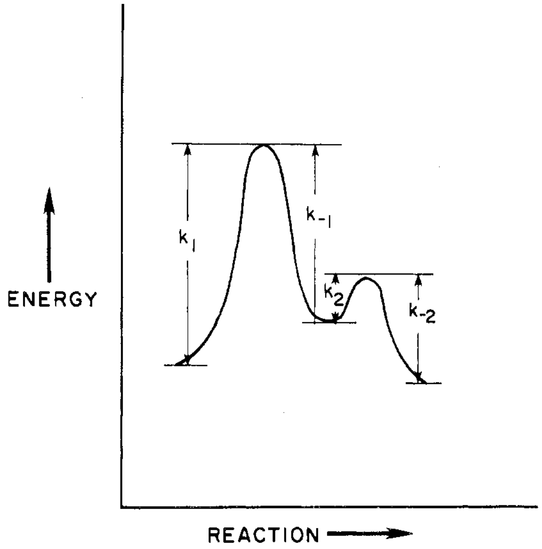

Figure 4. Diagramatic representation of the relative activation energies implied by the mechanism in eq 4.

that in eq 4 and makes an insignificant contribution to the total rate under the conditions studied. This is not unreasonable, as OH^- would be a poor leaving group relative to H_2O.

While the observed kinetics cannot rule out the formation of a ternary H^+–$(FeEDTAOH)_2$ complex, such a reaction is obviously unlikely on statistical grounds.

A final check of the validity of the proposed scheme is provided by the ratio of the rate of dimerization to monomerization, $\log k_D/k_M = \log K_{kinetic}$ which should equal $\log K_d$. The equilibrium constant thus determined ($\log K_{kinetic} = 2.4$) is in good agreement with the thermodynamic value (2.5 ± 0.2).

Thus, the mechanism for oxo bridging appears to involve dimerization of a hydrolyzed and nonhydrolyzed chelate to yield a hydroxo bridged intermediate. The stabilization of oxo bridged complexes, however, must depend on balancing the energy required for deprotonation of hydroxide against that gained by superexchange mediated delocalization. Delocalization will be maximal through a linear bridge[12] and minimal for a hydroxo bridged complex (with a bond angle of approximately 120°), in accord with experiment.[13,14] On formation of the

$$\overset{H}{M\text{–}O\text{–}M}$$

species, linearity of the bridge may be obtained simply by a molecular vibration, resulting in a configuration favorable for superexchange and concomitant deprotonation to yield the linear oxo bridge.

Thus, energy for the deprotonation of the hydroxo bridged intermediate is supplied by delocalization, and the inherent hydrolytic tendencies of iron(III), which is a strong Lewis acid. By contrast to the ferric complexes, cobalt(III) complexes, which are even stronger Lewis acids, cannot gain delocalization energy by superexchange since Co(III) complexes are generally spin paired. Thus Co(III) complexes do not form oxo bridges, but dimerize through two cis hydroxo bridges, as favored by a statistical (chelate) effect. Similarly, weaker Lewis acids which might be expected to exhibit superexchange such as nickel(II) cannot labilize the hydroxide proton and thus also do not undergo oxo bridging. For such ions, the energy of superexchange might overcome the energy required for deprotonation if the bridging group was less basic. Such appears to be the case with sulfide ($pK \cong 7$ for the first deprotonation $H_2S \rightarrow HS^-$ vs. $pK \cong 14$ for $H_2O \rightarrow OH^-$). Thus, linear sulfide bridges resulting in superexchange are well established for nickel(II)[15] and iron(II)[16] complexes.

Note Added in Proof. A kinetic study by Wilkins[17] of analogous $(FeL_2)O$ systems has come to our attention. The results are in substantial agreement with our own, but differ with respect to the $(FeLOH)_2$ dependent pathway. Temperature dependence studies are being performed to clarify the reason for the discrepancy.

