Photodetachment of Electrons from Alcoholate Ions in Liquid Ammonia

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Solvated electrons with a long lifetime (about 1 hr) are produced by photolysis of solutions of potassium ethanolate in ammonia. The quantum yield of $e_{an}^-$ produced by this photodetachment from the ethanolate ion is found equal to the theoretical yield of one electron formed per photon absorbed (for $\lambda$ 254 or 316 nm), thus indicating the negligible importance of reverse reactions of recombination, particularly in the cage. In the presence of molecular hydrogen, $\theta_{e_{an}^-}$ = 2 for both wavelengths; the formation of the supplementary $e_{an}^-$ being explained by the quantitative reaction of the radical $EIO$ with $H_2$ under these basic conditions.

Since the early work by Ottolenghi and Linschitz,1 it has been shown2 that both radiolysis and photolysis of liquid ammonia solutions of amide ions in the presence of hydrogen lead to the formation of amoniated electrons whose stability is comparable with that of electrons derived from dissolved alkali metals. Nevertheless, the quantum yields are small, of the same order of magnitude as those obtained for photodetachment processes in other solvents.3,4 This is due either to a large amount of recombination, possibly favored by a cage effect, between the free radical and the solvated electron or to a rate of deexcitation of the excited anion much greater than that of dissociation.

A solution of potassium ethanolate in liquid ammonia showed anomalies at room temperature which led us to suspect that, even without hydrogen, we should be able to observe the formation of stable solvated electrons by photolysis of this medium and a study of the system is briefly reported here.

The solutions were prepared as described previously2 taking all precautions concerning the purity of the reagents and the cleanliness of the silica cells, since any impurity increases the rate of disappearance of the solvated electron. The samples were given a preliminary test with a uv lamp; if a short exposure gave a blue color, persisting for more than 10 min, the sample was kept for further experiments.

The photolysis cell which served also for the spectrophotometric measurements (optical path 1.0 cm) was fitted with a side arm to contain the stock solution. The volume of the cell was calibrated before filling. The saturated ethanolate solutions were (3.1 $\pm$ 0.2) $\times$ 10$^{-2}$ M and the initial solution in the cell could be diluted with known amounts of ammonia distilled from the side arm.

For photolysis, we used a high-pressure mercury lamp (Hanau Q 600) and interference filters ($\lambda$ 254 nm, $\Delta \lambda$ = 19 nm, transmission $T$ = 0.21; $\lambda$ 316 nm, $\Delta \lambda$ = 16 nm, $T$ = 0.17; $\lambda$ 365 nm, $\Delta \lambda$ = 4 nm, $T$ = 0.34). Parker and Hatchard’s ferrioxalate method5 was used for actinometry.

Spectra were recorded between 220 and 3000 nm with a Beckman DK 1A double-beam spectrophotometer. For these, as for the kinetic measurements made at a selected wavelength, both sample and reference cells (containing also ethanolate ions) were kept in the dark to avoid errors due to stray light.

At room temperature, the ethanolate ion has an absorption spectrum which starts around 330 nm and increases gradually until it merges with the absorption band of ammonia near 230 nm. As is the case for other ions, this absorption is probably a charge-transfer to solvent band.3,4 At 250 nm, the extinction coefficient is $2 \times 10^3$ M$^{-1}$ cm$^{-1}$.

The ethanolate ion does not absorb at 365 nm and it was found experimentally that no photolysis occurred at this wavelength. Our studies were therefore confined to the wavelengths 254 and 316 nm.

The spectrum of the solvated electron in liquid ammonia is a large band covering the range between 600 nm, and beyond 2000 nm with a maximum at 1750 nm. Depending on the purity of the sample, the decay of the solvated electron was more or less slow, in some cases the half-life being


(22) See paragraph at end of paper regarding supplementary material.
(23) Unpublished work.
more than 1 hr. After photolysis, this decay was followed for each run, thus allowing an extrapolation to the zero time, i.e., that corresponding to the end of the irradiation. Knowing the extinction coefficients, the concentration of solvated electrons corresponding to the absorption of a known number of photons could be determined and hence the quantum yield.

