Inorg. Chem. **1992**, *31*, 1925–1930

Appendix

The extended Hückel method was used for calculations reported in Figures 1 and 2, parameters appear in Table V.

Ab initio MO calculations were performed using both the closed- and open-shell Hartree–Fock–Roothaan (HFR) methods.[27,28] All calculations were performed with the GAMESS package[29] on the Department of Chemistry FPS/UNIX 500EA computer. Ab initio calculations were carried out with several different basis sets, all derived from those of Huzinaga.[30] For the transition metals, double-ζ basis sets were derived from fully contracted (4333/43/4) primitive sets by splitting off the outermost primitive function in each case. 4p polarization functions are added for all the transition metals. For N a double-ζ basis was derived from Huzinaga's contracted (43/4) primitive set. The transition metal triple-ζ d basis sets were formed by augmentation with exponents one-third that of the most diffuse primitive. Nitrogen s–p diffuse functions were added as prescribed by Clark and co-workers.[31] For Li a fully contracted (43) primitive set was used. In the configuration–interaction calculations [all single- and double-excitations (SD–CI)], SCF optimization results were used as starting solutions. Unfortunately, convergence difficulties prevented us from carrying forward calculations for the two largest basis sets on $Fe(NLi_2)_3$. However, results for $Fe(NLi_2)_3$ obtained for the smaller basis sets are well in line with results obtained for the V and Cr analogues.

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(27) Roothaan, C. C. *Rev. Mod. Phys.* **1951**, *23*, 69.

(28) Roothaan, C. C. *Rev. Mod. Phys.* **1960**, *32*, 179.

(29) Guest, M. F., SERC Darebury Laboratory, Warrington, WA4 4AD U.K.

(30) *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier: Amsterdam, 1984.

(31) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem.* **1983**, *4*, 294.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics of Oxidation of Vanadium(IV) by Alkyl Hydroperoxides in Acidic, Aqueous Solution

Rong Ma, Andreja Bakac,* and James H. Espenson*

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The title reactions produce VO_2^+ and products derived from β-scission of alkoxy radicals, largely acetone, ethane, and methane (*tert*-butyl hydroperoxide) or ethane, ethylene, and *n*-butane (*tert*-amyl hydroperoxide). The minor amounts of methane from the first reaction and the excess amount of ethane from the second suggest a small contribution from the oxidation of VO^{2+} by $^{\bullet}CH_3$ and $^{\bullet}C_2H_5$, respectively. The kinetic dependence of the main reaction upon $[H^+]$ is consistent with the formation of an intermediate $OVOOR^+$ present at steady-state concentrations. This intermediate produces VO_2^+ and $RO^{\bullet}$ in a rate-limiting step. The yield of VO_2^+ is stoichiometric in the *t*-AmOOH reaction, whereas only about half this amount of VO_2^+ is produced from *t*-BuOOH. Although chloride ions affect neither reaction, Br^- changes the stoichiometry, products, and kinetics of the *t*-BuOOH reaction, but not those of the *t*-AmOOH reaction. These differences are accounted for by the relative reactivities of the intermediate alkoxy radicals, $RO^{\bullet}$, toward β-scission versus bromide oxidation. Addition of alcohols with α-H's (i.e., CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$) does not affect VO_2^+ production from *t*-AmOOH but does prevent VO_2^+ formation from *t*-BuOOH because VO_2^+ is reduced by the alcohol radical formed in the reaction between *t*-BuO$^{\bullet}$ and ROH. Several models are suggested, all of which feature β-scission of *t*-BuO$^{\bullet}$ and *t*-AmO$^{\bullet}$. The data pertaining to products and stoichiometry suggest an interaction or complexation of VO_2^+ by *t*-BuOOH (but not *t*-AmOOH), which is supported by product yields, ion-exchange isolation, and spectroscopic evidence.

Introduction

The reduction of peroxides by transition metal complexes is important in many contexts. This includes reactions that occur in biological systems and also certain metal-catalyzed oxidations. Vanadium toxicity may arise because of hydroxyl radicals formed in the reaction of vanadyl ions and hydrogen peroxide, which derives from superoxide reduction or disproportionation. Results have been reported concerning vanadate-dependent NADH oxidase present in cardiac cell membranes,[1] and both enzymatic[2-4] and nonenzymatic[4,5] oxidations by free-radical chains[6-8] have been identified. That hydroxyl radicals are produced[9] in the VO^{2+}–H_2O_2 reaction has been shown by spin-trapping and ESR detection.[10]

Also, reactions of peroxides are of importance in the context of oxygen activation.[11] Particular importance attaches to the *t*-BuOOH–$V^{IV}O$ system, the latter usually as $VO(acac)_2$. Epoxidation of alkenes is a fundamental and important reaction.[11,12] Vanadium-catalyzed selective peroxidation of olefins by alkyl hydroperoxides has become an important process for the manufacture of propylene oxide.[13,14] There has been no study of the kinetics of the VO^{2+}–*t*-BuOOH reaction, however, despite its importance, although it seems likely that free-radical intermediates are involved.

Peroxide reductions by metal ions continue to be of wide interest and are known to adopt a variety of mechanisms.[15] Among those one has to consider in the general case is the possibility of a group-transfer reaction that is, in effect, a two-electron process:

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(1) Erdman, E.; Krawietz, W.; Philipp, G.; Hackbarth, I.; Schmitz, W.; Scholz, H.; Crane, F. L. *Nature* **1979**, *282*, 335.

(2) Ramasarma, T.; MacKellar, W. C.; Crane, F. L. *Biochim. Biophys. Acta* **1981**, *646*, 88.

(3) Briskin, D. P.; Thornley, W. R.; Poole, R. J. *Arch. Biochem. Biophys.* **1985**, *236*, 228.

(4) Coulombe, R. A., Jr.; Briskin, D. P.; Keller, R. J.; Thornley, W. R.; Sharma, R. P. *Arch. Biochem. Biophys.* **1987**, *255*, 267.

(5) Vyskocil, F.; Teisinger, J.; Dlouha, H. *Nature* **1980**, *286*, 516.

(6) Darr, D.; Fridovich, I. *Arch. Biochem. Biophys.* **1985**, *243*, 220.

(7) Darr, D.; Fridovich, I. *Arch. Biochem. Biophys.* **1984**, *232*, 562.

(8) Liochev, S.; Fridovich, I. *J. Free Radicals Biol. Med.* **1986**, *250*, 139.

