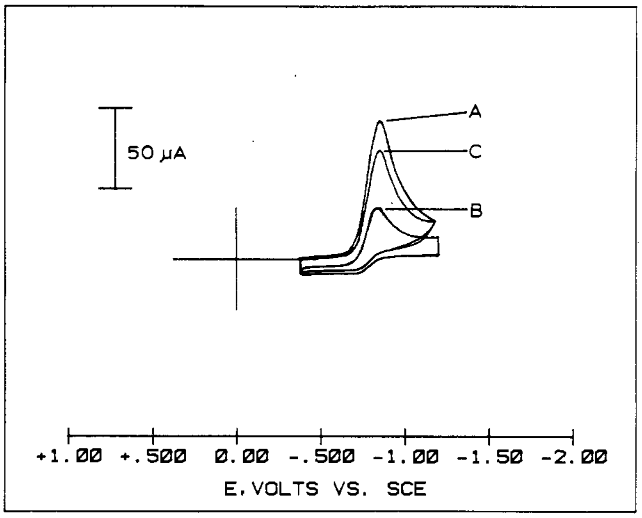

Figure 3. Thin-layer cyclic voltammograms of 1.0 mM $[Ni(slppy)]^+$ in 0.4 M TEAP/DMF (scan rate 5 mV): (A) initial cyclic voltammogram started at −0.300 V in negative direction; (B) second cycle showing a greatly diminished reduction wave; (C) cyclic voltammogram scan started after resting at −0.300 V for 15 min.

from which $E^{\circ\prime} = -1.527$ V and $n = 1.04$ are obtained. Thus, these techniques of spectroelectrochemistry allow relatively precise determination of $E^{\circ\prime}$ (to a few millivolts) and n as well as provide the spectra of otherwise rather inaccessible species.

For the copper systems the results are in accord with the general trends established by Patterson and Holm.[16] One point worth noting is that $E^{\circ\prime}$ is little changed whether the terminal group is a deprotonated phenolic oxygen or a deprotonated pyrrolic nitrogen. However, replacing either of these groups by a pyridine nitrogen gives rise to a dramatic positive shift in $E^{\circ\prime}$. Such a shift may result from a stabilization of the Cu(I) species or a destabilization of the Cu(II) moiety. Both of these may occur here. Pyridine, which is capable of significant back-bonding,[17] is expected to stabilize the Cu(I) moiety. That the $E^{\circ\prime}$ of Cu(sltsl) is significantly more positive than those of Cu(slesl), Cu(slpsl), Cu(slppl), and Cu(plppl) illustrates the fact that imposing pseudotetrahedral geometry also stabilizes Cu(I) while destabilizing Cu(II).[5,16]

Where measurable, the $E^{\circ\prime}$ values of the nickel complexes are much more negative than those of the corresponding copper systems (Table II), illustrating the fact that the Ni(I) state is much less accessible than is Cu(I). For the same reason the ligand-to-metal charge-transfer bands of Ni(II) proteins occur at much higher energies than the analogous bands of Cu(II) proteins.[8]

The thin-layer cyclic voltammogram of $[Ni(slppy)]^+$ is quite different from the normal case, as shown in Figure 3. The first scan, A, appears to represent an irreversible process. On the negative scan a reduction peak occurs, but on the positive scan no reoxidation wave is observed and no value of $E^{\circ\prime}$ may be assigned. This is most easily ascribed to some unknown chemical (or physical) reaction that occurs rapidly following electrochemical reduction to remove the reduced species so that the reverse oxidation is not electrochemically possible. Quite remarkably, the system still appears to be chemically reversible. Scan B, begun immediately after scan A, shows much less material available for reduction; however, if the system is held at a potential positive of the reduction potential for 15 min and then scan C is begun, the reduction wave, albeit somewhat reduced in magnitude relative to scan A, is again observed. Whether the ligand or the metal center is reduced and what the nature of the follow-up reaction is are questions that cannot be answered at present. Two possibilities that might explain the follow-up reaction are disproportionation of Ni(I) or precipitation of the reduced form of the complex.

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Registry No. $[Cu(slppy)]NO_3$, 75675-06-8; Cu(plppl), 21297-44-9; Cu(slppl), 75675-09-1; Cu(slpsl), 21051-65-0; Cu(slesl), 14167-15-8; $[Cu(pyppy)](ClO_4)_2$, 15772-23-3; $[Ni(slppy)]NO_3$, 75675-08-0; $[Ni(slppy)]BF_4$, 86688-20-2; Ni(slppl), 75675-10-4; Ni(plppl), 15158-90-4.

