Electron Spin Resonance Spectra of Oxyvanadium(V) Ions in Oxidation–Reduction Systems

Malkiat S. Bains,[1] Jett C. Arthur, Jr., and Oscar Hinojosa

Contribution from the Southern Regional Research Laboratory,[2] New Orleans, Louisiana 70119. *Received September 24, 1968*

Abstract: Interaction of free radicals, formed in Ce^{4+}–H_2O_2 and Fe^{2+}–H_2O_2 solutions, with oxyvanadium(V) ions generated an eight-line esr spectrum when recorded at low modulation amplitude. When recorded at high modulation amplitude, a doublet-like esr spectrum was obtained. The oxyvanadium(V)–free-radical complex in the Ce^{4+}–H_2O_2 system at 22° decayed with $k = -6.2$ sec^{-1} and $t_{1/2} = 0.1$ sec.

The esr detection and identification of the free-radical species in Ti^{3+}–H_2O_2 solution, using a flow–mix technique in the cavity of the esr spectrometer, were reported by Dixon and Norman.[3,4] Depending on the modulation amplitude and attenuation at which the spectrometer was operated, a singlet spectrum with a line width of about 2 G or a doublet spectrum with line widths of about 1 G each, spaced a few gauss apart, was obtained. The signal-generating species have been interpreted as $\cdot OH$, $HO_2\cdot$, and/or complexes of these radicals with Ti^{4+} ions.[3–14] Using the flow–mix technique, we have shown that Ti^{4+} ions and transition metal ions, such as Zr^{4+}, Hf^{4+}, Th^{4+}, and UO_2^{2+}, also form complexes with free radicals in Ce^{4+}–H_2O_2 and Fe^{2+}–H_2O_2 solutions and generate esr spectra.[5,6] Oxyvanadium(V) ions form an unstable complex with the free radicals generated in these redox systems. We are reporting the esr spectra and decay characteristics of these complexes.

Experimental Section

A Varian 4502-15 epr spectrometer system, operating at 100-kc field modulation and using an aqueous flow cell at 22°, was used. The flow rate of mixing was varied by pressurizing the two solution reservoirs with nitrogen (0.5 atm), by adjusting a clip on the exit line, and by measuring the rates of flow by meters inserted on the inlet sides of the mixing chamber to the aqueous cell.[3,6] The compositions of the solutions are shown in the legends for the figures.

In the kinetic studies, the flow-stop-flow technique was not applicable, since the constant of the instrumentation was relatively long as compared with the half-life of the radical complex. The half-life of the complex was calculated from the concentrations of the complex (as indicated by the intensities of the esr spectra) obtained under equilibrium conditions at different times after mixing of the solutions. The volume of the tubing from the point of mixing to the flattened portion of the aqueous flow cell in the resonant cavity was determined. From the rates of flow of the two solutions into the mixing chamber, the age of the mixed solutions, when they entered the flattened portion of the cell, was calculated. After equilibrium was reached, that is, the intensity of the esr spectrum became constant, the relative concentration of the oxyvanadium(V)–free-radical complex was determined. The rates of flow and mixing of the solutions were varied. From these types of data the rate of decay of the complex was estimated. In using this technique, it was assumed that the rate of formation of the radical complex was very rapid, as compared with the rate of decay of the radical complex.

Chemicals used were reagent grade; solutions were prepared with oxygen-free distilled water.

Spectra and Discussion

The esr spectrum, recorded on mixing equal volumes of solutions of ceric ammonium nitrate and of H_2O_2 containing NH_4VO_3 and recording at low modulation amplitude (80 units), is shown in Figure 1. If high modulation amplitude (800 units) was used, the esr spectrum recorded was similar to that shown in Figure 2. This spectrum appeared to be an intense doublet-like spectrum, without the fine structure generated on reduction of vanadium(V) to vanadium(IV). If Ce^{4+}, NH_4VO_3, or H_2O_2 was omitted from the solutions, no esr spectra with narrow line widths were generated.[15] If the concentration of Ce^{4+} was increased to greater than 0.003 M and the concentration of H_2O_2 was more than 0.1 M, an eight-line spectrum characteristic of vanadium(IV) was observed.