(9) Keller, R. J.; Coulombe, R. A., Jr.; Sharma, R. P.; Grover, T. A.; Piette, L. H. *Free Radical Biol. Med.* **1989**, *6*, 15.

(10) Ozawa, T.; Hanaki, A. *Chem. Pharm. Bull.* **1989**, *37*, 1407.

(11) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 9.

(12) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.

(13) Nishida, Y.; Yamada, K. *Inorg. Chim. Acta* **1990**, *174*, 1.

(14) Mimoun, H.; Mignard, M.; Brechot, P.; Scussine, L. *J. Am. Chem. Soc.* **1986**, *108*, 3711.

(15) Masarwa, M.; Cohen, H.; Meyerstein, D.; Hickman, D. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4293.

0020-1669/92/1331-1925$03.00/0

$M^{n+} + ROOH \rightarrow MO^{n+} + ROH$. The study of VO^{2+}–peroxide reactions is attractive, therefore, because this option is, of course, precluded. The number of alternatives is thus less, and one can search for evidence that will support one of the viable options over others. In particular, it seems likely that alkoxyl radicals are intermediates. The search for them has guided some of our experimental plan.

We have thus undertaken an investigation of the mechanism with the goal of identifying the various steps in the reaction sequence. Toward this end, we have examined the kinetics, stoichiometry, pH effects, and products. Because the *tert*-butoxyl radical is a likely intermediate, experiments were conducted to search for its presence by examining the effects of low concentrations of Br^- and high concentration of alcohols. For comparison purposes, the reaction of *tert*-amyl hydroperoxide was examined, because the rate of β-scission of its alkoxyl radical is so much faster than that of *t*-BuO•. The effect of bromide ions on the kinetics and products was also examined, as it could be expected to be different for the two as a result of the different relative reactivities of *t*-BuO• and *t*-AmO• toward β-scission and bromide oxidation. The alcohols prevent VO_2^+ formation from *t*-BuOOH but not from *t*-AmOOH, in effect turning the stoichiometric oxidation of *t*-BuOOH into a VO^{2+}-catalyzed reaction for peroxide decomposition. These are the issues addressed, along with the question of whether the subsequent alkyl radicals react exclusively by self-reactions or whether oxidation of VO^{2+} occurs.

Experimental Section

Reagents. Solutions of VO^{2+} in dilute perchloric acid were prepared by passing a solution of vanadyl sulfate through a column of Dowex 50W-X4 cation-exchange resin. The column, after washing to remove sulfate ions, was eluted with 1.6 M perchloric acid. The concentration of VO^{2+} was determined spectrophotometrically (ϵ_{760} = 17.5 L mol^{-1} cm^{-1}). *tert*-Butyl hydroperoxide was the commercial product (Aldrich), and *tert*-amyl hydroperoxide was prepared as in the literature.[16] Solutions of the hydroperoxides were analyzed by iodometric titration.[17] Solutions of VO_2^+ were prepared by dissolving V_2O_5 in 0.1 M perchloric acid. Lithium perchlorate, used to maintain constant ionic strength, was prepared from the carbonate and was recrystallized.

Stoichiometry. The consumption of VO^{2+} was monitored spectrophotometrically at 760 nm as successive increments of ROOH were added. The absorbance readings were taken only after 30-min reaction time. These experiments afforded values of $\Delta[VO^{2+}]/\Delta[ROOH]$. Because of the low molar absorptivity of VO^{2+}, these experiments entailed the use of higher concentrations than used in the kinetics, but nothing in the data indicated differences arising because of that. The production of VO_2^+ was monitored at 320 nm, on the side of an absorption band that rises steeply into the UV region, where the independently-determined value of the molar absorptivity of VO_2^+ is 390 L mol^{-1} cm^{-1}. These experiments were done at much lower concentrations, typically (1–4) × 10^{-3} M VO^{2+} and (1–3) × 10^{-4} M ROOH. These data allow the calculation of $\Delta[VO_2^+]/\Delta[ROOH]$.

Some experiments were done with added Br^-. The possible formation of Br_3^- was examined by recording the UV spectrum after complete reaction. The Br_3^- spectrum is characterized by a maximum at 280 nm. This was observed, although not clearly. The VO^{2+}:ROOH stoichiometry was also examined at 760 nm, to learn whether Br_3^- formation was accompanied by a change in reaction ratio. It should be noted that the oxidation of Br^- by VO_2^+ occurs *much* more slowly than the peroxide reaction, which we demonstrated by mixing this combination and also VO^{2+} with Br_2(aq). The effects of certain alcohols on the extent of VO_2^+ buildup were determined spectrophotometrically at 320 nm.

Kinetics. Reaction rates were determined by following the reaction progress spectrophotometrically. Most of the measurements were made at 320 nm, following the buildup of VO_2^+. In these experiments, the concentrations of VO^{2+} and H^+ were sufficiently large relative to that of ROOH that they remained constant in the experiment. The temperature was held at 25.0 °C in each kinetic run by thermostatting the reaction cuvette which was immersed in a water-filled cell holder with a jacket through which constant-temperature water was circulated. In successive experiments, the effects of concentration variables were determined by varying $[VO^{2+}]$, $[H^+]$, and $[Br^-]$. Many of the experiments were conducted at constant ionic strength of 1.0 M; in others, the effect of variable ionic strength was explored.

Under the conditions described, the reaction progress followed a single-exponential function, or pseudo-first-order kinetics. The absorbance (D)–time data were fit to the equation $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_\psi t)$ by a nonlinear least-squares program. The values of k_ψ were correlated with each of the concentration variables mentioned.

Products. VO_2^+ and Br_3^- were detected spectrophotometrically, as described above. Organic products were detected by gas chromatography, and their yields were estimated by comparisons with known standards. Polar molecules such as acetone and *tert*-butyl alcohol were separated on OV-101 by injection of liquid-phase samples. Low molecular weight hydrocarbons present in the headspace (methane, ethane, ethylene, and *n*-butane) were separated on VZ-10.

Results

Stoichiometry and Products. Several types of experiments were performed to determine the ratios in which the starting materials were consumed and products formed. Also, the inorganic and organic products were determined by spectrophotometric and gas chromatographic techniques as detailed in the Experimental Section.

First, the consumption of VO^{2+} was monitored at its 760-nm absorption maximum as increments of hydroperoxide were added. Values of $\Delta[VO^{2+}]/\Delta[ROOH]$ were so determined, being 0.59 for *t*-BuOOH and 1.0 for *t*-AmOOH. That these compounds give different results is consistent with other data and with the mechanism later proposed.

