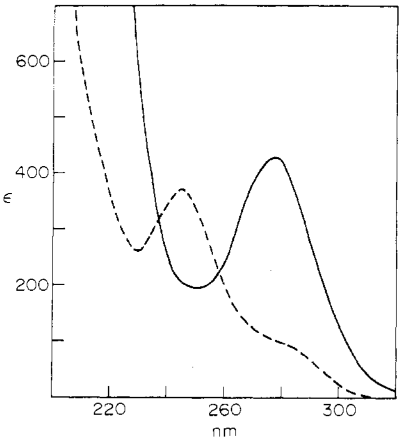

Figure 3. Electronic spectra of $K_3[Rh(CN)_5Cl]$ (—) and $K_3[Ir(CN)_5Cl]$ (- - -) in pH 6 aqueous buffer solutions at 300°K.

would be expected to be more readily observable in Ir(III) than Rh(III), because of the much larger spin-orbit coupling in the third-row central ion. We therefore attribute the weak low-energy feature in each of the $[Ir(CN)_5X]^{n-}$ complexes to the $^1A_1 \rightarrow {}^3E^a$ transition.

The positions of the $^1A_1 \rightarrow {}^1E^a$ bands in the $[M(CN)_5X]^{n-}$ complexes (Table III) are consistent with decreasing LF strength of X in the order $NCCH_3 > OH^- > H_2O > Cl^- > Br^- > I^-$ for both Rh(III) and Ir(III). A similar order has been obtained from an analysis of $[Co(CN)_5X]^{n-}$ spectra.[6]

For $[M(CN)_5X]^{n-}$ complexes with $X = Br^-$ or I^-, one or two relatively intense absorption bands are observed at higher energies than the $^1A_1 \rightarrow {}^1E^a$ transition. The spectrum of $[Rh(CN)_5I]^{3-}$, for example, shows well-resolved bands at 38.8 (ϵ 4200) and 45.5 (ϵ 42,000) kK, in addition to a $^1A_1 \rightarrow {}^1E^a$ band at 31.9 (ϵ 1500) kK (Figure 4). These additional bands are much too intense to be attributable to LF transitions, so they must represent ligand (X) → metal charge transfer (LMCT) excitation processes. There are two allowed LMCT transitions from halide valence p orbitals to a_1 (d_{z^2}), which is the lowest metal virtual orbital. These transitions are $^1A_1 \rightarrow {}^1E$ ($e\pi X \rightarrow a_1 d_{z^2}$) and $^1A_1 \rightarrow {}^1A_1$ ($a_1\sigma X \rightarrow a_1 d_{z^2}$), abbreviated π-LMCT and σ-LMCT, respectively. Simple theoretical reasoning, which places the σ bonding $a_1\sigma X$ orbital lower than the $e\pi X$ level, as well as established experimental patterns in the LMCT spectra of a variety of halometalate complexes,[13] lead us to expect that the σ-LMCT band will be of higher energy and have substantially greater intensity than the π-LMCT absorption. Thus we assign the 38.8- and 45.5-kK bands in $[Rh(CN)_5I]^{3-}$ to π-LMCT and σ-LMCT transitions, respectively. Analogous LMCT assignments are given in Table III for the intense bands observed in $[Rh(CN)_5Br]^{3-}$, $[Ir(CN)_5Br]^{3-}$, and $[Ir(CN)_5I]^{3-}$.

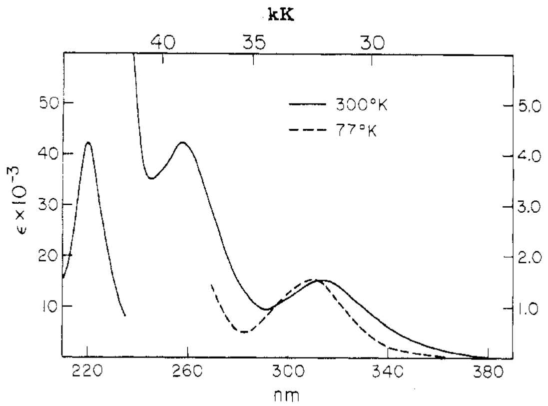

Figure 4. Electronic spectra of $K_3[Rh(CN)_5I]$ in pH 6 aqueous buffer solution at 300°K and in an aqueous LiCl glass at 77°K.

Acknowledgments. We thank Dr. V. Miskowski for several helpful discussions. This research was supported by the Army Research Office–Durham.

Registry No. $[Rh(CN)_5H_2O]^{2-}$, 42892-92-2; $[Rh(CN)_5OH]^{3-}$, 42892-93-3; $K_3[Rh(CN)_6]$, 20792-40-9; $K_3[Rh(CN)_5Cl]$, 42892-94-4; $K_3[Rh(CN)_5Br]$, 42892-95-5; $K_3[Rh(CN)_5I]$, 42892-96-6; $K_2[Rh(CN)_5NCCH_3]$, 42892-97-7; $[Co(NH_3)_6][Rh(CN)_5I]$, 42892-98-8; $[Co(NH_3)_6][Rh(CN)_5Br]$, 42892-99-9; $[Ir(CN)_5H_2O]^{2-}$, 42893-00-5; $[Ir(CN)_5OH]^{3-}$, 42893-01-6; $K_3[Ir(CN)_6]$, 20792-41-0; $K_3[Ir(CN)_5Cl]$, 42893-03-8; $K_3[Ir(CN)_5Br]$, 42893-04-9; $K_3[Ir(CN)_5I]$, 42893-05-0; $K_2[Ir(CN)_5NCCH_3]$, 42893-06-1; $[Co(NH_3)_6][Ir(CN)_5I]$, 42893-07-2; $[Co(NH_3)_6][Ir(CN)_5Br]$, 42893-08-3; $[Co(NH_3)_6][Ir(CN)_5Cl]$, 42893-09-4.

