Since ϕ is nearly pH independent in the pH 7–9 range, $Cr(YH)(CN)_2(H_2O)^{2-}$ clearly is not the primary photoactive form. We conclude that most if not all of the photochemistry is due to $Cr(Y)(CN)_2(H_2O)^{3-}$. That is, the photoaquation yield for the former complex could be comparable to that for the latter one but cannot be very much larger. There is a small increase in ϕ values between pH 7 and 9, even after correction for the fraction present in unprotonated form. This increase appears to be outside of our experimental error. Possibly, some further deprotonation occurs, e.g. of the coordinated water, to give a more photoactive species. No detailed studies were made, but qualitative results indicate that ϕ is not highly temperature dependent.

It is of interest to consider the application of the photolysis[18] and emission[19] rules for Cr(III) complexes. Figure 6 shows the four possible geometric isomers if the EDTA ligand in $Cr(Y)(CN)_2(H_2O)^{3-}$ is coordinated through two nitrogens and one carboxyl group. In three of these, C_1, C_2, and C_3, the cyano groups are cis, and in the fourth, T, they are trans. For all four cases, the photolysis rules predict the yield for cyanide aquation to be small, as observed, since the cyano group does not lie on the weak-field axis. In cases C_1, C_3, and T, the labilized group should be a coordinated nitrogen, for which permanent detachment and consequent net photolysis seem unlikely. In case C_2, either water exchange or aquation of a carboxyl group would be predicted, processes that we would not have been able to observe. According to the emission rules, the emission lifetime for C_1 might be observable since neither grop on the weak-field axis is substitutionally very labile. For C_2, C_3, and T, however, the emission lifetime should be short, as observed, since the weak-field axis contains a coordinated carboxyl group, which is substitutionally labile in the Cr(III)–EDTA family. The cis isomers seem to be preferred in this family, and our tentative conclusion is that the complex is in the form C_2 or C_3.

Summary

The complex $Cr(Y)(CN)_2(H_2O)^{3-}$ resembles the various cyano–aquo and cyano–ammine complexes of Cr(III) in that the thermal reaction is one of cyanide aquation, the rate increasing with decreasng pH. Unlike the other cases, however, there does not appear to be appreciable contribution to the rate from a path involving –CrCNH. It is possible that the aquation is assisted by internal protonation of a cyano group through hydrogen bonding from a noncoordinated but protonated carboxyl group.

While the cyano–ammine complexes show primarily *ammonia* photoaquation, the photochemistry of our complex is one of *cyanide* aquation only. A likely explanation, however, is that labilization of other ligands either is blocked or, if it does occur, is unobservable under our conditions. Both the quantum yield behavior and the emission behavior are consistent with the photolysis and emission rules proposed for Cr(III) complexes.

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Registry No. $Na_3[Cr(Y)(CN)_2(H_2O)]$, 86900-67-6; $Cr(YH)(H_2O)$, 15955-81-4.

Contribution from the Nuclear Research Centre Negev, Beer-Sheva, Israel,
Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel,
and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Reaction of $\cdot CH_2C(CH_3)_2OH$ Radicals with Cobalt(II) Tetrasulfophthalocyanine in Aqueous Solutions. A Pulse Radiolytic Study[1]

YACOV SOREK,[2a] HAIM COHEN,[2a] WILLIAM A. MULAC,[2b] KLAUS H. SCHMIDT,[2b]
and DAN MEYERSTEIN*[2a–c]

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The reaction of cobalt(II) tetrasulfophthalocyanine, $[Co^{II}(tspc)]^{4-}$, with $\cdot CH_2C(CH_3)_2OH$ free radicals was studied. The results indicate that the first product formed is $[(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-}$. This product loses water via β elimination to yield $[(tspc)Co^{III}CH{=}C(CH_3)_2]^{4-}$. The decomposition of the latter compound yields $[Co^{I}(tspc)]^{5-} + OCHCH(CH_3)_2$ at pH ≥ 9.5, $[Co^{III}(tspc)]^{3-} + CH_2{=}C(CH_3)_2$ at pH ~ 6, and mainly $[Co^{II}(tspc)]^{4-}$ plus equal amounts of $CH_2{=}C(CH_3)_2$ and $OCHCH(CH_3)_2$ at pH ~ 3. The results suggest that a p*K* of the water molecule trans to the aliphatic residue affects the mechanism of hydrolysis. A further reaction is observed, the exact nature of which is not fully understood. For comparison purposes the oxidation of $[Co^{II}(tspc)]^{4-}$ by $Br_2^{-}\cdot$ and its reduction by $CO_2^{-}\cdot$ were studied.

Introduction

Pulse radiolysis is a powerful technique for the study of the properties of short-lived intermediates with metal–carbon bonds formed in reactions of aliphatic free radicals with low-valent transition-metal complexes.[3–6] Of special interest is the possibility to measure the rate of β elimination of hydroxyl groups. Three reactions of this type have been studied so far in aqueous solutions:[7a]

$$[(H_2O)_5Cr^{III}CH_2C(CH_3)_2OH]^{2+} \rightarrow (H_2O)_5Cr^{III}CH{=}C(CH_3)_2 + H_2O \qquad (1)$$

$k_{obsd} = 1.0 \times 10^2 + (1.1 \times 10^3)[H_3O^+]\ \mathrm{s}^{-1}$[4]

$$[(H_2O)_nCu^{III}CH(CO_2){-}CH(OH)CO_2]^- \rightarrow [(H_2O)_nCu^{III}C(CO_2){=}CHCO_2]^- + H_2O \qquad (2)$$

$k = 2 \times 10^2\ \mathrm{s}^{-1}$[5]

$$Co^{III}L_1(CH(OH)CH_2OH) \rightarrow Co^{III}L_1(CH_2CHO) + H_2O \qquad (3)$$

$k = 4\ \mathrm{s}^{-1}$ at pH 5.0 and $k = 15\ \mathrm{s}^{-1}$ at pH 3.5[6]

where $L_1 \equiv$ 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-

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* To whom correspondence should be addressed at Ben Gurion University of the Negev.

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cyclotetradeca-4,11-diene. The last reaction is of special interest as it is a model reaction for that of the diol dehydratase enzyme which contains the coenzyme B_{12}.

We decided to extend these studies by a detailed study of the reaction

$$[\mathrm{Co^{II}(tspc)}]^{4-} + \cdot\mathrm{CH_2C(CH_3)_2OH} \rightarrow \text{products} \tag{4}$$

where tspc ≡ tetrasulfophthalocyanine.[7b]

This complex was chosen as it is expected to be a better model for the coenzyme B_{12} than CoL_1^{2+}[6] and because of the general interest in metal phthalocyanines as catalysts and photocatalysts in systems that involve free radicals.[9b] During this study Ferraudi and Patterson[10a] reported that the primary product in reaction 4 at pH 9.0 is indeed $[Co^{III}(tspc)CH_2C(CH_3)_2OH]^{4-}$ as expected but the chemical properties of the latter product were not reported. As our preliminary results indicated that the formation of $[Co^{III}(tspc)CH_2C(CH_3)_2OH]^{4-}$ is followed by three further reactions, we continued our study using spectrophotometry as well as conductometry as analytical techniques and report here our results.

