

Table I. Rate Constants for Ti(III) Reduction of Ru(C₂O₄)₃³⁻^a

[H ⁺], mM	[Ti] _T , mM	k _{obsd} , s ⁻¹	k ₂ , M ⁻¹ s ⁻¹ ^b	k _{calcd} , M ⁻¹ s ⁻¹
20	2.36	0.69	292	297
20	3.54	1.04	294	297
25	3.54	0.99	279	268
25	4.72	1.2	267	268
25	5.9	1.67	283	268
40	2.36	0.51	216	207
40	3.54	0.73	206	207
40	4.72	0.99	210	207
40	5.9	1.16	197	207
50	2.36	0.40	170	180
50	5.9	1.02	173	180
75	2.95	0.40	136	135
75	4.72	0.64	136	135
100	2.596	0.29	112	109
100	2.83	0.33	117	109
125	2.95	0.25	85	91
125	4.43	0.36	81	91
125	5.90	0.52	88	91
150	4.43	0.31	70	78
150	5.90	0.44	75	78

^a Conditions: in 1 M LiCl at T = 25 °C; [Ru(III)]_T = 2.0 × 10⁻⁴ M. ^b k₂ (M⁻¹ s⁻¹) = k_{obsd}/[Ti]_T.

Table II. Rate Constants for Ti(III) Reduction of Ru(C₂O₄)₃³⁻ in the Presence of Added Oxalate^a

[C ₂ O ₄] _T , mM	[H ⁺] _T , mM	k _{obsd} , s ⁻¹	k ₂ , M ⁻¹ s ⁻¹ ^b	k _{calcd} , M ⁻¹ s ⁻¹
7.5	159	0.82	320	426
10	164	1.20, 1.28	485	571
12.5	168	1.75	684	707
15	171	2.09, 1.97	793	832
17.5	175	2.25, 2.45	918	942
20	180	2.68, 2.73	1055	1039
22.5	185	2.77	1082	1125
25	188	3.43, 3.46	1344	1211
30	197	3.74	1461	1356

^a Conditions: in 1 M LiCl at T = 25 °C; [Ru(III)]_T = 2.0 × 10⁻⁴ M. ^b k₂ (M⁻¹ s⁻¹) = k_{obsd}/[Ti]_T.

is 2 orders of magnitude larger than the corresponding reactivities of TiC₂O₄⁺ or of uncomplexed Ti(III) (at [H⁺]_f = 0.150 M).

On Coulombic grounds, reaction of Ru(C₂O₄)₃³⁻ with Ti³⁺ or TiOH²⁺ would be expected to be faster than reaction of TiC₂O₄⁺ or Ti(C₂O₄)₂⁻. However, reaction of Ru(C₂O₄)₃³⁻ with Ti(C₂O₄)₂⁻ is 10 times faster than that with Ti(III). This effect was also noted⁵ in reduction of Co(NH₃)₅C₂O₄⁺. In both the present case and the case previously studied, nonbridging oxalate on the reductant side *increases* the rate of Ru(III)-Ti(III) ET through bridging oxalate ion. The result of the present study is that nonbridging oxalate on the oxidant side *reduces* the rate of Ru(III)-Ti(III) ET through bridging oxalate ion. That is, the effect on the redox rate of nonbridging oxalate located on ruthenium is just the opposite of the effect of nonbridging oxalate located on titanium. It does not appear that either the substitution reaction that leads to formation of the binuclear complex or the acid-base change that precedes ET within that intermediate accounts for this effect. Coordination of anionic oxalate should stabilize upper oxidation states, relative to lower ones. This is consistent with the effect of nonbridging oxalate on the reductant side, but contrary to the effect on the oxidant side. The most likely interpretation seems to be that interaction with the filled π orbitals on nonbridging oxalate raises the energy of the metal t_{2g} orbitals of the metal ions. This increases the rate when the nonbridging oxalate ions are on the reductant but decreases it when they are on the oxidant.