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[16] Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

[17] Elder, R. C. *Inorg. Chem.* **1968**, *7*, 2316.

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

Reactions of Bis(dimethylglyoximato)cobalt(II) Complexes with *tert*-Butyl Hydroperoxide

James H. Espenson* and Jon D. Melton

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The reaction of the cobalt(II) cobaloxime[1] $Co(dmgH)_2OH_2$ with various alkyl hydroperoxides $RC(CH_3)_2OOH$ leads, in aqueous or semiaqueous solution, to an organocobalt complex, $RCo(dmgH)_2OH_2$.[2] This product, the net stoichiometry (eq 5), and the rate law (eq 1) (shown here for *tert*-butyl hydroperoxide)

$$-d[Co(dmgH)_2OH_2]/dt = 2k_1[Co(dmgH)_2OH_2][(CH_3)_3COOH] \quad (1)$$

are all readily accounted for by the mechanism shown in Scheme I.

Scheme I

$$(CH_3)_3COOH + Co(dmgH)_2OH_2 \xrightarrow{k_1} HOCo(dmgH)_2OH_2 + (CH_3)_3CO\cdot \quad (2)$$

$$(CH_3)_3CO\cdot \xrightarrow{\text{fast}} (CH_3)_2CO + \cdot CH_3 \quad (3)$$

$$\cdot CH_3 + Co(dmgH)_2OH_2 \xrightarrow{\text{fast}} CH_3Co(dmgH)_2OH_2 \quad (4)$$

$$\text{net: } (CH_3)_3COOH + 2Co(dmgH)_2OH_2 = HOCo(dmgH)_2OH_2 + (CH_3)_2CO + CH_3Co(dmgH)_2OH_2 \quad (5)$$

In contrast, essentially the same reaction in benzene, carried out so as to produce the cobalt(II) complex by photolysis of an alkyl(pyridine)cobaloxime, was reported to produce (*tert*-butylperoxy)cobaloxime, $(CH_3)_3COOCo(dmgH)_2py$.[3] There can be little doubt of its identity, as the cumylperoxy analogue, obtained analogously, was characterized by single-crystal X-ray diffraction and all of the alkylperoxy compounds were characterized by spectroscopic methods.[3] A direct examination of the reaction between $Co(dmgH)_2py$ and $(CH_3)_3COOH$ in benzene was undertaken to seek an explanation for such a major effect of solvent change.

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[1] Cobaloxime = $Co(dmgH)_2$ (Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *4*, 97), where $dmgH^-$ represents the monoanion of dimethylglyoxime (=2,3-butanedione dioxime).

[2] Espenson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953.

[3] Giannotti, C.; Fontaine, C.; Chiaroni, A.; Riche, C. *J. Organomet. Chem.* **1976**, *113*, 57.

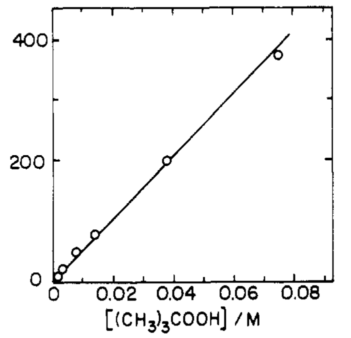

Figure 1. Illustration of the linear dependence of the pseudo-first-order rate constant upon the concentration of *tert*-butyl hydroperoxide. The kinetic data were taken in benzene at 25 °C.

Results

The stoichiometry of the reaction in benzene was determined by spectrophotometric titration of $(CH_3)_3COOH$ with $Co(dmgH)_2py$; a 1:1 end point was thus determined when the hydroperoxide was in excess throughout the reaction.[4] Chromatography on silica gel (TLC plates and column) yielded only two products, $(CH_3)_3COOCo(dmgH)_2py$ (R_f 0.61) and $HOCo(dmgH)_2py$; they were judged visually to have been produced in comparable amounts, but owing to extensive tailing of the latter, no quantitative determination was made. (The mechanism given below would lead to a 1:1 ratio.) Both products were identified by ^1H NMR, and the peroxide was also identified by elemental analysis.[5] No $CH_3Co(dmgH)_2py$ was detected; control experiments using the authentic material (by itself and added to reaction mixtures) were used to validate its absence in the benzene experiments. The kinetics of the reaction between $Co(dmgH)_2py$ and $(CH_3)_3COOH$ in benzene was studied under two sets of conditions. The most extensive measurements were made flash photolytically, by generating $Co(dmgH)_2py$ from the photolysis of an organocobaloxime (usually $(CH_3)_2CHCo(dmgH)_2py$) in the presence of a 10- to 500-fold excess of the hydroperoxide. The decay of the Co(II) absorption at λ 460 nm followed pseudo-first-order kinetics. The plot of k_{obsd} vs. $[(CH_3)_3COOH]$ was linear (Figure 1) with a slope $(4.93 \pm 0.8) \times 10^3$ M^{-1} s^{-1} at 25 °C.[6] The rate equation in benzene is thus