Experimental Section

The tetrasodium salt of Co^{II} 4,4′,4″,4‴-tspc was prepared by the procedure reported by Weber and Busch.[11] The UV–visible absorption spectrum was checked and was identical with that reported in the literature.[9,12] Anal. Calcd: C, 37.82; Co, 5.80. Found: C, 37.98, Co, 5.86.

Pulse radiolytic experiments using electron linear accelerators were carried out both at the Hebrew University of Jerusalem (5 MeV, 200 mAmp, 0.1–1.5 μs/pulse, dose per pulse 100–5000 rd) and at Argonne National Laboratory (12–18 MeV, 4–40 ns/pulse, dose per pulse 100–5000 rd).

Most of the spectra and all the spectrophotometric kinetic data were measured in Jerusalem; the conductometric measurements[13a–c] and some spectral measurements with the streak camera[13b] were carried out at Argonne.

The details of the experimental technique, including solution preparation and data analysis, are described elsewhere in detail.[4,6,13]

High integral dose irradiations were performed with a ^{60}Co γ source with a dose rate of 3×10^5 rd/h.

The 2-methylpropene content of solutions after irradiation was determined as follows: 25-mL quantities of N_2O-saturated solutions containing 4×10^{-3} M $[Co^{II}(tspc)]^{4-}$ and 0.1 M *tert*-Butyl alcohol at pH 3, 6.1, and 10.7 were irradiated for 133 min, with a dose rate of 5000 rd/min. Blank solutions, not containing $[Co^{II}(tspc)]^{4-}$, were also irradiated. The irradiated solution was injected into a 100-mL evacuated bottle, and water was added to complete solution volume to 90 mL. The solution was stirred with a magnetic stirrer, and aliquots from the gas phase, above the solution, were transferred into a P/Z gas chromatograph from LDC. The piezoelectric crystals of the detector were coated with Carbowax 400; calibration was done with pure 2-methylpropene obtained from Fluka.

Preparation of Free Radicals. The radiolysis of water, and dilute aqueous solutions, can be summed up by the equation[14]

$$\mathrm{H_2O} \xrightarrow{\gamma,\, e^-} e_{aq}^-,\ \cdot\mathrm{OH},\ \cdot\mathrm{H},\ \mathrm{H_2},\ \mathrm{H_2O_2},\ \mathrm{H_3O^+},\ \mathrm{OH^-(aq)} \tag{5}$$

These products are homogeneously distributed in the solution within less than 10 ns after absorption of the radiation. Their yields are $G(e_{aq}^-) = G(\cdot OH) = 2.65$, $G(\cdot H) = 0.60$, $G(H_2) = 0.45$, $G(H_2O_2) = 0.75$, $G(H_3O^+) \approx 3.65$, and $G(OH^-) \approx 1.0$.[14] (The G values are in units of molecules of product formed/100 eV absorbed in the solution.) In concentrated solutions the yield of the free radicals is somewhat higher and that of H_2 and H_2O_2 somewhat smaller.[14]

The hydrated electrons react with N_2O and H_3O^+:

$$e_{aq}^- + \mathrm{N_2O} \xrightarrow{\mathrm{H_3O^+}} \mathrm{N_2} + \cdot\mathrm{OH} \qquad k = 8.7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ {}^{15} \tag{6}$$

$$e_{aq}^- + \mathrm{H_3O^+} \rightarrow \cdot\mathrm{H} \qquad k = 2.3 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ {}^{15} \tag{7}$$

Thus in nitrous oxide saturated solutions, $[N_2O] \approx 2 \times 10^{-2}$ M, at pH ≥3 the hydrated electrons are transformed into hydroxyl radicals. Under these conditions ~90% of the free radicals formed by the radiation are ·OH radicals and the rest ·H atoms.

Preparation of $Br_2^-\cdot$. In nitrous oxide saturated solutions at pH ≥3 containing Br^- the following reactions occur:

$$\mathrm{Br^-} + \cdot\mathrm{OH} \rightarrow \cdot\mathrm{Br} + \mathrm{OH^-} \qquad k_8 > 10^9\ \mathrm{M^{-1}\ s^{-1}}\ \text{at pH} < 10^{16} \tag{8}$$

$$\cdot\mathrm{Br} + \mathrm{Br^-} \rightleftarrows \mathrm{Br_2^-}\cdot \qquad k_9 = 2 \times 10^5\ \mathrm{M^{-1}}\ {}^{16} \tag{9}$$

Thus all ·OH radicals are transformed into $Br_2^-\cdot$ radical anions, which have an absorption band with $\lambda_{max} = 360$ nm and $\epsilon_{max} = 8.2 \times 10^3$ M^{-1} cm^{-1}[17] and are strong oxidizing agents, $E°(Br^-/Br_2^-\cdot) = 1.77$ V.[18]

Preparation of $CO_2^-\cdot$. In N_2O-saturated solutions, at pH ≥3.0, containing HCO_2Na the following reactions occur:

$$\cdot\mathrm{OH}/\cdot\mathrm{H} + \mathrm{HCO_2^-} \rightarrow \mathrm{H_2O/H_2} + \mathrm{CO_2^-}\cdot \tag{10}$$

$$k_{\mathrm{OH+HCO_2^-}} = 3 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ {}^{19}$$

$$k_{\mathrm{H+HCO_2^-}} = 1.3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}\ {}^{20}$$

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(2) (a) Nuclear Research Centre Negev. (b) Argonne National Laboratory. (c) Ben-Gurion University of the Negev.

(3) (a) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43. (b) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882. (c) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1132. (d) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1977**, 934. (e) Brault, D.; Bizet, C.; Morlière, P.; Rougee, M.; Land, E. J.; Santus, R.; Swallow, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 1015. (f) Brault, D.; Neta, P. *Ibid.* **1981**, *103*, 2705. (g) Buxton, G. V.; Green, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

(4) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(5) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825.

(6) Elroi, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1978**, *100*, 5540.

(7) (a) In accord with the accepted nomenclature of organometallic compounds the oxidation state of the metal atom is calculated with the assumption that the alkyl group is a carbanion. (b) $[Co^{II}(tspc)]^{4-}$ appears in aqueous solutions as an equilibrium mixture of monomeric and dimeric forms.[8,9] The charges in the formulas $[Co^{II}(tspc)]^{4-}$ and $[Co_2(tspc)_2]^{8-}$ are formal, as due to ion pairing some of them are probably neutralized.

(8) (a) Schelly, Z. A.; Farina, R. D.; Eyring, E. M. *J. Phys. Chem.* **1970**, *74*, 617. (b) Schelly, Z. A.; Harward, D. J.; Hemmes, P.; Eyring, E. M. *Ibid.* **1970**, *74*, 3040.

(9) (a) Able, E. W.; Pratt, J. M.; Whelan, R. *J. Chem. Soc., Dalton Trans.* **1976**, 509. (b) Boucher, L. D. In: "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; p 461.

(10) (a) Ferraudi, G.; Patterson, L. K. *J. Chem. Soc., Dalton Trans.* **1980**, 476. (b) Day, P.; Hill, H. A. O.; Price, M. G. *J. Chem. Soc. A* **1968**, 90. (c) Rollman, L. D.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455. (d) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1975**, 360.

(11) Weber, J. H.; Busch, D. H. *Inorg. Chem.* **1965**, *4*, 469.

