Electron Spin Resonance Study of the Ionization of the Acetylaminyl Radical in Aqueous Solution

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Summary At pH 5·0 the acetylaminyl radical $\text{MeC=O}\dot{\text{N}}\text{H}$ is rapidly converted into the tautomeric imino-form $\text{MeC(OH)=N}\cdot$, while at pH 8·0 only the intermediate anion $\text{MeC(O}^-\text{)=N}\cdot$ is observed.

INTEREST in the aqueous chemistry of acylaminyl radicals, $\text{RCO}\dot{\text{N}}\text{H}$, stems from their potential significance in biological systems, and from the theoretical problem of their electronic structure and stability.[1,2] Using the e.s.r. flow technique we have examined the reduction of *N*-bromoacetamide by the $\text{CO}_2^{\cdot-}$ anion (equation 1). Oxidation of formate ion with titanium(III) complex of ethylenediaminetetra-acetic acid and hydrogen peroxide in aqueous solution is the initiating reaction.[3] The sensitive *N*-halogenoamide

$$\text{MeCONHBr} + \text{CO}_2\cdot \rightarrow \text{MeCO}\dot{\text{N}}\text{H} + \text{CO}_2 + \text{Br}^- \qquad (1)$$

must be added in a separate reactant solution employing a three-stream simultaneous mixing approach.

At pH 8·0 we observe an intense e.s.r. signal [$a_\text{N}(1)$ 1·10 ± 0·01 mT, $a_\text{H}(3)$ 0·24 mT, g 2·0034 ± 0·0001] assigned to the ionised acetylaminyl radical $\text{MeC(O}^-\text{)=N}\cdot$. At pH 5·0 a second spectrum is recorded having $a_\text{N}(1)$ 1·05 mT, $a_\text{H}(4)$ 0·15 mT, and g 2·0032. The multiplets have 1 : 4 : 6 : 4 : 1 intensity distribution. We assign the spectrum to the $\text{MeC(OH)=N}\cdot$ species with equivalence of the OH and Me hyperfine splitting constants at the resolution achieved. In neither experiment were any other resonances detected at high gain.

It is proposed that the initially formed acetylaminyl radical is deprotonated and preferentially reprotonated at oxygen in the pH 5·0 experiment (equation 2).

$$\text{MeC(OH)=N}\cdot \rightleftharpoons \text{MeC(O}^-\text{)=N}\cdot \rightleftharpoons \text{MeC=O}\dot{\text{N}}\text{H} \qquad (2)$$

In the steady state population of radicals under observation, the very rapid proton transfers that are involved may effectively establish the indicated tautomeric equilibration during the average radical lifetime. However, kinetically controlled reprotonation of the anion at oxygen would also be anticipated for a species with distinct σ radical character. Efficient conversion of the initially formed acylaminyl radical into the tautomeric hydroxyimino form is demonstrated. These results are in agreement with a previous study on OH addition to HCN.[2]

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