[13] W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5721 (1968).

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Preparation and Reactivity of Tris(oxalato)iridate(IV) Ion in Aqueous Acidic Solution[1]

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In aqueous acidic sulfate and perchlorate media, Ce(IV) rapidly and quantitatively oxidizes $Ir^{III}(C_2O_4)_3{}^{3-}$ to $Ir^{IV}(C_2O_4)_3{}^{2-}$. $Co_{aq}{}^{3+}$ also effects this rapid conversion, and the Ir(IV) complex is also produced by anodic oxidation. In solutions of a given acidity $Ir^{IV}(C_2O_4)_3{}^{2-}$ undergoes slow pseudo-first-order reaction to produce a highly reactive intermediate which we interpret to be $Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-}$. The latter species reacts very rapidly with $Ir^{IV}(C_2O_4)_3{}^{2-}$, Ce(IV), or O_2 with production of CO_2. In acidic sulfate media, the direct reaction of Ce(IV) with $Ir^{IV}(C_2O_4)_3{}^{2-}$ is a moderately slow process, in line with the redox reactivity exhibited by coordinated oxalate in related metal-oxalato complexes.

For some time we have been interested in the chemistry of iridium-oxalato complexes, particularly as the behavior may compare to observations which we and others have made on related rhodium and cobalt systems. While brief reports on the iridium system have been made,[2] the present paper represents the first detailed account of our progress. We describe here the preparation of $Ir(C_2O_4)_3{}^{2-}$, its thermal redox de-

[1] Supported by the National Science Foundation.

composition, and its reactivity toward Ce(IV).

Experimental Section

Materials. Reagent grade materials were used except where otherwise indicated. The purification of water and methods used to prepare stock solutions have been previously described.[3]

Potassium tris(oxalato)iridate(III) was prepared, using a modification of Delephine's procedure,[4] by heating 5.0 g of K_2IrCl_6, 80 g of $K_2C_2O_4 \cdot H_2O$, and 4 ml of water in an autoclave for 11 hr at 130°. After 45 ml of water had been added to the resulting mixture, it was filtered, the filtrate was allowed to evaporate slowly to dryness, and the best looking yellow crystals were separated. These were recrystallized twice from water, pulverized, and allowed to dry over Drierite. *Anal.*[5] Calcd for $K_3Ir(C_2O_4)_3 \cdot 4H_2O$: C, 11.16; K, 18.17; Ir, 29.8; H, 1.25; Cl, 0.00. Found: C, 11.20; K, 18.4; Ir, 29.5; H, 1.33; Cl, 0.03. The yield was ~30%. For the visible-uv spectral region, λ_{max} was at 286 nm (ϵ 4.10 × 10^3).

Preparation and Characterization of $Ir(C_2O_4)_3^{2-}$. In aqueous acidic solution (H_2SO_4 or $HClO_4$), $Ir(C_2O_4)_3^{3-}$ (yellow) is rapidly and quantitatively oxidized by Ce(IV) (yellow) to produce $Ir(C_2O_4)_3^{2-}$ (red) according to the stoichiometry of reaction 1. For this reaction,

$$Ir(C_2O_4)_3^{3-} + Ce(IV) \rightarrow Ir(C_2O_4)_3^{2-} + Ce(III) \quad (1)$$

spectrophotometric stopped-flow measurements (using a D-130 Durrum instrument) in 1.00 *M* H_2SO_4 at 25.0° (λ 460 nm) gave a bimolecular rate constant of 6.7 (±0.9) × 10^5 M^{-1} sec^{-1} (average of 6 runs). In 0.967 *M* $HClO_4$ at 25.0° we were only able to see the last ~10% reaction, from which we estimate (from several traces) $k_2 \approx 10^7$ M^{-1} sec^{-1}. Following this rapid reaction, slower changes occur.

In Figure 1 are shown visible spectra (in 1 *M* H_2SO_4) following the mixing of Ce(IV) with a slight stoichiometric excess of $Ir(C_2O_4)_3^{3-}$; spectra for the reactants Ce(IV) and $Ir(C_2O_4)_3^{3-}$ (each in 1 *M* H_2SO_4) are also shown (Cary 14 spectrophotometer). The uv spectrum for $Ir(C_2O_4)_3^{2-}$, corrected for Ce(III) and for $Ir(C_2O_4)_3^{2-}$ decomposition (discussed below), has a λ_{max} of 270 nm, with ϵ 4.55 × 10^3.

The stoichiometry of reaction 1 is supported by several lines of evidence.

