Supplementary Information

Static and Dynamic Scavenging of Ammoniated Electrons by Nitromethane

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Diagram of the high-pressure optical cell

Figure S1. High-pressure optical cell: B1, cell cap; B2 cell body (magnetic stirrer housing graved inside, not shown); G, gold seals; W, sapphire windows; S, spacer (radial holes allow fluid access); A, centring piece.

Diagram of the fluid handling equipment

Figure S2. High-pressure ancillary fluid handling equipment: (a) load, (b) injection. L, six-port low-dead-volume valve with a 10 μL sampling loop; C, high-pressure optical cell; R, 3 cm³ stainless steel auxiliary reservoir; B, stainless steel bottle with the nitromethane-ammonia mother solution; V, access port to the vacuum line; P, purge; T, access to high-pressure syringe pump filled with liquid ammonia and pressure transducer. Needle valves are represented by circles (in blue, open; in red, closed).
Electron distribution along the pathlength of the cell

The transient electron concentration decreases along the position $x$ of the optical path following the intensity drop of the UV light. For a given delay $\tau$, the transient electron concentration is: $c_{el}(x, \tau) = c_{el}(x = 0, \tau) I(x)/I_0$, where $I(x) = I_0 \times 10^{-\varepsilon_{CTTS}\text{KI}x}$, being $\varepsilon_{CTTS}$ the molar extinction coefficient of the iodide’s first CTTS band in liquid ammonia, and $c_{\text{KI}}$ the KI concentration. We used for $\varepsilon_{CTTS}$ the value $1.11 \times 10^4$ M$^{-1}$·cm$^{-1}$, which we determined carefully in a former stationary experiment. Finally, the transient electron concentration profile can be related with the measured solution transient absorbance by the expression: $\Delta A(\tau) = \varepsilon_{el} \int c_{el}(x, \tau)dx$, $x: 0 \rightarrow b$, where $\varepsilon_{el}$ represents the molar extinction of the solvated electron in liquid ammonia. We used for $\varepsilon_{el}$ the value $4.5 \times 10^4$ M$^{-1}$·cm$^{-1}$, which was measured by Quinn and Lagowski on ammoniated electrons produced by electrolitically-generated K-NH$_3$ solutions, at a wavelength of 1443 nm, and in presence of KI 0.1M.

In our experimental conditions, transient electron concentrations at the position of the front window were in the range of 2-5 mM, decreasing rapidly into the $\mu$m range when $x$ is $\sim 30 \mu$m. The mean electron concentration, $\bar{c}_{el}(\tau) = 1/b \int c_{el}(x, \tau)dx$, $x: 0 \rightarrow b$, can be related with the measured transient absorbance as: $\Delta A(\tau) = \bar{c}_{el}(\tau)\varepsilon_{el}b$.

Figure S3. Concentration of electrons along the optical cell’s pathlength, $x$. 
References