Next, spectrophotometric data were obtained by monitoring the final yield of VO_2^+ in the UV spectrum as described in the Experimental Section. Plots of D_{320} vs $[ROOH]_0$ were linear. The data gave the values of $\Delta[VO_2^+]/\Delta[ROOH]$ = 0.51 (*t*-BuOOH) and 0.95 (*t*-AmOOH). These are in essential agreement with those based on VO^{2+} consumption, establishing the internal consistency of both sets of results. The UV spectrum of the product corresponds to that of VO_2^+; although that is not a particularly definitive statement, given that the spectrum shows no distinctive features, there is little reason to suspect otherwise. That is particularly so in the light of experiments to be described later, where this absorbance change lessens or disappears in experiments where other intermediates seem to re-reduce VO_2^+ to VO^{2+}.

When Br^- was added, typically 0.05 M, the reaction with *t*-BuOOH produced Br_3^-, identified by its characteristic absorption spectrum. This product appeared at a rate corresponding to peroxide disappearance (see next section). Actually, the product band showed not only the 280-nm band of Br_3^- but a band about 30% as intense at 340 nm. The same spectrum resulted when solutions of Br^-, Br_2 and VO_2^+ were mixed at these concentrations. This suggests that some species containing both vanadium and bromine absorbs at 340 nm. Presumably, VO_2^+ was produced as well, although it was barely detectable beneath the stronger Br_3^- absorptions. When VO^{2+} and *t*-BuOOH were allowed to react to completion, and Br^- was then added, no Br_3^- was formed rapidly, although small concentrations of Br_3^- appeared after an hour as a result of the very slow oxidation of Br^- by VO_2^+. The reaction of VO^{2+} with *t*-AmOOH, conducted analogously with added Br^-, produced such a minor amount of Br_3^- as to be unimportant. Essentially, only VO_2^+ was seen in the UV spectrum. For both *t*-BuOOH and *t*-AmOOH, the same determinations were made with Cl^- added rather than Br^-. Here no differences were noted, and VO_2^+ is the only product for both.

The effect of Br^- on the *t*-BuOOH reaction is such that the stoichiometry also changes. As measured from the VO^{2+} consumption at 760 nm, the value of $\Delta[VO^{2+}]/\Delta[ROOH]$ is 0.85 at 0.050 M Br^-.

The organic products differ depending on the reaction conditions. The reaction with *t*-BuOOH in perchlorate or chloride media produces acetone (not quantitated, but presumably 100%), methane (31%), and ethane (69%). That with *t*-AmOOH yields acetone, ethane (28%), ethylene (18%), and butane (54%); a very small amount of methyl ethyl ketone is presumably present as well, but it was not detected. When Br^- was present in the *t*-BuOOH

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[16] Milas, N. A.; Sugenor, D. M. *J. Am. Chem. Soc.* **1946**, *68*, 643.

[17] (a) Johnson, R. M.; Siddigi, I. W. *The Determination of Organic Peroxides*; Pergamon: Oxford, England, 1966. (b) Mair, R. D.; Han, R. T. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. II, Chapter VI.

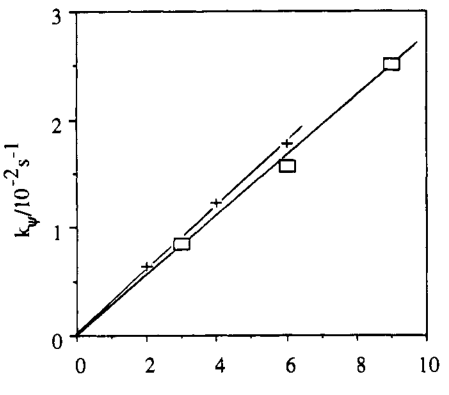

Figure 1. Plots showing the linear dependence of the pseudo-first-order rate constants on the concentrations of VO^{2+} for *t*-BuOOH (squares) and *t*-AmOOH (pluses). Reactions were conducted with $[VO^{2+}]_0 \gg [ROOH]_0$ at constant $[H^+]$. Data are shown at 0.14 M H^+, $T = 25.0$ °C, and $\mu = 1.0$ M.

reaction, no acetone was found, but *tert*-butyl alcohol was the major product.

Stoichiometric experiments were also conducted with primary and secondary alcohols added. High concentrations of methanol, ethanol, or 2-propanol were used, 1:1 by volume. The first two of these had no effect at all on the *t*-AmOOH reaction, the same concentration of VO_2^+ being formed as in the absence of alcohol. With 2-propanol, however, a considerable reduction in VO_2^+ yield was noted, to 15% of its former value. With *t*-BuOOH, *no* VO_2^+ was produced in the presence of any of these alcohols. These data are consistent (as detailed later) with the conversion of $RO^\bullet$ to $^\bullet C(R^1)(R^2)OH$, which then reduce VO_2^+.

To check certain issues arising during the formulation of a satisfactory mechanism, two other sets of stoichiometric experiments were performed. In one, the buildup of VO_2^+ was monitored with VO_2^+ pre-existing in the solution. For VO^{2+} (3×10^{-3} M) and *t*-BuOOH (3×10^{-4} M), the reaction produced 2×10^{-4}, 1×10^{-4}, and 6×10^{-5} M VO_2^+ when the preexisting concentrations of VO_2^+ were 0, 1, and 2 mM. In contrast, the same set of experiments with VO^{2+} + *t*-AmOOH gave the same yield of VO_2^+, $(3.0 \pm 0.3) \times 10^{-4}$ M, regardless of the amount of VO_2^+ added prior to reactions, if any.

In the other experiment, the effect of VO_2^+ on the yield of Br_3^- with 0.040 M Br^- was examined. Now, added VO_2^+ to 2×10^{-3} M is without effect, as $[Br_3^-]_\infty$ is the same as when $[VO_2^+]_0 = 0$. Also, when Br^- (0.04 M) and alcohol (50 vol %) are both present, Br_3^- production proceeds as if the alcohol were absent.