In a molar ratio experiment, illustrated in Figure 2, the initial concentration of $Ir(C_2O_4)_3^{3-}$ was held constant at 4.60 × 10^{-4} *M* while the concentration of added Ce(IV) was varied from 0 to 8.7 × 10^{-4} *M*. The ordinate of Figure 2, $A_i - A_c$, represents the difference between the *initial* absorbance at 460 nm for the solutions formed by mixing $Ir(C_2O_4)_3^{3-}$ and Ce(IV) (A_i), and the absorbance *calculated* for 460 nm on the assumption no reaction occurs (A_c). The data are summarized well by two straight lines (one of which is horizontal) which intersect at a molar ratio very close to 1.00. The absence of apparent curvature or of an effect when Ce(III) (of comparable concentrations to the iridium) is included in the reaction mixture, indicates that the equilibrium position for reaction 1 is well toward the product species.

Carbon dioxide is not produced in the initial rapid reaction between $Ir(C_2O_4)_3^{3-}$ and Ce(IV), but it is formed more slowly as $Ir(C_2O_4)_3^{2-}$ undergoes thermal redox decomposition, and it is also produced in a parallel reaction between $Ir(C_2O_4)_3^{2-}$ and any excess Ce(IV) (see below).

Carbon dioxide production was observed directly by sweeping nitrogen through reaction solutions and into $Ba(OH)_2$ solution and titrating the latter.[6] A more convenient method was devised, however, in which we determined the capacities of reaction solutions to oxidize Fe(II) to Fe(III) (oxidizing capacity). The method is based on the observation that $Ir(C_2O_4)_3^{3-}$, other iridium(III) species formed as products of reactions, and CO_2 do not oxidize Fe(II), while $Ir(C_2O_4)_3^{2-}$ (which we consider to be an Ir(IV) species; see Discussion), other iridium species with iridium oxidation states >3,[7] and Ce(IV) all rapidly and quantitatively oxidize Fe(II) to Fe(III). Each determination was made by adding an aliquot of reaction solution to a measured volume of standard iron(II) sulfate solution and determining the Fe(III) produced from the absorbance at 460 or 480 nm attributable to $FeNCS^{2+}$ formed on addition of a solution of potassium or sodium thiocyanate. Standardization of the method was achieved with use of standard solutions of Ce(IV). The latter solutions, reaction aliquots, and blank solutions were treated in the same manner; in all cases the stoichiometric concentrations of thiocyanate, Fe(III), and sulfuric acid were adjusted, respectively, to ~0.050 (constant for a given series of experiments), (1.5-15) × 10^{-4}, and 0.20 *M*. For these conditions the Fe(III) solutions were found to obey Beer's law.

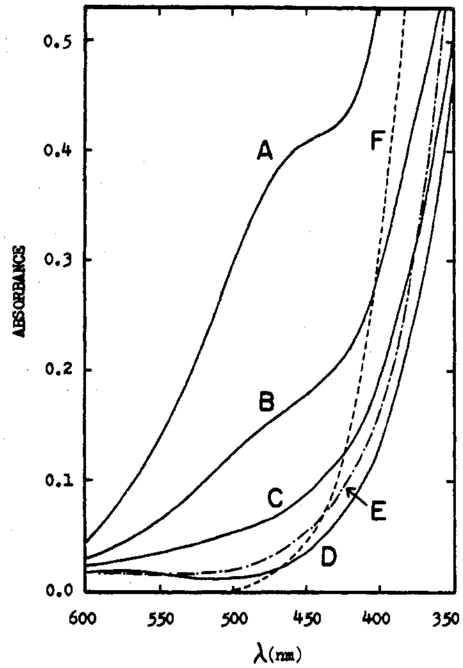

Figure 1. Spectra for solution 1.00 *M* in H_2SO_4 and initially 3.77 × 10^{-4} *M* in $Ir(C_2O_4)_3^{3-}$ and 3.04 × 10^{-4} *M* in Ce(IV), after ~2.5 min (A), ~17 min (B), ~33 min (C), and 220 min (D). Spectra for solutions 1.00 *M* in H_2SO_4 and 3.77 × 10^{-4} *M* in $Ir(C_2O_4)_3^{3-}$ (E); 1.00 *M* in H_2SO_4 and 3.04 × 10^{-4} *M* in Ce(IV) (F) (1-cm cell).

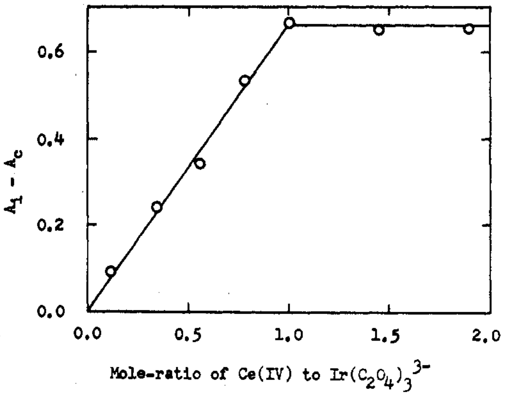

Figure 2. Molar ratio plot for solutions formed by mixing $Ir(C_2O_4)_3^{3-}$ (4.60 × 10^{-4} *M* before reaction) and Ce(IV) (0 to 8.7 × 10^{-4} *M* before reaction). All solutions 1.00 *M* in H_2SO_4, temperature 25.0°. A_i = initial absorbance at 460 nm on mixing solutions; A_c = calculated absorbance at 460 nm assuming no reaction occurs (1-cm cell).