$$-d[Co(dmgH)_2py]/dt = k_{exptl}[Co(dmgH)_2py][(CH_3)_3COOH] \quad (6)$$

The reaction was also studied by using stopped-flow methods to extend the measurements to solutions containing an excess of the Co(II) complex. Practical considerations limited the $[Co(II)]_0/[(CH_3)_3COOH]_0$ ratio to ≤10, owing to the light absorption of the excess reagent. Although a secondary (and unidentified) absorption change was detected, the principal reaction is as before. The rate constant, $k_{exptl} = (5.3 \pm 0.4) \times 10^3$ M^{-1} s^{-1}, agrees with the more accurate determinations employing excess hydroperoxide.

Finally, experiments were done in benzene with use of $(CH_3)_2CH(CH_3)_2COOH$. In that case an organocobaloxime identified as $(CH_3)_2CHCo(dmgH)_2py$ is formed. In effect, even in benzene, Scheme I is applicable[7] to this hydroperoxide but not to *tert*-butyl hydroperoxide. Thus, the explanation sought in the present instance is to be one that is unique to the latter.

Interpretation and Discussion

The results obtained lead us to suggest that $Co(dmgH)_2py$ reacts with excess *tert*-butyl hydroperoxide[6] in benzene according to the mechanism given in Scheme II. The first step

Scheme II

$$Co(dmgH)_2py + (CH_3)_3COOH \xrightarrow{k_7} HOCo(dmgH)_2py + (CH_3)_3CO\cdot \quad (7)$$

$$(CH_3)_3CO\cdot + (CH_3)_3COOH \xrightarrow{k_8} (CH_3)_3COH + (CH_3)_3COO\cdot \quad (8)$$

$$(CH_3)_3COO\cdot + Co(dmgH)_2py \xrightarrow{k_9} (CH_3)_3COOCo(dmgH)_2py \quad (9)$$

$$\text{net:}\quad 2(CH_3)_3COOH + 2Co(dmgH)_2py = HOCo(dmgH)_2py + (CH_3)_3COH + (CH_3)_3COOCo(dmgH)_2py \quad (10)$$

(eq 7) is identical with the first step in the aqueous reaction, save for the change in axial base from H_2O to py. The rate equation[8] associated with Scheme II, provided the reaction of eq 7 is rate limiting, is

$$-d[Co(dmgH)_2py]/dt = 2k_7[Co(dmgH)_2py][(CH_3)_3COOH] \quad (11)$$

which agrees with the experimental result of eq 6 with $k_7 = k_{exptl}/2 = (2.5 \pm 0.1) \times 10^3$ M^{-1} s^{-1} in benzene at 25 °C. The assignment of reaction 7 is consistent with the products observed in benzene, with the mechanism in aqueous solution, and with the first step of analogous reactions of Cr(II), Ti(III), and Fe(II).[9-11] Further evidence comes from the experiments involving $(CH_3)_2CH(CH_3)_2COOH$, which suggest that an alkyloxy radical is formed, which (unlike the *tert*-butyloxy radical in benzene) undergoes β-scission (eq 3b[7]).

The mechanism shown in Scheme II assigns the primary reaction of the *tert*-butyloxy radical in benzene as hydrogen abstraction from the parent hydroperoxide (eq 8), rather than β-scission. The rate constant has been measured: $k_8 = 2.5 \times 10^8$ M^{-1} s^{-1} in benzene.[12] On the basis of data using cyclohexane as a competing reagent for hydrogen atom abstraction,[13] the rate constant for β-scission is calculated to be

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(4) The reverse order of titration was not successful. There was evidence of a secondary reaction in that absorbances drifted with time. In addition, the titration plot was curved, indicating the stoichiometry was changing with the reactant ratio.

(5) The peroxide has ^1H NMR resonances at δ 2.23 and 0.90 in the expected 12:9 ratio. The inorganic product shows only a singlet at δ 2.10. (In addition, both display the expected pyridine resonances.) Anal. Calcd for $CoC_{17}H_{28}N_5O_6$: C, 44.64; N, 15.31; H, 6.17. Found: C, 43.64; N, 14.27; H, 6.18.

