# Detection and Characterization of Radical Cations Resulting from the Oxidation of Methyl and Acetyl Iron Complexes

*Sir:*

The oxidative degradation of alkyl transition-metal carbonyls, and $Cp(CO)_2FeR$[1] in particular, affords organic carbonyl products (esters, amides, acyl chlorides),[2–6] substitution products, RX (ethers, alkyl halides),[2,3,7] and organic dimers, $R_2$ (R = benzyl).[7] RX and $R_2$ are thought to result from nucleophilic attack on or homolytic scission of radical cation **1** whereas the organic carbonyls

$$Cp(CO)_2FeR \xrightarrow{-e} \underset{\mathbf{1}}{[Cp(CO)_2FeR]^+} \rightarrow \underset{\mathbf{2}}{[Cp(CO)(S)Fe(COR)]^+}$$

may arise from the solvated (or chelated) acyl cation radical **2**, derived from a facile migratory insertion in **1**.[2–5] We report direct characterization of the short-lived organometallic radicals generated by one-electron oxidation of $Cp(CO)_2FeCH_3$, **3**, and $Cp(CO)(L)Fe(COCH_3)$ [L = CO (**4a**), L = $PPh_3$ (**4b**)]. The evidence strongly supports rapid migratory insertion on oxidation of **3**.

When solutions of $Cp(CO)_2FeCH_3$ in alcohols, acetone, or tetrahydrofuran were treated with ceric ammonium nitrate or anhydrous cupric triflate at −78 °C, deep green solutions were obtained, whose color persisted for several minutes, but faded rapidly on warming. The short lifetime of the species responsible for the color suggested to us that we were observing formation and decomposition of an intermediate 17-electron cation radical.[8] In acetonitrile (AN) or AN/$CH_2Cl_3$ mixtures, the green species exhibited significantly greater stability ($\tau_{1/2}$ = 22 s, 20 °C, AN), facilitating its characterization as the acetyl cation radical, $[Cp(CO)(AN)Fe(COCH_3)]^{+\cdot}$ (**5c**). Similar oxidations in AN of the acetyl compounds **4a** and **4b** also yielded green species, which are formulated as the analogous cation radicals $[Cp(CO)(L)Fe(COCH_3)]^{+\cdot}$, L = CO (**5a**), L = $PPH_3$ (**5b**), respectively. **5a** is quite reactive ($\tau_{1/2}$ = 0.44 s, 20 °C, AN) whereas the phosphine cation radical persists for some time ($\tau_{1/2}$ = 177 s, 20 °C, AN).

Each of the oxidized species in acetonitrile shows two visible absorptions, a broad lower energy band around 600 nm and a somewhat more intense absorption around 450 nm (Table I), irrespective of whether Ce(IV) or Cu(II) was used as oxidant. Spectral titration of AN solutions of $Cp(CO)_2FeCH_3$ at 0 °C with ceric ammonium nitrate (monitoring the increase in absorbance at 630 nm) showed a sharp break at 1.2 equiv of Ce(IV),[9] in accord with a one-electron stoichiometry. A similar titration of **4b** (5 °C, AN, 585 nm) required 0.95 equiv of Ce(IV).

Table I. Visible Spectral Properties[a]

| species | $\lambda_{max}$, nm (log $\epsilon$) |
|---|---|
| 3, $Cp(CO)_2FeCH_3$ | 353 (2.91) |
| 5c, $[Cp(CO)(AN)Fe(COCH_3)]^+$ | 630 (2.3), 450 (2.9)[b] |
| 4a, $Cp(CO)_2Fe(COCH_3)$ | 322 |
| 5a, $[Cp(CO)_2Fe(COCH_3)]^+$ | ~580 (2.2), 445 (3.0)[c] |
| 4b, $Cp(CO)(PPh_3)Fe(COCH_3)$ | ~445 sh (2.51) |
| 5b, $[Cp(CO)(PPh_3)Fe(COCH_3)]^+$ | 584 (2.4), ~450 sh (2.8)[b] |

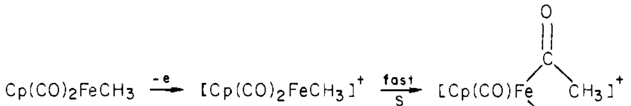
[a] Medium = anhydrous, deoxygenated acetonitrile. [b] At 0 °C, by oxidation with a deficiency of ceric ammonium nitrate, and $\epsilon$ based on a 1:1 oxidation. [c] At 20 °C, calculated from stopped-flow measurements of absorbancies observed on oxidation with a deficiency of cupric triflate.