If, to a solution containing $Ir(C_2O_4)_3^{3-}$, Ce(IV) is introduced to produce the red complex and if Fe(II) is now quickly added to determine the oxidizing capacity, the latter is found to be fully equivalent to the quantity of Ce(IV) which had been introduced (whether or not the Ce(IV) was in stoichiometric excess to the $Ir(C_2O_4)_3^{3-}$). This observation confirms that the initial reaction between $Ir(C_2O_4)_3^{3-}$ and Ce(IV) produces no CO_2 and provides additional support for the stoichiometry of reaction 1. Over a period of time, however, the oxidizing capacity of solutions prepared from $Ir(C_2O_4)_3^{3-}$ and Ce(IV) falls, accompanied by spectral changes and production of CO_2. The

(2) (a) H. G. Kruszyna, M. W. Hsu, and R. M. Milburn, *Proc. Int. Conf. Coord. Chem.*, 10, 302 (1967); (b) R. M. Milburn, paper presented at the 2nd Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct 1970; see Abstracts, p 67.

(3) (a) M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, 8, 2201 (1969); (b) H. G. Kruszyna and R. M. Milburn, *ibid.*, 10, 1578 (1971).

(4) M. Delephine, *Bull. Soc. Chim. Fr.*, [4] 21, 157 (1917).

(5) Analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

(6) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 246.

(7) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, 84, 123 (1950).

decrease in oxidizing capacity gives one a direct measure of the amount of CO_2 formed.

Anodic Oxidation of $Ir(C_2O_4)_3^{3-}$. Solutions of $Ir(C_2O_4)_3^{3-}$ were oxidized anodically in 1 *M* H_2SO_4 and in 2 *M* $HClO_4$. For this purpose we used a cell consisting of a platinum wire (cathode) in a glass tube with a sintered-glass bottom, the tube being surroundered by a platinum gauze cylinder (anode) in a slightly larger jar. Solutions containing $Ir(C_2O_4)_3^{3-}$ in acid were placed into the anode jar while the cathode compartment was filled to a slightly higher level with acid of a similar concentration. While stirring of the solution in the anode compartment was maintained, a dc current (~0.2 A) was passed for some minutes (variable). Electrolysis produced a red solution of similar appearance to the product of Ce(IV) oxidation. For a more quantitative comparison one can correct the spectra, observed for the anodically oxidized solutions, for the contributions from Ir(III) (which were estimated from the oxidizing capacity of the solution as measured by Fe(II) consumption together with an assumption that all Ir(III) exists as $Ir(C_2O_4)_3^{3-}$). While the resulting corrected spectra are very similar in shape and in position of maximum (270 nm) and shoulder (460 nm) to that observed for the initial product of the $Ir(C_2O_4)_3^{3-}$–Ce(IV) reaction (adjusted for cerium absorption), calculated absorbancy coefficients in the uv region for the electrolysis product are somewhat lower (*e.g.*, ~20% lower for a solution in 1 *M* H_2SO_4 which had been electrolyzed for 7 min). The apparent discrepancy arises because in the electrolyzed solutions there will be, on the average, somewhat fewer than three oxalates per iridium (for both the Ir(IV) and Ir(III) species present) even when the first spectral measurements are made (CO_2 being evolved during electrolysis). Our observations, from the time dependence of spectra for solutions prepared both by Ce(IV) oxidation and by electrolytic oxidation of $Ir(C_2O_4)_3^{3-}$, are that the intensities of the bands in the 250–350-nm region are lower in the chosen media for iridium species with fewer oxalates per metal center. This holds for both iridium(IV) and iridium(III) species. This feature is in agreement with the observations of Jorgensen[8] that the absorbancy coefficients for oxalato complexes in this region are dependent on the number of oxalates present.

Our electrolysis experiments indicate that the Ir(IV) species formed on oxidation of $Ir(C_2O_4)_3^{3-}$ by Ce(IV) and anodically are of similar type, except for the number of oxalates within the coordination sphere of the Ir(IV). These features provide further support for the stoichiometry represented by reaction 1.

Because the Ce(IV) oxidation is rapid and clean cut, we have in most cases used this method of preparation of $Ir(C_2O_4)_3^{2-}$ for kinetic studies on the complex.

Redox Decomposition of $Ir(C_2O_4)_3^{2-}$. In the absence of residual Ce(IV), solutions containing $Ir(C_2O_4)_3^{2-}$ soon fade from red to pale yellow as the complex undergoes internal redox decomposition. Spectral changes accompanying the reaction are shown in Figure 1. The production of CO_2 accompanied by loss in oxidizing capacity, the nature of the spectral changes, the straightforward kinetic behavior (see below), and the known substitution inertness of iridium(III) are consistent with the reaction stoichiometry.[9]

$$2Ir(C_2O_4)_3^{2-} + 2H_2O \rightarrow Ir(C_2O_4)_3^{3-} + Ir(H_2O)_2(C_2O_4)_2^{-} + 2CO_2 \quad (2)$$