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Conditions of Formation of α and β Phases of Germanic Nitride

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Germanic nitride is usually prepared by interaction of ammonia with elementary germanium or germanium dioxide between 700 and 750 °C. Popper and Ruddlesden[1] showed that the proportions of α and β crystalline phases varied depending upon the preparative conditions: heating germanium in ammonia at 750 °C gave a product which was almost entirely α phase, whereas heating germanium dioxide under the same conditions gave β phase with traces of α. Later, Lyutaya and co-workers[2] and other authors[3-6] observed the same phenomena. Labbe and co-workers[7] thought the β phase stabilized when oxide, oxygen, or steam were present, because this phase can be obtained in its pure form by having ammonia react with germanium dioxide and because the proportion of α phase is increased when purer ammonia is used. This assumption was at variance with the results of Wild and co-workers[8] who claimed the α phase of silicon and germanium nitrides to be, actually, oxynitrides $Si_{11.5}N_{15}O_{0.5}$ and

$Ge_{11.5}N_{15}O_{0.5}$. Based on the kinetics of nitriding germanium slices with ammonia in the presence of hydrogen and steam, these authors[9] proposed that the α phase was formed by interaction of ammonia with gaseous germanium monoxide. The effect of oxygen[7-9] upon the formation of either phase of germanic nitride is still under study.

Differences in the existing literature as to the methods and conditions for the preparation of germanium nitride show the need for further investigations of preparative conditions. Some results of these are given here. Three different methods have been used: reaction between pure ammonia and powdered elementary germanium; reaction between gaseous mixtures (ammonia–hydrogen) with variable compositions and powdered elementary germanium; reaction between pure ammonia and gaseous tetrachlorogermane using nitrogen as carrier gas.

Experimental Section

(1). Chemicals. Powdered elementary germanium (Cerac) had a purity of 99.999% (based on metallic impurities) and a particle size of 325 mesh (40 μm grain diameter). Oxygen percentage was 4.5 wt %. Before nitriding, the germanium was purified by sublimation of germanium monoxide;[10] the oxygen percentage was then below 0.2 wt %. Ammonia (Air Liquide) of purity 99.96% had a water content below 400 ppm. Before reacting with the germanium it was desiccated by flowing over sodium threads. Hydrogen and nitrogen (Air Liquide) had a purity of 99.995%. Liquid tetrachlorogermane (Merck) had a purity of 99.999%.

(2). Apparatus. A quartz boat containing elementary germanium was placed into the quartz tube or the refractory material tube in which the reaction was performed. Elementary germanium was nitrided under gaseous flow consisting of pure ammonia or an ammonia–hydrogen mixture, during 15 h. The composition of these mixtures was determined by gas chromatography. The flow and composition of the mixture were maintained at constant values by means of flow regulators (Brooks). The apparatus and the method of preparing germanic nitride by chemical vapor deposition with the mixture ($GeCl_4$–NH_3–N_2) were described previously.[11] The mixture ($GeCl_4$–NH_3–N_2) had a constant molar composition of 3% in tetrachlorogermane and a variable molar composition between 3.3 and 9.3% in ammonia. Nitrogen was used as carrier gas. The nitrogen flow was 24 l./h. Germanium nitride deposited on a substrate made of small quartz plates contained in the quartz tube in which the reaction was performed. Experiment times were 15 min.

(3). Analyses. Nitrogen determinations were carried out by alkaline fusion and by a microanalysis method perfected in our laboratory.[12] Oxygen determinations in germanium and germanium nitride were performed by LAREC Laboratory, ENSEEG, Institut Polytechnique de Grenoble, Grenoble, France. The percentage of elementary germanium in germanium nitride was calculated from weight differences assuming that nitrogen and oxygen combined with germanium as the nitride and oxide, respectively. The α and β phases were identified by analysis of x-ray patterns obtained by means of a Siemens diffractometer, F type, and by infrared absorption spectroscopy, using a double-beamed Perkin-Elmer 457 spectrometer.

Results and Discussion

(1). With Pure Ammonia. Between 630 and 800 °C, the nitriding of germanium yielded α and β phases simultaneously; the respective proportions were variable and unpredictable. The ammonia flow used was 14 l./h. Under these conditions, ammonia was partially dissociated. The exit gas composition was a function of temperature. At 630 °C, the exit gas consisted of 0.3% hydrogen, 0.1% nitrogen, and 99.6% ammonia; at 800 °C, the gas contained 15% hydrogen, 5% nitrogen, and 80% ammonia.

(2). With Ammonia–Hydrogen Mixture. Using a mixture containing 35% hydrogen and 65% ammonia, the α and β phases were obtained pure, at 630 and at 800 °C, respectively (Figure 1). At any intermediate temperature, the germanium nitride obtained was a mixture of α and β phases in which the percentage of pure β phase increased progressively since the percentage of pure α phase decreased progressively with increasing reaction temperature.