The AN acetyl cation radical **5c** was isolated as a green oil contaminated with acetonitrile by cupric triflate oxidation of a cold AN solution of $Cp(CO)_2FeCH_3$, precipitation of cuprous triflate by the addition of diethyl ether, filtration, and finally addition of petroleum ether to the filtrate (all manipulations were performed at −40 °C or lower). The x-band EPR spectra of the neat oil (−196 °C) or frozen AN or AN/ether solutions of the green oil exhibit an intense asymmetric signal with an average *g* value for the neat oil computed to be 2.04 G. The EPR spectrum of **5b**, which was obtained as a green oil in a similar manner except that silver tetrafluoroborate and $CH_2Cl_2$ were used as oxidant and solvent, also exhibited an intense asymmetric signal with an average *g* value of 2.24 G.

The infrared spectrum of the cation radical **5c**, generated in situ in $CH_2Cl_2$ at low temperatures in the presence of 1–2 equiv of AN, shows only one terminal carbonyl absorption (2020 cm$^{-1}$) and a strong acyl absorption at 1710 cm$^{-1}$, supporting an acetyl carbonyl rather than a dicarbonyl methyl structure. Although similar absorptions were observed for the isolated green oil spread on NaCl plates, the measurement was complicated by extensive thermal decomposition. The conversion of **4b** to **5b** ($AgBF_4$ in $CH_2Cl_2$) is readily followed by monitoring the decrease in carbonyl absorptions at 1910 and 1605 cm$^{-1}$ and concomitant increase in the absorptions at 1970 and 1650 cm$^{-1}$ attributed to **5b**.

Cyclic voltammetry experiments indicate a very rapid rearrangement on oxidation of $Cp(CO)_2FeCH_3$ (Pt electrode, AN/0.1 M TEAP). We concur with previous observations that oxidations of the $Cp(CO)_2FeR$ complexes are irreversible at scan rates as high as 100 V/s.[7,10] However, after the irreversible anodic wave at 0.88 V had been scanned, a reversible couple, not present in the initial scan, appeared at 0.18 V, and can be attributed to the reduction of **5c**. When $Cp(CO)_2FeCH_3$ was chemically oxidized with cupric triflate at 0 °C, a reversible couple at 0.19 V was observed when the potential was cycled between 0.4 and 0 V. We have found that the neutral acetyl complexes also exhibited reversible or quasi-reversible electrochemical oxidations (**4a**: 0.94 V, 1 V/s, $E_a - E_c$ = 140 mV. **4b**: 0.36 V, 50 mV/s, $E_a - E_c$ = 60 mV).

Predicted on these results, we believe the short-lived green species observed on one-electron oxidation of $Cp(CO)_2FeCH_3$, as well as $Cp(CO)(L)Fe(COCH_3)$ compounds, to be best described as acyl cation radicals. The migratory insertion on oxidation of $Cp(CO)_2FeCH_3$ is very rapid even at low temperatures[12]



$$Cp(CO)_2FeCH_3 \xrightarrow{-e} [Cp(CO)_2FeCH_3]^+ \xrightarrow[S]{fast} [Cp(CO)Fe(S)(C(=O)CH_3)]^+$$

and is most likely accompanied by solvent incorporation. We do not find a profound increase in the general lability of the formally Fe(III) complexes,[13] but rather dramatic activation of terminal

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[1] Abbreviations used: Cp = $\eta^5$-cyclopentadienyl, AN = acetonitrile, triflate = (trifluoromethyl)sulfonate, TEAP = tetraethylammonium perchlorate, S = solvent.

