2328 *Inorg. Chem.* **1992**, *31*, 2328-2333

Contribution from the Department of Chemistry, State University
of New York at Buffalo, Buffalo, New York 14214

Electrochemical Studies of Tris(acetylacetonato)ruthenium(III) in Ambient-Temperature Chloroaluminate Molten Salts

Jinsong Tang, Kunio Shimizu, and Robert A. Osteryoung*

Received November 27, 1991

The electrochemical behavior of tris(acetylacetonato)ruthenium(III), Ru(acac)$_3$, in a room-temperature molten salt composed of a mixture of aluminum trichloride and 1-ethyl-3-methylimidazolium chloride is studied as a function of melt composition. Ru(acac)$_3$ decomposes in acidic melts but is stable in neutral and basic melts, dissolving readily to give intense red solutions. The complex undergoes a Nerstian one-electron reduction process at a glassy-carbon electrode independent of the basic melt composition. The reduced Ru(acac)$_3^-$ complex, depending on the melt basicity, can react with AlCl$_4^-$ on the voltammetric time scale probably to form the adduct [Ru(acac)$_2$(acacAlCl$_3$)]$^-$, which gives a one-electron oxidation step at a more positive potential than that of Ru(acac)$_3^-$. When a small amount of Ru(acac)$_3$ is reduced by bulk electrolysis in the basic melt and allowed to stand for 1 day at room temperature, all remaining Ru(acac)$_3$ is transformed into the colorless hexachlororuthenium(III) anion, RuCl$_6^{3-}$. This reaction is initiated by the attack at an Ru–O bond in Ru(acac)$_3^-$ by AlCl$_4^-$, followed by the breakage of the Ru–O bond. In addition, the intermediate, Ru(acac)$_{3-n}$Cl$_{2n}^{(n+1)-}$, generated by the rupture of an Ru–O bond, acts as a redox catalyst for the ligand replacement of Ru(acac)$_3$ to form RuCl$_6^{3-}$.

Introduction

Acetylacetone (2,4-pentanedione, Hacac) and other β-dicarbonyl compounds constitute a class of important ligands which have been widely employed. They are very versatile and exhibit a great variety of coordination modes besides the usual bidentate behavior of the monoanion.[1]

The electrochemical properties of tris(β-diketonato) complexes involving many kinds of trivalent metal (e.g. chromium,[2-5] manganese,[2,3,6,7] iron[2,3,5,6,8-10] cobalt,[2,3,6,11] ruthenium,[12-16] and osmium,[13] etc.) have been studied in various protic and aprotic organic solvents. Most of these complexes undergo simple one-electron reduction and/or one-electron oxidation reactions. The use of (β-diketonato)metal complexes in photoinduced electron-transfer reactions has enhanced the interest in the electrochemical properties of these compounds.[17] Recently, studies of the electrochemistry and chemistry of tris(β-diketonato)ruthenate(II) and -ruthenium(III) were performed by Shimizu et al.[18-23]

Mixtures of aluminum chloride (AlCl$_3$) and 1-ethyl-3-methylimidazolium chloride (ImCl) are liquid over a broad range of compositions at room temperature and are intrinsically ionic conductors.[24-26] One of the most intriguing aspects of these molten salts is their adjustable Lewis acid–base properties. When the mole ratio of AlCl$_3$ to ImCl is less than 0.5, the melts are considered basic media because they contain chloride ion, a Lewis base, which is not covalently bound to aluminum; when the mole ratio is greater than 0.5, the melts are acidic, containing the chloride ion acceptor and the Lewis acid Al$_2$Cl$_7^-$.

In this paper, the electrochemical behavior of Ru(acac)$_3$ in ambient-temperature chloroaluminate molten salts is described.

Experimental Section

Ru(acac)$_3$ was prepared by the literature method and was purified by column chromatography (Merck silica gel 60/benzene).[18] The synthesis and purification of ImCl, ImHCl$_2$, and AlCl$_3$ were performed as previously described.[27-29] Co(acac)$_3$ and Fe(acac)$_3$ were obtained from Johnson-Mathey and used as received.

All electrochemical experiments in the melts were performed in a Vacuum Atmospheres Co. drybox under a purified nitrogen atmosphere. Oxygen and water levels were maintained below 2 ppm. Experiments in AlCl$_3$–ImCl melts were performed at 30 °C unless otherwise noted. All voltammetry and coulometry experiments were performed in glass cells with a Teflon cap fitted for introduction of electrodes. The assembled cells were maintained at constant temperature to within ±1 °C by insertion into an aluminum heating block.

Cyclic staircase (CS), normal pulse (NP), and reverse normal pulse (RP) voltammetries were performed using a Princeton Applied Research Model 273 potentiostat with a computer-controlled system as described previously.[30] Cyclic voltammetry (CV) was performed with an EG&G PARC 175 universal programmer in combination with a PARC Model 173 potentiostat. A glassy-carbon disk, area 0.071 cm^2, from Bioanalytical Systems was used in the voltammetric experiments as the working

---

(1) Mehrota, R. C.; Bohra, R.; Gaur, D. P. *Metal β-diketonates and Allied Derivatives*; Academic Press: San Francisco, CA, 1978.

(2) Bond, A. M.; Martin, R. L.; Masters, A. F. *Inorg. Chem.* **1975**, *14*, 1432.

(3) Gritzner, G. A.; Murauer, H.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 177.

(4) Handy, R. F.; Lintvedt, R. L. *Inorg. Chem.* **1974**, *13*, 893.

(5) Tsiamis, C.; Hadjikostas, G. G. *Inorg. Chim. Acta* **1988**, *143*, 17.