(12) (a) Gruen, L. C.; Blagrove, R. J. *Aust. J. Chem.* **1973**, *26*, 319. (b) Under the same conditions suggested by Gruen et al.[12a] we have found $\epsilon = 1.25 \times 10^5$ M^{-1} cm^{-1} at $\lambda_{max} = 663$ nm instead of 1.2×10^5 M^{-1} cm^{-1}.

(13) (a) Meisel, D.; Schmidt, K. H.; Meyerstein, D. *Inorg. Chem.* **1979**, *18*, 971. (b) Schmidt, K. H.; Ander, S. M. *J. Phys. Chem.* **1969**, *73*, 2846. (c) Schmidt, K. H. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 439. (d) Schmidt, K. H.; Gordon, S.; Mulac, W. A. *Rev. Sci. Instrum.* **1976**, *47*, 356. (e) Gordon, S.; Mulac, W. A.; Schmidt, K. H.; Syoblom, R. K.; Sullivan, J. S. *Inorg. Chem.* **1978**, *17*, 294. (f) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944. (g) Illan, Y. Ph.D. Thesis, Hebrew University of Jerusalem, 1977.

(14) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.

(15) Anbar, M.; Bambeneck, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1973**, *NSRDS-NBS 43*.

(16) Behar, D. *J. Phys. Chem.* **1972**, *76*, 1815. Zehavi, D.; Rabani, J. *Ibid.* **1972**, *76*, 312.

(17) Habersbergerovâ, A.; Janovský, I.; Teplý, J. *Radiat. Res. Rev.* **1968**, *1*, 109.

(18) Thoronton, A. T.; Laurence, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1632.

Thus all free radicals are transformed into $CO_2^-\cdot$ free radicals which have an absorption band with $\lambda_{max} = 250$ nm and $\epsilon_{max} = 2.25 \times 10^3$ M^{-1} cm^{-1} [17] and are strong reducing agents, $E°(CO_2/CO_2^-\cdot) = -1.3$ V.[21]

Preparation of $\cdot CH_2C(CH_3)_2OH$. In N_2O-saturated solutions, at pH ≥3.0, containing $(CH_3)_3COH$ the following reactions occur:

$$\cdot OH/\cdot H + (CH_3)_3COH \rightarrow H_2O/H_2 + \cdot CH_2C(CH_3)_2OH \qquad (11)$$

$$k_{OH+(CH_3)_3COH} = 4.2 \times 10^8\ M^{-1}s^{-1}\ ^{19}$$

$$k_{H+(CH_3)_3COH} = 8 \times 10^4\ M^{-1}\ s^{-1}\ ^{20}$$

Thus most of the free radicals are transformed into $\cdot CH_2C(CH_3)_2OH$ radicals. (As $k_{H+(CH_3)_3COH}$ is relatively low, the reactions of $\cdot H$ atoms with other substrates are often observed even when $(CH_3)_3COH$ is present in large excess. However, as the yield of $\cdot H$ atoms is ca. 10% of the free radical yield, their contribution to the reactions observed is often negligible.) The $\cdot CH_2C(CH_3)_2OH$ free radicals have no absorption at $\lambda > 300$ nm. They are expected to be relatively strong oxidizing and reducing agents,[21] forming $(CH_3)_3COH$ and $HOCH_2C(CH_3)_2OH$, respectively. However as they, as most aliphatic free radicals, react usually via the inner- and not via the outer-sphere mechanism, their redox potential has not been reported.[3a,6,22] (The measured polarographic half-wave potentials clearly involve large overpotentials.[21])

Significance of Measurement of Changes in Conductivity. In aqueous solutions the main changes in conductivity as a result of a redox reaction are due to the change in the concentration of H_3O^+ or OH^-. This is so because the specific conductivities of the two are considerably higher than those of all other ions and much higher than the change in conductivity due to the change in the oxidation state of a transition-metal complex.

Thus at pH <6.0, $[H_3O^+] \gg [OH^-]$, a reduction of a complex by free radicals produced in the pulse is accompanied by the formation of 1 equiv of H_3O^+ and therefore an increase in conductivity, and an oxidation process is accompanied by the consumption of 1 equiv of H_3O^+ and therefore in a decrease in the conductivity. At pH ≥8.0, $[OH^-] \gg [H_3O^+]$ and a reduction process results in a decrease in $[OH^-]$ and therefore in conductivity and oxidation in an increase in $[OH^-]$ and conductivity.[3a–c]

Results and Discussion

As the $\cdot CH_2C(CH_3)_2OH$ radicals may act as oxidizing and as reducing agents, we first studied the reaction of $[Co^{II}(tspc)]^{4-}$ with strong reducing, $CO_2^-\cdot$, and oxidizing, $Br_2^-\cdot$, reagents in order to obtain information on the properties of the reduced and oxidized forms of $[Co^{II}(tspc)]^{4-}$ under similar experimental conditions.

Reduction by $CO_2^-\cdot$. We chose $CO_2^-\cdot$ as the reducing radical as it is a powerful redox reagent[21] which in most systems reacts as an outer-sphere reducing agent. (The use of e_{aq}^- is complicated by the reactions of $\cdot OH$ or $\cdot CH_2C(CH_3)_2OH$.[10a] N_2O-saturated solutions containing $(1–5) \times 10^{-5}$ M $[Co^{II}(tspc)]^{4-}$ at different pHs were irradiated with a pulse of ca. 500 rd, producing ca. 3×10^{-6} M free radicals. The formation of a product with an absorption band around 460 nm was observed. From the dependence of the rate of formation of this product on $[Co^{II}(tspc)]^{4-}$ the rate of reaction 12, which

$$[Co^{II}(tspc)]^{4-} + CO_2^-\cdot \rightarrow [Co^{I}(tspc)]^{5-} + CO_2 \qquad (12)$$
$$k = (1.5 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}\ ^{25}$$

is independent of pH, was determined. The conclusion that the product is $[Co^{I}(tspc)]^{5-}$ is based on the observation that this reaction is acompanied by the concurrent consumption of 1 equiv of OH^- at pH 9.8[23a] as determined by the change in conductivity. The spectrum of $[Co^{I}(tspc)]^{5-}$ thus formed is plotted in Figure 1. (Note that the ordinate describes $\Delta\epsilon = \epsilon_{product} - \epsilon_{Co^{II}L}$ and not ϵ; all spectra in this paper are thus plotted.) This spectrum, which is nearly independent of pH in the range $3 < pH < 11$, is in good agreement with that obtained by Ferraudi et al.[10a] using other reducing agents and is similar to that of $[Co^{I}(tspc)]^{5-}$ [10b,c] and its aqueous[10d] solutions.

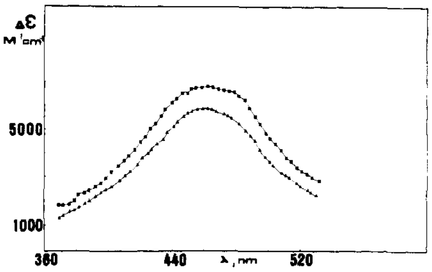

Figure 1. Difference spectra of products observed after a pulse producing 25 μM of free radicals (N_2O-saturated solution at pH 6.0, 6×10^{-5} M $[Co^{II}(tspc)]^{4-}$, 0.1 M HCO_2Na, 2-cm cell, streak camera spectra): (■) product 1 ms after pulse; (▲) permanent product. Absolute absorption coefficients were determined with use of a smaller pulse.

