

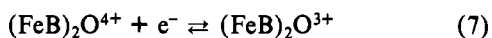
between FeB^{3+} and FeB^{2+} and the different anions, which might also account for the variation of the diffusion coefficient, D_0 , in the different media. Note that D_0 is smaller in buffers of diprotic acids (at pHs where appreciable concentrations of dianion are present) than in the presence of monoanions. The heterogeneous rate constant for electron transfer, k^0 , is also affected by the anions present in the medium (Tables II and III). While this may be partly ascribed to ion-pairing effects, specific interaction of the anions with the platinum electrode surface may also play a role. This is almost certainly the case for the results with iodide ion, which is known to be strongly adsorbed on a Pt surface.^{15,16} In slightly basic solutions, the wave shifts toward more negative values (line b) at -0.06 V/pH unit. This suggests addition of hydroxide ion to the FeB^{3+} species as an axial ligand with the redox reaction of line b corresponding to



From the usual means of analysis of potential-pH diagrams,¹⁴ we estimate $E^{\circ'}$ for this half-reaction as -0.48 V vs. SCE (pH 14) and the equilibrium constant of reaction 6 as $K_a = 6.3 \times 10^{-8}$.



The second voltammetric waves and those found in more basic solutions have been ascribed to reactions of the binuclear species. Line c of Figure 8 corresponds to reaction 7 with an



$E^{\circ'} = -0.54$ V vs. SCE. The deviation of the line from the expected pH independence in the less basic region (curve e) probably arises from the instability of the $(\text{FeB})_2\text{O}^{4+}$ form in these solutions (see reaction 3), as discussed previously. The voltammetric curves at different pHs (Figure 7) suggest that both forms exist at equilibrium at pHs near 8, with the monomeric form favored in more acidic solutions (eq 3). The existence of both dimeric and monomeric species of the couple

(15) Balashova, N. A.; Kazarinov, V. E. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; Vol. III.

(16) Lane, R. F.; Hubbard, A. T. *J. Phys. Chem.* 1975, 79, 808.

has also been demonstrated by magnetic moment measurements.⁴

At pHs above 11, the dimer redox wave shifts toward more negative potentials (line d, slope 0.12 V/pH unit; line f, slope 0.06 V/pH unit). The pH change that occurs upon dissolution of the iron(III) binuclear complex in 5 mM NaOH suggests loss of two protons; the subsequent coulometry showed $n_{\text{app}} = 2$ (i.e., reduction of both iron(III) centers). However, the decomposition reaction in strongly basic media to produce hydrous ferric oxide leads to some uncertainty in the values of potential obtained, and further studies are required to delineate the exact nature of the species under these conditions.

Conclusions

The results of this investigation indicate these complexes are promising materials for redox batteries and photoelectrochemical cells. They are highly soluble (FeBSO_4 , 4 M; $\text{FeB}(\text{OH})\text{SO}_4$, 2 M in H_2O at room temperature),¹² and both forms are stable for solutions in the range $5 < \text{pH} < 11$ upon repeated cycling between the iron(III) and iron(II) forms. For example, a 1 M 1:1 acetic acid/acetate buffer could be cycled coulometrically in exhaustive electrolyses of 1-h duration at least 22 times without apparent loss of species.¹² Application of these compounds to photoelectrochemical cells (0.5 M Na_2SO_4) at p-WSe₂ electrodes has also been reported.¹⁷

Acknowledgment. This work was supported in its early stages by a grant from Texas Instruments under TI/DOE cooperative agreement DE-FC01-79ER 10,000 and later by the Solar Energy Research Institute. The advice and suggestions of Dr. K. S. V. Santhanam are gratefully acknowledged.

Registry No. FeB^{3+} , 90269-23-1; FeB^{2+} , 59451-77-3; $(\text{FeB})_2\text{O}(\text{ClO}_4)_4$, 71882-22-9; $\text{FeB}(\text{OH})(\text{ClO}_4)_2$, 13963-71-8; $(\text{FeB})_2\text{O}^{3+}$, 71882-21-8; HNO_3 , 7697-37-2; KNO_3 , 7757-79-1; NaI, 7681-82-5; HCl, 7647-01-0; KCl, 7447-40-7; H_2SO_4 , 7664-93-9; Na_2SO_4 , 7757-82-6; NaOH, 1310-73-2; cyanoacetic acid, 372-09-8; trifluoroacetic acid, 76-05-1; acetic acid, 64-19-7; adipic acid, 124-04-9; tartaric acid, 87-69-4; propionic acid, 79-09-4; malonic acid, 141-82-2; succinic acid, 110-15-6.

(17) Abruna, H. D.; Bard, A. J. *J. Electrochem. Soc.* 1982, 129, 673.

