osmometric molecular weights for low-valent metal complexes as a result of reaction with oxygen.[14,15] $CoNO(PPh_3)_3$ also shows a single resonance with no evidence for phosphine dissociation. Since sterically demanding phosphines like PPh_3 maximize ligand dissociation,[16] eq 1 will lie farther to the left for analogous nitrosyl complexes containing mixed (alkyl)(aryl)phosphines. Phosphine dissociation thus occurs at most to a limited extent.

At 30°, exchange of phosphine coordinated to $RhNO(PPh_3)_3$ with free PPh_3 is detectable as line broadening of the free PPh_3 resonance. If an intramolecular redox process is energetically accessible, exchange might well occur *via* an associative mechanism. Substitution reactions of nitrosyl complexes frequently exhibit S_N2 kinetics.[17] For the exchange studied here, an associative mechanism predicts $\tau_L^{-1} \propto [RhNOL_3]$ and $\tau_{RhNOL_3}^{-1} \propto [L]$ where $L = PPh_3$. In fact, the phosphorus line width in $RhNO(PPh_3)_3$ is the same in all spectra recorded, including those without added phosphine. This line width is significantly greater than that of an internal standard, however.

Phosphine exchange by a dissociative pathway is shown in eq 1. For this equilibrium, the following relationships are valid

$$\tau_L^{-1} = k_1[RhNOL_3][L]^{-1} \qquad (2)$$

$$\tau_{RhNOL_3}^{-1} = k_1/3 \qquad (3)$$

Here τ_{RhNOL_3} represents the average lifetime of a complexed phosphine, which is the quantity measured experimentally. This mechanism correctly predicts the most obvious characteristic of the data in Table I: the line widths of the $RhNOL_3$ resonances are concentration independent. Values of k_1 derived from the line width of free triphenylphosphine (Table I) agree with those derived from eq 3. Since tetrahydrofuran is potentially a coordinating solvent, rate data were also obtained on a benzene solution of $RhNO(PPh_3)_3$ and PPh_3. The value of k_1 does not differ significantly from that in THF, suggesting that $RhNO(PPh_3)_2$ is a coordinatively unsaturated species and not the solvent (S) adduct $RhNO(PPh_3)_2S$.

Phosphine exchange of coordinatively saturated phosphine-metal-carbonyl complexes typically proceeds by a dissociative path. In contrast, the coordinatively unsaturated complexes MX_2L_2 (M = Fe, Co, Ni) all exchange phosphine by an associative pathway;[18] five-coordinative MX_2L_3 complexes are actually isolable in some instances. The mechanism of exchange of free phosphine with $RhNO(PPh_3)_3$ thus provides no evidence for NO functioning as an electron sink. However, this cannot be taken as evidence that linear-bent nitrosyl tautomerism is not catalytically significant. Steric factors are almost certainly important in this system. They may actually dominate the kinetics, since the bulkiness of triphenylphosphine promotes dissociation. Among six-coordinate complexes, a *fac*-$MX_3(PPh_3)_3$ complex, which bears an obvious structural similarity to $RhNO(PPh_3)_3$, has never been structurally characterized. An associative mechanism for phosphine exchange is probably sterically inaccessible to $RhNO(PPh_3)_3$. Excluding sterically atypical hydride complexes, there are no structurally characterized complexes with four triphenylphosphine ligands.[19] Solids of formula $M(PPh_3)_4$ may actually have one phosphine trapped in the lattice. Finally, steric effects have been shown to alter the mechanism of exchange of main group acid-base complexes.[20]

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Registry No. $CoNO(PPh_3)_3$, 18712-92-0; $RhNO(PPh_3)_3$, 51349-76-9; $Rh(NO)Cl_2(PPh_3)_2$, 40231-80-9; ^{31}P, 7723-14-0.

