

Nitrosation of N-Methylhydroxylamine by Nitroprusside. A Kinetic and Mechanistic Study

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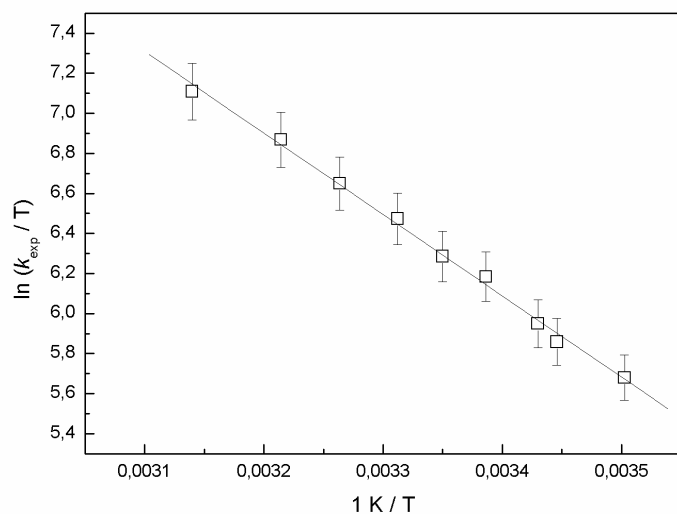
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Figure 1. ESR spectrum of the $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ radical, formed through cyanide labilization of $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ intermediate, in aqueous solution, room temperature, pH 9.3, 25 mM SNP, 20 mM MeHA, 200 mM isonicotinamide. $a_{\text{N}}(\text{NO}) = 1.47$ mT and $g = 2.0293$ vs tempo.



Figure 2. Eyring plot of the average rate constants, k_{exp} , at various temperatures. 25 mM MeHA; 0.2 mM SNP; 100 mM isonicotinamide; pH 8.0, $I = 1$ M (NaCl).^a



T, K	$10^5 k_{\text{exp}}, \text{M}^{-2}\text{s}^{-1}$
285.5	0.84 ± 0.01
290.2	1.0 ± 0.1
291.5	1.1 ± 0.1
295.3	1.4 ± 0.2
298.2	1.6 ± 0.2
301.9	2.0 ± 0.3
306.4	2.4 ± 0.3
311.1	3.0 ± 0.3
318.5	3.9 ± 0.4

^a Triplicate runs were averaged for each entry. The concentration of OH^- was computed from the pH, with $K_w = 1.0 \times 10^{-14}$