Contribution from the Departments of Chemistry, Mount Union College, Alliance, Ohio 44601, and Kent State University, Kent, Ohio 44242

Electron Transfer. 69. Mediation by Phenylglyoxylate¹

W. FAYE HOLLAWAY, VANGALUR S. SRINIVASAN,² and EDWIN S. GOULD*

Received September 19, 1983

Both the monomeric phenylglyoxylate derivative of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ (II) and the dimeric bridged $(\text{Co}^{\text{III}})_2$ complex (III) are reduced by Cr^{2+} via the chemical or radical-cation mechanism. Strongly absorbing Cr(III)-bound radical intermediates are observed in both instances. Internal electron transfer to Co(III) in the monomeric system proceeds at a specific rate of 93 s^{-1} and that in the dimeric system at 4.0 s^{-1} (25 °C, 1 M HClO_4). Reaction of the phenylglyoxylate derivative of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ (VII) with Cr^{2+} leads to yet another strongly absorbing (green) species having an association constant of $4.6 \times 10^3 \text{ M}^{-1}$. Here, it appears that the incoming Cr^{2+} ion has become attached to the keto group of the ligand, with the "extra" electron delocalized over the two chromium centers and the ligand (VIII). This novel green pigment is reduced by excess Cr^{2+} to a highly charged polymeric Cr(III) derivative of the corresponding α -hydroxy acid. In the absence of excess Cr^{2+} , the pigment decays at nearly a constant rate. The latter decay appears to be related to release of phenylglyoxylic acid by aquation of its $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ complex. A proposed mechanism for this bleaching, which results in a net 2e reduction of the ligand, features action of the keto acid as a reversible Cr(II) carrier that catalyzes disproportionation of the radical cation to the parent keto acid complex and the polynuclear hydroxy acid complex (IX).

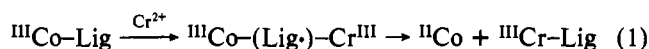
Operation of the inner-sphere or bridge mechanism for electron transfer between metal centers was demonstrated in 1953.³ Two years later it was shown that organic ligands

could function as redox bridges.⁴ Of the several mechanistic variations that have been characterized during the intervening

* To whom correspondence should be addressed at Kent State University.

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

30 years, the radical-ion or chemical mechanism has evoked particular interest, in part because of the suggestion that it may be utilized in certain biosystems.⁵ When applied to a reaction of an oxidizing center bearing a reducible ligand, this mechanism features preliminary reduction of the ligand to a radical cation, followed by intramolecular electron transfer, e.g.



Although sequence 1 is conceptually simple, the radical-cation intermediate is often elusive. With very few exceptions,⁶ evidence for this mechanism has been confined to heterocyclic systems and has been indirect.⁷ Detection of the intermediate has been accomplished with pyrazine-related species.⁸

The pyruvate group, $\text{CH}_3\text{C}(=\text{O})\text{COO}^-$, is an unusually effective mediator for inner-sphere reactions,⁹ and its parent acid is known to undergo 1e reduction readily.¹⁰ It might then be anticipated that mediation by ligated pyruvate would proceed by the chemical mechanism. However, close examinations of the reactions of the pyruvato derivative of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ with $\text{Cr}(\text{II})$,^{9,11} $\text{Eu}(\text{II})$,¹² and $\text{Ti}(\text{III})$ ¹³ give no hint that a radical-cation intervenes,¹⁴ and it therefore appears that the incoming electron in these reductions enters an acceptor orbital that embraces both the carbonyl function and $-\text{COO}-\text{Co}^{\text{III}}$, rather than just the ligand.

Phenylglyoxylato, $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{COO}^-$, in which a benzene ring replaces the methyl group in pyruvate, is an even more potent inner-sphere mediator than the latter^{12,13} and is still more easily reduced.¹⁰ In this contribution, we describe the $\text{Cr}(\text{II})$ reduction of complexes of this ligand and present evidence pointing to radical-cation intervention. This appears to be the first reported instance in which such an intermediate has been observed to arise from an oxidant devoid of both a nitro group and a heterocyclic unit. This system is further complicated by the occurrence of a mixed-valence dinuclear

Table I. Stoichiometry of Reductions of Phenylglyoxylato Complexes Using $\text{Cr}(\text{II})$ and $\text{Eu}(\text{II})$ (1.0 M HClO_4)

A. Reductant in Deficiency ^a	
	Co^{III} formed/ reductant taken
Co^{III} monomer (II) + Cr^{2+}	1.00
Co^{III} monomer + Eu^{2+}	0.53
Co^{III} dimer (III) + Cr^{2+}	0.90
Co^{III} dimer + Eu^{2+}	0.37
B. Reductant in Excess	
	Cr^{II} consumed/ oxidant taken
Co^{III} monomer + Cr^{2+} ^b	3.1 3.4 ^c 3.1 ^d
unbound carboxylic acid ^e	2.1

^a [oxidant] = 0.0050 M; [reductant] = 0.0020 M. See ref 6c.
^b [oxidant] = 0.0020 M; [Cr^{2+}] = 0.010 M. ^c Reaction in 4.0 M HClO_4 . ^d Reaction in 1.0 M $\text{CF}_3\text{SO}_3\text{H}$. ^e [Cr^{2+}] = 0.010 M; [carboxylic acid] = 0.0020 M.

complex of $\text{Cr}(\text{II})$ and $\text{Cr}(\text{III})$ exhibiting, in its behavior, additional elements of novelty, for which we can account only tentatively and in part.

