

Spin trapping of nitric oxide by *aci*-nitroalkanes

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Nitric oxide ($\dot{\text{NO}}$) is an important environmental and biological transient involved in numerous physiological processes. $\dot{\text{NO}}$ is a free radical but its successful trapping to afford EPR detection is a difficult task. We reported that $\dot{\text{NO}}$ adds to the *aci* anion of nitromethane, $\text{CH}_2=\text{NO}_2^-$, affording a spin adduct, $[\text{CH}(\text{NO})(\text{NO}_2)]^{2-}$, readily detectable with EPR (1). In the present work we extend these studies to include related nitroalkanes ($\text{CH}_3\text{CH}_2\text{NO}_2$, $\text{CH}_3(\text{CH}_2)_2\text{NO}_2$, $\text{CH}_3(\text{CH}_2)_3\text{NO}_2$, $\text{HC}(\text{CH}_3)_2\text{NO}_2$) in order to determine their suitability to trap $\dot{\text{NO}}$ in aqueous solutions, and to characterize EPR spectra of the resulting adducts. In 0.5 M NaOH all nitroalkanes, except 2-nitropropane, produced persistent EPR spectra of $\dot{\text{NO}}$ adducts with couplings to the nitrogen of the nitro group ($a_{\text{N}}^{\text{nitro}} = 12.45 \text{ G}$) and to the nitrogen from $\dot{\text{NO}}$ ($a_{\text{N}}^{\text{NO}} = 5.96\text{-}6.02 \text{ G}$). Additional couplings originating from interaction of the unpaired electron with hydrogen atoms on β - (and γ -) carbons were also resolved. Identification of the species was further verified by using ^{15}N -labeled $\dot{\text{NO}}$ and a NaOD solution ($\sim 0.5\text{M}$). The high stability of the spectra observed in 0.5M NaOH may be explained by dissociation of β -H in the primary spin adduct, $\text{RCH}(\text{NO})\text{NO}_2^-$, to give a dianionic radical, $\text{RC}(\text{NO}^-)\text{NO}_2^-$. In buffered solutions (pH 10-12) the dissociation does not occur and the adducts exist primarily in the form of monoanion radicals, as evident by EPR couplings. This study provides an extensive EPR characterization of the adducts of $\dot{\text{NO}}$ to *aci*-nitroalkanes, which may be useful for the development of $\dot{\text{NO}}$ spin traps for biological applications.

[1] Reszka, K.J. Bilski, P. and Chignell. C.F.. J. Am. Chem. Soc., 116, 4119, 1994