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The photochemistry of $[\text{Fe}^{\text{III}}\text{N}_3(\text{cyclam-ac})]\text{PF}_6$ at 266 nm

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1. Kinetic analysis of the step-scan FTIR spectra

A kinetic analysis of the step-scan FTIR spectra provides additional important insights into the thermal reactions accompanying the photolysis of **1**. Firstly, the normalized optical density of the 2006 cm^{-1} azide anion band is calculated according to $\Delta\text{OD}_{\text{norm}}(t) = [\Delta\text{OD}(t) - \Delta\text{OD}(\infty)] / [\Delta\text{OD}(0) - \Delta\text{OD}(\infty)]$, where $\Delta\text{OD}(0)$ and $\Delta\text{OD}(\infty)$ are the pump-induced optical densities at the earliest and the latest time delays of the step-scan experiment, i.e. at 500 ns and at 800 μs , respectively. Secondly, a similar normalized optical density is calculated at a frequency of 1638 cm^{-1} representing for the low-frequency components of the broad induced absorption seen in Figure 6. In Figure S1, this normalized rise of the 1638 cm^{-1} induced absorption is compared to the complement, $1 - \Delta\text{OD}_{\text{norm}}(t)$, of the asymmetric azide anion stretching band. It can be seen that during the first 200 μs , these two kinetic profiles nicely match. This indicates that the kinetics of these two spectral features are correlated and more precisely, that the 1638 cm^{-1} feature builds up at the expense of the azide absorption. In other words, a molecular species carrying an absorption at 1638 cm^{-1} is formed through a reaction in which azide anions are consumed.

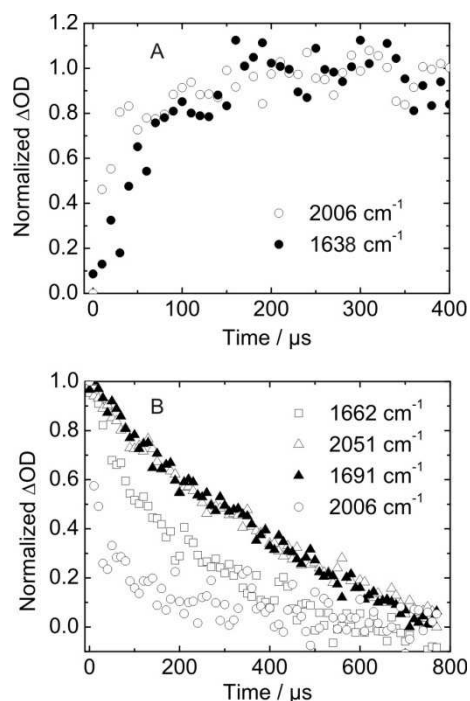


Figure S1. Normalized kinetic profiles recorded in step-scan experiments on Ar-saturated solutions of **1** in acetonitrile. A: Open circles represent the azide anion decay at 2006 cm^{-1} presented as a rise and closed circles illustrate the induced absorption rise recorded at 1638 cm^{-1} . B: Open squares and open circles illustrate normalized absorptions profiles recorded

at 1660 cm^{-1} and 2006 cm^{-1} , respectively. Open and closed triangles represent of the decay of the bleach of $[\mathbf{1}]\text{PF}_6$ at 2051 cm^{-1} and 1689 cm^{-1} , respectively.

All spectro-temporal traces measured in step-scan mode on Ar-saturated solutions of **1** in acetonitrile follow kinetics that are more complicated than simple first-order. This implies that secondary reactions of the primary photoproducts of **1** in the nanosecond-to-microsecond domain are bimolecular in nature. Figure S1B shows normalized profiles of the induced bleach recoveries of the parent's azido stretch (2051 cm^{-1}) and the parent's acetate-CO-stretch (1689 cm^{-1}). Their recoveries match nicely and occur on a time scale of hundreds microseconds. The high-frequency components of the induced absorption feature (i.e. at 1660 cm^{-1}) seen in Figure 6 decays significantly faster with a half-life of about $100\text{ }\mu\text{s}$. It is very likely that this feature is due to the azide radical whose asymmetric stretch was located at 1658 cm^{-1} in a cryogenic nitrogen matrix.^[14] Finally, the decay of the asymmetric stretching vibration of the azide anion at 2006 cm^{-1} shows the fastest kinetics and - as discussed in the text - matches the early time rise of the low-frequency components of the induced absorption feature (i.e. at 1638 cm^{-1}) shown in Figure S1A.

