

It is possible that species involving more than one peroxo ligand are (also) formed. The proposed species $O_3W(O_2)^{2-}$ corresponds to "O" in Scheme 1.

Radical spin trapping

Direct detection of radicals (by ESR) is usually extremely difficult because most are highly reactive and (often) present in low concentrations. As a result indirect methods must be utilized to obtain evidence for their presence and structure. There are two common indirect methods. The first is CIDNP⁴ (chemically induced dynamic nuclear polarization), which is an NMR technique in which resonances for radical species may be observed because the intensities of their resonances are much greater than expected for the concentration of the species present. This results from preferential polarization of nuclear spins by unpaired electron spins. Because these polarizations may be positive or negative the anomalously intense resonances may reflect absorption or emission. The second technique is spin trapping.⁵ Spin trapping reagents react with radicals to give a long-lived (persistent) radical which can be detected by ESR. The structure of the trapped radical is inferred on the basis of electron spin-nuclear spin coupling (hyperfine coupling) patterns in the persistent radical and/or by independent synthesis.

To successfully trap a highly reactive radical requires that the spin trap have a high rate of reaction (low activation energy) toward radicals, but not with other reaction components⁶ and that the product be sufficiently long-lived under reaction conditions for detection. It is usually necessary to use a large concentration of the trapping reagent to generate enough product for detection. Nitrones are efficient radical traps, but are otherwise relatively unreactive both chemically and photochemically. Certain derivatives, including **2**, have been used for in vivo biological applications.

In this experiment you will utilize **2** to trap a radical generated from a common initiator for radical polymerizations and detect the persistent nitroxide radical product by ESR.

Experimental

N-Benzylidene-tert-butylamine N-Oxide (2). In a 50-mL flask equipped with a stirring bar place *N-tert-butyl* benzylamine (5 mmol), $Na_2WO_4 \cdot 2H_2O$ (0.066 g, 0.20 mmol), and methanol (10 mL). Cool the solution in an ice bath and add to the stirred solution 30% aqueous hydrogen peroxide (1.70 g, 15.0 mmol). After addition is complete, remove the ice bath and stir the reaction mixture for at least one h, then stopper the flask and let it stand unstirred until the next lab period. Remove the methanol using a rotary evaporator and then transfer the residue to a separatory funnel using 25 mL of methylene chloride. Wash the methylene chloride solution twice with 10 mL portions of saturated aqueous sodium chloride, then dry the methylene chloride solution over anhydrous sodium sulfate. Remove the drying agent by filtration and evaporate the methylene chloride on a steam bath. The residue should crystallize upon cooling. The product should be recrystallized from a small amount of hexane. Collect the purified product by filtration and air dry the product. Obtain a melting point and ¹H NMR spectrum of

your purified product.

Trapping a radical using nitrone 2. Place 10 mg of nitrone and 15 mg of benzoyl peroxide, or 10 mg of 2,2'-azobisisobutyronitrile in a vial. Add 1 mL of benzene and then carefully sparge the solution with nitrogen for 2-3 min. Transfer about 0.5 mL of the solution to a serum-capped, nitrogen-flushed ESR sample tube. Heat the sample tube in a 60-70 °C water bath for about 5 min and immediately obtain the ESR spectrum.

Calculate the *g* value and hyperfine coupling constants for your spectrum. For information about ESR spectroscopy see reference 1. In preparing your report you should be careful to provide the structure of the radical whose spectrum you have recorded and to compare your results with a literature spectrum (give the literature reference to the data that you cite).

References and footnotes

(1) ESR is the equivalent of NMR for electrons. A physical model for the phenomenon is a spin flip of the electron in the magnetic field under resonance conditions. Electron spin-nuclear spin coupling occurs (hyperfine coupling) which provides structural information. A satisfactory introduction to the fundamentals to ESR spectral interpretation can be found in Atkins, P. *Physical Chemistry*, 6th Ed, W.H. Freeman, New York, NY, **1997**, Chapter 18, sections 10-11

(2) Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1997**, 70, 877.

(3) Espenson, J.H. *Chem. Commun.* **1999**, 479 and references cited.

(4) For an explanation of CIDNP see Pine, S.H. *J. Chem. Ed.* **1972**, 49, 664. Ward, H.R. *Acc. Chem Res.* **1972**, 5, 18. Lawler, R.G. *Acc. Chem. Res.* **1972**, 5, 25.

(5) A lucid article on this topic is Janzen, E.G. *Acc. Chem. Res.* **1971**, 4, 31.

(6) This includes electromagnetic radiation since many radicals are generated by photolysis.