The formation of $[Co^{I}(tspc)]^{5-}$ is followed by a second reaction with an observed rate of $1.0 \pm 0.2\ s^{-1}$. This process causes a decrease in the absorption due to $[Co^{I}(tspc)]^{5-}$ of ca. 10–15% over the whole spectral range (Figure 1). Addition of 4×10^{-7} M H_2O_2 to the solution, an amount similar to that formed by the pulse, increased the bleaching to ca. 25–30%, the rate observed being unchanged. We conclude that the reaction observed is

$$[Co^{I}(tspc)]^{5-} + H_2O_2 \rightarrow \text{oxidation products} \qquad (13)$$
$$k_{13} \approx 2.5 \times 10^6\ M^{-1}\ s^{-1}$$

The $[Co^{I}(tspc)]^{5-}$ remaining after the reaction with H_2O_2 is stable for many minutes as determined by low-dose-rate irradiation and measurement of the spectrum of the product using a Cary 17 spectrophotometer.

As most of the $[Co^{II}(tspc)]^{4-}$ in the formate solutions is in the form of a dimer, we expected that a process due to the reaction $[Co^{I}(tspc)Co^{II}(tspc)]^{9-} \rightarrow [Co^{I}(tspc)]^{5-} + [Co^{II}(tspc)]^{4-}$ would be observed but no spectral changes due to this reaction was observed. One plausible explanation is that the latter has a rate $\geq 2 \times 10^4\ s^{-1}$ and therefore reaction 12 is the rate-determining step.

Finally the reduction of $[Co^{II}(tspc)]^{4-}$ with $\cdot CH_2OH$, $\cdot CH(CH_3)OH$, $\cdot C(CH_3)_2OH$, and $\cdot CH(OH)CH_2OH$ was studied. In all cases the final product is $[Co^{I}(tspc)]^{5-}$; however, the mechanism of reduction is complex and was not studied in detail.[24]

Oxidation by $Br_2^-\cdot$. We chose $Br_2^-\cdot$ as the oxidizing agent and not the $\cdot OH$ radicals with the hope that this milder oxidizing reagent would attack only the central cobalt ion and not the ligand. N_2O-saturated solutions containing $(1–5) \times 10^{-5}$ M $[Co^{II}(tspc)]^{4-}$ and 0.1 M NaBr in the pH range 3 <

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(19) Dorfman, L. M.; Adams, G. E. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1976**, *NSRDS-NBS 46*.

(20) Anbar, M.; Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1975**, *NSRDS-NBS 51*.

(21) Henglein, A. *Electroanal. Chem.* **1976**, *9*, 164.

(22) Lati, J.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1105.

(23) (a) No conductivity measurements can be carried out in this system at pH ≤6.0 as the formate acts as a buffer under these conditions. One of the reviewers pointed out that the reaction $[Co^{II}(tspc)]^{4-} + CO_2^-\cdot \rightarrow [Co^{I}(tspc)]^{5-} + CO_2$ is not expected to cause a change in the conductivity as the half-time for the reaction $CO_2 + OH^- \rightarrow HCO_3^-$ is ca. 1 s at pH 10.[23b] The results however indicated a fast conductivity change, suggesting that the detailed mechanism if $[Co^{II}(tspc)]^{4-} + CO_2^-\cdot + OH^- \rightarrow [Co^{I}(tspc)]^{5-} + HCO_3^-$. (b) Kern, D. M. *J. Chem. Educ.* **1960**, *37*, 14.

(24) The most perplexing feature of these reactions is that 1 equiv of H_3O^+ is formed in two steps and not in one and that spectroscopically the formation of $[Co^{I}(tspc)]^{5-}$ is over before all the H_3O^+ was formed. These reactions were studied in the pH range $3 \leq pH \leq 6$.

Table 1. Dependence of the Observed Rate of Reaction 18 and the Optical Density at the End of Reactions 18 and 20 on Medium Composition[a]

10^5F (=[M] + 2[D]), M	[(CH$_3$)$_3$COH], M	10^6[M],[b] M	10^6[D],[b] M	10^6([M] + [D]), M	$10^{-4}k_{\text{obsd}}$,[c] s^{-1}	(OD)$_\infty$[d]	(OD)$_\infty$[e]
1	0.1	1.2	4.4	5.6	2.4	0.034[f]	0.019[f]
2[g]	0.1 + 0.1 M NaClO$_4$	0–1	9.5–10	10–10.5	4.7	0.046	0.029
2	0.1	1.8	9.1	10.9	4.8	0.048	0.034
2[g]	1.0	8–10	5–6	14–15	4.5	0.065	0.052
2[g]	2.0	14–16	2–3	17–18	3.7	0.085	0.069
3	0.1	2.2	13.9	16.1	6.8	0.052	0.034
5	0.1	2.8	23.6	26.4	10	0.048	0.034

[a] N$_2$O-saturated solutions at pH 6.0. [b] [M] and [D] were calculated in solutions containing 0.1 M (CH$_3$)$_3$COH by using the relation $K = [D]/[M]^2 = 2.5 \times 10^6$ M^{-1}.[8] The values obtained are in agreement with ϵ(M) and ϵ(D) at 663 nm.[12a] The spectra of solutions are not affected significantly by the addition of 0.1 M (CH$_3$)$_3$COH. [c] Observed rate of reaction 18. [d] The optical density measured (at 450 nm) in a cell with an optical path of 12.5 cm after reaction 18 is over. The total radical yield is 3.1×10^{-6} M. [e] The optical density measured after reaction 20 is over, with conditions as in footnote *d*. [f] The total radical yield is 2.3×10^{-6} M. [g] Concentrations of M and D calculated from measured spectra with the assumption that the change in composition of the solution does not affect their absorption coefficients at 663 nm.[12a]

pH < 10 were irradiated. The anion radical $Br_2^-\cdot$ was found to react with $[Co^{II}(tspc)]^{4-}$ with a specific rate of reaction of $(1 \pm 0.2) \times 10^8$ M^{-1} s^{-1}.[25] The spectrum of the transient formed in this reaction is plotted in Figure 2. The formation of this transient is followed by a first-order reaction with a rate of 4 ± 1 s^{-1}. The spectrum of the product of this reaction, which is stable for several minutes as measured with the Cary 17 after a low-dose-rate irradiation, is plotted in Figure 2.