Kinetics in Perchlorate Media. The parameter determined from the kinetic fit, k_ψ, is, by definition, $-\mathrm{d}\ln[ROOH]/\mathrm{d}t$ since the hydroperoxide was always taken in limiting concentrations. The values of k_ψ are directly proportional to $[VO^{2+}]$ over a range of concentrations, (3–9) $\times 10^{-3}$ M VO^{2+} (*t*-BuOOH) and (2–6) $\times 10^{-3}$ M VO^{2+} (*t*-AmOOH). The experiments cited refer to $[H^+] = 0.14$ M at 25.0 °C. This direct proportionality is shown in Figure 1, where k_ψ is shown to be a linear function of $[VO^{2+}]$ that passes through the origin. Values of the apparent second-order rate constants at 0.14 M H^+ are 2.81 ± 0.07 L mol^{-1} s^{-1} (*t*-BuOOH) and 3.21 ± 0.09 L mol^{-1} s^{-1} (*t*-AmOOH).

Experiments were then done to determine the effect on the rate constant of variable $[H^+]$, 0.1–1.0 M. The rate decreased with $[H^+]$ for both hydroperoxides, a somewhat surprising finding, since many peroxide reductions are $[H^+]$ independent. A plot of k_{app}^{-1} (where $k_{app} = k_\psi/[VO^{2+}]$) varies linearly with $[H^+]$, as shown in Figure 2. (Also, a plot of k_{app} vs $1/[H^+]$ is decidedly curved.) The functional form of the rate law is therefore given by

$$\frac{-\mathrm{d}[ROOH]}{\mathrm{d}t} = \frac{a[VO^{2+}][ROOH]}{1 + b[H^+]} \qquad (1)$$

The least-squares values of the parameters are $a = 4.2 \pm 0.4$ (*t*-BuOOH) and 4.0 ± 0.5 L mol^{-1} s^{-1} (*t*-AmOOH) and $b = 3.8 \pm 0.2$ (*t*-BuOOH) and 3.9 ± 0.7 L mol^{-1} (*t*-AmOOH).

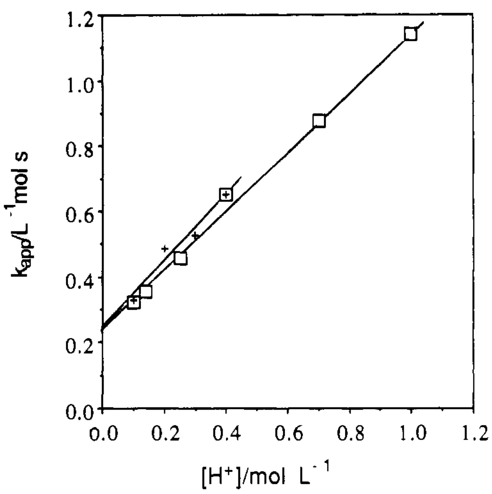

Figure 2. Plots illustrating that the apparent second-order rate constants at 25 °C for the reactions of VO^{2+} with ROOH depend on $[H^+]$ in such a way that $1/k$ varies linearly with $[H^+]$ as shown for *t*-BuOOH (squares) and *t*-AmOOH (pluses). This variation leads to the algebraic expression in eq 1.

The effect of variable ionic strength was explored for the *t*-BuOOH reaction. Experiments were conducted over the range $0.14 \le \mu \le 1.0$ M, and the value of k was found to remain unchanged to within <5%.

Kinetics in Chloride, Bromide, and Alcohol Media. Kinetics measurements were conducted with Cl^- and Br^- present. Addition of Cl^-, or substitution of Cl^- for ClO_4^-, has no effect on the reaction rate or products. Bromide, on the other hand, has a substantial effect on the *t*-BuOOH reaction. As in ClO_4^- media, experiments with $[VO^{2+}]_0 \gg [ROOH]_0$ follow pseudo-first-order kinetics with added Br^-. Again, values of k_ψ are directly proportional to $[VO^{2+}]$ at 0.050 M Br^-. Variation of Br^- over the range 8×10^{-3}–5.0×10^{-2} M yields values of k_{app} that are $[Br^-]$ independent. The values of k_{app}, however, are 1.7 times smaller than those in perchlorate medium. The same form of $[H^+]$ dependence (eq 1) is found in bromide solutions.

The rate of reaction of *t*-AmOOH, in contrast, is unaffected by bromide over the range 1×10^{-3}–0.1 M.

In a qualitative sense, the rates were the same in the presence of alcohol (50 vol %) as without. Because of the high levels of alcohol concentration needed to produce the stoichiometric effects, the reaction medium changed substantially. For that reason, quantitative kinetic evaluations in alcohol-containing solutions were not made.

Discussion

The variety of mechanisms that are possible when peroxides (a general term for H_2O_2 and ROOH, among others) are reduced by transition metal complexes have been considered in the literature.[15,18–28] In every case, some mode of coordination of peroxide to the metal in an essential pre-reaction step. When the metal complex undergoes slow ligand substitution, the peroxide reaction

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(18) (a) Czapski, G.; Levanon, H.; Samuni, A. *Isr. J. Chem.* **1969**, *7*, 375. (b) Samuni, A.; Czapski, G. *Isr. J. Chem.* **1970**, *8*, 563. (c) Czapski, G.; Samuni, A.; Meisel, D. *J. Phys. Chem.* **1971**, *75*, 3271.

(19) Johnson, G. R. A.; Nazhat, N. B.; Sandalla-Nazhat, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 407.

(20) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

(21) Espenson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953.

(22) Kochi, J. K. *Rec. Chem. Prog.* **1966**, *27*, 207.

(23) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; pp 33–43.

(24) Kristine, F. J.; Johnson, C. R.; O'Donnell, S.; Shepherd, R. E. *Inorg. Chem.* **1980**, *19*, 2280.

(25) Rush, J. D.; Bielski, B. H. J. *Inorg. Chem.* **1985**, *24*, 4282.

(26) Kim, H. P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1987**, *26*, 4090.

(27) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.

(28) (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713. (b) Sadler, N.; Scott, S. L.; Bakac, A.; Espenson, J. H.; Ram, M. S. *Inorg. Chem.* **1989**, *28*, 3951.

thus occurs slowly: the slow oxidation of $V(H_2O)_6^{2+}$ by H_2O_2 is an example.[25-26] Even the kinetically inert complex $Ru(NH_3)_6^{2+}$ is oxidized by an inner-sphere mechanism[24] at a very low rate because NH_3 is lost slowly. As far as we can discern,[27] reduction of peroxides by transition metal complexes never follows an outer-sphere mechanism. When the metal center is inaccessible, no reaction occurs, as is the case for the encapsulated species $Co(sep)^{2+}$.[29,30] Substitution is not, of course, a problem for VO^{2+}, as the rates of water substitution at both trans and cis positions are quite rapid.[31]

Once such a precursor forms, however, the reaction may then proceed in more than one direction. It often proceeds by what is called a Fenton mechanism, well established for $Cr(H_2O)_6^{2+}$ and $Ti(H_2O)_6^{3+}$ (but questionable[15] for Cu^+(aq) and likely for $Fe(H_2O)_6^{2+}$). If so, there is no kinetic manifestation of precursor complex formation, which occurs to a very minor extent, and the reaction occurs by an apparently uncomplicated bimolecular route, as shown for Cr^{2+}:

$$Cr(H_2O)_6^{2+} + ROOH \rightarrow (H_2O)_5CrOH^{2+} + H_2O + RO^\bullet \quad (2)$$

In this event, the rate is expected to be $[H^+]$ independent, which has been established for Cr^{2+} and many other complexes. The list of $[H^+]$-independent reactions includes some that adopt non-Fenton mechanisms, such as those of $Co(dmgH)_2$ and related complexes,[32] and is not an indication of mechanism.

