tion.[26,27] We hope to determine the extent of nonvertical acceleration in *exo*-norbornyl tosylate solvolysis by studying the ionization potentials of the appropriate structures.

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A Novel Vanadyl Pyrophosphate Trimer

Sir:

We wish to report the observation by esr spectroscopy and the preliminary characterization of a unique vanadium(IV) species: an anionic vanadyl pyrophosphate trimer.

The pH titration of a solution 0.02 *M* in $VO(ClO_4)_2$, 0.02 *M* in $Na_4P_2O_7$, 0.4 *M* in $NaClO_4$, and initially containing an excess of perchloric acid shows a sharp break at the point where all of the added acid has been titrated; see Figure 1. Thus, at the equivalence point, there are no protons remaining on pyrophosphate ions and all the pyrophosphates are bound in the complex. The esr spectrum at pH 1 shows the characteristic eight-line hyperfine spectrum due to interaction of the unpaired electron with the ^{51}V nucleus ($I = ^7/_2$), $a^V = 116$ G, $g = 1.965$, and is indistinguishable from that of the aquovanadyl ion. As base is added to the solution up to pH 2, the same eight-line spectrum persists. Above pH 2, the intensity of the original eight lines decreases and additional lines appear. To a first approximation, two new lines grow up between each pair of the original lines. At pH 5 the esr spectrum appears as in Figure 2. Twenty-two hyperfine lines are observed with intensity ratios very close to the expected ratios (1:3:6:10:15:21:28:36:42:46:48:48:46:42:. . .) for the interaction of an unpaired electron with three equivalent vanadium nuclei. The hyperfine splitting constant is 37 G, approximately one-third the usual splitting for monomeric vanadyl complexes; the *g* value is 1.964, very nearly the same as in the case of the aquo ion. As the titration is continued beyond pH 6, the 22-line spectrum decreases in intensity as a new eight-line spectrum grows up until, at pH 9, the trimer spectrum is gone and only a monomer spectrum is present with $a^V = 106$ G, $g = 1.965$. Addition of further base causes a decrease in the intensity of the esr spectrum, and at or above pH 11, no esr signal can be detected. The equilibria responsible for the buffer regions of pH 7–8 and pH 9.5–10.5 are, from the stoichiometry: (1) disproportionation of the vanadyl trimer to a monomeric vanadyl pyrophosphate (1:2) complex and an anionic vanadium(IV) species, perhaps $V_4O_9^{2-}$

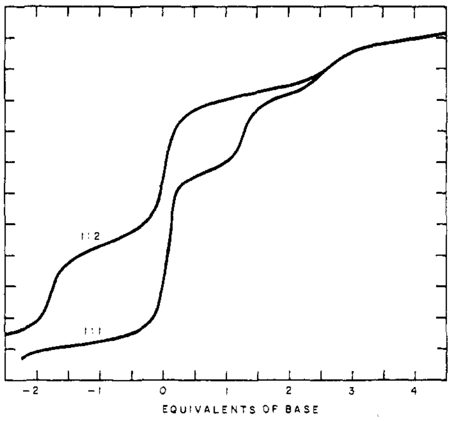

Figure 1. pH titration curve for the 1:1 and 1:2 VO^{2+}–$P_2O_7^{4-}$ solutions. Excess acid was added to the solutions to lower the initial pH to the desired value. The negative equivalents refer to the base needed to neutralize the excess acid added.

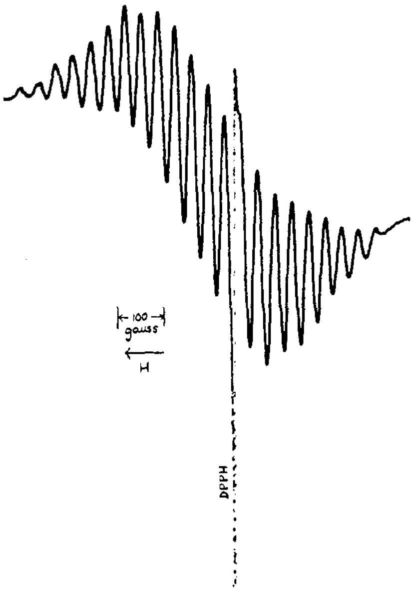

Figure 2. Esr spectra of $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$. The first derivative is plotted.

$$^1/_3(VO)_3(P_2O_7)_3^{6-} + {}^5/_4OH^- \rightleftharpoons {}^1/_2VO(P_2O_7)_2^{6-} + {}^1/_8V_4O_9^{2-} + {}^5/_8H_2O$$

and (2) base hydrolysis of the 2:1 complex to give $V_4O_9^{2-}$

$$^1/_2VO(P_2O_7)_2^{6-} + {}^5/_4OH^- \rightleftharpoons {}^1/_8V_4O_9^{2-} + {}^5/_8H_2O + P_2O_7^{4-}$$

The above interpretation is supported by the results of a pH titration and esr spectra of a solution 0.02 *M* in $VO(ClO_4)_2$ and 0.04 *M* in $Na_4P_2O_7$. The titration curve is shown in Figure 1. From the esr spectra, we find that the dominant species at the first break in the titration curve (pH 3.8) is the trimer mentioned above. In the buffer region, pH 4.5–6.5, the trimer is in equilibrium with the high-pH monomer ($a^V = 108$ G) which is dominant at the second break (pH 8). Again, between pH 9.5 and 10.5, the esr spectrum decreases in intensity and is gone at pH 11. Further support is given by the appearance of the characteristic brownish-yellow color of $V_4O_9^{2-}$ in the 1:2 solutions above pH 10. The 1:1 solutions turned brown beginning around pH 7.5.