We have examined the kinetics of the decomposition under several sets of conditions. Kinetic runs were in general initiated by addition of acidic Ce(IV) to solutions containing $Ir(C_2O_4)_3^{3-}$. In most of the experiments the molar amounts of Ce(IV) added were equal to or less than the molar amounts of the iridium(III) complex, so that the decomposition of $Ir(C_2O_4)_3^{2-}$ occurred in the absence of Ce(IV). Rates were measured by one or both of two methods: (1) by quenching aliquots of the resulting solution with Fe(II) and determining the Fe(III) with use of thiocyanate (oxidizing capacity method); (2) by following changes in the optical absorbance, usually at 460 nm (direct absorbancy method), and plotting ln $(A_t - A_\infty)$ *vs.* time. For these experiments

$$-d[\text{ox. capacity}]/dt = -d[Ir^{IV}]/dt = d[CO_2]/dt$$

In one set of experiments, the decomposition was allowed to take place under two types of conditions: (1) the reactant solutions were purged with He or N_2 (prewashed with solvent); (2) the reaction solutions were purged with O_2 (prewashed with solvent).[10] Table I summarizes the data. When the purging gas was He or N_2, first-order kinetics were observed for at least 2.5 half-lives. The final color of the solutions was pale yellow. When the purging gas was O_2, first-order kinetics were observed for at least 1.5 half-lives. Here, in some cases, the final solutions (>10 half-lives) were a very pale red, rather than pale yellow, and maintained a very slight oxidizing capacity (red color discharged immediately by Fe^{2+} solution). Separate experiments demonstrated that reaction of O_2 with the products of the redox decomposition in He or N_2 (*i.e.*, $Ir(C_2O_4)_3^{3-}$ and $Ir(C_2O_4)_2(H_2O)_2^{-}$) was too slow and too incomplete to interfere with our measurement of rate constants for the O_2-saturated solutions. For example, for a study in which the redox decomposition of 3.25 × 10^{-3} *M* $Ir(C_2O_4)_3^{2-}$ in 0.244 *M* $HClO_4$ was allowed to proceed to completion under He, subsequent bubbling of the yellow solution with O_2 for >100 hr resulted in a pale red solution with a regaining of only ~5% of the original oxidizing capacity.

Table I. Rate Constants for Redox Decomposition of $Ir(C_2O_4)_3^{2-}$

$[Ir(C_2O_4)_3^{3-}]_0$[a]	$[Ce(IV)]_0$[a]	Medium	Obsd first-order rate constants × 10^3, sec^{-1} [b,c] k_{He}	k_{O_2}	k_{O_2}/k_{He}
4.95×10^{-4}	4.79×10^{-4}	1.00 *M* H_2SO_4	1.87[d]	1.41[d]	0.75
4.52×10^{-4}	4.32×10^{-4}	1.00 *M* H_2SO_4	1.83[e]	1.26[e]	0.67
4.52×10^{-3}	4.47×10^{-3}	0.254 *M* $HClO_4$	0.727[e]	0.464[e]	0.64
4.56×10^{-3}	4.56×10^{-3}	0.254 *M* $HClO_4$	0.712[e]	0.458[e]	0.64
4.52×10^{-4}	4.47×10^{-4}	0.254 *M* $HClO_4$	0.734[e]	0.415[e]	0.57

[a] Initial concentrations after mixing, in mole per liter, if reaction 1 did not take place. [b] Temperature 25.0°. [c] Single determinations unless otherwise noted. [d] "Direct absorbancy method;" average of three traces using stopped-flow spectrophotometer; solutions purged prior to mixing. [e] "Oxidizing capacity method;" solutions continuously purged.

The rate constant in He- or N_2-saturated solutions is independent of the initial concentration of $Ir(C_2O_4)_3^{2-}$ (Table I). In separate studies where no purging precautions were taken, it was also shown that there was no apparent dependence of the rate constant on the concentration of $Ir(C_2O_4)_3^{2-}$ present at the start of the decomposition.

The effect of acidity on the decomposition was studied at 25° in perchlorate media. For these experiments, all solutions were carefully purged and kept under N_2. In check experiments at ionic strength 0.824, the rates measured by the oxidizing capacity method and the direct absorbancy method for 555 nm were found to be the same within experimental error limits (±5%). The direct absorbancy method at 555 nm was then used to study the acid dependence of the reaction in $NaClO_4$–$HClO_4$ media at ionic strength 1.00, with $[Ir(C_2O_4)_3^{2-}]_0 = 3.04 \times 10^{-3}$ *M*. First-order rate plots were linear over 2 half-lives. Results are $[H^+] = 0.367$ *M*, $k_1 = 5.88 \times 10^{-4}$ sec^{-1}; $[H^+] = 0.567$ *M*, $k_1 = 6.22 \times 10^{-4}$ sec^{-1}; $[H^+] = 0.887$ *M*, $k_1 = 8.83 \times 10^{-4}$ sec^{-1}; $[H^+] = 0.967$ *M*, $k_1 = 1.10 \times 10^{-3}$ sec^{-1}.

Reaction of $Ir(C_2O_4)_3^{2-}$ in Presence of Residual Ce(IV). When solutions containing Ce(IV) and $Ir(C_2O_4)_3^{3-}$ in acidic sulfate or perchlorate media are mixed under conditions where the initial Ce(IV):$Ir(C_2O_4)_3^{3-}$ molar ratio is >1, the rapid initial reaction leading to the formation of $Ir(C_2O_4)_3^{2-}$ (red) is followed by slower reactions which now lead to blue rather than pale yellow solutions. These slow visual and spectral changes are accompanied by steady production of CO_2 and losses in oxidizing capacities of the solutions. The blue color fades only very slowly (over many days) but is immediately discharged by Fe^{2+}.

