Primary Processes Studied by Pulse Radiolysis of Liquid Ammonia. 2. Influence of a Chemically Inert Electrolyte

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The main reaction of solvated electrons in irradiated liquid ammonia appears to be with the oxidizing radicals NH₂ and NH although the product, the NH₂⁺ ion, is not observed in the pure medium. Addition of a chemically inert salt such as NaClO₄ makes this observation possible. Such a result, interpreted as a screening effect on the electrostatic attraction between the geminate pair, strongly supports the proposed hypothesis of ion pairing between the electron and a cation prior to reaction with radicals in the pure medium. This hypothesis is discussed in relation to some earlier results and to the present results and permits an estimation of the distance between the geminate ions (85 Å).

Introduction

In the preceding paper we elucidate the nature of the UV absorption bands induced by pulse radiolysis of liquid ammonia. We are now interested in the fate of the solvated electron in this medium. The relatively high value of the amoniated electron yield has been interpreted as a result of the slow reaction of e⁻ with NH₄⁺. Nevertheless, an important question remained about the fate of e⁻; the product NH₂⁺ expected from its reaction with NH₃ and NH radicals has never been observed in the pure medium, at least in sufficient amounts to support the hypothesis of this reaction. A low intermediate concentration would have been interpreted in terms of a high rate constant for the reaction of NH₂⁺ with NH₄⁺. In metal-ammonia solutions, though NH₂⁻ has been observed, its rate of neutralization with NH₄⁺ has been found to be slow. To explain this conflicting situation, we suggested that the electrostatic perturbation caused by the added electrolyte Na⁺ + e⁻ has a determining importance, even at the low concentrations used. Thus, to distinguish chemical scavenging from the electrostatic effect, we studied solutions of chemically inert electrolytes.

Experimental Section

The pulse-radiolysis set up, the optical detection, and the procedure for preparing solutions have been described in part 1. NaClO₄·6H₂O was from BDH and NH₄ClO₄ from Prolabo.

Results

The chemically inert electrolyte used was NaClO₄. The ClO₄⁻ ion is well known for its nonreactivity toward e⁻ or radicals produced radiolytically in water and also in liquid ammonia, both from radiolysis and pulse radiolysis results.

We used NaClO₄ in the same concentration range as metal-ammonia solutions in order to obtain a comparable electrostatic effect. Contrary to what happens in the pure medium, and in the same way as in metal ammonia solutions, a build up of amide ions is observed after the pulse (Figure 1). Although the end-of-pulse spectrum (Figure 1, curve a) and the decay of e⁻ in the infrared are not appreciably altered with respect to the pure medium, the UV spectrum changes into a new one during the first 150 ns (Figure 1, curve b). The increase of absorbance near 330 nm is correlated with the decay of e⁻ and, at 150 ns, the optical density of e⁻ is about half its initial value.

When subtracting the decay of both X and Y bands, supposed to be identical with that of e⁻ in the same solution, the true evolution in time of the new species is obtained (insert of Figure 1), and its spectrum at 150 ns (Figure 1, curve c) is very close to that of NH₂⁺ (Figure 1, curve d).

The absorbance at 330 nm, measured 150 ns after the pulse, which corresponds to the maximum in time, is plotted vs. NaClO₄ concentration in Figure 2; above 10⁻⁴ M there is an appreciable increase in optical density, up to a plateau value reached for 10⁻³ M. The corresponding G(NH₂⁺) is then about 1.5, i.e., half the value of the initial Gₑ⁻ and exactly the same as the yield of e⁻ consumed within the same time. It is noteworthy that in these NaClO₄ solutions the risetime of NH₂⁺ absorbance is considerably shorter (150 ns) than that (~400 ns) deduced from homogeneous kinetics in Na solutions with kₑ⁻ = 3.5 × 10⁻¹⁰ M⁻¹ s⁻¹. This means that the spatial distribution of radiolytic species e⁻ and NH₂⁺ is still nonhomogeneous in this time range.

Beyond 150 ns, the decay of NH₂⁺ is assumed to be due to the recombination with NH₄⁺. If the concentration of the cation is deduced from charge balance, a second-order rate constant is estimated at (5 ± 1) × 10⁻¹⁰ M⁻¹ s⁻¹ close to the calculated diffusion-controlled rate constant (Table 1). This value is a factor of 40 larger than the corresponding value in Na solutions. The difference is discussed below in relation to the electrostatic interactions between ions.

The most important feature of the NaClO₄ effects lies, contrary to the results obtained in the pure medium, in the important yield of NH₂⁺ quite unexpected from classical ionic strength effects. Indeed such an influence of chemically inert electrolytes on the evolution of species has never been observed so far in radiolysis. It is therefore of interest to mention that the results of this work concern numerous solutions in separate runs.

We also reinvestigated solutions of NH₄ClO₄ at concentration up to 10⁻¹ M; no noticeable difference in spectrum and kinetics (markedly in the UV range) was observed with respect to the pure solvent, at least during the first microsecond.