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[8] Related 17-electron cobaloxime cation radicals have been reported. See: Topich, J. A.; Halpern, J. *Inorg. Chem.* **1979**, *18*, 1339–1343, and references therein.

[9] This titration is complicated by decomposition of the cation radical. Up to 1.8 equiv of Ce(IV) were needed to deplete all of **3**, if the green species was allowed to decay completely between additions.

[10] Reduction potentials vs. SCE (22 °C, 50 mV/s) unless otherwise noted. This behavior contrasts with the nearly reversible oxidation of $CpFe(diphos)CH_3$ in which no carbonyl ligand is present.[11] For $CpFe(PPH_3)(CO)Me$, we have observed reversible redox behavior in $CH_2Cl_2$ with $Bu_4NClO_4$ as supporting electrolyte.

[11] Treichel, P. M.; Wagner, K. P.; Mueh, H. J. *J. Organomet. Chem.* **1975**, *86*, C13–C16.

[12] The rearrangement is much faster than could be accounted for by migratory insertion in **3**. See: Nicholas, K. M.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *78*, 133–137.

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carbon monoxide toward migratory insertion,[2-4,14] both kinetically and thermodynamically.

Decomposition of the acetyl cation radicals, **5a-c**, was found to be first order for three half-lives in AN at 20 °C (monitoring the decrease in the low-energy absorption maximum, with [Fe] $\sim 3 \times 10^{-3}$ M and [oxidant] $\sim 1 \times 10^{-3}$ M). This contrasts with the second-order decomposition in cation radical observed for alkyl cobaloxime(IV) complexes, for which a disproportionative mechanism has been proposed.[15] The evidence suggests that acyl cation radicals are the immediate precursors to one-electron oxidative decomposition products previously reported for $Cp(CO)_2FeR$ systems.[2-7] The possibility cannot be dismissed that organic products arise from nucleophilic attack at the acyl carbonyl (esters, amides, etc.), nucleophilic displacement at the $\alpha$ carbon of the acyl (ethers, alkyl halides), or homolytic scission of the acyl carbonyl-$\alpha$ carbon bond (organic dimers). In support of this, $PhCH_2CO_2CH_3$, $PhCH_2OCH_3$, and $PhCH_2CH_2Ph$ all resulted from the Ce(IV) oxidation of $Cp(CO)_2Fe(COCH_2Ph)$ in methanol.

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**Roy H. Magnuson,* Samu Zulu, Wen-Ming T'sai**
**Warren P. Giering***
*Department of Chemistry, Boston University*
*Boston, Massachusetts 02215*

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## Photochemical Preparation of an *O*-Sulfinato Complex of Cobalt(III)

*Sir:*

The ability of sulfinic acids, $RSO_2H$, to coordinate to main group and to transition-metal ions is well-known, and the structure and bonding have been studied in some detail.[1,2] The bonding may be via one or both oxygen atoms, sulfur, or a sulfur-oxygen $\pi$ system. To our knowledge, however, all reported Co(III) complexes containing sulfito, sulfinato, or sulfenato ligands show only Co-S bonding.[3] The only indication otherwise is a recent observation[4] of a transient in the reaction of $SO_2$ with $Co(NH_3)_5(OH)^{2+}$, tentatively assigned as $Co(NH_3)_5(OSO_2)^{2+}$. We report here the synthesis and characterization of what appears to be the first example of a *robust* Co(III) complex containing an O-bonded sulfinato ligand.

The observations are a sequel to an earlier photochemical study of Co(III) chelate complexes containing a Co-S bond,[5] of the type $Co(en)_2L^{n+}$, where L is a bidentate ligand containing sulfur, and en denotes ethylenediamine. Upon extension of the photochemical investigations to the complex $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$, here designated as CoSOON, an unusually clean photochemistry was observed. On photolysis at various wavelengths in the 350-450-nm region, the spectral changes that occur with an aqueous solution of the perchlorate salt maintain very good isosbestics up to essentially complete conversion to product, accompanied by a color change from yellow to red. Ion-exchange chromatography with Sephadex SP-25 confirmed that a single product was present. The electronic absorption spectra of aqueous CoSOON and of the photoproduct are shown in Figure 1, with details included in Table I. Quantum yields decreased from 0.1 to 0.01 over the wavelength range 313-460 nm; details on this aspect are to be included in a later report.