For two series of solutions in 1.00 *M* sulfuric acid with initial $[Ce(IV)]/[Ir(C_2O_4)_3^{3-}]$ molar ratios >1, measurements of the rate of loss of oxidizing capacity indicated that the reaction rate, for two initial values of $[Ir(C_2O_4)_3^{3-}]$, is not entirely independent of the initial [Ce(IV)]. The results are consistent with a two-term rate law of the form

$$-\frac{d[\text{ox. capacity}]}{dt} = \frac{d[CO_2]}{dt} = k'[Ir(C_2O_4)_3^{2-}] + k''[Ir(C_2O_4)_3^{2-}][Ce(IV)] \quad (3)$$

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(8) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 196.

(9) In the case of sulfate media the possibility exists that some sulfate may become incorporated into the iridium coordination sphere.

(10) In most cases "continuous" purging was maintained throughout the reaction. In a few cases, where the stopped-flow spectrophotometric apparatus was used to examine the decomposition by the direct absorbancy method, reactant solutions were purged only up to the time of mixing. In these cases $[Ir(C_2O_4)_3^{2-}]_0$ was ~5 × 10^{-4} *M*, while the solubility of O_2 in O_2-saturated solutions at 1 atm and 25° is ~1.3 × 10^{-3} *M*.

where the initial values of $[Ir(C_2O_4)_3{}^{2-}]$ and [Ce(IV)] are those which will exist immediately after completion of the very rapid reaction 1. The form of the rate law and approximate values of k' and k'' were obtained from a study of initial rates, this procedure being utilized to avoid interference from secondary reactions. Initial values of $-d[\text{ox. capacity}]/dt$ (initial rates) were determined for each of 11 reaction solutions (6 with $[Ir(C_2O_4)_3{}^{2-}]_0 = 1.69 \times 10^{-3}\ M$; 5 with $[Ir(C_2O_4)_3{}^{2-}]_0 = 6.84 \times 10^{-4}\ M$) from plots of [capacity] *vs.* time, and from these, two plots were made of $-(d[\text{capacity}]/dt)/[Ir(C_2O_4)_3{}^{2-}]_0$ *vs.* $[Ce(IV)]_0$. These plots gave $k' = 1.4\ (\pm 0.3) \times 10^{-3}\ \text{sec}^{-1}$ and $k'' = 6\ (\pm 2) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. The solutions were not in this case purged with He or N_2, but consideration of results from the above-described oxygen studies, together with reactant and possible oxygen concentrations, leads to the conclusion that the above approximate k'' value would not be influenced significantly by this factor.

Discussion

As has been described, Ce(IV) in acidic solution rapidly and quantitatively oxidizes $Ir(C_2O_4)_3{}^{3-}$ (yellow) to $Ir(C_2O_4)_3{}^{2-}$ (red) according to the stoichiometry of reaction 1. We have also observed, in preliminary studies, that certain other strong oxidants such as $Co_{aq}{}^{3+}$ can effect this process. In addition, the oxidation can be achieved electrolytically, although the slowness of the process now results in interference arising from competing decomposition of the $Ir(C_2O_4)_3{}^{2-}$.

Several reasons lead us to regard $Ir(C_2O_4)_3{}^{2-}$ as a complex of Ir(IV) rather than of Ir(III) (to which a $C_2O_4{}^{-}$ radical ion could be considered to be coordinated).[11] Support for this position comes particularly from the rapidity of the Ce(IV)-$Ir(C_2O_4)_3{}^{3-}$ reaction ($k_2 \approx 7 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ in 1 M H_2SO_4 at 25°), the quantitative nature of this process, and the slowness with which $Ir(C_2O_4)_3{}^{2-}$ reacts with any excess Ce(IV). Accumulated observations in acidic sulfate media have shown that the Ce(IV) oxidations of coordinated oxalate in such formally similar complexes as $Rh(C_2O_4)_3{}^{3-}$, $Co(C_2O_4)_3{}^{3-}$, and $Cr(C_2O_4)_3{}^{3-}$ are slow processes.[3] In the case of $Rh(C_2O_4)_3{}^{3-}$ the one-electron oxidation by Ce(IV), in 1 M H_2SO_4 at 25°, to produce the presumed intermediate $Rh(C_2O_4)_3{}^{2-}$ proceeds with a second-order rate constant of only $6 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$; the rate constant for the Ce(IV)-$Ir(C_2O_4)_3{}^{3-}$ reaction is $\sim 10^9$ times greater than this. Even free oxalic acid reacts with Ce(IV) under these conditions with an apparent k value for the initial one-electron oxidation of only $28\ M^{-1}\ \text{sec}^{-1}$.[3a,12] Again, if it were appropriate to regard $Ir(C_2O_4)_3{}^{2-}$ as an Ir(III) complex, it is difficult to see why the radical ion ligand would not react very rapidly with any excess Ce(IV). All evidence we have to date is in accord with the view that $C_2O_4{}^{\cdot -}$, whether free or coordinated to a metal center, reacts extremely rapidly with Ce(IV). In summary, our view is that the odd electron in $Ir(C_2O_4)_3{}^{2-}$ is predominantly metal centered ($Ir^{IV}(t_{2g})^5$) rather than predominantly ligand centered. For clarification in further discussion, roman superscripts will be used to designate the presumed oxidation state of the iridium center.

