5,5-Dimethylpyrroline *N*-oxide: A Trap for the Unwary

By ANTHONY T. BULLOCK,* DAVID L. GAVIN, and MALCOLM D. INGRAM
(*Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland* AB9 2UE)

Summary The nitroxides formed by radical addition to the spin trap 5,5-dimethylpyrroline *N*-oxide are extensively dimerized in aqueous solution and this constitutes a serious limitation to the use of the trap in quantitative studies of radical production.

THE spin trap 5,5-dimethylpyrroline *N*-oxide (DMPO) is finding increasing usage in the detection of free radicals generated in aqueous solution. As examples, •OH and HO_2• radicals have been trapped in photolysed aqueous solutions of H_2O_2[1] whilst e^-_{aq}, H• and •OH have all been trapped in water irradiated with 3 MeV electrons.[2] We have used DMPO to demonstrate the generation of H• and •OH radicals in the glow discharge electrolysis of aqueous solutions.[3] The purpose of this communication is to point out that the use of DMPO in quantitative studies is severely limited by the fact that nitroxides resulting from radical addition to the trap are extensively dimerized.

The main evidence is found in the variation of e.s.r. signal strength (I) with temperature for the hydrogen atom adduct (Figure). The temperature dependence is almost completely reversible, deviations being attributable to the decay of radicals with time during successive heating and cooling cycles. (The instability of the radicals limited the number of observations for each heating and cooling cycle to four).

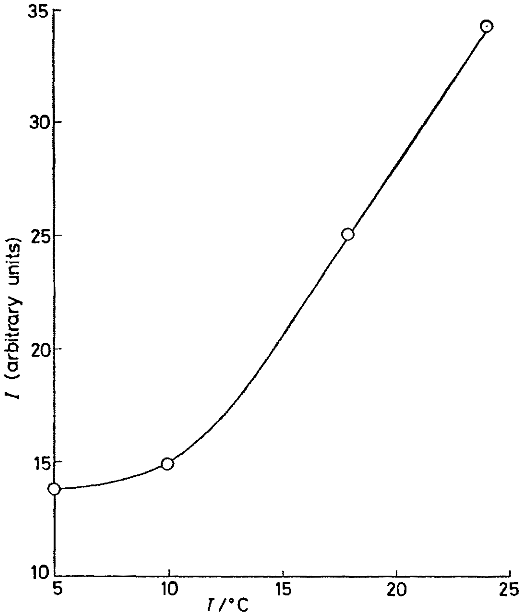

FIGURE. The temperature dependence of the e.s.r. signal intensity (I) for the hydrogen atom adduct to DMPO in aqueous solution.

The hydroxyl radical adduct shows much the same behaviour, *viz*, a 2–3 fold increase in signal intensity as the temperature is raised from 5 to 24 °C.

Steric hindrance to dimerization is expected to increase as the size of the adduct radical increases. Thus, the nitroxides produced by reaction of DMPO with $\cdot CH_2OH$ and $Me_2\dot{C}OH$ (formed by reaction of $\cdot OH$ with the alkanols during glow discharge electrolysis) indeed do show considerably smaller signal intensity variations with temperature than do the $\cdot H$ and $\cdot OH$ adducts. However, the increases are still substantial, being 40 and 48% for $\cdot CH_2OH$ and $Me_2\dot{C}OH$, respectively, as the temperature is raised from 5 to 24 °C.

It is possible to estimate ΔH for the dissociation of the dimer. If attention is confined to the initial portion of the curve shown in the Figure, the degree of dissociation of the dimer is small and a plot of $\ln I$ *vs.* $1/T$ has a slope of $-\Delta H/2R$. A value of 50 ± 7 kJ mol^{-1} was obtained and may be compared with the value of 54 kJ mol^{-1} found for dissociation of the dimer of tetraphenylpyrrol-1-oxyl in CH_2Cl_2 solution.[4]

A further complication arises when using DMPO as a spin trap in aqueous solution and has its origin partly in the sensitive dependence of radical concentration upon temperature, discussed above, and partly on microwave heating effects. These are due to non-resonant dielectric absorption by the water molecules. At an incident microwave power of 40 mW, they are sufficient to cause the hydrogen adduct signal intensity to rise by 50% before levelling off after 3 min.

Despite the reservations implicit in this note, DMPO is still an extremely useful spin trap for use in aqueous solutions. An attempt is presently being made to obtain more quantitative data on the dimerization of various radical adducts with the trap.

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