(6) Sock, O.; Lemoine, P.; Gross, M. *Electrochim. Acta* **1981**, *26*, 99.

(7) Gritzner, G.; Murauer, H.; Gutmann, V. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 185.

(8) Shimizu, K.; Morinaga, K.; Nakano, K. *Nippon Kagaku Zasshi* **1969**, *90*, 564.

(9) Murray, R. W.; Hiller, L. K., Jr. *Anal. Chem.* **1967**, *39*, 1221.

(10) Kalinowski, M. K.; Cmiel, A. *Inorg. Chim. Acta* **1981**, *49*, 179.

(11) Tsiamis, C.; Cambanis, S.; Hadjikostas, C. *Inorg. Chem.* **1987**, *26*, 26.

(12) Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285.

(13) Everett, G. W., Jr.; Horn, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 2087.

(14) Endo, A.; Watanabe, M.; Hayashi, S.; Shimizu, K.; Sato, G. P. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 800.

(15) Endo, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2733.

(16) Lewis, N. A.; Sishta, B. K. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1428.

(17) Wilkinson, F.; Tsiamis, C. *J. Am. Chem. Soc.* **1983**, *105*, 767.

(18) Endo, A.; Kajitani, M.; Mukaida, M.; Shimizu, K.; Sato, G. P. *Inorg. Chim. Acta* **1988**, *50*, 25.

(19) Hoshino, Y.; Endo, A.; Shimizu, K.; Sato, G. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *246*, 225.

(20) Endo, A.; Hoshino, Y.; Hirakata, K.; Takeuchi, Y.; Shimizu, K.; Furushima, Y.; Ikeuchi, H.; Sato, G. P. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 709.

(21) Hoshino, Y.; Yukawa, Y.; Maruyama, T.; Endo, A.; Shimizu, K.; Sato, G. P. *Inorg. Chim. Acta* **1990**, *174*, 41.

(22) Hoshino, Y.; Takahashi, R.; Shimizu, K.; Sato, G. P.; Aoki, K. *Inorg. Chem.* **1990**, *29*, 4816.

(23) Kasahara, Y.; Hoshino, Y.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1990**, 381.

(24) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum Publishing Corp.: New York, 1981; pp 407–423.

(25) Hussey, C. L. In *Advances in Molten Salt Chemistry*; Mamantov, G., Mamantov, C. B., Eds.; Elsevier: Amsterdam, 1987; pp 195–230.

(26) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum Press: New York, 1983; Vol. 1, pp 55–78.

(27) Carter, M. T.; Osteryoung, R. A. *J. Electrochem. Soc.*, in press.

(28) Zawodzinski, T. A.; Osteryoung, R. A. *Inorg. Chem.* **1988**, *27*, 4383.

(29) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.

(30) Brumleve, T. R.; O'Dea, J. J.; Osteryoung, R. A.; Osteryoung, J. *Anal. Chem.* **1981**, *53*, 702.

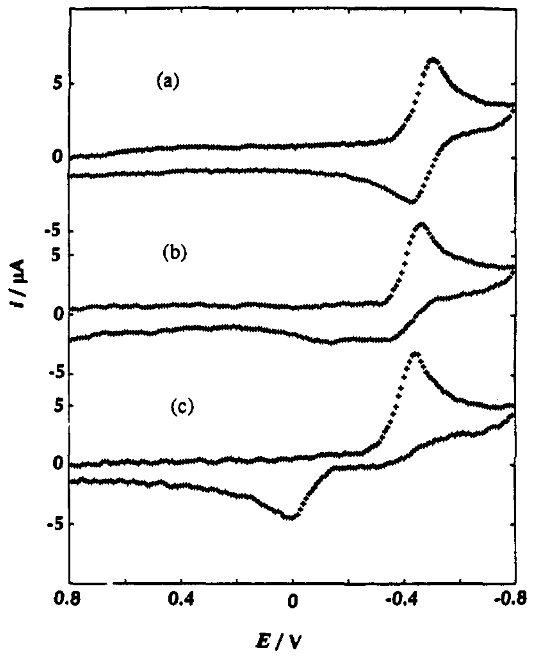

Figure 1. Staircase cyclic voltammograms for $Ru(acac)_3$ in (a) 0.6:1.0, (b) 0.8:1.0, and (c) 1.0:1.0 melts. Conditions: concentration of $Ru(acac)_3$, 2.7 mmol dm^{-3} in 0.6:1.0 and 1.0:1.0 melts and 2.6 mmol dm^{-3} in 0.8:1.0 melt; scan rate, 0.1 V s^{-1}; temperature, 30 °C.

electrode. The counter electrodes were Pt coils. The reference electrode was an aluminum wire immersed in a 1.5:1.0 $AlCl_3$–ImCl melt and separated from the bulk solution by a Vycor frit. For the work in ImCl melts, a Pt flag was used as quasireference electrode. Rotating-disk (RD) voltammetry employed a glassy-carbon disk electrode, area 0.126 cm^2, sealed in Teflon and was performed with a Pine Instruments Co. Model MSR speed controller and a Pine ASR rotator. CV and RD voltammograms were recorded with a Houston Omnigraph Model 2000 X-Y recorder.

Constant-potential coulometry was performed using a PARC Model 173 potentiostat combined with PARC Model 179 digital coulometer. A cylindrical glassy-carbon rod was used as the working electrode for controlled-potential coulometry.

UV and visible absorption spectra were recorded with a Hewlett-Packard HP 8452A diode array spectrophotometer using a 10-mm cell for acetonitrile solutions and a 0.1-mm cell (Wilmad Glass Co.) for melts at 30 °C.