At pH 4.0 the conductivity in the bromide solutions decreases after the pulse and remains at its low value for at least 1 s, and at pH 9.8 it increases after the pulse and remains high. These observations are in accord with the expectation that $[Co^{II}(tspc)]^{4-}$ is oxidized. The mechanism of oxidation observed was not studied in detail. The results fit either Scheme I or Scheme II. Scheme I assumes an inner-sphere oxidation as was reported for many oxidations by $Br_2^-\cdot$ including the reaction $Br_2^-\cdot + B_{12r}$.[26a] (Reaction 15 might be an equilibrium process if under the experimental conditions some of the bromide stays bound to the cobalt.[26b])

Scheme I

$$[Co^{II}(tspc)]^{4-} + Br_2^-\cdot \rightarrow [(tspc)Co^{III}Br]^{4-} + Br^-$$
$$(\text{or } [Co^{II}(tspc)]_2^{8-} + Br_2^-\cdot \rightarrow [(tspc)Co^{III}Br]^{4-} + Br^- + [Co^{II}(tspc)]^{4-}) \quad (14)$$

$$[(tspc)Co^{III}Br]^{4-} \rightarrow [Co^{III}(tspc)]^{3-} + Br^- \qquad k \approx 4\ s^{-1} \quad (15)$$

Scheme II

$$[Co^{II}(tspc)]_2^{8-} + Br_2^-\cdot \rightarrow [Co^{III}(tspc)Co^{II}(tspc)]^{7-} + 2Br^- \quad (16)$$

$$[Co^{III}(tspc)Co^{II}(tspc)]^{7-} \rightarrow [Co^{III}(tspc)]^{3-} + [Co^{II}(tspc)]^{4-} \qquad k \approx 4\ s^{-1} \quad (17)$$

The features of the spectrum of the final product, presumably $[Co^{III}(tspc)]^{3-}$, differ from those reported by Ferraudi; i.e., the isobestic point (Figure 2) in this study is at 460 ± 10 nm whereas it is around 550 nm in Ferraudi's study.[10a] The source of these discrepancies might stem, at least in part, from the lower reactivity of $Br_2^-\cdot$ toward the ligand, which might result in more side products when $[Co^{II}(tspc)]^{4-}$ is oxidized by ·OH radicals, as suggested by Ferraudi.[10a]

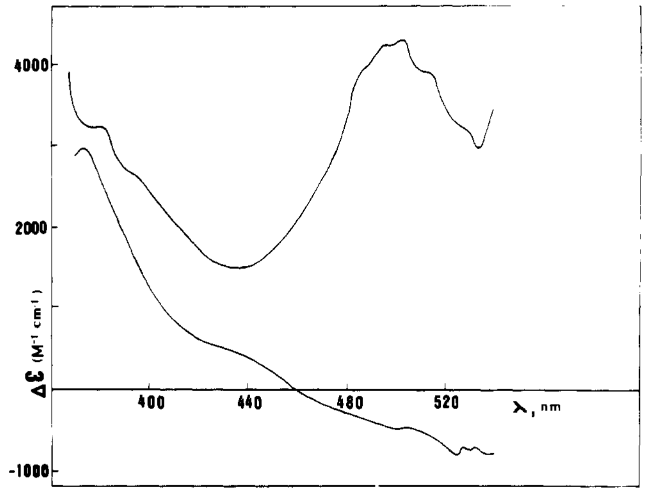

Figure 2. Difference spectra of products observed 300 μs (upper curve) and 1 s (lower curve) after a pulse producing 25 μM of free radicals (N$_2$O-saturated solution at pH 6.1, 6×10^{-5} M $[Co^{II}(tspc)]^{4-}$, 0.1 M NaBr, 2-cm cell, streak camera spectra). Absolute absorption coefficients were determined with use of a smaller pulse.

Reactions with ·CH$_2$C(CH$_3$)$_2$OH Radicals. When N$_2$O-saturated solutions containing $(1–5) \times 10^{-5}$ M $[Co^{II}(tspc)]^{4-}$ in the pH range 3 < pH < 12 are irradiated, three to four consecutive processes, depending on pH, are observed spectrophotometrically. Only one of these processes is accompanied by a conductivity change. Spectra of the products obtained at pH 6.1 at different times after the pulse are plotted in Figure 3.

The first reaction observed obeys a first-order rate law both in $[Co^{II}(tspc)^{4-}]$ and in $[\cdot CH_2C(CH_3)_2OH]$. This reaction is not accompanied by a change in conductivity and is therefore probably not a redox process. We conclude therefore, in agreement with Ferraudi et al.,[10a] that in this stage a transient with a cobalt–carbon bond is formed

$$[Co^{II}(tspc)]^{4-} + \cdot CH_2C(CH_3)_2OH \rightarrow [(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-} \quad (18)$$

or

$$[Co^{II}(tspc)]_2^{8-} + \cdot CH_2C(CH_3)_2OH \rightarrow [Co^{II}(tspc)(tspc)Co^{III}CH_2C(CH_3)_2OH]^{8-} \ (\text{or } [Co^{II}(tspc)]^{4-} + [Co^{III}(tspc)CH_2C(CH_3)_2OH]^{4-})^{27} \quad (18a)$$

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(25) This rate is calculated with the assumption that all the $[Co^{II}(tspc)]^{4-}$ is in its monomeric form; however, under the experimental conditions most of it exists in the solutions in the dimeric form. Thus, the specific rate of reaction is clearly higher but no effort was made to measure exactly the rate of reaction with these two forms of $[Co^{II}(tspc)]^{4-}$.

(26) (a) Meyerstein, D.; Espenson, J. H.; Ryan, D. A.; Mulac, W. A. *Inorg. Chem.* **1979**, *18*, 863. (b) Ferraudi, G. *Ibid.* **1979**, *18*, 1005.

(27) The results in this study indicate either that the monomeric form $Co^{III}(tspc)CH_2C(CH_3)_2OH$ is the only product of reaction or that it and the dimeric form have very similar chemical properties.

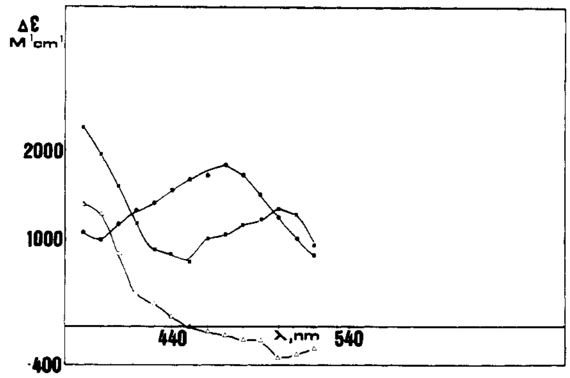

Figure 3. Difference spectra of products observed after a pulse producing 3 μM of free radicals (N_2O-saturated solution at pH 6.1, 2×10^{-5} M $[Co^{II}(tspc)]^{4-}$, 0.1 M $(CH_3)_3COH$, 12.5-cm optical path): (●) 100 μs after pulse; (■) 2 ms after pulse; (▲) 2 s after pulse.