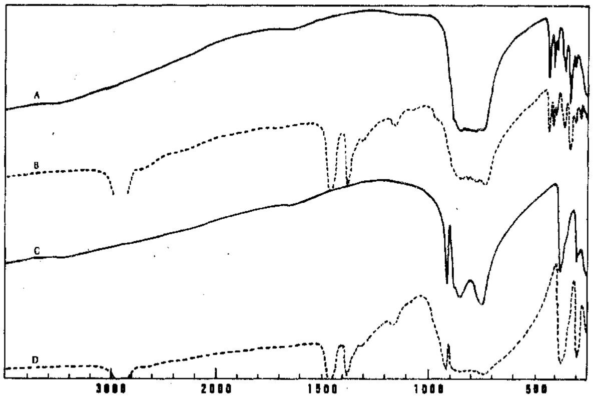

Figure 1. Infrared spectra (4000–250 cm^{-1}) for: (A) α-Ge_3N_4 with KBr; (B) α-Ge_3N_4 (Nujol mull); (C) β-Ge_3N_4 with KBr; (D) β-Ge_3N_4 (Nujol mull).

(3). Chemical Vapor Deposition. The reaction was carried out between 660 and 800 °C. In this temperature range, nitride crystallized. Below 660 °C, amorphous nitride was obtained[13,14] and the deposition rate was very low.[11] Above 800 °C, the nitride film contained elementary germanium. The x-ray diffraction pattern of germanium nitride contained lines of the α and β phases. β phase proportion was greater in films prepared at high temperature. This confirmed the results obtained in the preparation of powdered nitride.

Nitrogen determinations on films prepared at 760 °C were performed by means of the microanalysis apparatus.[12] The mean value for nitrogen was 20.2 wt % (theoretical for stoichiometric germanium nitride, Ge_3N_4, is 20.46 wt %).

(4). Infrared Absorption Spectroscopy. The infrared absorption spectra (Figure 1) of the pure α and pure β phases prepared under the given procedures differed both in the number and the positions of the absorption bands. Continuous lines correspond to spectra obtained from a pelletized mixture of germanium nitride crystalline powder and KBr. Dotted lines correspond to spectra obtained from crystalline germanium nitride powder mulls prepared on CsI plates using predried Nujol.

The spectrum of the α phase had more absorption bands than the spectrum of the β phase within the 1000–250-cm^{-1} range. The absorption bands common to both spectra (A and B, and C and D) occupy the following positions: α phase, 840, 815, 775, 430, 410, 395, 355, 330, and 310 cm^{-1}; β phase, 910, 845, 740, 370, and 290 cm^{-1}. This result confirms Ukhanov and co-workers',[15] though there is no evidence of the presence of their 550-cm^{-1} band for the α phase spectrum or the 355-cm^{-1} band for the β phase spectrum. The absorption band near 810 cm^{-1} was ascribed to the asymmetric valence oscillations ν_3 (F_2) of the Ge–N bond in the GeN_4 tetrahedron. The bands between 250 and 500 cm^{-1} were ascribed to deformation oscillations or to lattice oscillations. In this range, the number of absorption bands ascribed to the α phase was greater than the number of absorption bands ascribed to the β phase (Figure 1). This increasing in the number of absorption bands was ascribed to the canceling of degeneracy and to an increasing in the couplings and interactions connected with the decreasing in symmetry between the β phase and the α phase.

Spectra (Figure 2) of germanium nitride prepared at 730 and at 790 °C showed a transition to the more ordered phase (β phase) with increase in deposition temperature. Generally, films become more ordered as the deposition temperature is increased.[16]

Conclusion

Preparation of the pure α and β phases of germanic nitride requires a rigorous control of composition of nitriding gas and

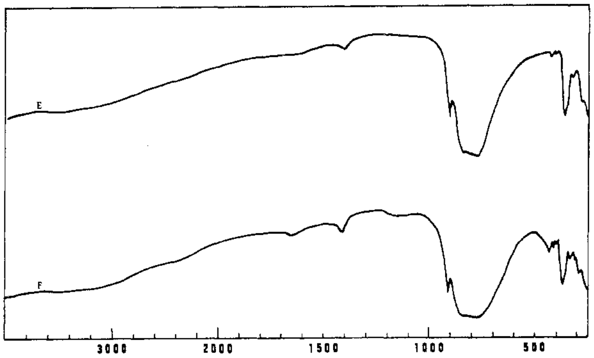

Figure 2. Infrared spectra (4000–250 cm^{-1}) for: (E) Ge_3N_4 prepared at 790 °C by the CVD process; (F) Ge_3N_4 prepared at 760 °C by the CVD process.

temperature. For a given ammonia–hydrogen mixture the β phase was obtained at a higher temperature than the α phase. The β phase can be prepared pure by reaction of ammonia and elementary germanium. Thus, oxygen is not necessary for the formation of either crystalline phase. The progressive increase in the percentage of β phase with increasing deposition temperature suggests that the α and β phases are two polymorphic varieties of germanic nitride, though we have verified the impossibility of the α–β transition at any temperature; this result confirms those obtained by Labbe[6] and by Bradley and co-workers.[4]

Registry No. Ge_3N_4, 12065-36-0.