2. Step-scan FTIR spectra of **1** with excess azide

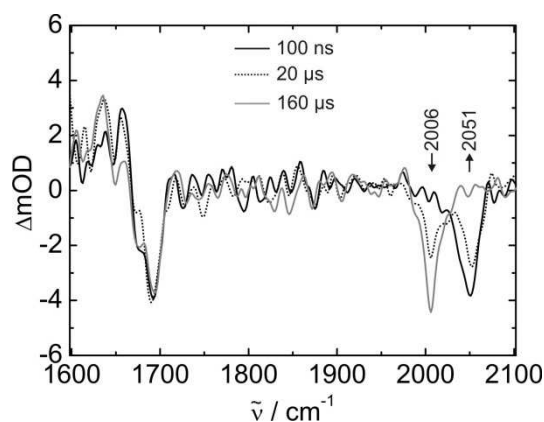
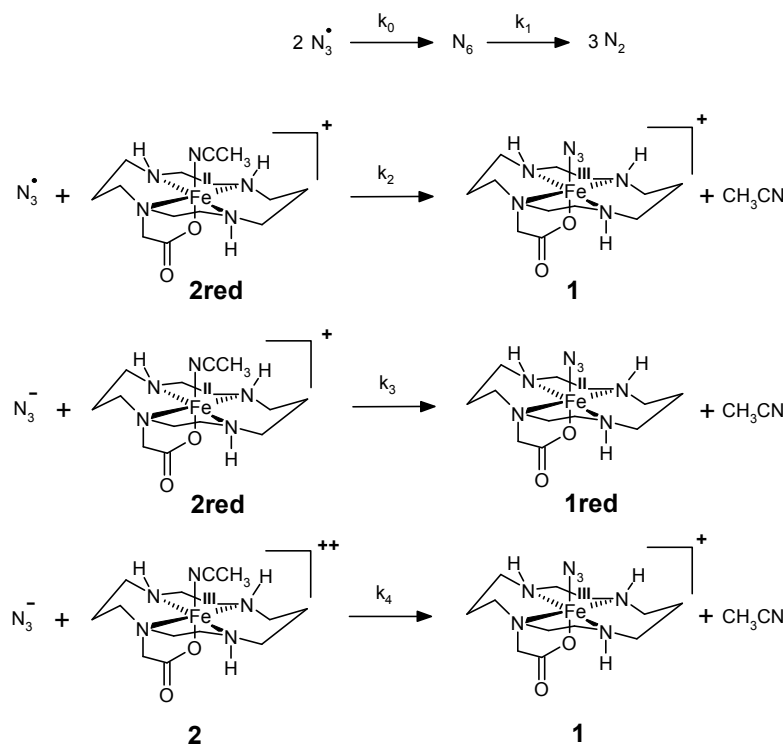


Figure S2. Step-scan time-resolved FTIR spectra recorded 100 ns (black-solid line), 20 μs (dot line), and 160 μs (grey line) after the 266-nm laser pulse in an argon saturated solution of [(cyclam-ac)FeN₃]PF₆ (0.85 mmol/L) with added tetrabutylammonium azide (0.85 mmol/L) in acetonitrile.

The step-scan spectra on Ar-purged solutions of complex **1** in the presence of an excess of azide anion demonstrate, that immediately after 266 nm-illumination, the asymmetric stretching band of the azide anion is not bleached. This is an unequivocal evidence for a negligible direct photolysis of the azide ions. Only after several microsecond can an azide bleach be detected, which indicates that the ions are consumed through a thermal chemical reaction, presumably with **2red** under formation of **1red**.

3. Kinetic model simulations

To simulate the time-resolved infrared data obtained from the photolysis experiments on **1** in Ar-purged solutions, the reaction mechanism shown in Scheme S1 was employed. This sequence of elementary reactions constitutes the simplest reaction mechanism that can be constructed to account for all the experimental observations we have presented in this paper. It was assumed that the azide radical, the azide anion and the iron complexes **2** and **2red** are generated instantly with the photolysis laser pulse. Azide radicals can decompose into dinitrogen via self-quenching involving two consecutive elementary reactions with an intermediate formation of the presumed N_6 . Since N_6 was never observed in our experiments, this pathway is controlled by the initial bimolecular encounter of two azide radicals. Azide radicals can furthermore react with **2red** to recover the parent while the azide anions are allowed to react with **2** and **2red** in two parallel bimolecular reactions. The time-dependent concentrations of all the species (N_6 and N_2 excluded) involved in this reaction scheme are given by the following system of coupled differential equations, which are integrated numerically using a fourth-order Runge-Kutta method embedded in a non-linear least-squares fitting routine based on the Levenberg-Marquardt algorithm.