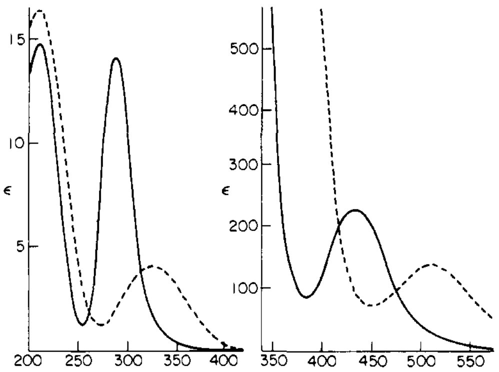

Figure 1. Absorption spectrum of aqueous CoSOON (—) and CoOSON (- - -).

Table I. Spectral Data for $Co(en)_2[S(O)_2CH_2CH_2NH_2]^{2+}$ and $Co(en)_2[OS(O)CH_2CH_2NH_2]^{2+}$

A. Electronic Absorption ($H_2O$, 25 °C)

| complex | $\lambda_{max}$ ($\epsilon$) | $\lambda_{max}$ ($\epsilon$) |
|---|---|---|
| $Co(en)_2(S(O)_2CH_2CH_2NH_2)(ClO_4)_2$ | 432 (220) | 288 (14 200) |
| $Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$ | 512 (134) | 326 (4100) |

B. 100-MHz $^1H$ NMR ($D_2O$, 25 °C, HDO internal reference)

| complex | $\tau$ from HDO (shape, assignment) |
|---|---|
| $Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$ | −2.0 (br, en $CH_2$)<br>−1.5 to −1.9 (complex m, $NCH_2RSO_2$-)<br>−1.24 (m, $NRCH_2S$)<br>−0.6 (v br, $NH_2$)<br>+0.4 (br, $NH_2$) |
| $Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$ | −2.3 to −1.9 (complex m, $NCH_2RSO_2^-$)<br>−2.0 (br, en $CH_2$)<br>−1.55 (m, $NRCH_2S$) |

C. Vibrational[a] Data (IR; KBr pellet; Raman, $H_2O$, 647.1 nm)

| complex | IR,[b] $cm^{-1}$ | Raman,[c] $cm^{-1}$ |
|---|---|---|
| $Co(en)_2(S(O)_2CH_2CH_2NH_2)^{2+}$ | 1190 (s) | 1204 (w) |
| $Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+}$ | 950 (m) | 950 (w sh on $ClO_4^-$ peak) |
|  | 1030-1037 (s) | 1038 (w) |

[a] Only frequencies not common to both complexes are listed. [b] Halide salts. [c] $ClO_4^-$ salts.

The photoproduct was isolated on a preparative scale by nearly complete photolysis of a stirred, nearly saturated aqueous solution of the perchlorate salt of CoSOON, using white light ($\lambda > 400$ nm), followed by evaporation to dryness to obtain the product as an essentially pure red solid. Elemental analyses of the product were consistent with the formulation, $Co(en)_2(SO_2CH_2CH_2NH_2)(ClO_4)_2 \cdot H_2O$.[6] As a check, further purification was accomplished by dissolving the material in minimal wet methanol, filtering the solution, and then precipitating the product by the addition of acetone and ether, with no change in properties except that a methanol solvate was obtained.[6] The

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[6] Anal. Calcd: C, 14.29; N, 13.89; H, 4.80. Found: C, 14.36; N, 13.82; H, 4.65. That the water was of crystallization and not coordinated was indicated by analysis of the product obtained by evaporation of a methanolic solution. Calcd for $[Co(en)_2(NH_2CH_2CH_2SO_2)](ClO_4)_2 \cdot CH_3OH$: C, 16.02; N, 13.51; H, 5.06. Found: C, 15.95; N, 13.46; H, 4.65.

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