Results and Discussion

Voltammetry in Chloroaluminate Melts. $Ru(acac)_3$ dissolved readily in basic and neutral melts, which were slightly basic in practice, to give intensely red solutions which were stable for several months at room temperature. In the acidic melts, however, $Ru(acac)_3$ immediately decomposed to give a dark brown solution, which was not studied further; hence all electrochemical experiments were limited to basic and neutral melts.

CS, NP, RP, and RD voltammetries for the reduction of $Ru(acac)_3$ were carried out as a function of melt composition. Typical CS voltammograms of the complex in melts of three compositions in which the $AlCl_3$:ImCl mole ratios were 0.6:1.0, 0.8:1:0, and 1.0:1.0 are shown in Figure 1, and CS and NP voltammetric data are summarized in Table I. The CS voltammogram in the 0.6:1.0 melt gave coupled cathodic and anodic peaks in which both cathodic and anodic peak currents, i_{pc} and i_{pa}, were equal in magnitude. The separation of the peak potentials was in reasonable agreement with the theoretical value; at the slowest scan rate, a 60-mV peak separation was obtained; see Table I.[31] The faster potential scans gave larger potential separations than the theoretical value; we attribute this to *ir* drop in the melts. The voltammogram of the complex in the 0.6:1.0 melt was fit to a theoretical model for the simple reversible one-electron reaction

$$Ru(acac)_3 + e^- = Ru(acac)_3^- \qquad (1)$$

using the COOL algorithm.[32]

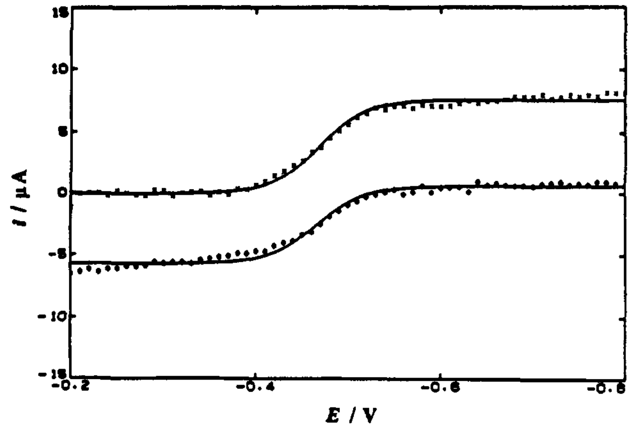

Figure 2. Normal (upper) and reverse normal (lower) pulse voltammograms. Conditions: solution, as in Figure 1a; t_p, 200 ms; t_g, 10 s. Solid line is COOL algorithm fit for reversible, one-electron process.

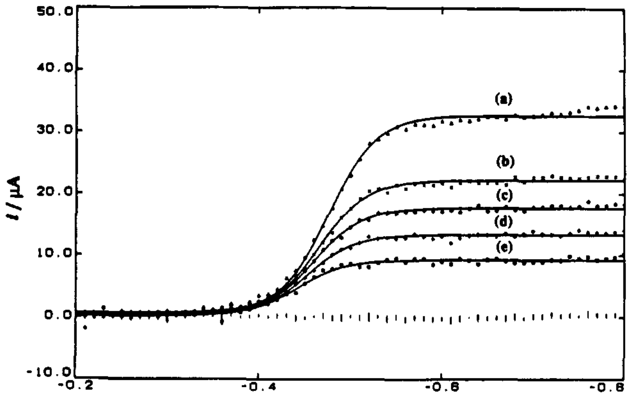

Figure 3. Normal pulse voltammograms of $Ru(acac)_3$ in 0.8:1.0 melt. t_p/ms: (a) 20; (b) 40; (c) 60; (d) 100; (e) 500. Points are experimental data; solid lines are the best fitted theoretical voltammograms for a one-electon process; bars show the differences between the experimental and calculated curves. Other conditions are as in Figure 1.

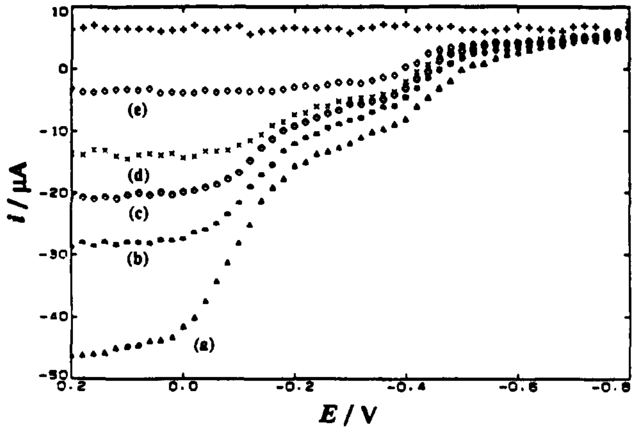

Figure 4. Reverse normal pulse voltammograms for 2.9 mmol dm^{-3} $Ru(acac)_3$ in 0.8:1.0 melt. t_g = 1 s. t_p/ms: (a) 20; (b) 40; (c) 60; (d) 100; (e) 500.

The NP and RD voltammograms of the complex in the 0.6:1.0 melt showed a single reduction step with the limiting current diffusion or convective-diffusion controlled. The NP and RP fit to the reversible reaction are shown in Figure 2 and confirm that the complex in the 0.6:1.0 melt undergoes a Nernstian one-electron reduction process without any complicating chemical reactions coupled with the electron-transfer process.[33]

---

(31) Christie, J. H.; Lingane, P. J. *J. Electroanal. Chem.* **1965**, *10*, 176.

(32) O'Dea, J. J.; Lane, T.; Osteryoung, J. *J. Phys. Chem.* **1986**, *90*, 2761.