In order to check whether the free radicals react with the monomeric form, $[Co^{II}(tspc)]^{4-}$ (M), or the dimeric form, $[Co^{II}(tspc)]_2^{8-}$ (D), the media composition was changed so that one of the two forms prevails. The results obtained are summarized in Table I. The results point toward several conclusions: (1) Both $[Co^{II}(tspc)]^{4-}$ and $[Co^{II}(tspc)]_2^{8-}$ react with the free radicals. (2) The rate of reaction of the monomeric form is over twice lower than that of the dimeric form. (The difference in rates observed might also stem from the changes in the medium composition. We cannot differentiate between this effect and its effect on the equilibrium D $\rightleftarrows$ 2 M.) (3) The rate of reaction 18a is $k_{18} = (4.5 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. This value is over 1 order of magnitude higher than that reported by Ferraudi et al.,[10a] and we have no explanation for this discrepancy. (4) The optical density after reactions 18 and 18a are over, at 450 nm, is higher in solutions containing the monomeric form, $[Co^{II}(tspc)]^{4-}$. This result suggests that $\epsilon_{max}([(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-}) > \epsilon_{max}([Co^{II}(tspc)(tspc)Co^{III}CH_2C(CH_3)_2OH]^{8-})$. However, this result might also be due to a solvent effect on the spectrum of the transient.[27]

The second reaction observed spectrophotometrically obeys a first-order rate law, the rate of reaction being independent of $[Co^{II}(tspc)^{4-}]$, pH, pulse intensity, and wavelength. The specific rate constant of this reaction $k = 2000 \pm 200$ s^{-1} is in reasonable agreement with $t_{1/2} = 0.3$ ms reported by Ferraudi et al.[10a] This reaction causes no conductivity changes and therefore is probably not a redox process. The absolute change in absorbance at 450 nm due to this reaction (Table I) is independent of the ratio [D]/[M], and thus it is unreasonable to assume that the reaction observed is

$$[Co^{II}(tspc)(tspc)Co^{III}CH_2C(CH_3)_2OH]^{8-} \rightarrow [Co^{II}(tspc)]^{4-} + [(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-} \quad (19)$$

as suggested by Ferraudi.[10a] This conclusion is also in accord with the fact that the reaction causes a decrease in the absorbance whereas an increase would have been expected from point 4 in the preceding paragraph. Also the reverse reaction of reaction 19 does not fit the results as the rate is independent of $[Co^{II}(tspc)^{4-}]$. We suggest that the reaction observed is[28]

$$[(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-} \rightarrow [(tspc)Co^{III}CH{=}C(CH_3)_2]^{4-} + H_2O \quad (20)$$

$$[Co^{II}(tspc)(tspc)Co^{III}CH_2C(CH_3)_2OH]^{8-} \rightarrow [Co^{II}(tspc)(tspc)Co^{III}CH{=}C(CH_3)_2]^{8-} + H_2O \quad (20a)$$

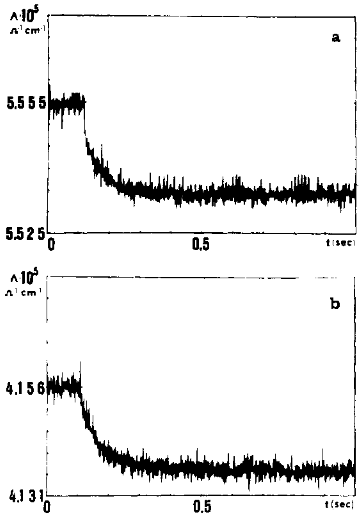

Figure 4. Changes in conductivity after a pulse of 1000 rd (N_2O-saturated solution containing 6×10^{-5} M $[Co^{II}(tspc)]^{4-}$ and 0.1 M $(CH_3)_3COH$): (a) pH 9.5; (b) pH 5.3.

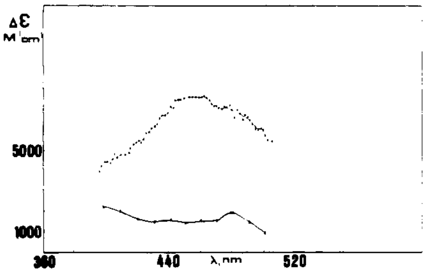

Figure 5. Difference spectra of products observed after a pulse was delivered into an N_2O-saturated solution at pH 10.8 containing 0.1 M $(CH_3)_3COH$: (■) product 200 ms after the pulse, radical concentration 3.1×10^{-6} M, $[Co^{II}(tspc)^{4-}] = 2 \times 10^{-5}$ M, 12.5-cm optical path; (●) permanent product, radical concentration 25 μM, $[Co^{II}(tspc)^{4-}] = 6 \times 10^{-5}$ M, 2-cm cell, streak camera spectrum.

Table II. pH Effect on the Rates of Reaction[a]

pH	$10^{-4}k_{18} \times [Co^{II}(tspc)^{4-}]$, s^{-1}	k_{20}, s^{-1}	k_{21}(op),[b] s^{-1}	k_{21}(con),[c] s^{-1}	k_{last},[d] s^{-1}
1.7	4.7	2200	<33		0.3
3.1	4.8	2100	18		0.3
3.7	4	1700	*e*		5.5
4		1900	*e*		4.6
5.3				12.5	
6.0	4.0	1800	*e*	17.9	2.5
9.5	4.2	1800	22		0.2
9.8				15.6	
10.7	3.9	2000	20		0.2

[a] N_2O-saturated solutions containing 2×10^{-5} M $[Co^{II}(tspc)]^{4-}$ and 0.1 M $(CH_3)_3COH$. [b] k_{21} as measured spectrophotometrically at 450 nm. [c] k_{21} as measured by using changes in conductivity. [d] Rate of the last reaction observed (see text). [e] As the rate of the last reaction at this pH differs only by a factor of 4–7 from that of k_{21} and as larger optical changes occur in the last reaction k_{21} could not be measured spectrophotometrically.

This suggestion is corroborated by the observation that in neutral and acidic solutions $CH_2{=}C(CH_3)_2$ is a final product. The observation that the absorbance at the end of the reaction is larger in the 2 M $C(CH_3)_3OH$ solution than in 0.1 M $C(CH_3)_3OH$ + 0.1 M $NaClO_4$ stems from reasons similar to

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(28) The possibility that the product of the reaction is $[(tspc)Co^{III}CH_2{-}C(CH_3){=}CH_2]^{4-}$ cannot be ruled out, but as for the chromium system[4] we prefer the vinylic product.

(29) In the pH range $3 \leq pH < 7$ this reaction is followed by a fourth reaction, with a similar rate, which causes larger changes in the absorbance, and therefore the third reaction is not observed under these conditions.

those suggested above for $[(tspc)Co^{III}CH_2C(CH_3)_2OH]^{4-}$. The spectrum of the transient formed in reaction 20 is plotted in Figure 3.

The third reaction observed causes a decrease in conductivity at pH ≤6.0 and at pH ≥9.5 (Figure 4). This reaction obeys a first-order rate law with $k = 15 \pm 3\ s^{-1}$. A reaction with the same rate (Table II) is observed spectrophotometrically, at pH ≥9 and at pH ≤3.1. The decrease in conductivity at pH >9.0, equivalent to the consumption of 1 equiv of OH^-, caused by this reaction suggests a reduction of the cobalt center (see Experimental Section) in accord with the spectrum of the final product in this pH range (Figure 5). Thus, the reaction observed is

$$[\mathrm{(tspc)Co^{III}CH{=}C(CH_3)_2}]^{4-} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co^{I}(tspc)}]^{5-} + (\mathrm{HO{-}CH{=}C(CH_3)_2} \leftrightarrow \mathrm{OCH{-}CH(CH_3)_2}) + \mathrm{H_3O^+} \tag{21}$$

$$[\mathrm{Co^{II}(tspc)(tspc)Co^{III}CH{=}C(CH_3)_2}]^{8-} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co^{II}(tspc)Co^{I}(tspc)}]^{9-} + (\mathrm{HO{-}CH{=}C(CH_3)_2} \leftrightarrow \mathrm{OCH{-}CH(CH_3)_2}) + \mathrm{H_3O^+} \tag{21a}$$