(6) We are grateful to a reviewer for calling to our attention the partial dimerization of alkyl hydroperoxides in nonpolar solvents. The equilibrium constant for $(CH_3)_3COOH$ is 1.98 dm^3 mol^{-1} ($\Delta H° = 23.8$ kJ mol^{-1}) at 20 °C in CCl_4 (Yablonskii, O. P.; Lastochkina, N. S.; Belyayev, V. A. *Pet. Chem. USSR (Engl. Transl.)* **1973**, *13*, 261; *Neftekhimiya* **1973**, *13*, 851). That corresponds to a maximum decrease of ~15% at 25 °C in the monomer concentration as compared to the stoichiometric value at the highest concentration employed. The concentrations used in the kinetic analysis were not corrected for this equilibrium, however, since values applicable to benzene do not appear to have been reported. The very slight downward curvature in Figure 1 may, in fact, reflect the effect of dimerization and its nearly negligible extent. In particular, the curve shown does not exhibit a quadratic dependence on hydroperoxide concentration, which would be the case were the dimer the reactive form.

(7) With, of course, appropriate changes in the formulas such that eq 3, for example, becomes

$$(CH_3)_2CHC(CH_3)_2O\cdot \rightarrow (CH_3)_2CO + (CH_3)_2\dot{C}H \quad (3b)$$

(8) We call attention to the correct inclusion of the stoichiometric factor of 2 in the rate law of eq 11, despite the stoichiometric reaction being one in which the reactants are consumed in a 1:1 ratio.

(9) Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. *Trans. Faraday Soc.* **1951**, *47*, 462.

(10) Samuni, A.; Meisel, D.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1273.

(11) (a) Kochi, J. K.; Mocadlo, P. E. *J. Org. Chem.* **1965**, *30*, 1133. (b) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

(12) Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

$\sim 3 \times 10^4$ s^{-1} in benzene, many times smaller than in water. Thus, the fraction of *tert*-butyloxy radicals undergoing β-scission would be ~8% at the lowest concentration of *tert*-butyl hydroperoxide. The corresponding low yield of methylcobaloxime would have been below the detection limit. That this explanation is a reasonable one is demonstrated from known solvent effects. Polar solvents, particularly those capable of hydrogen bonding, accelerate greatly the rate of β-scission of *tert*-butyloxy radicals by stabilizing the transition state.[13,14] Polar solvents also decrease the rate of hydrogen atom abstraction because of the greater solvation of alkyloxy radicals.[14] Both effects favor β-scission over hydrogen atom abstraction in water but the reverse in benzene. The rate of β-scission of $(CH_3)_2CHC(CH_3)_2O\cdot$ (eq 3b) is so much higher[14b,15] that, even with this effect, β-scission remains the major pathway in benzene.

The final step in the mechanism is assigned to a rapid bimolecular reaction between $Co(dmgH)_2py$ and the alkylperoxy radical. Although no examples can be cited, the analogous coupling of $Co(dmgH)_2py$ and alkyl radicals occurs quite rapidly. In addition, eq 9 leads to the product actually isolated under the experimental conditions.

The situation where $Co(dmgH)_2py$ was in excess over $(CH_3)_3COOH$ is not as clearly defined. Secondary reactions were observed, however, and thus the expectation[13] of a substantial yield (~60%) of methylcobaloxime (<25% was detected) was based on estimates that were not able to allow for all the reactions occurring.

Conclusions

The change in products and stoichiometry between aqueous and benzene solution arises from the solvent effect on the rate constant for β-scission of the first radical intermediate, $(CH_3)_3CO\cdot$. In benzene, this is so slow that hydrogen atom abstraction occurs instead, leading to a second oxygen-centered radical, $(CH_3)_3COO\cdot$, and finally to the isolated product $(CH_3)_3COOCo(dmgH)_2py$.

Experimental Section

Flash photolytic measurements were made by photolyzing 2×10^{-4} M $(CH_3)_2CHCo(dmgH)_2py$ in benzene with visible light in a Xenon Corp. Model 710C system. Absorbance changes were monitored at 460 nm, where the molar absorptivity of the Co(II) complex, the principal absorbing species, is ca. 2.1×10^2 M^{-1} cm^{-1}. Stopped-flow measurements were made with a Canterbury SF-3A instrument at a wavelength of 520 nm. Samples spotted on TLC plates were eluted with a 2:2:1 mixture of ethyl acetate, chloroform, and methanol. Column chromatography was done similarly, with a second elution using a 7:7:1 mixture of the same solvents and a jacketed column held at 0 °C and wrapped with aluminum foil. Crystalline products were isolated by rotary evaporation.

tert-Butyl hydroperoxide was the commerical (90%) material, and 2,3-dimethyl-2-butyl hydroperoxide was prepared according to the literature method[16] as were the cobaloximes.[17]

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82.