Table I. CV and NP Voltammetric Data for $Ru(acac)_3$ in Basic and Neutral Melts[a]

CV					NP			
v/V s^{-1}	$i_{pc}v^{-1/2}/10^{-6}$ A $(V\ s^{-1})^{-1/2}$	E_{pc}/V	E_{pa1}/V	E_{pa2}/V	t_p/s	$i_l t_p^{1/2}/10^{-6}$ A $s^{1/2}$	$E_{1/2}$/V	$S^{-1\,b}$/mV
0.6:1.0 Melt								
0.02	16.9	−0.495	−0.435	n[c]	0.02	3.27	−0.479	−58
0.05	17.1	−0.498	−0.432	n	0.04	3.33	−0.474	−60
0.10	17.4	−0.500	−0.430	n	0.06	3.23	−0.469	−58
0.20	17.8	−0.503	−0.425	n	0.10	3.13	−0.468	−58
0.50	17.9	−0.510	−0.415	n	0.20	3.11	−0.461	−66
0.8:1.0 Melt								
0.02	21.2	−0.450	−0.350	n	0.02	4.51	−0.473	−59
0.05	21.2	−0.455	−0.350	−0.150	0.04	4.52	−0.463	−59
0.10	20.6	−0.465	−0.340	−0.130	0.06	4.60	−0.457	−59
0.20	20.7	−0.470	−0.340	−0.110	0.10	4.40	−0.453	−55
0.50	21.2	−0.480	n	−0.085	0.20	4.55	−0.443	−48
1.0:1.0 Melt								
0.02	25.6	−0.425	n	−0.045	0.02	5.92	−0.422	−72
0.05	25.2	−0.440	n	−0.030	0.04			
0.10	23.7	−0.450	n	−0.020	0.06	5.68	−0.416	−64
0.20	21.2	−0.460	n	−0.010	0.10	5.72	−0.412	−66
0.50	23.7	−0.470	n	0.005	0.20	5.72	−0.402	−71

[a] $[Ru(acac)_3]$: 2.7 mmol dm^{-3} in 0.6:1 and 1:1 melts; 2.6 mmol dm^{-3} in 0.8:1 melt. [b] Slope of lot plot. [c] No peak observed.

Table II. Diffusion Coefficients and Stokes Radii of $Ru(acac)_3$ in $AlCl_3$–ImCl

melts	technique	C/mmol dm^{-3}	$\eta/10^{-1}$ g cm^{-1} s^{-1}	$D/10^{-7}$ cm^2 s^{-1}	$(\eta D/T)/10^{-10}$ g cm s^{-2} K^{-1}	r^a/nm
0.6	NP	2.7	7.155	0.79	1.87	0.39
0.6	RDE	2.7	7.155	0.72	1.70	0.43
0.8	NP	2.6	2.915	2.0	1.92	0.38
0.8	NP	6.6	2.915	2.1	2.02	0.37
1.0	NP	2.7	1.548	3.5	1.79	0.41

[a] Stokes–Einstein equation; $r = kT/6\pi\eta D$; 30 °C.

In both the 0.8:1.0 and the approximately 1.0:1.0 melts, NP and RD voltammograms of the complex also gave a single reduction step which could be fit to the Nernstian one-electron reduction process; the half-wave potentials were, however, shifted to less negative values, as shown in Table I. NP voltammograms with different pulse times, t_p, in the 0.8:1.0 melt are shown in Figure 3. The limiting currents of the NP and RD voltammograms were again diffusion or convective-diffusion controlled. CS and RP voltammograms, however, indicated the existence of homogeneous chemical reactions coupled with the electron transfer as shown in Figures 1b,c and 4. The one-electron-reduced species, $Ru(acac)_3^-$, reacts with a species in the melt to give another ruthenium(II) species which is oxidized at less negative potentials, an EC mechanism. This reaction will be discussed below.

Diffusion Coefficient of $Ru(acac)_3$. The values of the diffusion coefficients of $Ru(acac)_3$ at different melt compositions were evaluated on the basis of the Cottrell and Levich equations using the limiting currents of NP and/or RD voltammograms, respectively. As an example, the plots of the limiting current, i_{lim}, against $t_p^{-1/2}$ for the NP voltammograms in the 0.6:1.0, 0.8:1.0 and 1.0:1.0 melts are shown in Figure 5. Table II shows the diffusion coefficients, D, obtained from the slope of the linear lines through the original points, the ηD product, where η is the melt viscosity, the Stokes radii, calculated from the D value using the Stokes–Einstein equation, and the viscosity of the melts.[34]

The ηD product is quite constant; the r values obtained are almost independent of the melt composition, concentration of the complex, and the two techniques used here. Furthermore, the r values in the melts are also nearly equal to the value obtained in acetonitrile solutions, 0.415 nm, and that calculated on the basis

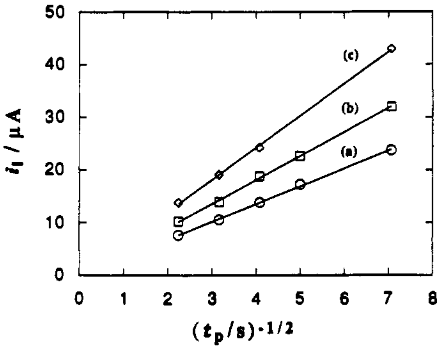

Figure 5. Plots of the limiting current of normal pulse voltammograms vs $t_p^{-1/2}$. Melt composition: (a) 0.6:1.0; (b) 0.8:1.0; (c) 1.0:1.0. Other conditions are as in Figure 1.