Scheme S1. Kinetic scheme invoked for the simulating the photolysis of **1** in Argon-purged acetonitrile solutions

$$\frac{d[N_3]}{dt} = -2k_0[N_3]^2 - k_2[N_3][2red]$$

$$\frac{d[2red]}{dt} = -k_2[N_3][2red] - k_3[N_3^-][2red]$$

$$\frac{d[N_3^-]}{dt} = -k_3[N_3^-][2red] - k_4[N_3^-][2]$$

$$\frac{d[1]}{dt} = k_2[N_3][2red] + k_4[N_3^-][2]$$

$$\frac{d[2]}{dt} = -k_4[N_3^-][2]$$

$$\frac{d[1red]}{dt} = k_3[N_3^-][2red]$$

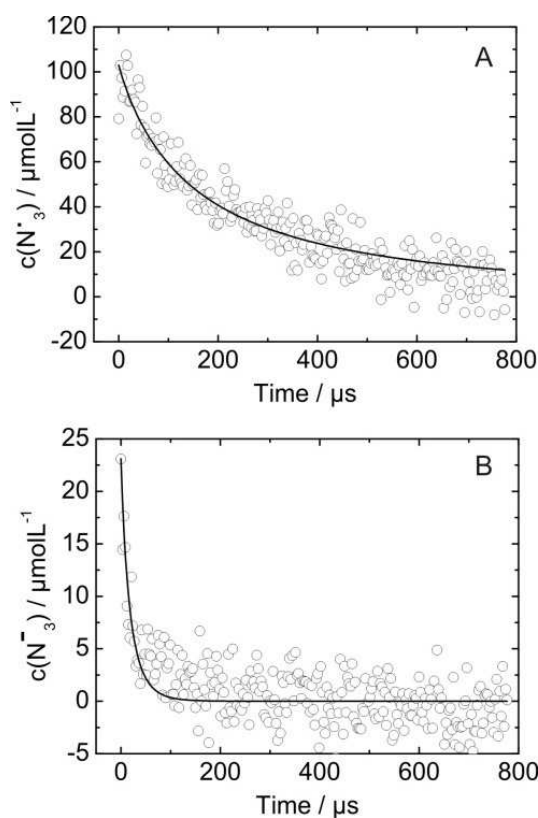


Figure S3. Concentrations-time traces for the azide radical (A), and the azide anion(B). The experimental data are shown as open symbols and the simulation is given by the solid curves.

The concentration-times traces representative for the azide radical, the azide anion and the parent complex **1** were simulated simultaneously using the rate constants k_0 , k_2 , k_3 , and k_4 as global fitting parameters. The obtained rate constants are collected in Table S1 and the fitting results for the azide radical and azide anion concentrations are shown in Figure S3.

Table S1. Rates constants k_i , (see Scheme 6) evaluated from experimental kinetic data. Standard deviations are indicated within the parentheses

i	$k_i / \text{Lmol}^{-1}\text{s}^{-1}$
0	$1.6(0.1) \times 10^7$
2	$4.2(0.6) \times 10^7$
3	$5.4(1.4) \times 10^8$
4	$1.4(2.4) \times 10^8$

The agreement between experiment and simulation is satisfactory. Unfortunately, our inability to observe bands connected with **2** and the fact that absorptions of **2red** and **1red** are strongly overlapping the obtained rate constants have to be accepted with caution. If one omits the last step in the reaction mechanism and reduces the number of floating parameters similar values for k_0 , k_2 , and k_3 are obtained. Although, these we cannot compare these values with literature data, it seems that all rate constants are well below the diffusion limit ($k_{\text{diff}} = 1.9 \times 10^{10} \text{ Lmol}^{-1}\text{s}^{-1}$) at room temperature with acetonitrile as solvent.^[19, 33] This suggests that these reactions are thermally activated over a barrier. Notice, that k_4 is smaller than k_3 , which probably reflects a stronger iron-nitrogen bond in the iron(III) complex **2** as compared to the iron(II) complex **2red**. Notice also that k_3 is about 10 times larger than k_2 , which might reflect a higher reactivity of the good electron donor, N_3^- , with regard to ligand exchange in this system as compared to the azide radical.