Registry No. $(CH_3)_3COOCo(dmgH)_2py$, 86561-35-5; $HOCo(dmgH)_2py$, 15688-61-6; $Co(dmgH)_2py$, 36451-60-2; $(CH_3)_3COOH$, 75-91-2; benzene, 71-43-2.

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(13) The ratio of rate constants for H atom abstraction from cyclohexane to that of β-scission is $k_H/k_\beta = 48.6$ M^{-1} in benzene at 298 K (Walling, C.; Wagner, P. J.; *J. Am. Chem. Soc.* **1964**, *86*, 3368). This ratio and the independently determined value $k_H = 1.6 \times 10^6$ M^{-1} s^{-1} in benzene (Scaiano, J. C., personal communication) afford the value cited for k_β.

(14) (a) Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 49. (b) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(15) Choo, K. Y.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 833.

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(17) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

Contribution from the Dipartimento di Chimica
and Istituto di Mineralogia e Cristallografia,
Università di Perugia, 06100 Perugia, Italy

Exchange Interaction in Multinuclear Transition-Metal Complexes. 4.[1] Relative Magnetic Coupling in Hydroxo- and Methoxo-Bridged Dinuclear Complexes of Iron(III) with the Heptadentate Schiff Base Trisalicylidenetriethylenetetramine

B. Chiari, O. Piovesana,* T. Tarantelli, and P. F. Zanazzi

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There is a continuing interest, from both an experimental[2] and theoretical[3,4] point of view, in determining whether the magnetic properties of exchange-coupled transition-metal compounds can be examined in terms of their geometrical and chemical features.

Combined magnetic and structural information is so far available for about 10 dinuclear iron(III) compounds having Fe_2O_2 bridging units, which have been briefly reviewed elsewhere.[5,6] As has been noted by us[5,6] and by others,[7] variations in weak antiferromagnetic coupling ($7 < |J| < 17$ cm^{-1}) within this series defy unified and comprehensive interpretation in terms of geometrical and chemical changes. Also, the behavior of these compounds seems to raise doubts about the proposed general applicability of the MO formalism that has been widely and successfully used to rationalize the magnetic properties of a number of copper(II)[4] or chromium(III)[8] coupled dimers. It must however be recognized that the analysis of the magnetic data for the Fe_2O_2 series is complicated by the fact that fully characterized compounds generally involve different ligands and coordination geometries.

Recently, we have described[6] the X-ray structure and magnetic properties of $Fe_2L(OCH_3)Cl_2$ (L^{3-} is the anion of the heptadentate Schiff base trisalicylidenetriethylenetetramine) having an Fe–OMe–Fe–OPh bridging unit.

Tasker et al.[9] have performed an X-ray analysis of the tetrahydrofuran solvate of the hydroxy analogue, $Fe_2L(OH)Cl_2\cdot C_4H_8O$, using crystals taken from ill-defined mixtures. The synthesis of the compound was not achieved.

In order to test the effect of changing the electron density at the bridging atom on the metal–metal coupling for a magnetically condensed iron(III) system, we have now completed the synthesis of $Fe_2L(OH)Cl_2\cdot C_4H_8O$, verified by X-ray methods that its X-ray structure is the same as that reported in the literature, and examined the magnetic behavior of the compound in the temperature range ~4–200 K.

A comparison of X-ray data for the hydroxy and methoxy compounds shows that, except for the substituent linked to one bridging oxygen, the dinuclear molecules are virtually identical. Since, in addition, the electronic structures of the methoxy and hydroxy bridges are likely to be very similar, one has a situation where the relative J values for the two species should provide a reliable test of general expectations of MO theory regarding the effect on magnetic coupling of variations in electron density at the bridging atom.[4]

Experimental Section

Preparation. The LH_3 ligand has been prepared according to known procedures.[10]

$Fe_2L(OH)Cl_2\cdot C_4H_8O$. LH_3 (0.46 g, 1 mmol) was dissolved, at room temperature, in a 25-mL portion of a solution composed of 50 mL of tetrahydrofuran, 0.25 mL of triethylenetetramine, and 0.25 mL of water. The remaining portion of this solution was used to dissolve 0.54 g (2 mmol) of $FeCl_3\cdot 6H_2O$. The iron chloride and LH_3 solutions

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* To whom correspondence should be addressed at the Dipartimento di Chimica.

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