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Photoinduced Oxidation of Tertiary Arylphosphines

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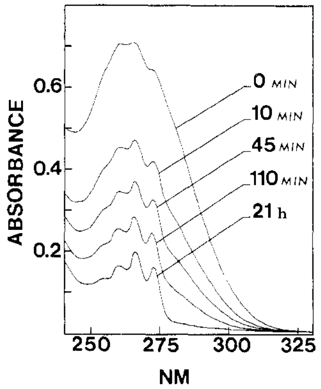

Figure 1. Electronic absorption spectral changes during irradiation with a fluorescent desk lamp of an 8.8 × 10^{-5} M oxygen-saturated CH_2Cl_2 solution of triphenylphosphine.

Tertiary phosphines are an important class of ligands in inorganic and organometallic chemistry, in part due to their unique σ-donor and π-acceptor properties and their resistance to chemical transformation. Unlike trialkylphosphines, tertiary phosphines that contain at least one aryl group are not very sensitive toward autoxidation. Triphenylphosphine, for example, yields only a trace of its oxide when heated under an oxygen atmosphere in benzene.[1] Under similar conditions, most trialkylphosphines readily undergo a free-radical chain autoxidation process yielding as principal products the corresponding phosphine oxides and phosphinate esters.[1] Triarylphosphines can be oxidized by molecular oxygen, however, by treatment with a radical initiator, and triphenylphosphine yields its oxide exclusively under these conditions.[1]

In the course of our investigations into the photochemical properties of some transition metal–phosphine complexes, we have discovered that uncoordinated arylphosphines are readily oxidized by molecular oxygen when irradiated with ultraviolet light or with fluorescent room light. Since this observation is of importance to workers investigating the photochemical properties of phosphine complexes, we have examined these photoreactions in some detail and report our results herein. Although the photoinduced oxidation of triphenylphosphine to triphenylphosphine oxide has been briefly mentioned in the literature,[2,3] quantum yield data have not been presented and the high photosensitivity of arylphosphines in the presence of oxygen has apparently not been generally appreciated.

Experimental Section

Triphenylphosphine was obtained from Aldrich Chemical Co. and was recrystallized from EtOH before use. $PMePh_2$, $PEtPh_2$, PMe_2Ph, and PEt_2Ph were synthesized from PPh_2Cl and $PPhCl_2$ and the appropriate Grignard reagent following an adaptation of the literature procedure.[4] Methyldiphenylphosphine oxide was prepared by heating $PMePh_2$ with ethylene carbonate[5] and was characterized by its melting point (110–111 °C[6]), its infrared spectrum ($\nu_{P=O}$ 1122 cm^{-1}), and its ^1H NMR spectrum (δ 1.95 and 2.16[7]). A low-pressure Hg-arc lamp (254 nm), a Hanovia 450-W medium-pressure Hg-arc lamp equipped with Corning 0-52 and 7-37 glass filters (366 nm), an Ultraviolet Products B-100A lamp (366 nm), and a Sylvania F40/CW 40-W fluorescent desk lamp were used as the irradiation sources for the photochemical studies. Quantum yields were measured at 254 nm in oxygen-saturated CH_2Cl_2 solutions using ferrioxalate actinometry ($I = 2.2 \times 10^{-7}$ einstein/min). Electronic absorption spectral changes were monitored with a Cary 17 spectrophotometer, infrared spectral changes were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer, and ^{31}P NMR spectra were recorded on a JEOL PS-100-FT Fourier-transform NMR spectrometer. Reported chemical shifts are relative to external H_3PO_4.

Results and Discussion

Photolysis of an 8.8 × 10^{-5} M oxygen-saturated CH_2Cl_2 solution of PPh_3 with a fluorescent desk lamp results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds, the intense band centered at 270 nm steadily decreases in intensity and the final spectrum obtained is identical with that of triphenylphosphine oxide. In the infrared spectral region the PPh_3 band at 1080 cm^{-1} decreases in intensity with increased irradiation time, and Ph_3PO bands