The marked $[H^+]$ dependence of the rate of the VO^{2+}–ROOH reactions signals a different type of interaction, in which the ROO^- anion rather than ROOH itself is bound to the metal. Also, the form of the rate law establishes that there is an intermediate species $OVOOR^+$. This differs from the normal Fenton scheme, where $M(ROOH)^{n+}$ is not kinetically evident, and may merely represent the composition of the transition state (for eq 2, for example) and not a genuine intermediate.[33] For the VO^{2+} reactions, the algebraic form of the rate law is consistent with the following scheme:

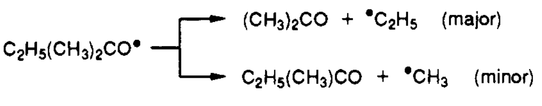
$$VO^{2+} + ROOH \rightleftarrows OVOOR^+ + H^+ \quad (3)$$

$$OVOOR^+ \rightarrow VO_2^+ + RO^\bullet \quad (4)$$

The alkoxyl radical reacts further, as described below, in reactions that are rapid compared to these steps. If one makes the steady-state approximation for the concentration of $OVOOR^+$, the predicted rate has the same form as that observed. This proposal identifies the experimental parameters a and b of eq 1 as $a = k_3$ and $b = k_{-3}/k_4$. Actually, for the *t*-BuOOH reaction, where the stoichiometry points to an additional fast step consuming a second mole of *t*-BuOOH, the parameter a is equal to $2k_3$.

The reaction steps that follow are those known and expected for the alkoxyl radicals and for the alkyl radicals that derive from them. In perchlorate medium, the $RO^\bullet$ radicals react by β-scission, eqs 5 and 6, a process which is much faster for the *tert*-amyloxyl radical.[34] This is expressed as $k_6 \gg k_5 = 1.4 \times 10^6$ s^{-1} at 25 °C.[34]

$$(CH_3)_3CO^\bullet \longrightarrow (CH_3)_2CO + {}^\bullet CH_3 \quad (5)$$



$$C_2H_5(CH_3)_2CO^\bullet \longrightarrow (CH_3)_2CO + {}^\bullet C_2H_5 \ \text{(major)} \quad (6a)$$

$$C_2H_5(CH_3)_2CO^\bullet \longrightarrow C_2H_5(CH_3)CO + {}^\bullet CH_3 \ \text{(minor)} \quad (6b)$$

The difference in the rates of β-scission can be invoked to explain the other stoichiometric and kinetic differences in the two systems. With *t*-AmOOH, steps 3, 4, and 6 occur in sequence, giving rise to a reaction of 1:1 stoichiometry. The features referred to are not altered by addition of VO_2^+, Br^-, or ROH.

Addition of VO_2^+ reduces the amount of VO^{2+} consumed in the *t*-BuOOH reaction. It is as if *t*-BuOOH were only partially consumed once VO_2^+ is added. This is not necessarily so, however, in that the VO_2^+ that is formed could instead be partially re-reduced to VO^{2+}. The alkyl radicals produced in eqs 5 and 6 for the most part undergo only self-reactions, resulting mostly in C_2H_6 (from $^\bullet CH_3$) and C_2H_4, C_2H_6, and n-C_4H_{10} (from $^\bullet C_2H_5$). There is, however, some CH_4 produced in the *t*-BuOOH reaction and an extra[35] amount of ethane from *t*-AmOOH, beyond that expected as a result of eq 6b. Both of these results are accounted for if we postulate the occurrence of a relatively inefficient reduction of the alkyl radicals by vanadium(IV) (eq 7).

$$R^\bullet + VO^{2+} + H_2O \rightarrow RH + VO_2^+ + H^+ \quad (7)$$

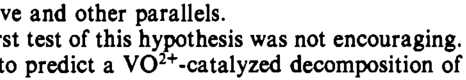
The occurrence of the VO^{2+}–$R^\bullet$ reaction is also substantiated in a minor way by the *t*-BuOOH:VO^{2+} stoichiometry. Consumption of additional VO^{2+} by eq 7 may account for some of the deviation from the 1:1 stoichiometry expected from reactions 3 and 4. The major cause of the deviation, however, lies elsewhere.

We suggest three possible reasons why the *t*-BuOOH reaction with VO^{2+} proceeds differently from that of *t*-AmOOH. One possibility is that additional *t*-BuOOH is consumed by an interaction with VO_2^+, presumably tight binding of a sort. Another is that the $^\bullet CH_3$ radical may reduce *t*-BuOOH, but $^\bullet C_2H_5$ does not react with *t*-AmOOH as efficiently. Still a third invokes reduction of *t*-BuO$^\bullet$ (but not *t*-AmO$^\bullet$) by VO_2^+. In the next sections we consider each of these in turn, seeking both positive evidence or falsifying experiments.