The esr spectra, generated on mixing equal volumes of solutions of ferrous ammonium sulfate (0.005 M) and of H_2O_2 (0.1 M) containing NH_4VO_3 (0.005 M) and recorded at different modulation amplitude, are shown in Figure 3. The doublet-like spectrum, recorded at high modulation amplitude (800 units, Figure 3B), apparently resulted from an averaging of the eight-line esr spectrum in which the second half of the first line was out of phase with the first half of the second line and so on. At the critical modulation amplitude (in this case about 800 units), the esr spectrum recorded resulted from the first half of the first line and the second half of the eighth line. The adjacent out of phase components of the esr spectrum apparently cancelled each other. At modulation amplitudes greater than or less than the

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[1] National Academy of Science–National Research Council Postdoctoral Research Associate, 1966–1968.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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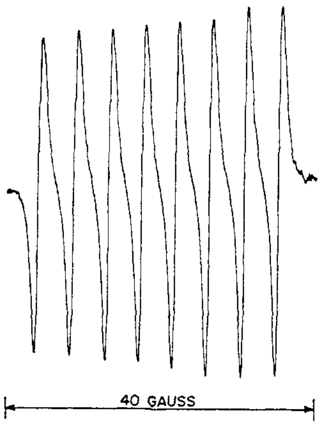

Figure 1. Esr spectra generated by the Ce^{4+}–H_2O_2 system containing NH_4VO_3 at 22° (Solution 1: Ce^{4+}, 0.001 *M;* 5 ml of concentrated acid $l.^{-1}$; H_2SO_4, 2 ml of concentrated acid $l.^{-1}$. Solution 2: NH_4VO_3, 0.01 *M;* H_2O_2, 0.05 *M;* HCl, 5 ml of concentrated acid $l.^{-1}$. pH 1.3. Modulation amplitude 80 units). Magnetic field increases from left to right.

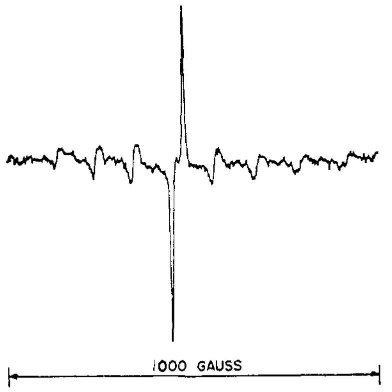

Figure 2. Esr spectra generated by the Fe^{2+}–H_2O_2 system containing NH_4VO_3 at 22° (Solution 1: Fe^{2+}, 0.002 *M;* H_2SO_4, 2 ml of concentrated acid $l.^{-1}$. Solution 2: NH_4VO_3, 0.01 *M;* H_2O_2, 0.1 *M;* H_2SO_4, 2 ml of concentrated acid $l.^{-1}$. pH 1.3. Modulation amplitude 800 units). Magnetic field increases from left to right.

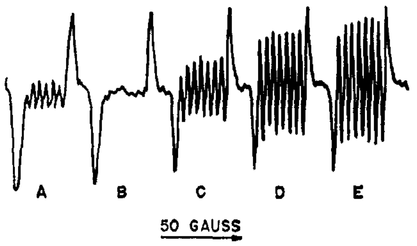

Figure 3. Effect of modulation amplitude on the esr spectra generated by the Fe^{2+}–H_2O_2 system containing NH_4VO_3 at 22° (A, modulation amplitude, 1000 units; B, 800; C, 630; D, 500; E, 400. Solution 1: Fe^{2+}, 0.005 *M;* H_2SO_4, 2 ml of concentrated acid $l.^{-1}$. Solution 2: NH_4VO_3, 0.005 *M;* H_2O_2, 0.1 *M;* H_2SO_4, 2 ml of concentrated acid $l.^{-1}$. pH 1.3). Magnetic field increases from left to right.