Evidence on the thermal decomposition of $Ir^{IV}(C_2O_4)_3{}^{2-}$, as described above, is in accord with the stoichiometry of reaction 2. The observations suggest that the decomposition, in the absence of excess Ce(IV) or of O_2, proceeds according to the two-step mechanism[9]

$$Ir^{IV}(C_2O_4)_3{}^{2-} \xrightarrow{\text{slow}} Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-} \tag{4}$$

$$Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-} + Ir^{IV}(C_2O_4)_3{}^{2-} \xrightarrow{\text{fast}} Ir^{III}(C_2O_4)_2(H_2O)_2{}^- + Ir^{III}(C_2O_4)_3{}^{3-} + 2CO_2 \tag{5}$$

This reaction scheme compares closely with that pertinent to the acid-promoted thermal decomposition of $Co^{III}(C_2O_4)_3{}^{3-}$, which in its most essential features may be represented by[3b,13]

$$Co^{III}(C_2O_4)_3{}^{3-} \xrightarrow{\text{slow}} Co^{2+} + 2C_2O_4{}^{2-} + C_2O_4\cdot^- \tag{6}$$

$$C_2O_4\cdot^- + Co^{III}(C_2O_4)_3{}^{3-} \xrightarrow{\text{fast}} Co^{2+} + 3C_2O_4{}^{2-} + 2CO_2 \tag{7}$$

Here, $Co(C_2O_4)_3{}^{3-}$ may be taken to include protonated and ring-opened forms; $C_2O_4{}^{2-}$ to include $HC_2O_4{}^-$ and $H_2C_2O_4$; and $C_2O_4{}^{\cdot -}$ to include its protonated form (or $CO_2{}^{\cdot -}$ and $CO_2H\cdot$).[13] An important difference between the thermal decompositions of $Ir^{IV}(C_2O_4)_3{}^{2-}$ and $Co^{III}(C_2O_4)_3{}^{3-}$ arises because of the great difference in substitution rates at Ir(III) and Co(II) centers. Thus, the Co(II) center is labile and, once formed, quickly releases (under acidic conditions) its oxalate into solution. But because Ir(III) forms inert complexes and because reaction 5 can be presumed to be very rapid, we believe it to be unlikely that $Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-}$ will have time to release $C_2O_4\cdot^-$ into solution before it reacts with $Ir^{IV}(C_2O_4)_3{}^{2-}$.

When solutions containing $Ir^{IV}(C_2O_4)_3{}^{2-}$ were swept with a steady stream of O_2, diminished rates of Ir(IV) reduction were observed (as measured by both the oxidizing capacity and the direct absorbance methods). The values of the rate constants measured over the first 1.5 half-lives, during which the reaction exhibits good first-order behavior, in fact at low complex concentrations approach half of the values measured under He purging, indicating that O_2 can compete successfully with $Ir^{IV}(C_2O_4)_3{}^{2-}$ in scavenging for the coordinated radical in $Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-}$. In a separate presentation[13] we have shown how $C_2O_4\cdot^-$, produced in the redox decomposition of $Co(C_2O_4)_3{}^{3-}$, can be successfully scavenged by O_2 (in competition with $Co(C_2O_4)_3{}^{3-}$).

When the initial molar ratio of Ce(IV) to $Ir(C_2O_4)_3{}^{3-}$ exceeds 1, $Ir(C_2O_4)_3{}^{2-}$, which is formed rapidly as before by reaction 1, now decomposes slowly to produce blue solutions. The blue species are likely to be complexes of Ir(IV) containing fewer than three oxalates; consistent with this view the blue color is discharged immediately by Fe^{2+}. In the presence of sufficient Ce(IV) it is clear that all oxalate initially present in $Ir(C_2O_4)_3{}^{3-}$ will ultimately be oxidized to CO_2. The first steps of such a process are likely to proceed by a mechanism which involves reaction 1 followed by[9]

$$Ir^{IV}(C_2O_4)_3{}^{2-} \xrightarrow{\text{slow}} Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-} \tag{4}$$

$$Ir^{III}(C_2O_4)_2(C_2O_4\cdot^-)^{2-} + Ce(IV) \xrightarrow{\text{fast}} Ir^{III}(C_2O_4)_2(H_2O)_2{}^- + Ce(III) + 2CO_2 \tag{8}$$

$$Ir^{III}(C_2O_4)_2(H_2O)_2{}^- + Ce(IV) \xrightarrow{\text{fast}} Ir^{IV}(C_2O_4)_2(H_2O)_2 + Ce(III) \tag{9}$$

$$Ir^{IV}(C_2O_4)_2(H_2O)_2 \xrightarrow{\text{slow}} \text{etc.}$$

As oxidation by Ce(IV) proceeds, it is likely that the iridium species become more closely related to the Ir(IV) species observed by Dwyer and Gyarfas.[7]

It is of interest to note the dissimilar behavior of the formally similar complexes $Co(C_2O_4)_3{}^{3-}$, $Rh(C_2O_4)_3{}^{3-}$, and $Ir(C_2O_4)_3{}^{3-}$ toward Ce(IV) in acidic solution. Thus, addition of the oxidant Ce(IV) to solutions containing $Co(C_2O_4)_3{}^{3-}$ results in an accelerated reduction of the cobalt(III) center.[3b] In the case of $Rh(C_2O_4)_3{}^{3-}$, the addi-

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(11) Otherwise the odd electron could be considered to be delocalized.

(12) Y. El-Tantawy and G. A. Rechnitz, *Anal. Chem.*, 36, 1774 (1964).