Does $^\bullet CH_3$ React with *t*-BuOOH? Consider the reaction represented by eq 8. We seek to find if it occurs and if its rate

$$^\bullet CH_3 + t\text{-BuOOH} \rightarrow CH_3OH + t\text{-BuO}^\bullet \quad (8)$$

constant falls in the correct range. If so, it could account for one of the principal findings about the reaction between VO^{2+} and *t*-BuOOH: An excess of *t*-BuOOH is consumed as compared to the 1:1 ratio expected here and actually found for that between VO^{2+} and *t*-AmOOH. In the absence of data, there is much to be said for reaction 8: it parallels that for Cr^{2+} (and many other reduced metal ions) and ROOH's. This is a telling point, because in many cases, Cr^{2+} and alkyl radicals $R^\bullet$ undergo reactions analogous to those of Cr^{2+} *at comparable rates*. To cite one example, consider the reactions shown in eqs 9 and 10, with $k_9 = 6 \times 10^5$ and $k_{10} = 1.8 \times 10^4$ L mol^{-1} s^{-1}.



$$Co(NH_3)_5Cl^{2+} \xrightarrow{Cr^{2+}} CrCl^{2+} + Co(NH_3)_5^{2+} \quad (9)^{36a}$$

$$Co(NH_3)_5Cl^{2+} \xrightarrow{^\bullet CH_3} CH_3Cl + Co(NH_3)_5^{2+} \quad (10)^{36b}$$

After the above considerations, we included reaction 1 into the overall scheme, to see if a reasonable value of k_8 could account for the "extra" consumption of hydroperoxide. Over the concentrations used, it seemed as if a value $k_8 \sim 10^5$ L mol^{-1} s^{-1} could suffice on the basis of numerical simulations. Since the rate constant for the reaction of Cr^{2+} and *t*-BuOOH is 3×10^4 L mol^{-1} s^{-1}, this seemed entirely feasible on the basis of the comparison cited above and other parallels.

The first test of this hypothesis was not encouraging. Surely it led us to predict a VO^{2+}-catalyzed decomposition of the hydroperoxide. That is, reaction 8 and the β-scission process of eq 5 are circular, with a net effect in the limit: $(CH_3)_3COOH \rightarrow$

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(29) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(30) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624.

(31) Wüthrich, K.; Connick, R. E. *Inorg. Chem.* **1968**, *7*, 1377. See also: Johnson, M. D.; Murmann, R. K. *Inorg. Chem.* **1983**, *22*, 1068.

(32) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.

(33) Incidentally, it is unlikely that such species would deprotonate to yield $M(ROO)^{(n-1)+}$, since that would only lead to a less stable product, MO^+, in the next step, as in eq 2, rather than MOH^{2+}.

(34) (a) Erben-Russ, M.; Michael, C.; Bors, W.; Saran, M. *J. Phys. Chem.* **1987**, *91*, 2362. See also: (b) Gilbert, B. C.; Marshall, P. D. R.; Norman, R. O. C.; Pineda, N.; Williams, P. S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1392. (c) Walling, C.; Padwaz, A. *J. Am. Chem. Soc.* **1963**, *85*, 1587. (d) Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053.

(35) The yields of C_2H_6, C_2H_4, and n-C_4H_{10} expected from the self-reactions of $^\bullet C_2H_5$ in aqueous solution have been determined: Bakac, A.; Espenson, J. H. *J. Phys. Chem.* **1986**, *90*, 325.

(36) (a) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766. (b) Kelley, D. G.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1990**, *29*, 4996.

$(CH_3)_2CO + CH_3OH$. Thus, if this is a correct model, there should be ratios of VO^{2+} to t-BuOOH at which substantial amounts of the hydroperoxide are lost per mole of VO^{2+}. That proved not so—the consumption ratio remained ~1.7:1 (t-BuOOH:VO^{2+}), even with peroxide in excess, which should have favored the catalytic aspect.

We then turned to experiments that would search more directly for evidence of reaction 8. Solutions of $CH_3Co(cyclam)H_2O^{2+}$ were photolyzed with visible radiation, in the absence and presence of t-BuOOH. This photolysis is known[37] to yield $^\bullet CH_3$ quite clearly. In both experiments, ethane was the only product detected gas chromatographically. And its yield was essentially the same, irrespective of the hydroperoxide concentration. This shows that reaction 8 is unimportant under any circumstance. This conclusion is supported by other literature data as well.[38]

Does VO_2^+ Oxidize t-BuO$^\bullet$? Such a reaction is without precedent. One possibility is the reaction shown in eq 11.

$$VO_2^+ + (CH_3)_3CO^\bullet \xrightarrow{H^+} VO^{2+} + CH_3OH + (CH_3)_2CO \tag{11}$$

Although this is not a known reaction, it could explain the data, in that partial regeneration of VO^{2+} in eq 11 is equivalent to an extra consumption of t-BuOOH. Moreover, this could occur for t-BuO$^\bullet$, but not t-AmO$^\bullet$, given their rates of β-scission. If reaction 3 is to occur comparably to β-scission of t-BuO$^\bullet$, it must have $k_{11} \geq 10^9$ L mol^{-1} s^{-1}, given the concentrations used. Also, the importance of reaction 11 relative to reaction 5 would be greater the more VO_2^+ added initially. This is consistent with our finding that less VO_2^+ is formed when more is added initially. That is, re-reduction to VO^{2+} becomes more prevalent but not entirely dominant.

We performed experiments with added VO_2^+ (up to 10 mM) and found no change in the organic products. This suffices to rule out eq 11, which is additionally suspect because of the very high rate constant required.

Does VO_2^+ "Bind" t-BuOOH? We return to this possibility because it does suffice as an explanation for the 1:1.7 VO^{2+}:t-BuOOH stoichiometry, with certain provisions. First, one must accept that this interaction, complexation or whatever, does not occur appreciably between VO_2^{2+} and t-AmOOH, perhaps because of steric reasons. Second, it occurs over a wide range of VO^{2+}:t-BuOOH ratios, since their consumption ratio remains about the same, 1:1.7 (but never quite 1:2).

We therefore conducted some experiments to detect directly a VO_2^+–t-BuOOH interaction. At higher concentrations (0.1 M each), there is clear evidence for it in the electronic spectrum; a new peak develops with a maximum at 370 nm.

We then carried out the reaction between VO^{2+} and t-BuOOH so as to determine the yield of acetone. With respective concentrations of 3.0 and 2.0 mM, the GC yield was 1.4 mM acetone. In comparison, however, t-BuOOH itself (1.0 mM, this being the expected amount of VO^{2+}:t-BuOOH complex) yielded 0.4 mM acetone because of the decomposition in the GC. More to the point, the same reaction solution was passed through a column of Dowex 50W-X8 cation-exchange resin. The acetone yield of the eluent now matched that of the 1.0 mM standard. The VO_2^+ portion absorbed on the column (a VO_2^+–t-BuOOH complex), once eluted with 2.6 M perchloric acid, showed an "acetone" yield of 0.4. This clearly establishes holdback of organic material, presumably t-BuOOH, with the VO_2^+ fraction.

The same experiment with VO^{2+} + t-AmOOH showed the same acetone yield before and after chromatography, suggesting no column holdback. Moreover, once the yellow VO_2^+ fraction was eluted, no acetone whatever was detected in it.