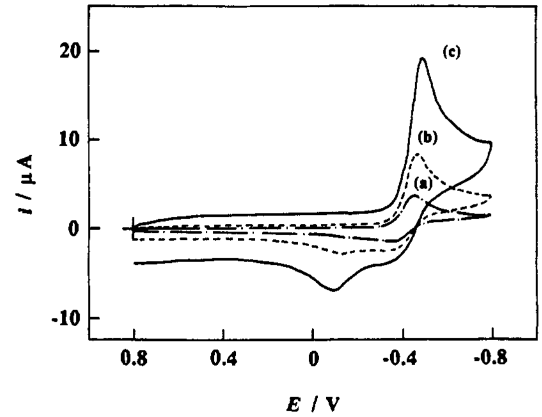

Figure 6. Cyclic voltammograms for $Ru(acac)_3$ in 0.8:1.0 melt. Scan rate/mV s^{-1}: (a) 20; (b) 100; (c) 500.

of the molar volume of the crystal (0.463 nm).[18] This suggests that the difference in formation energy of the second sphere of $Ru(acac)_3$ between the ions composing the melt and the acetonitrile molecules is too small to give different values for the Stokes radius in each medium. This result suggests that $Ru(acac)_3$ is a fairly bulky, spherically symmetrical, and noncharged molecule.

Chemical Reaction on the Voltammetric Time Scale. As indicated above, a chemical reaction following the electron-transfer step was observed in both CS and RP voltammetries in the 0.8:1.0 and 1.0:1.0 melts.

In the 0.8:1.0 melt, only a single reduction wave with a peak potential at ca. −0.46 V can be seen on the forward scan in CV,

---

(33) Osteryoung, J.; Kirowa-Eisner, E. *Anal. Chem.* **1980**, *52*, 62.

(34) Fannin, A. A., Jr.; Floriani, D. A.; King, L. A.; Sanders, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, *88*, 2614.

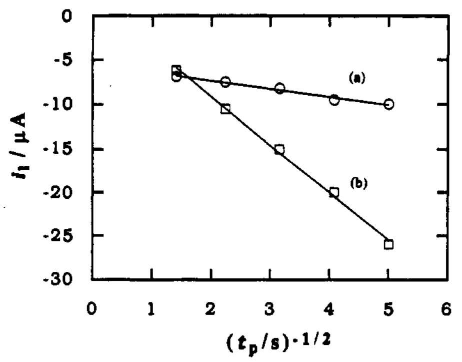

Figure 7. Limiting currents of reverse pulse voltammograms of Ru(acac)$_3$ vs $t_p^{-1/2}$: (a) limiting currents of the first oxidation at −0.3 V; (b) total limiting current at 0.2 V. The experimental conditions are the same as in Figure 4.

but two oxidation peaks with $E_{pa1} = -0.35$ V and $E_{pa2} = -0.15$ V are observed on the reverse scan. The more negative wave corresponds to the reversible one-electron oxidation of Ru(acac)$_3^-$, while the second is due to the oxidation of the product generated by the reaction between Ru(acac)$_3^-$ and some melt species. Both the first and the second oxidation peak currents, i_{pa1} and i_{pa2}, decreased with a decrease in potential scan rate (see Figure 6), but the decrease of the magnitude of the current for i_{pa2} was much greater than for i_{pa1}. Only the first, more negative wave remained at scan rates less than 0.05 V s^{-1}. RP voltammograms, as shown in Figure 4 for the 0.8:1.0 melt, also gave two oxidation steps corresponding to the oxidation peaks of the cyclic voltammograms. As t_p increases, the magnitude of the second wave also decreases.

The analysis of RP voltammograms gave more definitive evidence of the existence of chemical kinetics between Ru(acac)$_3^-$ and another Ru(II) species. We postulate that the Ru(II) species is an AlCl$_3$ adduct, as shown in eq 2.

$$\mathrm{Ru^{II}(acac)_3^- + AlCl_4^- \rightleftharpoons Ru^{II}(acac)_2(acacAlCl_3)^- + Cl^-} \quad (2)$$

$$K = [\mathrm{Ru^{II}(acac)_2(acacAlCl_3)^-}][\mathrm{Cl^-}]/[\mathrm{Ru^{II}(acac)_3^-}][\mathrm{AlCl_4^-}] \quad (3)$$

Figure 7 shows plots of the limiting currents of the first wave and the sum of the first and second waves for the RP voltammogram against $t_p^{-1/2}$ in the 0.8:1.0 melt. The straight line for the first oxidation wave with the small slope and the large intercept suggests that, for the most part, the limiting current for this wave is controlled by the kinetics of the reverse of eq 2 to generate Ru(acac)$_3^-$. The total limiting-current plot, which passes almost through the origin, indicates that the total current was diffusion controlled. The equation of the line in Figure 7 for the total limiting current in the RP experiment is $i_{\mathrm{lim}} = -5.44t_p^{-1/2} + 1.77$ and the equation for the NP line in Figure 5 for the 0.8:1.0 melt is $i_{\mathrm{lim}} = +4.52t_p^{-1/2} + 0.02$: i/uA and t_p/s. Thus the similarity, to within 20%, of the slopes suggests that all of the product was conserved.

Further, the decrease in the ratio of the limiting current of the first wave to the total current, $i_{\mathrm{lim1}}/(i_{\mathrm{lim1}} + i_{\mathrm{lim2}})$, from 0.95 to 0.27 by changing the generation time, t_g, in RP voltammetry, from 0.05 to 10 s, is also strong evidence for a preceding reaction, i.e., a CE mecahnism, in the reoxidation of the proposed Ru$^{\mathrm{II}}$(acac)$_2$(acacAlCl$_3$)$^-$ species.