The decrease in conductivity at pH 6.0 and 5.3, slightly less than expected if 1 equiv of H_3O^+ is consumed, suggests that the cobalt center is oxidized. This conclusion is in agreement with the spectrum of the final product at pH 6.1 (Figure 3). Thus, we suggest that the reaction occurring is

$$[\mathrm{(tspc)Co^{III}CH{=}C(CH_3)_2}]^{4-} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co^{III}(tspc)}]^{3-} + \mathrm{CH_2{=}C(CH_3)_2} + \mathrm{OH^-} \tag{22}$$

$$[\mathrm{Co^{II}(tspc)(tspc)Co^{III}CH{=}C(CH_3)_2}]^{8-} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co^{II}(tspc)(tspc)Co^{III}}]^{7-} + \mathrm{CH_2{=}C(CH_3)_2} + \mathrm{OH^-} \tag{22a}$$

In order to check the suggested mechanisms of reaction, the yield of $CH_2{=}C(CH_3)_2$ was determined after extended low-dose irradiations.[30] The yield of $CH_2{=}C(CH_3)_2$ was equivalent to 80 ± 5% of the ·OH radical yield at pH 6.0, and no $CH_2{=}C(CH_3)_2$ was observed at pH 11.0 in accord with reactions 21 and 22.

It is of interest to note that reactions 21 and 22 have the same rate of reaction (Table II) though the product is different. One plausible explanation of the pH effect is that $[(tspc)Co^{III}CH{=}C(CH_3)_2]^{4-}$ has a pK in this pH region, i.e.[31]

$$[\mathrm{H_2OCo^{III}(tspc)CH{=}C(CH_3)_2}]^{4-} \rightleftarrows [\mathrm{HOCo^{III}(tspc)CH{=}C(CH_3)_2}]^{5-} + \mathrm{H_3O^+} \tag{23}$$

In the acidic form the cobalt center is a stronger nucleophile than in the alkaline form; therefore, it is reasonable that when H_2O reacts with the Co–C bond the OH group attacks the carbon atom in the alkaline form and the cobalt center in the acidic form. This result indicates again how "minor" structural effects change the mechanism of decomposition of metal–carbon bonds in aqueous solutions.[4-6,32-38]

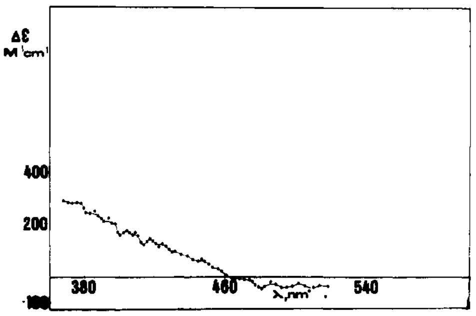

Figure 6. Difference spectrum of the permanent product after a pulse producing 25 μM of free radicals (N_2O-saturated solution at pH 3.1, 6×10^{-5} M $[Co^{II}(tspc)]^{4-}$, 0.1 M $(CH_3)_3COH$, 2-cm cell, streak camera spectrum).

At pH <4 only small changes in conductivity were observed, suggesting only a small yield of $[Co^{III}(tspc)]^{3-}$. Also the spectrum of the final product (Figure 6) suggests that the yield of $[Co^{III}(tspc)]^{3-}$ is only ca. 10% of that expected. The yield of $CH_2{=}C(CH_3)_2$ at this pH is 46 ± 4% of the ·OH radical yield. We suggest therefore that at this pH reaction 24 is fast and therefore only ca. 50% of the $[(tspc)Co^{III}CH{=}C(CH_3)_2]^{4-}$ decomposes via reaction 22.

$$[\mathrm{Co^{III}(tspc)}]^{3-} + [\mathrm{(tspc)Co^{III}CH{=}C(CH_3)_2}]^{4-} \xrightarrow{\mathrm{H_2O}} 2[\mathrm{Co^{II}(tspc)}]^{4-} + \mathrm{OCH{-}CH(CH_3)_2} + \mathrm{H_3O^+} \tag{24}$$

Finally a fourth first-order reaction with rates depending slightly on pH (Table II) is observed spectrophotometrically. The nature of this reaction is not clear. The easiest explanation would be a dissociation of a dimer product, i.e $[Co^{II}(tspc)(tspc)Co^{III}]^{7-} \rightarrow [Co^{II}(tspc)]^{4-} + [Co^{III}(tspc)]^{3-}$ or $[Co^{II}(tspc)(tspc)Co^{I}]^{9-} \rightarrow [Co^{II}(tspc)]^{4-} + [Co^{I}(tspc)]^{5-}$. However, we did not observe the analogous reaction in the blank experiments, i.e. oxidation with $Br_2^-\cdot$ and reduction with $CO_2^-\cdot$. The only other explanation available at present is that the unsaturated aliphatic products $HOCH{=}C(CH_3)_2$ and $CH_2{=}C(CH_3)_2$, formed in reactions 21 and 22, remain somehow complexed to $[Co^{I}(tspc)]^{5-}$ and $[Co^{III}(tspc)]^{3-}$, respectively, prior to their final release.

Conclusions. The results presented corroborate earlier conclusions that the reactions of aliphatic free radicals with planar divalent cobalt complexes are fast and that transients with cobalt–carbon bonds are formed.[6,32] The β-hydroxyl elimination reaction, from the $CH_2C(CH_3)_2OH$ group bound to the cobalt center, was followed and found to be relatively fast, $k = 2000\ s^{-1}$. This result points out again that cobalt complexes induce such eliminations and thus corroborates the free-radical mechanism for the diol dehydratase enzymes[32,39] as the complex used is a good model for B_{12r}. However, we note that the analogous elimination was not observed when reactions of $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH(OH)CH_2OH$ with B_{12r} were studied.[32] The reason for these differences might stem from subtle structural and media effects which strongly affect the chemistry of cobalt–carbon bonds in aqueous solutions.[6,32,33,35-37] The last point is demonstrated here by the pH effect on the mechanism of hydrolysis of the $[(tspc)Co^{III}CH{=}C(CH_3)_2]^{4-}$ group.

The results also indicate that a pK of a water molecule coordinated trans to the aliphatic residue has a major effect

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(30) The 25-mL portions of N_2O-saturated solutions containing 4×10^{-3} M $[Co^{II}(tspc)]^{4-}$ and 0.1 M $C(CH_3)_3OH$ were irradiated with a total dose of 3.3×10^5 to 6.6×10^5 rd. At pH 6.1, 4.0×10^{-5} and 7.8×10^{-5} mol of $CH_2{=}C(CH_3)_2$ were found respectively. At pH 3.0, 2.2×10^{-5} and 4.5×10^{-5} mol of $CH_2{=}C(CH_3)_2$ were found respectively. At pH 10.7, no 2-methylpropene was found.

(31) One of the reviewers has pointed out that such a pK should cause a change in conductivity, which was not observed (see above). We thank the reviewer for pointing out this discrepancy. It might stem from a more complicated charge distribution in the complex which already has a high negative charge, i.e. association of H^+ to another site on the complex.

(32) Mulac, W. A.; Meyerstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 4124.