Discussion

Neutralization Rate Constant Between NH₂⁻ and NH₄⁺. Reasons for the difference (Table 1) of kₜh₂⁻+nh₄⁺ in Na and NaClO₄ solutions must be found. First of all, the...
d) NH₃ spectrum at -50 °C, normalized at 330 nm. Insert shows the evolution of absorbance at 330 nm in NaCIO₄ solutions in liquid ammonia at -50 °C (NaCIO₄ ≈ 5 × 10⁻⁴ mol L⁻¹); (curve a) end-of-pulse spectrum; (curve b) spectrum 150 ns after the pulse (R(NH₃) = 2.3 × 10⁻⁴ mol L⁻¹; Δ [NaCIO₄] = 6.2 × 10⁻⁴ mol L⁻¹); (curve c) difference b - a/2; (curve d) NH₂ spectrum at -50 °C, normalized at 330 nm. Insert shows the evolution of absorbance at 330 nm in NaCIO₄ = 9.8 × 10⁻⁴ mol L⁻¹; (dashed curve) experimental result; (dotted curve) absorbance in pure solvent; (full curve) difference between the two preceding ones (see text).

decays from which the rate constants were determined are too slow to be still disturbed by nonhomogeneous distribution. Secondly, concentrations of Na and NaCIO₄ used are comparable and are in a such range that NH₃ is strongly paired with Na⁺ (Kₐ = 2.2 × 10⁻⁵ M at -33 °C), and probably reacts as a pair in both cases. The only possible difference therefore arises from the cation NH₄⁺. The CIO₄⁻ anion is probably less associated with cations than is e-am, the pairing of which with alkali cations is well known. In fact, if NH₄⁺ forms ion pairs with added e-am in Na solutions, their lifetime must be long according to the Smoluchowski-Debye equation assuming R(NH₃) = 1 A and R(NH₄⁺, Na⁺) = 4 A, respectively. b Reaction radius (sum of radii of reactants): R(e-am⁺, NH₄⁺) = 3.1 Å (from molar volume = 70 mL mol⁻¹); R(NH₃⁺) = 2.3 Å (Stokes-Einstein radius). c Diffusion-controlled rate constant at zero ionic strength, calculated according to the Smoluchowski-Debye equation (δ(NH₃) = 23.5 at -50 °C). d In metal-ammonia solutions ([Na⁺] = 3.2 × 10⁻⁴ M). e In NaCIO₄ solutions (=10⁻⁴ M). The value has been deduced from the Fig. 1 (inset, full line). The experimental error on k₁ includes any eventual formation of NH₃ slowly occurring in the 0.1-1 μs time range beyond the maximum observed.

Moreover the IR spectrum is not modified in the experiments where NH₄CIO₄ is added to ammonia, although the pair has already been formed by a diffusion-controlled process. This implies the identity of the spectra of e-am⁻ and (e-am⁺, NH₄⁺).

Reexamination of the Fundamental Processes in Pure Liquid Ammonia: Fate of the Solvated Electron. In contrast to solutions of electrolytes, the only ions present in irradiated neat ammonia are the species e-am⁻ and NH₄⁺. Concerning the formation and direct observation of NH₃ in this medium, it must be pointed out that the electron is strongly attracted by the cation.

The competition between the diffusion of e-am⁻ toward NH₄⁺ and the diffusion of e-am⁺ toward the neutral radical NH₂ is then in favor of the reaction

\[ e_{am}^- + NH_4^+ \rightarrow (e_{am}^+, NH_2^-) \]

(17)

This is true for both free and geminate ions since the secondary cation NH₄⁺ radical, resulting from an ion-molecule reaction, are closely spaced. Thus, the NH₂ radical, when reacting with e-am⁻, actually encounters the pair (e-am⁻, NH₄⁺) which has quite a low probability of disappearance by itself. In spurs, therefore, the diffusion of the electron toward the radical is assisted by the attractive field of the neighboring cation. The subsequent reaction of NH₂ with NH₄⁺ is then so fast that a stationary NH₂ concentration is never observed, even at long times, when spurs have diffused (at least at low temperatures):

\[ NH_2^- + (e_{am}^-, NH_4^+) \rightarrow (NH_2^-, NH_4^+) + 2NH \]

(18)

This qualitative interpretation is also consistent with temperature effects in pure NH₃. We observed that the decay of absorption at the maximum of the NH₂ spectrum near 340 nm is slowed down by raising the temperature from -50 to 0 °C. Perkey and Farhataziz observed at 23 °C a slight increase in the absorption near 380 nm which lasts 60 ns. These features may be attributed to a small NH₂ concentration, indicating a slowing down of the recombinetion NH₄⁺, NH₂^- with raising temperature; a possible explanation would be that ion pairing is weakened under such conditions. This interpretation is consistent with NH₄CIO₄ results as well; the presence of the NH₂⁻ ion can only enhance the formation of the pair (e-am⁻, NH₂⁻) in a first step according to (17); then, due to mechanism 18, NH₂⁻ is not observed as a transient.