Experimental Section

Materials. Solutions of $\text{Cr}(\text{ClO}_4)_2$ ¹⁵ and $\text{Eu}(\text{ClO}_4)_2$ ¹² were prepared as described. The bridged phenylglyoxylato dimeric $\text{Co}(\text{III})$ complex^{6c} and the monomeric phenylglyoxylato derivative¹² of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ were prepared as their perchlorates by published methods. A portion of the latter was converted to its hexafluorophosphate by treatment with NaPF_6 in solution and recrystallized twice from dilute NaPF_6 solution.

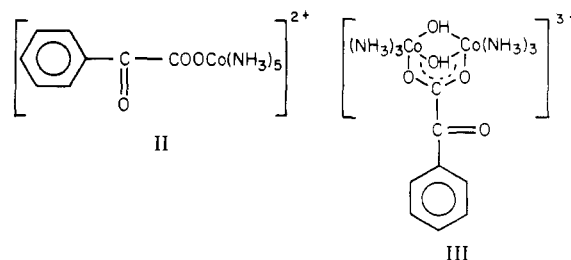
Anal. Calcd for $\text{Co}(\text{NH}_3)_5\text{C}_8\text{H}_5\text{O}_3(\text{PF}_6)_2$: Co, 10.11; H, 3.46; C, 16.47. Found: Co, 10.0;¹⁵ H, 3.31; C, 17.36.

Rate Measurements. Kinetic studies of the more rapid reactions were carried out by using absorbance changes are measured on the Durrum-Gibson stopped-flow spectrophotometer. Slower reactions were generally monitored on the Beckman 5260 or Cary 14 recording spectrophotometer. All reactions were carried out under N_2 . The reaction medium was generally 1.0 M HClO_4 . Where possible, formation and decay of transient species were followed at their absorption maxima; when the development of very high absorbances made this impractical, measurements were carried out at a position removed from the maximum at which absorbance changes were of convenient magnitude.

Stoichiometric Studies. Stoichiometries of reactions involving a $\text{Co}(\text{III})$ oxidant and a known deficiency of Cr^{2+} were determined by measurement of the $\text{Co}(\text{II})$ released as CoCl_4^{2-} in HCl (692 nm) as described.¹⁵ For reactions with Cr^{2+} in excess, unreacted Cr^{2+} was consumed by addition of $\text{Cl}(\text{NH}_3)_5\text{Co}(\text{ClO}_4)_2$ and the resulting $\text{Co}(\text{II})$ determined as above. Discrepancies between the Cr^{2+} added and the Co^{2+} formed were attributed to reduction of the ligand. Representative results appear in Table I.

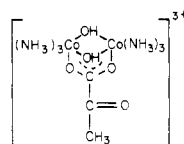
Results and Discussion

Reduction of the monomeric phenylglyoxylato derivative of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ (II) with a deficiency of Cr^{2+} is seen (Table I) to yield Co^{2+} quantitatively. The visible spectrum of the



Cr^{III} product (λ_{max} 560 nm (ϵ 25), 400 s (27) in 1.0 M HClO_4),

- (2) On leave from Vivekananda College, Mylapore, Madras, India.
- (3) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 4118.
- (4) Taube, H. *J. Am. Chem. Soc.* **1955**, *77*, 4481.
- (5) See, for example: LaMer, G. N.; Del Gaudio, J. In "Bioinorganic Chemistry II"; Raymond, K. N., Ed.; American Chemical Society: Washington, DC, 1977; *Adv. Chem. Ser.* No. 162, p 207.
- (6) Gould, E. S. *J. Am. Chem. Soc.* **1966**, *88*, 2983. (b) Diaz, H.; Taube, H. *Inorg. Chem.* **1970**, *9*, 1304. (c) Srinivasan, V. S.; Singh, A. N.; Wiegardt, K.; Rajasekar, N.; Gould, E. S. *Ibid.* **1982**, *21*, 2531.
- (7) See, for example: (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Itzkowitz, M. M.; Nordmeyer, F. *Inorg. Chem.* **1975**, *14*, 2124. (c) Radlowski, C. A.; Gould, E. S. *Ibid.* **1979**, *18*, 1289. (d) Goli, U. B.; Gould, E. S. *Ibid.* **1984**, *23*, 221.
- (8) (a) Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 4360. (b) Spiecker, H.; Wiegardt, K. *Inorg. Chem.* **1977**, *16*, 1290. (c) Dunne, T. G.; Hurst, J. K. *Ibid.* **1980**, *19*, 1152.
- (9) Price, H. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1.
- (10) Fleury, M. B.; Moiroux, J.; Fleury, D.; Dufresne, J.-C. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *81*, 365. Reduction potentials (1e, pH 0, vs. NHE) reported by these workers are -0.268 V for pyruvic acid and $+0.002$ V for phenylglyoxylic acid.
- (11) Gould, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 2373.
- (12) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.
- (13) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.
- (14) (a) The chemical mechanism appears to operate in the Eu^{2+} reduction of the μ -pyruvato dimeric complex (I).^{6c}