(33) Mulac, W. A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 4016.

(34) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(35) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2274.

(36) Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 541.

(37) Tsou, T. T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623.

(38) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, 1838.

(39) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 371. Abeles, R. H.; Dolphin, D. *Ibid.* **1976**, *9*, 114.

on the chemical behavior of the metal–carbon bond. This seems to be the first observation of this type and calls for further studies.

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Registry No. [Co^{II}(tspc)]Na_4, 14586-48-2; [(tspc)$Co^{III}CH_2C(CH_3)_2OH]^{4-}$, 86766-36-1; [(tspc)$Co^{III}CH{=}C(CH_3)_2]^{4-}$, 86766-37-2; [$Co^{I}$(tspc)]$^{5-}$, 86766-38-3; [$Co^{III}$(tspc)]$^{3-}$, 69087-63-4; $\cdot CH_2C(CH_3)_2OH$, 5723-74-0; $Br_2^{-}\cdot$, 68565-50-4; $CO_2^{-}\cdot$, 34496-91-8; $CH_2{=}C(CH_3)_2$, 115-11-7; $OCHCH(CH_3)_2$, 78-84-2.

Contribution from the Department of Material Science,
Technological University of Nagaoka, Nagaoka, Niigata 949-54, Japan

Reconstituted Myoglobins with Rhodium(III) Complexes of Meso- and Deuteroporphyrin IX

YASUHIRO AOYAMA, KATSUHIRO AOYAGI, HIROO TOI, and HISANOBU OGOSHI*

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Reconstitution of sperm whale apomyoglobin with rhodium(III) complexes of meso- and deuteroporphyrin IX afforded stable rhodium(III) myoglobins (Meso-Rh(III)-Mb and Deut-Rh(III)-Mb) in a 1:1 (Rh to protein) stoichiometry. Inertness of Meso-Rh(III)-Mb toward external anions and reducing agents indicated that it is not a native ferrimyoglobin analogue but rather an analogue of an internal hemichrome. An organometallic Rh(III)–CH_3 derivative of mesoporphyrin IX was also successfully reconstituted into myoglobin (Meso-CH_3-Rh(III)-Mb). The ^1H NMR spectra indicated that the methyl group bonded to Rh(III) resonated at lower magnetic field by about 2 ppm upon incorporation into the protein, probably due to a compression effect of the amino acid residue(s) at the distal site. Prosthetic group exchange reactions between rhodium and iron myoglobins indicated a significant reduction in stability of Meso-CH_3-Rh(III)-Mb relative to Meso-Rh(III)-Mb.

Introduction

An interesting and important research area in the study of hemoproteins concerns metal substitution in the prosthetic heme.[1] The successful preparation of the oxygen-carrying cobalt(II)-reconstituted hemoglobin and myoglobin has provided valuable information as to the influence of an apoprotein on the reactivity of a prosthetic group and also as to the electronic structure, spin distribution in particular, in a prosthetic group.[1] Rhodium is a fifth-row transition metal in the homologous series with cobalt. The chemistry of rhodium porphyrins is rather well characterized.[2-4] The formation of dioxygen adducts of rhodium(II) porphyrins has also been reported.[3] Rhodium-reconstituted hemoproteins, however, have never been reported to our knowledge. In the present work, we have prepared myoglobins reconstituted with rhodium(III) meso- and deuteroporphyrin IX including a novel rhodium–methyl derivative as the first organometalloporphyrin incorporated into apohemoprotein. The physicochemical properties of rhodium myoglobins have been studied by spectroscopic means and exchange reactions with the protohemin.

Experimental Section

Electronic absorption, IR, mass, and routine ^1H NMR spectra were obtained with a Hitachi 320 spectrophotometer, a Hitachi 260-10 IR spectrometer, a Hitachi RMU-7M mass spectrometer, and a JEOL JNM-PMX 60 NMR spectrometer, respectively. For measurement of 270-MHz ^1H NMR spectra of rhodium myoglobins (Rh(III)-Mb), an aqueous solution of a Rh(III)-Mb was filtered with a millipore filter (Immersible CX-10) to give a concentrated solution (approximately 1 mL) containing 1–2 mM Rh(III)-Mb. Most of remaining water was further removed by centrifugal filtration (3000 rpm, 15 min) at 2 °C with a Hitachi 18PR-52 automatic high-speed refrigerated centrifuge equipped with membrane cones (Amicon, CF-25). ^2H_2O ($\geq$1 mL) buffered at pD 7 with 50 mM phosphate was added, and the mixture was similarly filtered as described above. Addition–filtration procedures of ^2H_2O were repeated five times to remove traces of H_2O. The NMR spectrum of the final solution was measured with a JEOL FX 270 NMR spectrometer at 25 °C.

Preparation of Rh(III) Complexes. Rhodium(III) complexes of meso- and deuteroporphyrin IX (Meso-Rh(III) and Deut-Rh(III)) were prepared according to the procedure of Grigg et al. for the preparation of Rh(III) etioporphyrin.[4] Thus, mesoporphyrin IX dimethyl ester[5] (300 mg) was dissolved in 30 mL of chloroform containing sodium acetate (1.5 g). A chloroform solution (30 mL) of $[Rh(CO)_2Cl]_2$ (300 mg) was added and the mixture stirred at room temperature for 2 h. Inorganic salts were removed by filtration, and the filtrate was stirred for 1 h after addition of iodine (200 mg). The course of the reaction was monitored by TLC, and when necessary, further iodine (100 mg) was added to complete the oxidation of the Rh(I) complex. The chloroform was evaporated in vacuo and the residue chromatographed on alumina (Brockman, activity grade II–III) with chloroform as eluant. The dimethyl ester of (mesoporphyrinato)rhodium(III) iodide (MesoDME-Rh(III)) thus obtained was further purified by preparative TLC (Merck Sharp and Dohme, Kieselgel 60 PF_{254}) with chloroform–acetone (95:5 v/v) as eluant, followed by recrystallization from methanol to give 130 mg (31.3%) of dark orange crystals. IR (KBr disk): 1725 cm^{-1} ($\nu_{C=O}$). ^1H NMR (in C^2HCl_3): δ 1.90 (t, 6 H, CH_2CH_3), 3.30 (t, 4 H, $CH_2CH_2CO_2CH_3$), 3.53 (s, 6 H, 1- and 3-CH_3), 3.67 (s, 12 H, 5- and 8-CH_3 and CO_2CH_3), 4.10 (q, 4 H, CH_2CH_3), 4.44 (t, 4 H, $CH_2CH_2CO_2CH_3$), 10.11 (s, 4 H, meso-H). Mass spectrum: *m/e*

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(1) Hoffman, B. M. *Porphyrins* **1979**, *7*, 403–444 and references cited therein.

(2) (a) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461. (b) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* **1975**, 572. (c) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869. (d) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983.

(3) (a) Wayland, B. B.; Newman, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 6472. (b) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3039. Also see: James, B. R.; Stynes, D. V. *J. Am. Chem. Soc.* **1972**, *94*, 6225.

(4) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1395.

(5) Caughey, W. S.; Alben, J. O.; Fujimoto, W. Y.; York, J. L. *J. Org. Chem.* **1966**, *31*, 2631.

0020-1669/83/1322-3046$01.50/0