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Contribution from the Departments of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106, and University of California at Riverside, Riverside, California 92521

Oxidation of (Tetraphenylporphyrin)chromium(III) Chloride by Styrene Ozonide

Ernst S. Schmidt,[†] Thomas C. Bruice,^{*,†} Robert S. Brown,[‡] and Charles L. Wilkins^{*,†}

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Oxygen atom transfer to (*meso*-tetraphenylporphyrinato)-metal(III) salts has received considerable attention in the modeling of peroxidase and cytochrome P-450 reactions. Searches continue for new oxygen-transfer agents that provide insights into the mechanisms of formation and reactions of higher valent metallooxoporphyrin species. Oxygen-transfer agents that can act as substrates after having delivered the oxygen atom to a metalloporphyrin are of particular interest. For example, the *p*-cyano-*N,N*-dimethylaniline formed upon oxygen transfer from *p*-cyano-*N,N*-dimethylaniline *N*-oxide serves as a substrate for the higher valent metallooxoporphyrin.¹ The use of this type of oxygen-transfer reagent in the study of the dynamics of oxygen transfer and subsequent substrate oxidation has definite advantages. Percarboxylic acids serve well as oxygen-transfer agents, yielding metallooxoporphyrins two-electrons oxidized above the (porphyrinato)metal(III) state.² Ozonides are known to transfer oxygen to carboxylic acids to yield percarboxylic acids and two oxidizable aldehyde fragments.³ It occurred to us that ozonides should be explored as possible double agents for oxygen transfer to (porphyrinato)metal(III) salts. We report herein the results of a study of the reaction of styrene ozonide with (*meso*-tetraphenylporphyrinato)chromium(III) chloride ((TPP)Cr^{III}Cl).

Experimental Section

The LD/FTMS system employs a Tachisto 215G pulsed TEA carbon dioxide laser coupled with a Nicolet FTMS-1000 Fourier transform mass spectrometer operated at a 3 T, with a 5.08 cm³ analyzer cell constructed of 80 Transmissive etched stainless steel.² For the LD mass spectra reported here, the laser delivered approximately 0.3–0.4 J per 40-ns pulse at 10.6 μm. The laser beam was focused by a 10.16-cm focal length zinc selenide lens to a diameter of approximately 1 mm on the stainless-steel probe tip. Power density at the probe tip is estimated to be in the range of 10⁸–10⁹ W/cm². Negative ions were trapped in the cell by application of a -1.0-V trapping potential.

The sample (~0.5 mg) was dissolved in methanol and applied dropwise to a stainless-steel probe tip. The solvent was allowed to evaporate in air and then placed in the FTMS and pumped down until a gauge pressure of 1.0 × 10⁻⁸ Torr was obtained. In a typical experiment sequence, ions were formed by triggering the laser pulse with the FTMS filament off. Following a 3-s pump down delay, after the negative ions formed were trapped, an FTMS spectrum was obtained. Each spectrum resulted from a single laser pulse, and no spectral coaddition was employed.

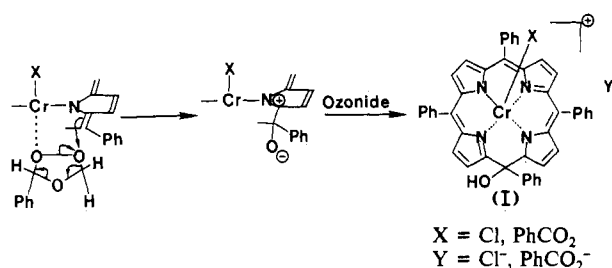
The UV-vis spectra were measured on a Cary 118C spectrophotometer. Styrene ozonide was prepared according to Criegee et al.¹⁰

Synthesis of Isoporphyrin I. A 200-mg sample of (tetraphenylporphyrinato)chromium(III) chloride (0.286 mmol) and 100 mg of styrene ozonide (0.657 mmol) were stirred in 10 mL of CH₂Cl₂ for 1 h at room temperature. The course of the reaction was monitored by UV-vis spectroscopy. The solvent was rotary-evaporated and the residue washed with 3 × 4 mL *n*-pentane. The residue was dissolved in 2 mL of CH₂Cl₂ and chromatographed on silica gel (100 g, 70–230 mesh), eluting with CH₂Cl₂ containing 3 M MeOH. The main band (R_f 0.85) was collected. Recrystallization from CH₂Cl₂/hexane afforded 72 mg (30%, based on I: X = Cl, Y = PhCO₂⁻) of a dark microcrystalline material. UV-vis: 423 (ε = 3.6 × 10⁴), 447 (ε = 3.6 × 10⁴), 800 (ε = 8.8 × 10³), 880 nm (ε = 1.6 × 10⁴).