(b) For evidence against occurrence of the chemical mechanism in the reaction of $\text{Cr}(\text{II})$ with the pyruvato complex of $(\text{NH}_3)_5\text{Cr}^{\text{III}}$, see: Liu, C.-L.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1831.

(15) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

Table II. Reduction of Phenylglyoxylate-Bridged Dimer (III) with Cr^{2+} : Growth (k_1) and Decay (k_2) of Intermediate (19 °C, 1.2 M HClO_4 , 440 nm)

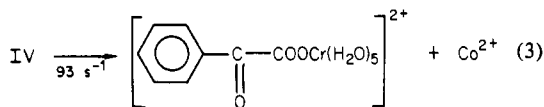
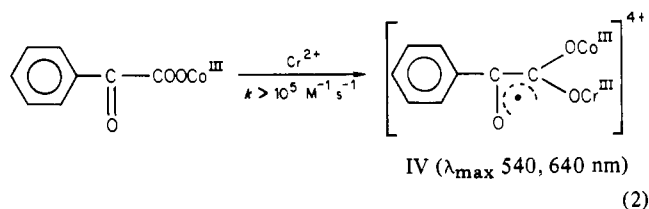
$[\text{Co}^{\text{III}} \text{ dimer}], \text{M}$	$[\text{Cr}^{2+}], \text{M}$	k_1, s^{-1}	k_2, s^{-1}
0.00526	0.0010	5	3.6
0.00820	0.0010	8	4.3
0.0116	0.0010	12	4.2

^a Estimated uncertainty: in k_2 , 0.3 s^{-1} ; in k_1 , 1 s^{-1} .

as well as its cation-exchange elution behavior, corresponds¹⁵ to the expected carboxylate derivative, $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{COOCr}(\text{H}_2\text{O})_5^{2+}$. When the pH is raised, this is converted reversibly to its conjugate base (λ_{max} 550 nm (ϵ 27), 431 (34)), with the two forms coexisting in equal concentrations at pH 2.17.^{16,17} Aquation of this Cr^{III} complex to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ proceeds with a half-life period of 2.5 h in 1 M HClO_4 at 25 °C.

Kinetic profiles of the reduction of the monomeric complex II point to the intervention of a strongly absorbing intermediate exhibiting maxima near 640 nm (ϵ 2×10^2) and 500 nm (ϵ 7×10^2). Formation of this intermediate is essentially complete within the time of mixing, and the specific rate at which it disappears ($93 \pm 7 \text{ s}^{-1}$ at 20 °C) is found to be independent of $[\text{Co}^{\text{III}}]$ taken, of $[\text{Cr}^{2+}]$, and of acidity (within the range 0.4–1.2 M HClO_4). No such species is observed to intervene in the rapid ($k = 4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$)¹² reduction of complex II with Eu^{2+} .

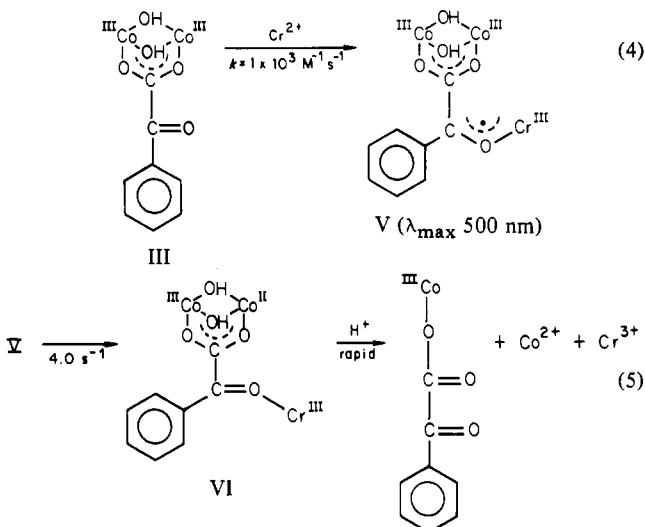
The spectral and decay properties of this intermediate are thus consistent with those of a Cr(III)-bound radical cation (IV), analogous to those thought to intervene in analogous pyrazine systems⁸ but significantly more reactive (eq 2 and 3).