In the 1.0:1.0 melt, the first oxidation wave on CS and RP voltammograms disappeared and only the second wave, with the limiting current controlled by diffusion, remained. Thus, the flux of Ru(acac)$_3^-$ coming to the electrode surface decreases in less basic melts because Ru(acac)$_3^-$ is being replaced at the electrode surface by the chemical reaction product, Ru$^{\mathrm{II}}$(acac)$_2$(acacAlCl$_3$)$^-$.

The effect of the melt composition on the reversible half-wave potential of the Ru(acac)$_3$/Ru(acac)$_3^-$ reaction also supports the existence of a following chemical reaction. The half-wave potential will be more positive than in the absence of the perturbation. In fact, the half-wave potential shifted from −0.47 to −0.41 V when the melt composition changed from 0.6:1.0 to 1.0:1.0 (Table I).

The reaction for the oxidation of Ru(acac)$_3^-$ can be explained by the reversible reaction between Ru(acac)$_3^-$ and AlCl$_4^-$ shown in eq 2. The concentration ratio of Ru(acac)$_3^-$ to the AlCl$_3$ adduct may be expressed as

$$[\mathrm{Ru(acac)_3^-}]/[\mathrm{Ru(acac)_2(acacAlCl_3)^-}] = K([\mathrm{Cl^-}]/[\mathrm{AlCl_4^-}]) = P \quad (4)$$

The concentrations of chloride and tetrachloroaluminate in the basic melts are easily calculated from the melt composition because the formation constant for the reaction of AlCl$_3$ + ImCl to give Im$^+$ + AlCl$_4^-$ is extremely large.[27] The concentration ratios, [Cl$^-$]/[AlCl$_4^-$], are 0.67, 0.25, and 0 for the 0.6:1.0, 0.8:1.0, and 1.0:1.0 melts, respectively. In the more basic melt, a larger P value can be obtained. Thus, the CS and RP voltammograms are dependent on the melt composition.

A similar reaction between AlCl$_4^-$ in basic melts and oxygen of the anion radical of 9,10-anthraquinone, which is generated by electochemical reduction in basic melts, has been proposed by Carter and Osteryoung.[27]

The voltammetry of Ru(acac)$_3$ in pure molten ImCl was examined to show that the AlCl$_4^-$ species actually takes part in the chemical reaction coupled with electron transfer. This melt contains no chloroalumimate species and therefore might be expected to display simple, reversible electron-transfer behavior. The CS voltammogram of Ru(acac)$_3$ in an ImCl melt at 100 °C (melting point of ImCl = ~90 °C) gave single, coupled cathodic and anodic waves which corresponded to a simple, reversible one-electron process. This result seems to support the conjecture that the AlCl$_4^-$ species in this chloroaluminate molten salt takes part in the subsequent chemical reaction, eq 2, but the temperature effects on the chemical reaction rate must also be considered.

Voltammetry in an AlCl$_3$–ImCl melt at higher temperature was also performed. CV and RP voltammograms of Ru(acac)$_3$ in the 0.8:1.0 melt were obtained at 50, 70, and 100 °C. As mentioned above, two oxidation waves were observed on CS and RP voltammograms at 30 °C. Increasing the temperature reduced the current ratio of the second wave to the first, i_{p2}/i_{p1}, in CV and the ratio $i_{\mathrm{lim1}}/(i_{\mathrm{lim1}} + i_{\mathrm{lim2}})$ in RP. At temperatures above 70 °C, only the first wave, corresponding to the oxidation of Ru(acac)$_3^-$ to Ru(acac)$_3$, remained. This indicates that at higher temperatures either the kinetics required to establish the equilibrium in eq 2 are too fast to give the kinetic properties of the oxidation current for Ru(acac)$_3^-$ or else the equilibrium constant itself decreases significantly, or possibly both. Hence, the voltammetric results in pure ImCl melt at 100 °C do not unambiguously support the evidence for the participation of AlCl$_4^-$ in the reaction. As is described later, however, constant-potential coulometry in a pure ImCl melt strongly supports the participation of AlCl$_4^-$ in the reaction.

Another experiment was carried out to further elucidate the properties of Ru(acac)$_3^-$ in the melts. The AlCl$_3$ in the proposed adduct, Ru(acac)$_2$(acacAlCl$_3$)$^-$, acts as a Lewis acid, presumably combining with an oxygen atom on the coordinating acetylacetonate in the complex. Voltammetry of a 0.6:1.0 melt containing ImHCl$_2$ as a source of proton, a Bronsted acid, revealed behavior similar to that seen in the case of the 0.8:1.0 proton-free melt, where AlCl$_4^-$ takes the place of the proton. NP voltammograms of Figure 8 show a single reduction step corresponding to the Nernstian one-electron process, but the half-wave potentials, −0.42V, are shifted to more positive values than those obtained in the 0.6:1.0, melt which was free of ImHCl$_2$. CS and RP voltammograms corresponding to NP voltammograms in Figure 8 are shown in Figures 9 and 10, respectively. When 0.2 mol dm^{-3} ImHCl$_2$ was added to the 0.6:1.0 melt, a second oxidation wave similar to that observed in the 0.8:1.0 melt appeared in the CS and RP voltammograms. This suggests that the proton in the basic melts behaves similarly to AlCl$_4^-$ in its interaction with Ru(acac)$_3^-$:

$$\mathrm{Ru^{II}(acac)_3^- + HCl_2^- \rightleftharpoons Ru^{II}(acac)_2(Hacac) + 2Cl^-} \quad (5)$$

The replacement reaction of Ru$^{\mathrm{III}}$(acac)$_3$ to form Ru$^{\mathrm{III}}$(acac)$_2$(AN)$_2^+$ (AN = acetonitrile) in AN in the presence of a small amount of perchloric acid was reported by Kasahara et al.[23]