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Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Barium Pernitride from Thermal Decomposition of Barium Azide

Stuart Salot and James C. Warf*

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Various substances described as alkaline earth pernitrides have been reported.[1] All are black, reactive materials which yield X-ray diffraction patterns typical of amorphous compounds. The strontium pernitride prepared by vacuum pyrolysis of strontium amide proved to have a small magnetic moment which increased with rising temperature.[2] The most easily prepared and most thoroughly studied higher nitrides are those resulting from the decomposition of barium, strontium, and calcium azides under hydrocarbons.[1e] Of these, the barium compound is most nearly stoichiometric, being approximately Ba_3N_4. Attempts by Linke and coworkers[3] further to characterize these pernitrides by infrared, Raman, and mass spectrometry resulted in few revealing results. They showed that considerable hydrazine is formed during slow hydrolysis of the pernitrides and conjectured that the nitrogen atoms in pernitrides exist in some sort of polymeric chain or net structure. Barium pernitride has been employed to effect aldol and ester condensations and to prepare anhydrous hydrazine and alkaline earth hydrazides.[4] It converts dimethyl sulfoxide to an amorphous polymeric substance.[5]

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Experimental Part

Materials. Barium azide was recrystallized by dissolving in hot water and precipitating with ethanol. The resulting $Ba(N_3)_2 \cdot H_2O$ was dehydrated over sulfuric acid, which gave needles 0.01-0.04 mm wide and 0.1-0.4 mm long. Decalin was purified by shaking several days with alkaline permanganate, drying, refluxing with sodium, and collecting the center fraction during distillation. Fluorolube oil, from the Hooker Electrochemical Co., was degassed by evacuation. Decafluorobiphenyl was supplied by Imperial Smelting Corp., Ltd., Bristol, England.

Preparation of Pernitrides. Earlier procedures[1e,3] were followed when the azides were decomposed under decalin. Barium pernitride was also synthesized employing *n*-nonane or xylene as the liquid phase; a glass apparatus pressurized with argon was used so that the temperature could be raised to 200°. Mineral oil or Fluorolube was the liquid phase in some runs, in which case the composition could be monitored by weight loss. Kinetic observations were made in which barium azide was heated under mineral oil in a closed nickel bomb, using a constant-temperature furnace. The rise in nitrogen pressure was observed as a function of time, and at the end the total nitrogen was determined volumetrically. Two runs were made in which barium azide was decomposed under the very inert compound, decafluorobiphenyl (mp 68°). These reactions were carried out in pressurized glass vessels under nitrogen.

Hydrolysis and Ammonolysis of Barium Pernitride. Treatment with water was carried out as described by earlier workers.[3b] The gases evolved were dried and collected in a bulb for mass spectrometric analysis. A Consolidated Electrodynamics Corp. Model 103C mass spectrometer was employed. For ammonolysis, the barium pernitride specimens, from which the volatile hydrocarbon had been removed by distillation, were in glass vessels capable of withstanding the vapor pressure of liquid ammonia at room temperature (*ca.* 10 atm). These vessels were equipped with Kovar seals and stainless steel valves. Anhydrous ammonia was distilled in and the vessel was warmed and shaken. After the apparatus had stood 1 hr at room temperature, by which time bubbling had ceased, the reaction gases were collected over 6 *M* H_2SO_4, dried, and drawn into a bulb for mass spectrometric analysis. After removal of all ammonia from the reaction vessel and evacuation, an excess of hydrochloric acid of near azeotropic composition (8 *M*) was distilled in using liquid nitrogen, and the mixture was warmed slowly. The resulting solution was analyzed for hydrazine by iodate titration.[6]

Deuterium Exchange. To aid in identifying the barium compounds, other than the pernitride, which resulted from the decomposition of the azide under hydrocarbons, a barium pernitride specimen of composition $BaN_{1.06}$ was made under decalin. After all the decalin was removed, the residue was maintained at 100-105° in contact with 99.8% deuterium gas for 70 hr, after which the gas phase was analyzed mass spectrometrically. The solid phase was hydrolyzed using ordinary water, and the gases produced were analyzed.

Amalgamation Experiments. Apparatus was assembled in which barium pernitride (N:Ba = 1.14) was prepared under *n*-nonane, the hydrocarbon removed, and an excess of mercury added. After heating to 100° the mercury was poured into a side arm holding a sintered-glass filter, and this arm was drawn off in the flame. The mercury was centrifuged through the filter and treated with hydrochloric acid in an apparatus which permitted collection of the gases evolved for mass spectrometric analysis.

Esr Study. Barium pernitride (N:Ba = 1.37) was made under decalin, the hydrocarbon removed, and the specimen transferred to two silica capillaries, all under vacuum. One capillary held about 20 mg of pernitride, and the other about 1 mg. A second 1-mg specimen was made similarly and exposed briefly to air before sealing in order to find whether paramagnetic materials are generated by this treatment. Spectra were taken at 25, 50, 100, 150, 200, and 250° for each specimen, using a Varian E-12 (X-band) esr spectrometer. The 250° spectra were repeated at high resolution.