Further evidence supporting this interpretation arises from the Cr^{2+} reduction of the bridged dimeric (Co^{III})₂ complex (III). Here again an intermediate intervenes, the spectral characteristics of which (λ_{max} 500 nm (ϵ 1.1×10^3), 630 nm (7×10^2)) are similar to those of the species interceding in reduction of the monomeric oxidant. Both its formation and destruction proceed at measurable rates. Kinetic profiles with Cr^{2+} in deficiency indicate the superposition¹⁸ of two consecutive pseudo-first-order reactions, with the specific rate of the slower very nearly independent of [oxidant] and that for the faster (determined less precisely) very nearly proportional to it (Table II).

The usual kinetic ambiguity in assigning specific rates to the first and second steps in such a series¹⁸ does not operate

here since the formation of the intermediate may reasonably be expected to be first order in oxidant and that for its destruction (by intramolecular electron transfer) independent of oxidant. Arguments developed earlier^{6c} that the initial electron transfer to such $\text{Co}(\text{III})$ dimers determines the kinetic characteristics of the reaction may be taken to apply here and allow us to write the sequence¹⁹ (4) and (5). In the Co^{III}



dimer, the carboxyl group is "tied up" by coordination to a second $\text{Co}(\text{III})$ center; attack by Cr^{2+} is therefore represented as occurring at the keto group of the ligand (V). Both the initial electron transfer from Cr^{2+} and the internal transfer within the radical-cation intermediate are seen to be much more rapid in the monomeric than in the dimeric system, confirming the greater effectiveness of the carboxyl as a lead-in group for this ligand, a point that has earlier been emphasized.^{6c}

Note also that Eu^{2+} reductions, both of the monomeric and dimeric oxidant, yield much less than the equivalent quantity of Co^{2+} (Table I), indicating that irreversible reduction of the carbonyl group competes with reduction of $\text{Co}(\text{III})$. Previous work¹⁹ points to reduction to a $>\dot{\text{C}}\text{O}$ radical (remaining after loss of the extremely substitution-labile Eu^{III} center), followed by dimerization to a pinacol-like species. The departure from 1:1 stoichiometry is, not unexpectedly, more severe for the Co^{III} dimer ($k_{\text{Eu}} = 86$)^{6c} than for the more effectively mediated reduction of the monomer ($k_{\text{Eu}} = 4 \times 10^4$).¹² This diversion does not play a major role in the corresponding Cr^{2+} reductions, presumably reflecting the reluctance of the $\text{Cr}(\text{III})$ -bound radicals (IV and V) to dimerize.

Treatment of the phenylglyoxylate complex of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ with Cr^{2+} yields still another strongly absorbing (green) species (λ_{max} 640 nm (ϵ 1.5×10^2), 500 (1.8×10^2)), persistent enough to be studied by ordinary mixing techniques. This pigment may also be made by addition of more than 1 equiv of Cr^{2+} to Co^{III} complex II or more than 2 equiv of Cr^{2+} to dimer III. It is similar in appearance to several reported $\text{Cr}(\text{III})$ -bound pyrazine radicals,^{8bc,20} but apparently unlike any long-lived species we have yet encountered in carbocyclic systems. Absorbance data, taken at 640 nm (Table III), indicate that this species is a 1:1 $\text{Cr}(\text{II})$ - $\text{Cr}(\text{III})$ complex having an association constant of $(4.6 \pm 0.6) \times 10^3 \text{ M}^{-1}$ (25 °C, 1 M

(16) An isobestic point at 405 nm is associated with this protonation equilibrium. Attempts to prepare the phenylglyoxylate derivative of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ from $\text{Cr}(\text{ClO}_4)_3$ and the parent carboxylic acid, using the ligation procedure of Hamm¹⁷ and several modifications thereof, yielded only minor amounts of the desired product, together with intractable solid materials.

(17) Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4469.

(18) See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; pp 65–70.

(19) The collapse of the $\text{Co}(\text{III})$ - $\text{Co}(\text{II})$ species (VI) is taken to be very rapid in view of the substitution-labile character of the $\text{Co}(\text{II})$ center. The departure of the keto-bound $\text{Cr}(\text{III})$ from VI (almost certainly by acid-catalyzed carbon-oxygen bond breakage) may also be considered to be rapid. See, for example: Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929.