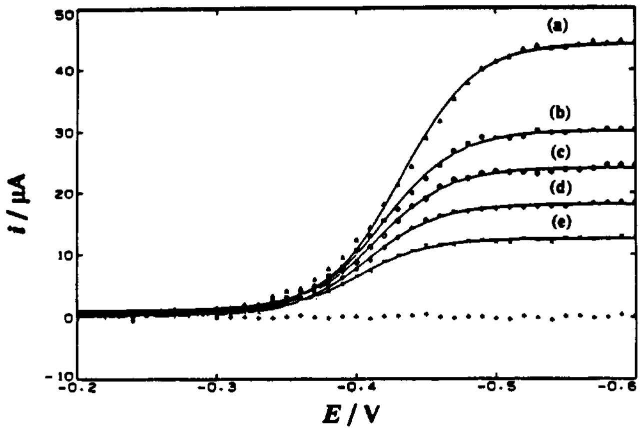

Figure 8. Normal pulse voltammograms for the reduction of $\mathrm{Ru(acac)_3}$ in 0.6:1.0 melt containing 0.2 mol $\mathrm{dm^{-3}}$ $\mathrm{ImHCl_2}$. t_p/ms: (a) 20; (b) 40; (c) 60; (d) 80; (e) 200. Solid line is COOL algorithm fit for reversible, one-electron process.

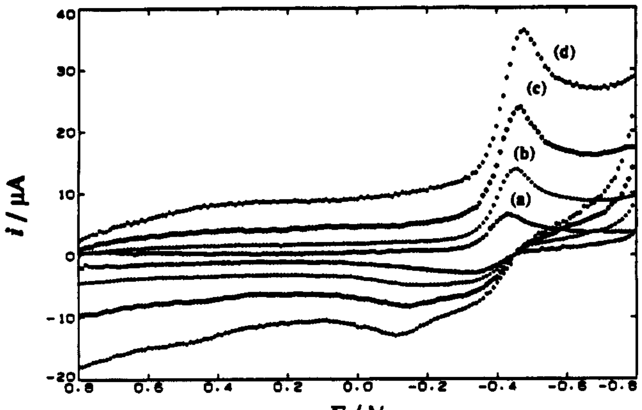

Figure 9. Staircase cyclic voltammograms for $\mathrm{Ru(acac)_3}$ in 0.6:1.0 melt containing 0.2 mol $\mathrm{dm^{-3}}$ $\mathrm{ImHCl_2}$. Scan rate/V $\mathrm{s^{-1}}$: (a) 0.05; (b) 0.20; (c) 1.0. Concentration of $\mathrm{Ru(acac)_3}$ is ca. 3.0 mmol $\mathrm{dm^{-3}}$. Other conditions are as in Figure 1.

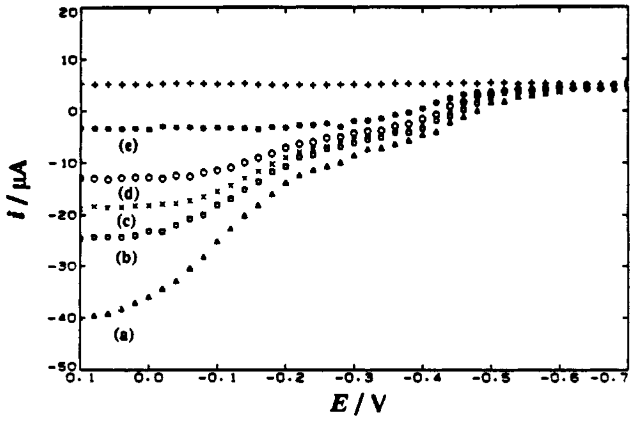

Figure 10. Reverse normal pulse voltammograms for $\mathrm{Ru(acac)_3}$ in 0.6:1.0 melt containing 0.2 mol $\mathrm{dm^{-3}}$ $\mathrm{ImHCl_2}$. t_g = 1 s. t_p/ms: (a) 20; (b) 40; (c) 60; (d) 100; (e) 500. Other conditions are as in Figure 8.

They proposed that the reaction was initiated by attack at an Ru–O bond by protons, forming an intemediate with a dangling ligand. In a basic molten salt, a similar reaction can be expected between $\mathrm{Ru(acac)_3^-}$ and $\mathrm{AlCl_4^-}$, with $\mathrm{AlCl_4^-}$ serving as a source of the Lewis acid $\mathrm{AlCl_3}$.

Chemical Reactions during Bulk Electrolysis. Constant-potential coulometry in bulk melt indicated another interesting chemical reaction following the formation of the $\mathrm{AlCl_3}$ adduct. When about 8% of the $\mathrm{Ru(acac)_3}$ was reduced at –0.7 V at a glassy-carbon electrode in the 0.6:1.0 melt and then allowed to stand for 1 day at room temperature, a colorless melt resulted. A cyclic voltammogram of the colorless compound gave a reversible oxidation and an irreversible reduction wave, as shown in Figure 11c. The limiting currents of both the anodic, $E_{1/2}$ = 0.54 V, and the cathodic, $E_{1/2}$ = –0.90 V, steps, on the RD voltammogram, corresponding to the cyclic voltammetric CV waves, are equal in magnitude. The resulting colorless melt was then completely oxidized at +0.7 V to give a wine red melt whose electronic spectrum agreed with that of $\mathrm{Ru^{IV}Cl_6^{2-}}$ reported by Hussey et al.[35,36]