Esr observations were also carried out during the course of decomposition of barium azide under mineral oil. These studies were conducted with the probe at 195°. They were repeated at 175°, at which temperature the formation of the pernitride was much slower. Successive 30-sec scans were made at the higher temperature; the scan time was raised to 120 sec at the lower temperature.

Results

Formation of Barium Pernitride. Decomposition of barium azide under the various hydrocarbons, Fluorolube, or molten decafluorobiphenyl was carried out at temperatures ranging from 150 to 200°. The gas evolved, when decalin was the liquid phase, was shown by mass spectrometric analysis to be nitrogen with 0.1% hydrogen. The N:Ba ratio fell to approximately 1.30 in 35 min at 190° in a typical run, and further loss of nitrogen was much slower. Decomposition of barium azide under mineral oil at 196° in the nickel bomb began after an induction period of 12-15 min. Plots of log (N:Ba) *vs.* time were linear over 93% of the reaction, corresponding to a first-order reaction of rate constant 0.0038 sec^{-1}.

On several occasions, especially when the liquid phase caused part of the azide to adhere to the upper walls of the vessel, the reaction was initiated by a flash and sound, with sudden rise in pressure. Decomposition under molten decafluorobiphenyl, using 166 mg of $Ba(N_3)_2$, resulted in a mild explosion.

Hydrolysis and Ammonolysis of Barium Pernitride. The gases evolved on hydrolysis of $BaN_{1.09}$ (made under mineral oil) proved to be 65% nitrogen, 29% hydrogen, and 6% acetylene. Some $BaN_{1.10}$ which had been made by heating barium azide under Fluorolube (a polymer of chlorotrifluoroethylene) was hydrolyzed and the residue examined. The residue was found to contain barium fluoride, barium chloride, and traces of carbon. Similarly, the product which resulted from the decomposition of barium azide under molten decafluorobiphenyl was hydrolyzed. The gases evolved were found to consist mostly of nitrogen (79%) and acetylene (13%), with a little hydrogen (2%) and carbon dioxide (6%). The residue was washed with chloroform, and was found to contain both barium fluoride and carbon.

On treating barium pernitride samples, prepared under decalin or *n*-nonane, with liquid ammonia, not the slightest blue color could be detected at any temperature from the melting point of ammonia to 25°. Gas evolution commenced between 0 and 10°; the gas consisted of nitrogen and hydrogen only. After removal of ammonia and acidifying, iodate titration revealed that of the total nitrogen originally present as pernitride, 3.1% had been converted to hydrazine.

Deuterium Exchange. After exposure of the barium pernitride, made under decalin, to deuterium at an elevated temperature, the final composition of the gas phase was 1.7% H_2, 6.0% HD, and the remainder D_2. No deuterated ammonia was produced. Hydrolysis of the residue with ordinary water gave a complicated mixture containing H_2, HD, D_2, C_2H_2, C_2HD, C_2D_2, and N_2, but no quantitative estimate of the composition of the original solids could be made. The composition of the hydrolysis gases could be accounted for by partial exchange of $Ba(HC_2)_2$ and BaH_2 with D_2.

Formation of Barium Amalgams. The amalgams, made as described earlier and treated with acid, evolved a gas which proved to be 99.6% hydrogen and 0.4% nitrogen. This disclosed the ready formation of barium amalgam under conditions yielding barium pernitride.

Esr. All samples showed no signal when examined over a field sweep of 0-1000 G and at temperatures ranging from room temperature to 250°. This disclosed that the materials were not paramagnetic.

The esr search for paramagnetic intermediates during formation of barium pernitride gave negative results. The only response was minor, random spikes in the signal which resulted from the formation of nitrogen bubbles in the mineral oil.

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Discussion

The results of this study confirm that barium pernitride results from the thermal decomposition of the azides under a liquid phase. The exact composition of the pure compound is still unknown, but the substance appears to be either nonstoichiometric Ba_3N_4 or mixtures of Ba_3N_4 with the orthonitride (Ba_3N_2), both in a microcrystalline state. There is insufficient evidence to confirm beyond doubt the ideal formula often quoted, Ba_3N_4.