We thus conclude that the data support formation of a complex of sorts between VO_2^+ and t-BuOOH. This work has not been directed toward defining its structure, but some comments may nonetheless be made. The bright orange species formed from hydrogen peroxide[39] may be a useful point of comparison:

$$VO_2^+ + H_2O_2 \rightarrow OV(OO)^+ + H_2O \tag{12}$$

If we imagine an η^2 interaction of the peroxide, then the *tert*-butyl group may be less prohibitive than the *tert*-amyl.

When VO^{2+} and t-BuOOH are mixed at 0.1 M, a precipitate forms. This material is soluble in methanol and shows a peak at 370 nm. (Vanadium(V) is not methanol soluble and has no UV peak.) When H_2O_2 is injected, the 370-nm peak decreases in intensity after each injection, as if the so-called VO_2^+–t-BuOOH complex is destroyed with each occurrence of reaction 12.

Effects of Chloride and Bromide Ions. The reactions were entirely the same when Cl^- was used instead of ClO_4^-, which means that the effects of Br^- in the t-BuOOH reaction are specific ones. We propose that Br^- is oxidized by the *tert*-butoxyl radical, leading to Br_3^- (eqs 13 and 14). Consistent with that, the organic product

$$(CH_3)_3CO^\bullet + Br^- + H^+ \rightarrow (CH_3)_3COH + Br^\bullet \tag{13}$$

$$Br^\bullet + Br^- \rightarrow Br_2^-;\ 2Br_2^- \rightarrow Br_3^- + Br^- \tag{14}$$

was now found to be *tert*-butyl alcohol rather than acetone, and ethane and methane were not formed. That bromide ions have no effect on the t-AmOOH reaction is simply a manifestation that the rate of the β-scission reaction of the *tert*-amyloxyl radical is much faster than that of the *tert*-butoxyl radical.[34]

The bromide also changes the stoichiometry of the VO^{2+}–t-BuOOH reaction to 1:1 and reduces the rate by a factor of 1.7 at 0.14 M H^+. An explanation that will satisfy these observations seems to require that Br^- somehow prevents the interaction of VO_2^+ with t-BuOOH. Although truly unexpected, a complex of VO_2^+ with Br^- may interfere sufficiently with the VO_2^+–t-BuOOH interaction to affect the stoichiometry and with it the kinetics.

Effects of Alcohols. Primary alcohols, although without effect on the t-AmOOH reaction, prevent VO_2^+ formation in the reaction of t-BuOOH with VO^{2+}, as does 2-propanol. The following equations account for this:

$$t\text{-BuO}^\bullet + R^1R^2CHOH \rightarrow t\text{-BuOH} + {}^\bullet C(R^1)(R^2)OH \tag{15}$$

$$^\bullet C(R^1)(R^2)OH + VO_2^+ + H^+ \rightarrow (R^1)(R^2)CO + VO^{2+} + H_2O \tag{16}$$

The first of these is well-known,[20,40] and leads, as shown, to hydrogen atom abstraction from primarily but not exclusively the α-carbon. The resulting α-hydroxyalkyl radical is a strong one-electron reducing agent.[40] Although the rates of reduction of VO_2^+ by such radicals have not been reported, eq 16 seems fully consistent with the known reactivity of such radicals. Indeed, our findings can be taken as evidence that vanadium(V) is rapidly reduced by $^\bullet CH_2OH$, $^\bullet CH(CH_3)_2OH$, and $^\bullet C(CH_3)_2OH$.

The effect of 2-propanol on the t-AmOOH reaction suggests that to a small extent this alcohol can intercept t-AmO$^\bullet$ prior to the β-scission reaction of eq 6 but that the other alcohols cannot. This can be interpreted to mean that only the secondary alcohol, being more reactive, can compete with eq 6.

Comparisons with H_2O_2. The reaction of VO^{2+} with H_2O_2 forms hydroxyl radicals.[9,10] The kinetics of this reaction were examined by ESR techniques,[41] which pointed to the same mechanism as shown in eqs 3 and 4. The nature of the subsequent reactions with HO$^\bullet$ was different, however, resulting in certain algebraic and kinetic differences. That aside, the values of k_3 (eq 3) are 52, 4.2, and 4.1 L mol^{-1} s^{-1} for H_2O_2, t-BuOOH, and t-AmOOH, respectively; and the values of the ratio k_{-3}/k_4 are 250, 3.8, and 3.9 L mol^{-1} for the same three cases.

The value of k_3 might be expected to be about twice as high for H_2O_2 as compared to ROOH, for statistical reasons. Indeed, reductions by $Cr(H_2O)_6^{2+}$ and $V(H_2O)_6^{2+}$ of these reagents follow

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(37) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 3091.

(38) Reynolds, W. L.; Kolthoff, I. M. *J. Phys. Chem.* **1956**, *60*, 969.

(39) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.

(40) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1982** *NSRDS-NBS70.*

(41) Brooks, H. B.; Sicilio, F. *Inorg. Chem.* **1971**, *10*, 2530.

that pattern with $k_{H_2O_2}/k_{ROOH}$ typically 3–5.[20,26] Perhaps it is better to compare the composite of constants k_3k_4/k_{-3} for the VO^{2+} reactions. This composite represents the net reaction flux through both steps and is thus comparable to the "simple" bimolecular rate constants for Cr^{2+} and V^{2+} where peroxide binding and peroxide cleavage steps are not separated. The values for VO^{2+} are 0.21 (H_2O_2), 1.1 (*t*-BuOOH), and 1.0 (*t*-AmOOH). The statistical factor is not evident—indeed, it is reversed—but the reactivities are more comparable than would be concluded from k_1 values alone.