[†] University of California at Santa Barbara.

[‡] University of California at Riverside.

Scheme I



Discussion and Results

Reaction of iodobenzene and percarboxylic acids with (TPP)Cr^{III}Cl provides a mixture of (TPP)Cr^VO(Cl) and (TPP)Cr^{IV}O. The latter arises from the reaction of the two-electron-oxidized product (i.e., (TPP)Cr^VO(Cl)) with unreacted (TPP)Cr^{III}Cl.⁴ The reaction of the comparatively reactive ozonide derived from styrene with (TPP)Cr^{III}Cl did not afford (TPP)Cr^VO⁺ or (TPP)Cr^{IV}O species. However, an isoporphyrin was formed as established by its quite distinctive electronic spectrum.⁵ To our knowledge this is the first report of an isoporphyrin derived from a chromium(III) porphyrin.

Spectral titration of a solution of (TPP)Cr^{III}Cl (6×10^{-5} M in CH₂Cl₂) with a solution of styrene ozonide results in the disappearance of the (TPP)Cr^{III}Cl absorbances at 563 and 602 nm accompanied by the formation of new maximal absorbances at 800 ($\epsilon = 8.8 \times 10^3$) and 880 nm ($\epsilon = 1.6 \times 10^4$) and a decrease in the intensity of the Soret band (446 nm) with concurrent broadening to provide double maxima at 423 ($\epsilon = 3.6 \times 10^4$) and

447 nm ($\epsilon = 3.6 \times 10^4$). Isosbestic points were observed at 620, 460, and 403 nm. For completion of the spectral transformation, a ratio of ozonide to (TPP)Cr^{III}Cl of 2:1 was required. In the presence of a 1.0 M concentration of MeOH, no reaction occurred. Purification of a preparative reaction of ozonide and (TPP)Cr^{III}Cl (ratio 2:1) by column chromatography (silica gel eluting with CH₂Cl₂ containing 3% MeOH) provided a product (R_f 0.85) in 30% yield, which exhibited the UV-vis spectral features of an isoporphyrin. Recrystallization from CH₂Cl₂/hexane afforded a black crystalline material. In view of the paramagnetic nature of Cr^{III}, the product could not be characterized by NMR spectroscopy. Multiple crystallizations from CH₂Cl₂/hexane provided only microcrystalline material unsuitable for X-ray structural determination.⁶ Field desorption mass spectrometry failed to afford the necessary structural information.

Laser desorption Fourier transform mass spectrometry⁷ yielded a well-resolved ($m/\Delta m$ 10 000 at half-height) negative ion spectrum, consistent with formation of chromium tetraphenylisoporphyrins of structure I with either benzoate or chloride as counter ions. Furthermore, ions corresponding to loss of H₂, possibly by bridging the *meso*-hydroxy group to the β -pyrrole position of the corresponding isoporphyrin II, either during the synthesis or in the mass spectrometer,⁸ were observed. Ions derived from II containing both ligands and counterions were present. Also, decomposition ions consistent with these structural interpretations (e.g., chloride loss and hydroxide ions) were detected. Exact mass measurements were not possible due to the difficulty of calibrating under the experimental conditions. However, the combination of UV-vis spectral characteristics, which establish an isoporphyrin structure, and the mass spectral data lead us to conclude that the structural interpretations are reasonable.

A mechanism for formation of these isoporphyrins is outlined in Scheme I. We assume that one ozonide molecule coordinates with the Cr^{III} moiety and transfers an oxygen atom to a *meso* position of the porphyrin ligand. Methanol occupies the axial position in (TPP)Cr^{III}Cl⁹ and, thus, prevents isoporphyrin formation. The intermediate then abstracts a proton from a second ozonide molecule, generating the hydroxyisoporphyrin with benzoate or chloride as counterion and formaldehyde. It is well established that the solvolysis of ozonides leading to carboxylic acids and aldehydes is initiated by a proton abstraction.¹⁰ The intermediacy of a Cr^V-oxo species can be ruled out, since electrochemically generated (TPP)Cr^VO⁺ species did not afford an isoporphyrin with styrene ozonide.

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