In the case of the solutions without hydrogen, the quantum yield is \( \Phi_{\text{em}} = 1 \) up to absorbed energies of \( 3 \times 10^{19} \) photons \( \text{l}^{-1} \), the corresponding concentration in ammonia, equivalent to \( 3 \times 10^{-3} \) \text{M} for both wavelengths 254 and 316 nm. For larger doses up to \( 8 \times 10^{19} \) photons \( \text{l}^{-1} \), the quantum yield decreases to \( \Phi_{\text{em}} = 0.8 \).

In the case of solutions in the presence of hydrogen, the quantum yield is \( \Phi_{\text{em}} = 2 \) for both lines mentioned above. The initial yields remain constant as a function of ethanolate ion concentration in the range \( 10^{-4}-3 \times 10^{-2} \) \text{M}.

Discussion

Applying Stein's scheme of photodetachment of electrons from anions to our case of ethanolate ions in liquid ammonia, we have

\[
\text{EtO}^- \xrightarrow{\text{hv}} \text{EtO}^{*} \xrightarrow{\text{deexcite}} (\text{EtO} + e^-) \xrightarrow{\text{recombination}} \text{EtO} + e^-_{\text{em}}.
\]

As we obtain a quantum yield equal to the theoretical yield of one electron per photon, we may suppose that the reverse reactions are negligible. In particular the deexcitation of the excited state EtO* must be very slow compared to the photodetachment. Moreover, the recombination between the radical and the electron, solvated or not, hardly proceeds at all, whether they are still in the cage or separated by diffusion. This recombination should be most probable when the radical and \( e^- \) remain close to each other in the cage, but this seems not to hold in the case of photodetachment. In effect, according to the experiments of Rentzepis, et al., on Fe(CN)\(_6\)\(^{3-}\) in aqueous solution, the electron is ejected to distances of several molecular diameters before the solvation shell of the initial ion is adjusted to the new valency state.

Therefore we are led to conclude that the oxidizing radicals, either the initial ethoxy radical or the a-hydroxyethyl radical which could be formed by rearrangement, react between themselves or with the solvent giving stable compounds at rates much higher than that of recombination with \( e^-_{\text{em}} \). At high absorbed doses, when the concentration of \( e^-_{\text{em}} \) increases markedly, this competition may be reversed and we observed indeed a decrease of \( \Phi_{\text{em}} \). The most probable product of the reaction of the oxidizing radicals would be glycol or its anion.

The quantum yield \( \Phi_{\text{em}} = 2 \) found in presence of hydrogen can be explained by the hypothesis of a quantitative reaction of the oxidizing radical leading to a second solvated electron. Such reactions are known for OH radicals in water\(^1\) and for NH\(_3\) in liquid ammonia.\(^2\)\(^,\)\(^3\) These mechanisms involve either an intermediate formation of a hydrogen atom giving then a solvated electron in the basic solvent or the reaction of the anionic form of the radical with the hydrogen. In the case of the ethanolate solutions, the reaction "f" with the a-hydroxyethyl radical in its neutral form seems improbable as the reverse reaction "r" is known in liquid ammonia, i.e.

\[
\text{CH}_3\text{CHOH} + H_2 \xrightarrow{\text{r}} \text{CH}_3\text{CH}_2\text{OH} + H^-.
\]

We suggest that the hydrogen molecule rather reacts directly with the anionic form of the a-hydroxy ethyl radical \( \text{CH}_2\text{CHO}^- \) or with the primary ethoxy radical \( \text{CH}_3\text{CH}_2\text{O}^- \).

We summarize the whole mechanism proposed by Scheme I.

Thus the solutions of alcohole ions in liquid ammonia allow us to study the photodetachment of electrons without recourse to scavengers which are normally necessary in media reactive toward the electron. The fact that the quantum yield attains the theoretical values shows that the recombination processes, even in the cage, do not occur.

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References and Notes