(13) N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, 11, 2272 (1972).

tion of Ce(IV) leads to stepwise oxidation of coordinated oxalate without evidence for change in oxidation state of the rhodium center.[3a] The greater accessibility of higher oxidation states in the case of third-row transition elements is clearly illustrated by the rapid and quantitative Ce(IV) oxidation of $Ir(C_2O_4)_3^{3-}$.

Acknowledgment. We wish to thank Dr. D. H. Fortnam, who made some initial observations on the $Ir(C_2O_4)_3^{3-}$-Ce(IV) system. We are also indebted to Matthey Bishop, Inc., Malvern, Pa., for the generous loan of some potassium hexachloroiridate(IV).

Registry No. $Ir(C_2O_4)_3^{2-}$, 42401-85-4; $Ir(C_2O_4)_3^{3-}$, 18307-27-2; Ce^{4+}, 16065-90-0.

Contribution from the Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan

Studies on Interactions of Isocyanides with Transition Metal Complexes. IX.[1] Single and Multiple Insertion of Isocyanide into Palladium-to-Carbon σ Bonds[2]

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Reactions of trans square-planar complexes of palladium alkyls with isocyanides have led to the preparation of four classes of new complexes: *trans*-$PdL_2X[C(R){=}NR']$ (type I) (R = CH_3, Ph, *o*-$C_6H_4CH_3$; R' = C_6H_{11}, $(CH_3)_3C$, $PhCH_2$, Ph; X = Br, I; L = PPh_3, $PPh(CH_3)_2$, $P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$, $PPh_2(C_6H_{11})$), $[Pd\{PPh_2(CH_3)\}I\{C(CH_3){=}NR'\}]_2$ (type II) (R' = C_6H_{11}, $(CH_3)_3C$), *trans*-$PdL_2I[(C{=}NC_6H_{11})_2(CH_3)]$ (type III) (L = PPh_3, $PPh_2(CH_3)$, $PPh(CH_3)_2$, $P(CH_3)_3$), and $Pd[PPh_2(CH_3)]I[(C{=}NC_6H_{11})_3(CH_3)]$ (type IV). The type I complex (R = CH_3; R' = C_6H_{11}; X = I; L = $PPh(CH_3)_2$, $P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$) and the type II complex (R' = C_6H_{11}, in the presence of $PPh_2(CH_3)$) were converted to the corresponding type III complex; the type III complex (L = $PPh_2(CH_3)$) was converted to the corresponding type IV complex, when treated with cyclohexyl isocyanide. The steric effects of ligands and the incoming isocyanide were observed in these insertion reactions. The possible insertion pathways of isocyanide into palladium-to-carbon bonds were discussed.

Introduction

Many examples of the insertion reactions of small molecules such as carbon monoxide, olefins, acetylenes, and sulfur dioxide into carbon-transition metal σ bonds are well-known.[3] This type of reaction is one of the most essential reactions in organometallic chemistry and is thought to be an important intermediate step in catalytic processes. There have also been several insertion reactions of isocyanides which are isoelectronic with carbon monoxide.[4]

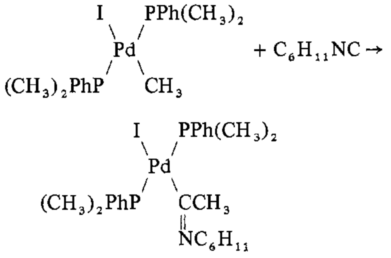
Otsuka, *et al.*, reported that tetrakis(*tert*-butyl isocyanide)nickel undergoes multiple successive insertion of isocyanide molecules, when allowed to react with methyl iodide or benzoyl chloride.[5] Such a multiple insertion occurs in the reactions with trans square-planar palladium alkyls.[6] Recently, we found that dicarbonyl-π-cyclopentadienylbenzyliron leads to a successive insertion of three isocyanide molecules to produce π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2Ph)]$, when treated with cyclohexyl isocyanide.[7] These multiple insertions are considered as an intermediate process of the coordinated polymerization of isocyanides catalyzed by transition metal complexes.[8,9]

In this paper, we wish to report more fully on the single and multiple insertion of isocyanides into the palladium-carbon σ bond, on which we have already communicated briefly.[6]

Results and Discussion

Single Insertion. When *trans*-iodobis(dimethylphenylphosphine)methylpalladium is treated with an equimolar amount of cyclohexyl isocyanide in benzene at 5°, yellow crystals, formulated as a 1:1 adduct on the basis of the elemental analysis and molecular weight determination, are obtained in good yield. They can be handled in air, but decompose when exposed to the atmosphere for longer periods of time in the solid state. The infrared spectrum shows a characteristic band at 1625 cm^{-1} assignable to a carbon-nitrogen double bond. The reaction with hydrogen peroxide gives *N*-cyclohexylacetamide.

These results suggest *trans*-iodobis(dimethylphenylphosphine)(1-cyclohexyliminoethyl)palladium for the complex in question (eq 1). The stereochemistry is provided by the



(1)

proton nmr spectrum. The spectrum in $CDCl_3$ shows a triplet at τ 7.76 (C-CH_3, J_{P-H} = 1.5 Hz) and a well-defined

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[1] Part VIII: Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 11, 211 (1972).

[2] Presented at the Symposium of Organometallic Chemistry: Osaka, Japan, Oct 7, 1969 (see Preprints, p 172); Kiryu, Japan, Oct 13, 1970 (see Preprints, p 171).

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