Addition of ethanol to a solution containing $VO(ClO_4)_2$ and $Na_4P_2O_7$ (1:1) at pH 6 causes precipitation of a greenish-gray solid which we believe to be $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$. *Anal.* Calcd. for $Na_6(VO)_3(P_2O_7)_3 \cdot 18H_2O$: V, 12.8; P, 15.7; Na, 11.7; H, 3.0.

Found: V, 12.0; P, 14.9; Na, 12.1; H, 2.6. Esr of a solution of the solid gave the 22-line spectrum described above. The esr of a glycerol–water solution at −170° showed a complicated spectrum in the vicinity of $g = 2$, and a single strong feature at approximately 1650 G. The latter, which most likely corresponds to a $\Delta m_S = 2$ transition, and some preliminary magnetic susceptibility studies ($\mu_{\text{eff}} = 3.6$ BM) suggest that the trimer contains three unpaired electrons.

Since the solution esr spectrum at room temperature shows an uncomplicated 22-line pattern, the three unpaired electrons must be relatively strongly coupled so that the exchange term in the spin Hamiltonian

$$\sum_{i \neq j} J_{ij}\vec{S}_i \cdot \vec{S}_j$$

is large compared with the hyperfine terms. This situation is analogous to that observed for the vanadyl *dl*-tartrate dimer where the V–V distance is 4.08 Å. In the vanadyl *d*-tartrate dimer, the V–V distance is larger, 4.35 Å, and the exchange coupling is smaller, resulting in a much more complex spectrum.[1]

Since the three vanadium nuclei are magnetically equivalent and apparently in rather close proximity, a cyclic structure is suggested with each pyrophosphate acting as a bidentate ligand with each of two vanadyl ions. Further work on this and related systems is in progress.

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α-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone. A Novel Probe for Radical Detection and Identification

Sir:

The detection and identification of short-lived free radicals by electron spin resonance trapping techniques has recently received wide attention.[1-5] Janzen and coworkers[3-5] showed that nitrones (*e.g.*, phenyl-*tert*-butylnitrone) function as convenient probes for studying, in solution, the mechanisms of reactions which involve short-lived radical intermediates. Nitrones react with short-lived radicals to produce stable nitroxide radicals ("spin adducts").[6] The magnitude of the β-hydrogen and nitrogen hyperfine couplings (hfc) of the spin adduct define the structure of the trapped radical.

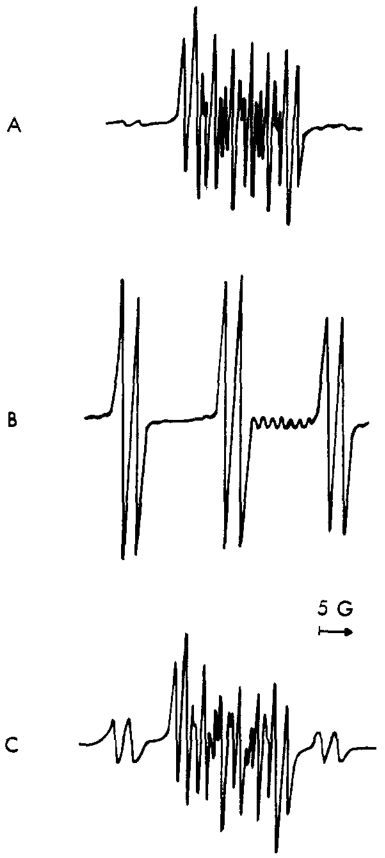

Figure 1. (A) The esr spectrum of II obtained by reaction of benzoyloxy radical from thermal decomposition of benzoyl peroxide in benzene at 70° with nitrone I. (B) The esr spectrum of the phenyl spin adduct of nitrone I obtained from phenyl radicals generated from the thermal decomposition of PAT at 70°. (C) The esr spectrum obtained from the thermal decomposition of benzoyl peroxide in benzene at 70° in the presence of nitrone I.

We report that α-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone[7] (I) serves as a novel probe for differentiation between oxy radicals and carbon radicals.[9] Some preliminary results with known radical sources are presented in Table I. The concentrations of the radical sources and the nitrone were *ca.* 0.01 and 0.1 *M* in benzene, respectively, except where otherwise noted. The samples were purged with dry nitrogen for several minutes prior to thermolysis or photolysis. The stable radicals produced were detected and identified by esr analysis of the reaction mixtures at room temperature.[10] The color changes, in initially colorless solutions, upon reaction of the nitrone and the short-lived species, gave a qualitative indication of the reaction course. Solutions in which only phenoxyl radicals

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(6) The term "spin adduct" designates the addition product of the reaction of the short-lived radical and the nitrone.[3-5]

(7) I was prepared in 92% yield by reaction of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (Aldrich Chemical Co., Inc.) with *N*-*tert*-butylhydroxylamine[8] in ethanol. The compound is a white, crystalline solid: mp 200° dec; ir ($CHCl_3$) 3640 cm^{-1} (s, OH); nmr ($CDCl_3$) 1.45 (s, 18 H), 1.58 (s, 9 H), 5.60 (s, 1 H), 7.40 (s, 1 H), and 8.17 ppm (s, 2 H). *Anal.* Calcd for $C_{19}H_{31}NO_2$: C, 74.71; H, 10.23; N, 4.58. Found: C, 74.57; H, 10.23; N, 4.55.

(8) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).

(9) The terms "oxy radical" and "carbon radical" refer to radicals in which the odd electron is primarily localized on an oxygen atom and on a carbon atom, respectively.

(10) The esr spectra were recorded in standard esr sample tubes with the Varian Associates V-4500-10 EPR spectrometer by using 100-kHz modulation at a frequency of about 9300 MHz.