Contrary to earlier reports, the hydrocarbon under which the $Ba(N_3)_2$ decomposes is seriously degraded, evidently resulting in BaH_2 and $Ba(HC_2)_2$ (and possibly BaC_2), along with some elemental carbon. The presence of these substances is revealed by the composition of the gases formed on hydrolysis. The acetylides generally constitute an estimated 3–5% of the total solids. The two proton nmr lines observed by Linke and Lingmann[3b] might be ascribable to $Ba(HC_2)_2$ and BaH_2. Even the normally inert halocarbons are degraded when heated with barium azide, Fluorolube to BaF_2 and $BaCl_2$, and decafluorobiphenyl to BaF_2; barium acetylide and carbon are formed as well. Mineral oil is attacked when heated at 280° with sodium azide; hydrolysis of the resulting mixture yields no nitrogen, but acetylene, along with some hydrogen. Pernitrides of barium, strontium, and calcium only are known.

Linke, *et al.*,[3d] reported a temperature-dependent paramagnetism of Ba_3N_4 using the Gouy method. The result is in direct conflict with the observations in the present study by esr, that Ba_3N_4 is not paramagnetic from room temperature to 250° and that no paramagnetic intermediates are detected during its formation.

It is by no means clear how the liquid phase changes the manner of decomposition of barium azide. There is an extensive literature on the thermal and photolytic decomposition of alkaline earth azides.[7,8] Insufficient studies are available to draw a detailed picture, but an approximate course of events is as follows. On heating dry barium azide, nuclei appear on the crystal surfaces and grow as the net reaction $4Ba(N_3)_2 \rightarrow Ba_3N_2 + Ba + 11N_2$ occurs.[8c–f] Neutral N_3 radicals might be an intermediate.[8] Esr studies of barium azide irradiated with ultraviolet indicate[8] formation of the N_2^- molecule ion, which can be further converted reversibly to N_2 by electron transfer: $N_2^- + N_3^- \rightleftarrows N_2 + N_3^{2-}$. The molecule ion is thus believed to be the precursor of elemental nitrogen. Esr studies of $Ba(N_3)_2$ irradiated with X-rays at 77°K[8h] also show N_3^{2-} and in addition a species which is evidently a paramagnetic, neutral nitrogen atom. Photodecomposition of aqueous solutions of barium azide yield nitrogen, ammonia, hydrazine, and hydroxylamine.[8a]

But when crystals of the azide are covered with a relatively inert liquid and the temperature raised to 140–200°, the course of the reaction is changed dramatically. The liquid is evidently adsorbed at the sites of decomposition nuclei, and quenches or arrests complete decomposition to the orthonitride. Since no paramagnetic intermediate could be detected during the course of decomposition of barium azide to the pernitride under mineral oil, the N_2^-, N_3^{2-}, or N radicals which are reported to result by irradiation either are not formed or do not persist long enough for detection at the elevated temperatures.

The formation of barium amalgam when the azide is decomposed could readily result from the dissolution of nascent metal by mercury. When the pernitride preparation is treated with liquid ammonia, no trace of the intense blue color (ammoniated electron) which would result were metallic barium present is observed, and there is no initial gas evolution.

Since crystallographic, infrared, and esr studies yield little useful information concerning these intractable substances, it might well be that solid-state broad-line ^{14}N nmr or better, multipulse nmr techniques[9] using ^{15}N-enriched samples would be able to distinguish any N_2 or N_4 groups or even more highly polymerized units of nitrogen atoms. Electron spectroscopy of the 1s shell (ESCA) of nitrogen and barium would reveal any nonequivalency in these types of atoms. There might also be a difference in behavior between the anhydrous barium azide which crystallizes out of aqueous solution above 52.5°[10] and the material usually made by dehydrating the monohydrate, which is obtained below this temperature.

Registry No. Ba_3N_4, 12047-80-2; $Ba(N_3)_2$, 18810-58-7.

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Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201

Carbon Monosulfide Used in Synthesis of Halosulfur Compounds

Kenneth J. Klabunde,* Curt M. White, and Howard F. Efner

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Relatively little is known about the general chemical properties and uses of carbon monosulfide (CS). This reactive molecule has been observed in significant amounts in the upper atmosphere[1] and as an intermediate in the photolysis and combustion of carbon disulfide (CS_2).[2] Numerous spectroscopic studies have been reported for CS.[3–9] However, only Steudel[5,8,9] has reported results where CS has

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