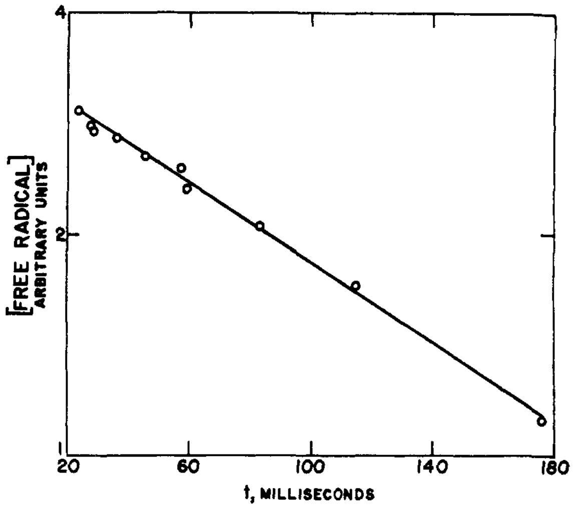

Figure 4. Decay of oxyvanadium(V)–free-radical complex in the Ce^{4+}–H_2O_2 system containing NH_4VO_3 at 22° (Solution 1: Ce^{4+}, 0.001 *M;* SO_4^{2-}, 0.2 *M*. Solution 2: NH_4VO_3, 0.0025 *M;* H_2O_2, 0.025 *M;* SO_4^{2-}, 0.2 *M*. pH 1.0).

critical modulation amplitude, the eight-line esr spectrum was recorded. However, the relative intensities of the lines were dependent on modulation amplitude. If concentrations of Fe^{2+} (0.01 *M*) and NH_4VO_3 (0.01 *M*) were increased and the concentration of H_2O_2 was 0.1 *M* at pH 1.0–1.3, the esr spectrum generated was characteristic for vanadium(IV).

The appearance of vanadium(IV) in Ce^{4+}–H_2O_2 solutions indicated that the free radicals formed reduced vanadium(V) to vanadium(IV). This reduction was much greater in Fe^{2+}–H_2O_2 solutions, as shown by the relative intensities of the esr signals due to both of the oxidation states of vanadium. Ce^{4+} or H_2O_2 did not separately reduce vanadium(V); however, Fe^{2+} is a strong reducing agent for vanadates. Also, in Ce^{4+}–H_2O_2 solution, $HO_2\cdot$ radicals are formed in the primary reaction. In Fe^{2+}–H_2O_2 solution, $\cdot OH$ radicals are formed in the primary reaction, and then these radicals react with H_2O_2 to yield $HO_2\cdot$ radicals.

The *g* values, line widths, and line separations for the esr spectrum, shown in Figure 1, are recorded in Table I. Compared with the esr spectrum of oxyvanadium(IV) ions having d electrons with unpaired spins, the data show that the esr spectrum obtained was not generated by a reduced form of vanadate ions, but was generated by a radical species formed on interaction of oxyvanadium(V) ions with radicals present in the redox systems. For example, (1) the *g* values were higher than the free-electron value while those due to unpaired d electrons were lower than the free-electron value (this may indicate the absence of spin–orbit coupling, characteristic of d electrons in transition metal ions); (2) the

Table I. Line Widths, *g* Values, and Separations of the Hyperfine Components of the Esr Spectrum Generated by the Ce^{4+}–H_2O_2 System Containing NH_4VO_3 at 22° (Figure 1)

Line[a]	*g* Value	Line width, G	Separation from preceding line, G
1	2.0203	1.25	...
2	2.0177	1.12	4.4
3	2.0150	1.20	4.3
4	2.0124	1.12	4.3
5	2.0098	1.08	4.3
6	2.0073	1.12	4.2
7	2.0046	1.08	4.4
8	2.0021	1.20	4.3

[a] Reading esr spectrum (Figure 1) from left to right.

line widths were much less than those for systems having free-spin d electrons (usually 15–25 G);[16–18] (3) the spectroscopic splitting factor was very small and was less by a factor of two orders than for systems having free-spin d electrons.[19] Oxyvanadium(V) ions have a higher charge to radius ratio than Ti^{4+} ions. Therefore, the $HO_2\cdot$ radicals may be attached laterally with oxyvanadium(V) ions in solution and linearly or angularly with Ti(IV) species.[20] For vanadate ions the radical end of $HO_2\cdot$ may interact strongly with t_{2g} orbitals of these ions which results in generating an eight-line spectrum, $I = {}^7/_2$ for ^{51}V. For Ti^{4+} ions, if the radical ligands are linearly or angularly attached, the interaction of the radical site with the t_{2g} orbitals would be weak, and no hyperfine splitting would occur.[9]

The oxyvanadium(V)–free-radical complex was unstable and decayed as a first-order reaction, probably by interaction of the complex with the solvent, as shown in Figure 4. For the Ce^{4+}–H_2O_2 system shown, $k = -6.2$ sec^{-1} and $t_{1/2} = 0.1$ sec.

