Photochemical Reductive Elimination of Nitrogen from Triazidogallium(III).
Generation of Luminescent Gallium(I)

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The irradiation of Ga(N₃)₃ in CH₃CN leads to a reductive elimination of nitrogen according to the equation Ga(N₃)₃ —> Ga⁺ + 3N₂ (φ = 0.002 at λₑ = 254 nm). Ga⁺ in CH₃CN is characterized by its absorption (λₘₐₓ = 298 nm) and emission (λₘₐₓ = 475 nm) spectrum.

Introduction

Azide complexes of Ga(III) have attracted considerable attention in recent years owing to their importance as precursors for the formation of GaN [1-4]. Gallium nitride is a rather stable III-V semiconductor with interesting optical properties which can be utilized for optoelectronic applications including blue light-emitting diodes and lasers [5-7]. The thermal decomposition of Ga(N₃)₃ seems to proceed according to the simple stoichiometry Ga(N₃)₃ —> GaN + 4N₂ [4]. In distinction of the thermal behavior the light sensitivity of Ga(N₃)₃ has not yet been studied. We explored this possibility in the present investigation which is based on our previous experience with azido complexes of other s² metals such as [Sn(N₃)₆]²~ and [Pb(N₃)₆]²~ [8]. Generally, s² complexes undergo photochemical reductive eliminations which lead to the corresponding s³ complexes [9-11]. These photoredox reactions are induced by ligand-to-metal charge transfer (LMCT) excitation.

2. Experimental

2.1. Materials

Anhydrous GaCl₃ was commercially available (Aldrich) and used as received. Ga(N₃)₃ was prepared according to a published procedure [4b]. All solvents were spectrograde, carefully dried and saturated with argon.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption spectrometer. Emission and excitation spectra were obtained on a Hitachi 850 spectrophotofluorimeter equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

2.3. Photolyses

The light source was an Osram HBO 200 W/2 lamp for white light or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp for irradiation at selected wavelengths. Monochromatic light was obtained by means of a Schoeffel GM 250/1 high-intensity monochromator (band width 23 nm). The photolyses were carried out in freshly prepared acetonitrile solutions in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV-visible spectrophotometry. The photoproduct was identified by its absorption and emission spectrum. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by actinometry and equipped with a R&P-345 detector.

3. Results

The spectroscopic and photochemical studies are conducted in acetonitrile solutions which are transparent in the UV region. The electronic spectrum of Ga(N₃)₃ in CH₃CN (Fig. 1) displays an absorption at λₘₐₓ = 265 (ε = 1200 dm³ M⁻¹ cm⁻¹). The photolysis of this solution leads to the evolution of N₂ which escapes as gas bubbles. The concomitant spectral changes (Fig. 1) include an isosbestic point at 282 nm and the appearance of a new absorption

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Fig. 1. Spectral changes during the photolysis of 1.85 × 10^{-4} M Ga(N₃)₃(CH₃CN) in CH₃CN under argon at (a) 0, 2, 4, 8, and (e) 30 min irradiation times, with white light (Osram HBO 200 W/2 lamp) in a 1-cm cell.

at λ_{max} = 298 nm. The formation of this new species is monitored by the increase of the optical density at 245 nm. The quantum yield for the generation of this photolysis product is φ = 0.002 at λ_{irr} = 254 nm. While Ga(N₃)₃ in CH₃CN is not emissive, the photoproduct shows an intense blue luminescence (Fig. 2) at λ_{max} = 475 nm. The excitation spectrum matches the absorption spectrum of the photolyzed solution. In the presence of oxygen the spectral changes which accompany the irradiation take a different course and the photolyzed solution does not emit anymore.

4. Discussion

In donor solvents Ga(N₃)₃ dissolves with the formation of Lewis-base adducts such as Ga(N₃)₃(THF) [4b,c]. It is thus assumed that in solutions of CH₃CN the neutral complex Ga(N₃)₃(CH₃CN) is present. Simple complexes of s° metal ions display only LMCT absorptions in their electronic spectra [9 - 11]. Accordingly, the band of Ga(N₃)₃(CH₃CN) at λ_{max} = 265 nm (Fig. 1) is assigned to a N₃⁻ → Ga^{III} LMCT transition. In analogy to a variety of other s° complexes [9 - 11] including those with azide ligands [8], LMCT excitation of Ga(N₃)₃(CH₃CN) is assumed to result in a reductive elimination according to the equation:

\[
Ga^{III}(N_3)_3 \rightarrow hν \rightarrow Ga^+ + 3N_2
\]

The evolution of nitrogen is accompanied by the appearance of a new absorption at λ_{max} = 298 nm (Fig. 1) which is attributed to Ga^+. While absorption spectra of Ga⁺ in solution have not yet been reported, the spectra of Ga⁺ doped in alkali halides were studied in quite some detail [12]. The metal-centered \(^1\text{S}_0 \rightarrow ^3\text{P}_1\) sp transition [12, 13] of Ga⁺ depends somewhat on the matrix but occurs around 280 nm [12] in agreement with the spectrum of the photolyzed solution. Moreover, complexes of s² metal ions are generally luminescent [12, 13]. This emission originates from the sp-excited state \(^3\text{P}_1\). In the case of Ga⁺ in alkali halide matrices it appears around 500 nm [12, 14]. In the photolyzed solution this luminescence occurs at λ_{max} = 475 nm. The Stokes shift of the \(^1\text{S}_0 \rightarrow ^3\text{P}_1\) transition of Ga⁺ in the photolyzed solution (Δν = 12500 cm⁻¹) is also comparable to that of other s² complexes in solution [13]. The disappearance of the emission upon exposure of the photolyzed solution to oxygen is certainly due to the facile oxidation of Ga(I) to Ga(III).

Originally, we expected that a secondary photolysis would proceed according to the reaction sequence:

\[
\begin{align*}
Ga^+ N_3^- & \rightarrow hν \rightarrow Ga^+ + \bullet N_3 \\
\bullet N_3^- & \rightarrow N + N_2 \\
Ga^+ + N & \rightarrow GaN
\end{align*}
\]

This expectation was based on the following considerations. In suitable cases s² metal ions undergo a further reduction induced by LMCT excitation [9, 10, 15, 16]. If this would apply to GaN₃ the primary photochemical step should yield Ga⁺ and azide radicals which decompose to nitrogen atoms and N₂ [11, 17]. Finally, Ga⁺ and N are expected to
recombine to GaN. Such photoreactions which lead to the conversion of azide to nitride complexes are well known for transition metals (e.g. \([\text{Cr}^{\text{III}}\text{L}_5\text{N}_3]^{2+} \rightarrow \text{Cr}^{\text{V}}\text{L}_5\text{N}]^{2+} + \text{N}_2\) \([11, 18]\)). Unfortunately, gallium nitride which can be easily identified as insoluble material is apparently not accessible by the photolysis of gallium azide complexes.

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