(20) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

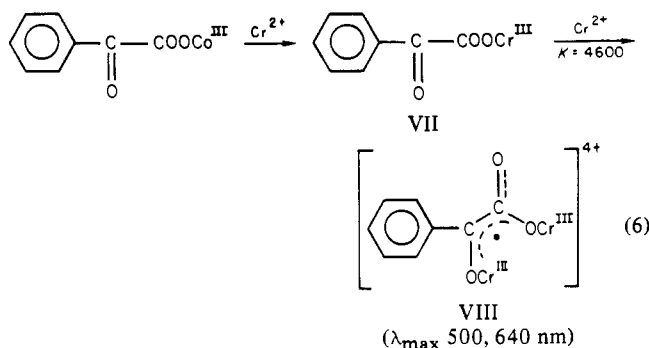
Table III. Absorbance Data for the Binuclear Cr(II)-Cr(III)-Phenylglyoxylato Complex^a

[Cr ²⁺] _{added} , M × 10 ⁻³	abs(640 nm) ^b	[complex] ^c , M × 10 ⁻³	[Cr ²⁺] _{present} ^d , M × 10 ⁻³	[Cr ^{III}] _e , M × 10 ⁻³	K _{eq} ^f , M ⁻¹ × 10 ³
0	0	0.00	0	0	
2.0	0.065	0.45	0.15	0.95	3.1
2.6	0.128	0.87	0.33	0.53	5.0
2.9	0.145	0.99	0.51	0.41	4.7
3.2	0.158	1.08	0.72	0.32	5.1
3.5	0.170	1.16	0.94	0.24	5.2
4.2	0.208	1.40	1.40	~0	
5.1	0.205	1.38	2.30	~0	

$$K_{eq}(\text{av}) = (4.6 \pm 0.6) \times 10^3 \text{ M}^{-1}$$

^a Measurements at 25 °C in a 1.00-cm cell. The reaction medium was 1.0 M HClO₄. Each solution was 0.00140 M in the phenylglyoxylato derivative of (NH₃)₅Co^{III} (oxidant II) before reaction. This consumes 1-equiv quantity of the added Cr²⁺. ^b Extrapolated to zero time after mixing. ^c [complex] assumed to be proportional to absorbance. ^d [Cr²⁺]_{present} = [Cr²⁺]_{added} - [Co^{III}]_{consumed} - [complex]_{formed}. ^e [Cr^{III}]_e = [Co^{III}]_{consumed} - [complex]_{formed}. ^f Calculated as [complex]/[Cr²⁺]_{present}[Cr^{III}]_{present}.

HClO₄). Since the development of this pigment is accompanied by a decrease of the α-keto absorbance (at 254 nm) of the phenylglyoxylato complexes, it may be inferred that coordination of Cr(II) to that carbonyl function is occurring (VIII). If the Cr(III) "precursor" (VII) is allowed to undergo



partial aquation before addition of more Cr²⁺, less of the pigment is formed. When this delay is extended to 2.5 h (the half-life period for aquation of VII in 1.0 M HClO₄), the maximum concentration of the green complex that can be generated is likewise halved. The green complex is very rapidly destroyed by addition of (NH₃)₅CoCl²⁺ or uncomplexed phenylglyoxylic acid.

Although the green species may be regarded as a mixed complex of Cr(III) and Cr(II), the similarity of its visible spectrum to those of binuclear radical intermediates IV and V indicates that the "extra" electron is delocalized, embracing the ligand and, possibly, both chromiums. We have therefore designated it as a radical anion bound to two Cr(III)'s.²¹

The decay of the green complex in the presence of excess Cr²⁺ is first order in each in pigment and in Cr²⁺ (Table IV), and in the process, one phenylglyoxylato unit ultimately consumes 2 equiv of reductant.²² The ligand has thus undergone a 2e reduction to the hydroxy acid (C₆H₅CHOH-COOH) level, but the resulting solution is found to contain no detectable Cr(H₂O)₆³⁺. All Cr(III) is instead present as a highly charged polynuclear species that is eluted from sulfonic acid resins only in minor part with 0.5 M Th(ClO₄)₄. Since, on the average, three Cr(III) centers are bound to each unit of the reduced ligand, it appears that the principal product is or is related to the trinuclear complex (IX) (having a carboxylato-bridged unit similar to that in the Co(III) dimer

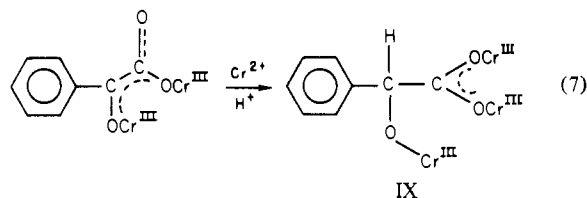
Table IV. Kinetic Data for Reaction of the Cr(II)-Cr(III)-Phenylglyoxylato Complex (VIII) with Excess Cr²⁺^a

medium	[Cr ²⁺] _b , M × 10 ⁻³	k, s ⁻¹
1.0 M HClO ₄	1.56	0.0140
	1.96	0.0170
	2.36	0.0180
	3.1	0.028
	3.5	0.029
	3.9	0.032
1.0 M CF ₃ SO ₃ H	1.50	0.0150
	3.3	0.029

$$\text{rate} = 8.7 \text{ M}^{-1} \text{ s}^{-1} [\text{VIII}] [\text{Cr}^{2+}]$$

^a Reactions were carried out at 25 °C. Complex VIII was generated from the monomeric Co(III) derivative (II) either as its perchlorate or its hexafluorophosphate salt. ^b [Cr²⁺] values adjusted for initial reduction of Co(III) and for formation of VIII (sequence 6 in text). ^c k = -d ln [VIII]/dt.