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Triplet State of Vanadyl Tartrate Binuclear Complexes and Electron Paramagnetic Resonance Spectra of the Vanadyl α-Hydroxycarboxylates[1]

R. L. Belford, N. D. Chasteen, H. So, and R. E. Tapscott

Contribution from the W. A. Noyes Chemical Laboratory and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

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Abstract: The oriented single-crystal epr spectra of tetrasodium divanadyl *d*-tartrate *l*-tartrate dodecahydrate and the liquid (pH ~7) and frozen solution epr spectra of vanadyl ion complexed with *d*- and *dl*-tartrate, glycolate, mandelate, and benzilate anions (both hydroxyl and carboxyl protons removed) were investigated. Within experimental error $g_\parallel = 1.953$ and $g_\perp = 1.983$ for all the α-hydroxycarboxylate complexes, except the glycolate complex. Observation of the half-field ($g \sim 4$) "forbidden" transitions for both tartrate complexes confirms the existence of triplet-state binuclear species in solution. Their spectra are interpreted in terms of the usual axially symmetric $S = 1$ spin Hamiltonian, axial symmetry being a better approximation for the *d*-tartrate than the *dl*-tartrate complex. The D values (0.0335 cm^{-1}, *d*-tartrate, frozen solution; 0.0334 and 0.0338 cm^{-1}, *dl*-tartrate, frozen solution and single crystal) are accounted for by simple magnetic dipole calculations. An unusual frequency dependence in the room-temperature solution spectra of the *d*-tartrate is reported. Assignments of the ligand-field transitions in the α-hydroxycarboxylates are discussed utilizing the epr results.

The anionic complexes of VO^{2+} ion with α-hydroxycarboxylate anions, in which both hydroxyl and carboxyl protons are removed, exhibit novel structural, optical, and magnetic properties. Three of their structures, monomeric sodium tetraethylammonium bis(benzilato)oxovanadium(IV) di-2-propanolate,[2] binuclear tetrasodium divanadyl(IV) *d*-tartrate *l*-tartrate dodecahydrate,[3] and binuclear tetraammonium divanadyl(IV) bis(*d*-tartrate) dihydrate[4] have been determined by X-ray methods. In the solid, the active and racemic tartrate complexes consist of two VO^{2+} ions bridged by two tetranegative tartrate anions, $O_2CC(O)H \cdot C(O)HCO_2^{4-}$, with *trans* and *cis* arrangements about the vanadyl group, respectively. The brown *cis-dl* isomer exhibits a three-band optical spectrum in solid and solution,[5] in contrast to the four bands displayed by both the purple *trans-dd* isomer[5,6] and *trans*-vanadyl bisbenzilate chelate.[2]

A 15-line X-band epr spectrum of the *dl*-tartrate complex in aqueous solution at pH ~7 and a similar but more complicated X-band spectrum of the *dd*-tartrate complex (Figures 2 and 3) were reported from this laboratory.[5] We attributed the 15-line spectrum to electron exchange between two vanadium metal nuclei (^{51}V, $I = {}^7/_2$). Seven- and 15-line solution spectra of some copper[7] ($I = {}^3/_2$) and cobalt[8] ($I = {}^7/_2$) chelates have been presented as evidence for dimers in solution; however, these were mixed valence complexes in which only one unpaired electron was shared by both metal nuclei. In addition to the epr results, osmometer formula weight determinations and potentiometric titrations as well as the strikingly different optical spectra for active and racemic tartrate complexes led us to conclude that dimeric species also exist in solution.[5]

Recently, Dunhill and Smith[9] reported epr spectra of

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