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Contribution from the Institut für Anorganische Chemie,
Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Germany

Electron-Transfer-Induced Isomerization η^2(C=C) → η^1(N) of the Tetracyanoethylene Complex $(C_6N_4)W(CO)_5{}^{0/\bullet-}$

Thomas Roth and Wolfgang Kaim*

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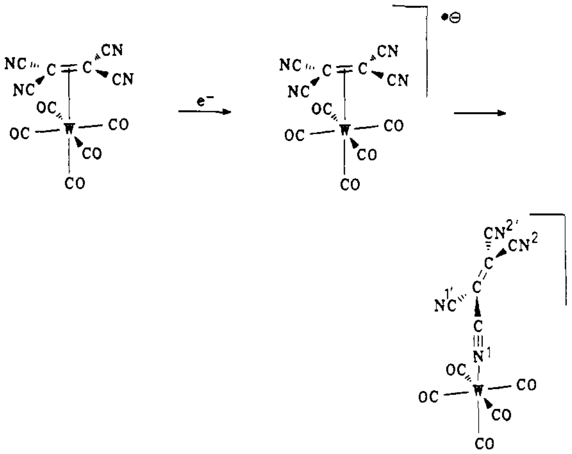
Single-electron transfer to the π(C=C)-bonded tetracyanoethylene (TCNE) ligand in the blue complex with $W(CO)_5$ leads to a yellow isomerized anion-radical product in which $TCNE^{\bullet-}$ coordinates via one nitrile nitrogen lone pair. The high-resolution EPR, UV/vis, and infrared data of the singly reduced complex clearly illustrate the lowered symmetry and diminished π-back-donation in the anionic form. Cyclic voltammetric experiments at variable scan rates show two distinctly separate second reduction processes of the π- and σ-coordinated complexes in what appears to be an organometallic example of "molecular hysteresis" (Sano, M.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 2327).

Introduction

Cyanoolefins, and especially tetracyanoethylene (TCNE), have long been recognized as ambidentate ligands toward metal centers.[1-4] Both the electron-acceptor-substituted C=C bond and the N lone pairs of the nitrile functions are well established to coordinate inorganic and organometallic 16-valence-electron complex fragments.[1-3] Whereas hard-metal centers prefer the σ(N) coordination mode,[2] "soft" and π-electron-rich organometallics prefer the π(olefin) coordination.[1] The prediction of the type of coordination mode is not always easy, as the reformulation of $(C_5R_5)(CO)_2Mn(TCNE)$ from a π(C=C)-[4a,b] to a σ(N)-coordinated complex has shown.[3,5] In this contribution we present detailed electrochemical and spectroscopic evidence for the coordination of the $W(CO)_5$ fragment by TCNE in both ways, depending on the *oxidation state* of this ligand (1).[6]



Scheme I

$$\begin{tikzcd}
(\eta^2\text{-TCNE})W(CO)_5 \arrow[r, shift left, "-0.19\ V"] & {[(\eta^2\text{-TCNE})W(CO)_5]^{-\bullet}} \arrow[l, shift left] \arrow[r, shift left, "-1.12\ V"] \arrow[d] & {[(\eta^2\text{-TCNE})W(CO)_5]^{2-}} \arrow[l, shift left] \arrow[d, "fast"] \\
(\eta^1\text{-TCNE})W(CO)_5 \arrow[u, "fast"'] & {[(\eta^1\text{-TCNE})W(CO)_5]^{-\bullet}} \arrow[l, "(+0.20\ V)"'] \arrow[r, shift left, "-0.96\ V"] & {[(\eta^1\text{-TCNE})W(CO)_5]^{2-}} \arrow[l, shift left]
\end{tikzcd}$$

Experimental Section

The synthesis of blue $(C_6N_4)W(CO)_5$ was described previously.[3,4] The singly reduced form was preferably generated as a yellow persistent species in polar but noncoordinating acetone via addition of KBH_4 or *n*-Bu_4NBH_4. In a typical experiment, a solution of 500 mg (1.1 mmol) of $(TCNE)W(CO)_5$ in 50 mL of acetone was combined with a 385-mg (1.5 mmol) amount of *n*-Bu_4NBH_4 at room temperature. The yellow-brown solution formed was kept for 48 h at −30 °C. Concentration of this solution by removal of solvent in vacuo gave a dark, noncrystalline, and air-sensitive material which could not be redissolved in acetone and was not characterized further.

Instrumentation. For cyclic voltammetry a Princeton Applied Research potentiostat/function generator 273/175 and a three-electrode configuration with glassy-carbon working electrode, Pt counter electrode, and Ag/AgCl as reference were used. Internal calibration was done with the ferrocene/ferrocenium pilot system in dichloromethane/0.1 M *n*-Bu_4NPF_6. For EPR measurements a Bruker spectrometer ESP 300 in the X band was used. *g* factors were determined by using a Bruker NMR gaussmeter ER035M and a HP 5350B microwave counter. Computer simulations of EPR spectra were performed using available programs.[7a] For IR spectrometry a Perkin-Elmer spectrometer 684 was employed, and for UV/vis a Bruins Instruments spectrometer Omega 10 was used.

HMO/McLachlan perturbation calculations of π spin populations ρ were carried out using standard routines[7b,9] with the parameters h_N =

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(1) Baddley, W. H. *Inorg. Chim. Acta, Rev.* **1968**, *2*, 7.

(2) (a) Rettig, M. F.; Wing, R. M. *Inorg. Chem.* **1969**, *8*, 2685. (b) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432. (c) McQueen, A. E. D.; Blake, A. J.; Stephenson, T. A.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1533.

(3) (a) Olbrich-Deussner, B.; Gross, R.; Kaim, W. *J. Organomet. Chem.* **1989**, *366*, 155. (b) Olbrich-Deussner, B.; Kaim, W.; Gross-Lannert, R. *Inorg. Chem.* **1989**, *28*, 3113.

(4) (a) Herberhold, M. *Angew. Chem.* **1972**, *84*, 773. (b) Herberhold, M. *Angew. Chem.* **1968**, *80*, 314; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 305. (c) Kaim, W.; Olbrich-Deussner, B.; Roth, T. *Organometallics* **1991**, *10*, 410.

(5) Braunwarth, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1989**, *372*, C23.

(6) (a) For a general discussion of structural consequences of electron transfer see: Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275. Potential applications of such systems in the field of molecular electronics are described in: Kölle, U. *Angew. Chem.* **1991**, *103*, 970; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 956. (b) Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888. (c) Geiger, W. E.; Salzer, A.; Edwin, J.; von Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113. (d) Sano, M.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 2327.

(7) (a) Modification of the program described by Oehler, U. M.; Janzen, E. G. *Can. J. Chem.* **1982**, *60*, 1542. (b) Heilbronner, E.; Bock, H. *The HMO Model and its Application*; Wiley: New York, 1976. McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

(8) (a) Bell, S. E.; Field, J. S.; Haines, R. J.; Sundermeyer, J. *J. Organomet. Chem.*, in press. (b) Bell, S. E.; Field, J. S.; Haines, R. I.; Moscherosch, M.; Matheis, W.; Kaim, W. Submitted for publication in *Inorg. Chem.*

0020-1669/92/1331-1930$03.00/0