(III)). The spectral features of the product (λ_{max} 580 nm (ε per Cr^{III} 35), 417 (38)) are consistent with this formulation.



Pigment VIII also decomposes when prepared with a deficiency of Cr²⁺, but here the kinetic behavior is quite different. Decay curves are nearly zero order (linear), rather than exponential,²³ but as successive small "shots" of Cr²⁺ are added, slopes are seen to decrease. As decay proceeds, absorbance at 254 nm (attributable to the keto group) becomes *partially* restored. After a total of slightly more than 2 equiv of Cr²⁺ per phenylglyoxylato group has been added, no further green pigment can be generated. As with Cr²⁺ in excess, the ligand is reduced to the hydroxy acid level, and the Cr(III) product appears to be the highly charged species represented here as IX.

The observed zero-order decay of radical cation VIII indicates that it is being consumed by the action of another entity that is generated slowly, and at nearly a constant rate, from a major species in the solution. The bleaching agent here is doubtless the uncomplexed keto acid, formed in the slow aquation of VII; for if addition of Cr²⁺ to VII is delayed for

(21) ESR measurements are not informative as to this point. Like some,^{8c} but not all,^{8b} Cr(III)-bound pyrazine radicals, pigment VIII is virtually ESR silent.

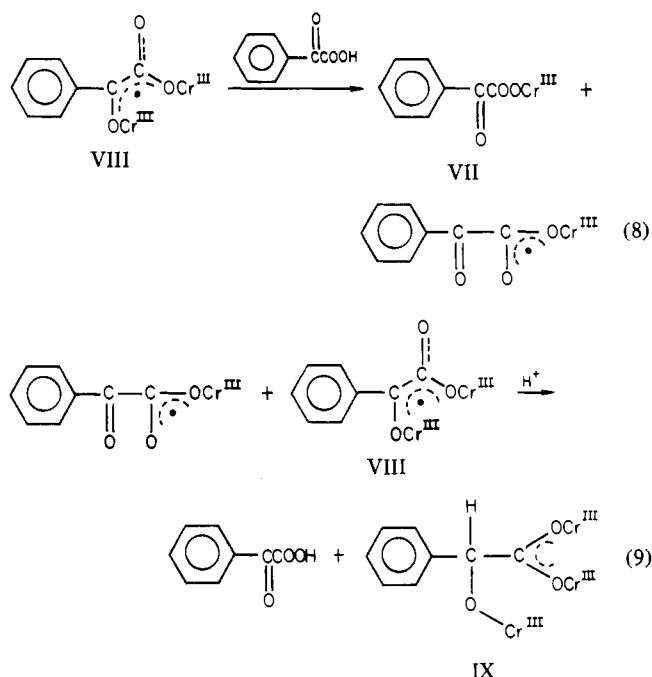
(22) This stoichiometry may be derived from entries in Table I, Section B, which indicates that Co(III) monomer consumes slightly more than 3 equiv of Cr²⁺. Of this, 1 equiv is used in reduction of the Co(III) center.

(23) Typically, when 6 × 10⁻⁴ M Cr²⁺ is added to a 2 × 10⁻³ M solution of the Cr(III)-phenylglyoxylato complex (VII) in 1 M HClO₄, pigment VIII is quickly formed and then decays at a nearly constant rate of 2.2 × 10⁻⁶ M s⁻¹, a rate not significantly altered by carrying out the same reaction in 1 M CF₃SO₃H.

a period corresponding to the half-life for aquation (2.5 h), the slopes of the decay curves are diminished by half.²⁴

Note, however, that the rate at which the keto acid is released from VII differs, by a large factor, from the rate at which pigment VIII disappears. When, for example, the pigment is generated from a 0.0014 M solution of the parent chromium(III) complex, it is found to disappear at the rate $1.5 \times 10^{-6} \text{ M s}^{-1}$; but, under the same conditions, phenylglyoxylic acid is released at a rate of only $1.1 \times 10^{-7} \text{ M s}^{-1}$. One molecule of the keto acid then results in the loss of 13 units of radical cation VIII. Recyclic is thus occurring. For the overall bleaching process, we favor the sequence (8) and (9), in which the keto acid acts as a reversible Cr^{2+} carrier, transporting this cation from the poorly coordinating keto-like group of radical VIII to the more basic carboxyl-like site of another unit of VIII, restoring, in part, the keto absorbance at 254 nm and reducing one of the two radical cations to the hydroxy acid level (IX). Chain termination is not represented here but may be presumed to involve bimolecular reaction between two of the radical species to yield a pinacol derivative. The observed 2:1 (rather than 1:1) stoichiometry of the overall reduction indicates, however, that the latter process plays only a minor role.