Mechanism 18 proposed above (e₋-radical reaction in the vicinity of the cation) to explain the lack of NH₂⁻ observation in the pure solvent is the only one which can explain the influence of NaCIO₄. The effect of added electrolyte consists essentially in perturbing the specific attraction between the charges of the geminate pair. This screening effect makes the probability of encounter of e-am⁻ with NH₂⁻ or NH₂ possible so that the electron en-

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**TABLE I: Rate Constants in Liquid Ammonia at -50 °C**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(D_{am}^c \text{ cm}^2 \text{s}^{-1})</th>
<th>(k_{dift}^c \text{ L mol}^{-1} \text{ s}^{-1})</th>
<th>(k_{obs}^c \text{ L mol}^{-1} \text{ s}^{-1})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e_{am}^- + NH_4^+)</td>
<td>1.7 × 10⁻⁴</td>
<td>4.45 × 10⁻⁵</td>
<td>10⁴</td>
<td>11-12</td>
</tr>
<tr>
<td>(e_{am}^- + NH_3)</td>
<td>2.0 × 10⁻⁴</td>
<td>6.2 × 10⁻⁵</td>
<td>3.5 × 10⁻⁴</td>
<td>1</td>
</tr>
<tr>
<td>((NH_2^+, Na^+) + NH_2^- d)</td>
<td>4.5 × 10⁻⁴</td>
<td>7.0 × 10⁻⁵</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>((NH_3^+, Na^+))</td>
<td>3.8 × 10⁻⁴</td>
<td>1.7 × 10⁻⁴</td>
<td>(6 to 1) × 10⁻⁴</td>
<td>This work</td>
</tr>
</tbody>
</table>

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**Figure 1.** Transient absorption spectra in NaCIO₄ solutions in liquid ammonia at -50 °C ([NaCIO₄] ≥ 5 × 10⁻⁴ mol L⁻¹): (curve a) end-of-pulse spectrum; (curve b) spectrum 150 ns after the pulse (\(\text{[NaCIO}_4\text{]} = 2.2 \times 10^{-4} \text{ mol L}^{-1}\); \(\Delta \text{[NaCIO}_4\text{]} = 6.2 \times 10^{-4} \text{ mol L}^{-1}\)); (curve c) difference b - a/2; (curve d) NH₂ spectrum at -50 °C, normalized at 330 nm. Insert shows the evolution of absorbance at 330 nm in NaCIO₄ = 9.8 × 10⁻⁴ mol L⁻¹; (dashed curve) experimental result; (dotted curve) absorbance in pure solvent; (full curve) difference between the two preceding ones (see text).
counters either the cation to form the long-lived pair $e_{\text{em}}$-$\text{NH}_4^+$ as in the pure medium, or the radical to form NH$_4^-$ outside the range of the NH$_4^+$ interaction (reaction 3).

Because of this, the amide ion is observed during its relaxation time is very short as in water. In this respect, we can obtain the most probable distance $\rho(r)$ between an electron and the nearest neighbor ion:

$$\rho(r) \, \text{dr} = 4\pi r^2 n \exp(4\pi r^3/3)$$ (19)

The parameter $n$ is the total number of ions per unit volume supposed randomly distributed. From relation 18, we can obtain the most probable distance $\bar{r}$ between an electron and the nearest neighbor ion:

$$\bar{r} = (2\pi n)^{-1/3}$$ (20)

Now, if we insert the concentration of NaClO$_4$ corresponding to half the maximum effect (Figure 2), i.e., $2 \times 10^{-4}$ M, we find $\bar{r} \approx 85$ Å. This value may be considered as an estimate of the mean distance between NH$_4^+$ and $e_{\text{em}}$ in liquid ammonia at $-50$ °C. It is much higher than corresponding distances in water.$^{21-23}$ In this respect, ammonia resembles alcohols$^{22}$ or hydrocarbons$^{24}$ although the relaxation time is very short as in water.

With regard to the formation of a long-lived pair ($e_{\text{em}}$-$\text{NH}_4^+$), it would be of interest to reexamine some mechanisms for which a species such as NH$_4$ was invoked to account for certain anomalous results.$^{25,26}$ A pair, stoichiometrically equivalent and with spectral properties near those of the isolated electron, could be a more likely transient.

In conclusion, in an irradiated liquid which has a low dielectric constant and where the main reaction of disappearance of $e_{\text{em}}$ is that with the parent radical as in ammonia, the perturbations introduced by the addition of a chemically inert electrolyte are observed through the formation of the resulting anion; the probability of first encounter by diffusion of the electron is in favor of the cation in the pure solvent, but becomes the same for the radical as for the cation in the presence of the electrolyte. This makes possible the observation of the anion as a distinct step.

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References and Notes