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Photoregeneration of Faded Alkali Metal Solutions¹

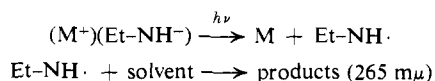
Sir:

Solutions of alkali metals in ammonia or amines decompose to form the corresponding amides. We have found that illumination of such faded solutions regenerates the metal or solvated electron components characteristic of the original metal-solvent combination. In addition to its general interest in connection with the fundamental properties of these systems, the regeneration reaction affords a convenient method for the preparation of metal solutions of controlled concentration, particularly in amine solvents.

In ethylamine solution, the absorption spectra of potassium or rubidium exhibit two bands near 650 and 850 m μ ,^{2,3} which we have previously shown to be due, respectively, to monomer and dimer species.² The 650-m μ band of potassium is associated with an e.s.r. spectrum having a characteristic hyperfine pattern.² Illumination of faded potassium or rubidium ethylamine solutions in the amide absorption region (~ 315 m μ) regenerates the original optical bands, as shown in Figure 1a,b. The e.s.r. patterns of the regenerated potassium solutions are likewise identical with the original spectra, and the fading rates are also similar. Repeating the cycle of fading and photorecovery gradually develops a strong absorption at 265 m μ , presumably due to some irreversible reaction associated with the process. This absorption does not correspond to *sym*-diethylhydrazine.

In ammonia, the photoregeneration of potassium solutions shows two phases, which are conveniently studied by flash technique, using apparatus previously described.⁴ Flashing potassium amide solutions in ammonia, in the region 240-390 m μ , produces an infrared transient whose absorption spectrum (at least as far as 1000 m μ) closely resembles the solvated electron band of metal-ammonia systems.⁵ Most of this transient disappears rapidly ($\tau \approx 40$ μ sec.), but a residual absorption, having the same spectrum, persists for as long as a minute (Figure 1c).

Under the conditions of these experiments, the metal amides in ethylamine solution are probably highly ion-paired, and it appears that the relevant reactions are



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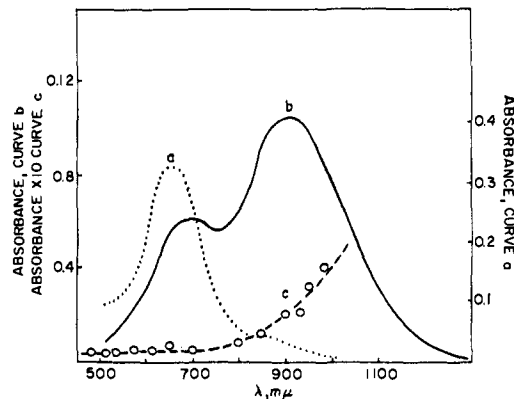


Figure 1. Photoregeneration of decomposed metal solutions (Hanovia Type HS (150 w.) quartz mercury arc, 10 cm. from sample): (a) absorption spectrum of decomposed potassium ethylamine solution (amide $\sim 10^{-3}$ M), 5-min. irradiation, 1-cm. Pyrex cell, -78° ; (b) decomposed rubidium ethylamine solution (amide $\sim 10^{-3}$ M), 7-min. irradiation, 1-cm. quartz cell, room temperature; (c) flash transient spectrum, potassium amide in ammonia ($\sim 10^{-4}$ M), time after flash, 20 μ sec., 5-cm. cell, -75° .

In ammonia, where ion-unpairing is more extensive,⁶ it is possible that charge transfer occurs from excited amide ions directly to solvent to yield solvated electrons. This is evidently closely related to the formation of hydrated electrons by photoionization of negative ions in water.⁷

Quantitative aspects of this work will be presented shortly.

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The Catalytic Versatility of Carbonic Anhydrase from Erythrocytes. The Enzyme-Catalyzed Hydration of Acetaldehyde

Sir:

Although several workers have studied the catalytic effect of erythrocyte carbonic anhydrase (EC4.2.1.1) upon the reversible hydration of carbon dioxide,^{1a-f} the accelerative effect of this enzyme in the hydration of other carbonyl systems does not appear to have been considered. We have recently established that the catalytic effect of carbonic anhydrase is not limited to CO₂ hydration, but that the enzyme very powerfully and reversibly catalyzes the hydration of acetaldehyde and many other related carbonyl systems. The hydration of acetaldehyde was studied in the ultraviolet by following the decrease in the carbonyl band at 278 m μ (ϵ 16.8). For the determination of the catalytic constant k_{enz} the initial concentration of acetaldehyde

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