In sum, our results demonstrate the extraordinary ease with which bound phenylglyoxylate undergoes 1e reduction by Cr^{2+} ,



leading to Cr^{3+} -bound radical species. When this ligand is Co(III) bound, the radical collapses as internal electron transfer occurs. When, however, it is Cr(III) bound, the keto group of the ligand ultimately suffers 2e reduction via a chainlike process that appears to be unique to this ligand.

(24) To carry out time-delay experiments of this type, it is necessary to destroy the keto acid formed during the delay period (using Eu^{2+} or Cr^{2+}) before generating the green radical cation by addition of further Cr^{2+} .

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Reaction between Permanganate Ion and Chlorine(III): Kinetics and Mechanism of the Initial Reaction and Dissociation of Chlorous Acid¹

CHRISTINE AHLSTROM, DONALD W. BOYD, IRVING R. EPSTEIN,* KENNETH KUSTIN,* and JOHN H. ROMANOW

Received August 18, 1983

In the pH range 1.3–5.0, chlorine(III) and permanganate react rapidly, yielding mixtures of products and unexpended reactants that are stable for approximately 10 s to 1 min, before the further occurrence of slower reactions leading to higher chlorine oxidation states. At $25.0 \pm 0.5 \text{ }^\circ\text{C}$ and ionic strength 1.0 M (NaClO_4), the spectrophotometrically determined stoichiometry of this initial reaction is $\text{MnO}_4^- + 5\text{ClO}_2^- + 8\text{H}^+ \text{ (or } 3\text{H}^+) = \text{Mn}^{2+} + 5\text{ClO}_2 + 4\text{H}_2\text{O}$. Under the same conditions the rate law is $1/5 d[\text{ClO}_2^-]/dt = -d[\text{MnO}_4^-]/dt = k_{\text{app}}[\text{MnO}_4^-][\text{Cl(III)}]$. It was found that the $[\text{H}^+]$ dependence of the pseudo-first-order rate constant $k = k_{\text{app}}[\text{Cl(III)}]$ is given by $k = (a + b[\text{H}^+])/(1 + c[\text{H}^+])$. A mechanism consisting of the rapidly established chlorous acid–chlorite protolytic equilibrium, $K_a = [\text{H}^+][\text{ClO}_2^-]/[\text{HClO}_2]$, and the two rate-limiting steps $\text{MnO}_4^- + \text{ClO}_2^- = \text{MnO}_4^{2-} + \text{ClO}_2$ (k_1) and $\text{MnO}_4^- + \text{HClO}_2 = \text{MnO}_4^{2-} + \text{ClO}_2 + \text{H}^+$ (k_2) leads to the following rate parameter values: $1/c = K_a = (2.70 \pm 0.45) \times 10^{-3} \text{ M}$, $a = k_1 = 24.4 \pm 2.0 \text{ M}^{-1} \text{ s}^{-1}$, $b/c = k_2 = 92 \pm 29 \text{ M}^{-1} \text{ s}^{-1}$. No significant variation of k_{app} with ionic strength was observed in the range 0.01–0.10 M (NaClO_4); a slight increase is observed in the range 0.1–2.0 M (NaClO_4). Variation of specific ions showed no observable change in k_{app} when Li^+ , or $(\text{CH}_3)_4\text{N}^+$, replaces Na^+ . The kinetically measured value of K_a at ionic strength 1.0 M, though smaller than other experimentally determined or extrapolated values, is considered more reliable than static determinations, since the latter are impaired by decomposition of chlorous acid. The experimental k_1 and k_2 greatly exceed the values predicted by the outer-sphere Marcus cross-reaction theory, and we find $k_2 > k_1$ while the Marcus theory predicts $k_1 > k_2$. Therefore, the rate-limiting steps are better described by an inner-sphere mechanism.

Introduction

The system acidic chlorite–iodide is capable of oscillating in a continuous-stirred tank reactor, behavior that may persist when oxidant or reductant is added. In an effort to determine whether such systems represent new oscillators or are per-

turbations on the fundamental ClO_2^- – I^- system, more complex mixtures of the type ClO_2^- – I^- – X , where X = oxidant or reductant, were studied.² The ClO_2^- – I^- – MnO_4^- system possesses a third stable steady state in addition to the two bistable states of ClO_2^- – I^- and oscillates in a narrower pH range than

(1) Systematic Design of Chemical Oscillators. 18. Part 17: Alamgir, M.; Epstein, I. R. *J. Am. Chem. Soc.* 1983, 105, 2500.

(2) Orbán, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* 1982, 104, 5911.