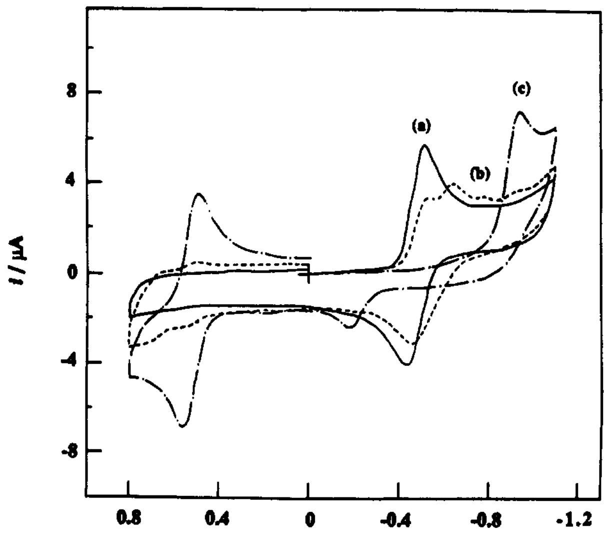

Figure 11. Cyclic voltammograms recorded during bulk electrolysis of $\mathrm{Ru(acac)_3}$ in 0.6:1.0 melt: (a) before electrolysis; (b) immediately after the reduction of 8% of amount of the $\mathrm{Ru(acac)_3}$; (c) 12 h later. Concentration of $\mathrm{Ru(acac)_3}$ is 3.6 mmol $\mathrm{dm^{-3}}$; scan rate is 0.1 V/s. Other conditions are as in Figure 1.

The oxidation and reduction half-wave potentials of the oxidized species corresponding to the Ru(III)/Ru(II), 0.86 V, and the Ru(III)/Ru(II), –0.52 V, couples, respectively, also agreed with those reported by Hussey et al.[35,36] These results, together with those for the chemical reaction observed on the CV and RP voltammetric time scales, lead us to propose the following reactions for the generation of $\mathrm{Ru^{III}Cl_6^{3-}}$:

$$\mathrm{Ru^{II}(acac)_2(acacAlCl_3)^- + 2\mathit{n}Cl^- \rightarrow (Ru^{II}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}})^{(\mathit{n}+1)-} + acacAlCl_3^- + (\mathit{n}-1)acac^-} \quad (6)$$

$$\mathrm{Ru^{III}(acac)_3 + Ru^{II}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}}{}^{(\mathit{n}+1)-} \rightarrow Ru^{II}(acac)_3^- + (Ru^{III}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}})^{\mathit{n}-}} \quad (7)$$

Thus, the overall reaction for eqs 2, 6, and 7 is

$$\mathrm{Ru^{III}(acac)_3 + 2nCl^- \rightarrow (Ru^{III}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}})^{\mathit{n}-} + \mathit{n}acac^-} \quad (8)$$

The half-wave potential for the $\mathrm{Ru^{II}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}}{}^{(\mathit{n}+1)-}}$ species must then be more negative than that for the $\mathrm{Ru^{III}(acac)_3/Ru^{II}(acac)_3^-}$ couple.

After about 8% of the total amount of $\mathrm{Ru^{III}(acac)_3}$ initially present in the melt had been reduced to $\mathrm{Ru(acac)_3^-}$ by constant-potential electrolysis, the reactions occurring in the melt were followed with CV and RD voltammetry. The time dependence of the cyclic voltammograms recorded in the 0.6:1.0 melt is shown in Figure 11b,c. Three new oxidation peaks can be seen during the course of the reaction, which are presumed to result from $\mathrm{(Ru^{III}(acac)_{3-\mathit{n}}Cl_{2\mathit{n}})^{\mathit{n}-}}$ species. This number of peaks could correspond to species with n = 1, 2, and 3. As expected, similar results were obtained in the 0.8:1.0 melt during constant-potential electrolysis as in the 0.6:1.0 melt.

Constant-potential coulometry of $\mathrm{Ru(acac)_3}$ also was carried out in pure ImCl at 100 °C. When half of the $\mathrm{Ru(acac)_3}$ was

---

(35) Ward, E. H.; Hussey, C. L. *Anal. Chem.* **1987**, *59*, 213.

(36) Hussey, C. L.; Barnard, P. A.; Sun, I. W. *J. Electrochem. Soc.* **1991**, *139*, 2590.

reduced, the melt color varied from red to deep red and a new redox couple, together with the redox peaks of the $Ru(acac)_3/Ru(acac)_3^-$ couple, appeared at −0.01 V in the cyclic voltammogram; here the potential in pure ImCl melt is converted to the potential against the Al/Al(III) reference electrode in the 1.5:1.0 melt at 30 °C using the redox potential of $Ru^{III}(acac)_3/Ru^{II}(acac)_3^-$ as an internal standard. The color and cyclic voltammogram of the melt did not change after it was left overnight at 100 °C. These results strongly suggest that $AlCl_4^-$ in the melt induces the ligand exchange of $Ru^{III}(acac)_3$ to form $Ru^{III}Cl_6^{3-}$.

Other acac Complexes. $Fe(acac)_3$ dissolved in the basic melt; however, it decomposed almost immediately to form the $FeCl_4^-$ complex, as indicated by the half-wave potential and spectrum.[37]

$Co(acac)_3$ gave an irreversible reduction wave in a 0.8:1.0 melt; the cathodic peak potential in a CS voltammogram shifted from −0.48 to −0.58 V as the scan rate varied from 0.02 to 0.5 V s^{-1}. The values of λ_{max} from UV–vis spectroscopy of 259 and 328 nm were in good agreement with those for this complex in acetonitrile, 258 and 324 nm, respectively, previously reported.[11] The diffusion coefficient was evaluated from NP voltammograms, assuming a one-electron reduction. For a solution containing 7.8 mmol dm^{-3}, a D value of 1.8×10^{-7} cm^2 s^{-1} and an r value of 0.41 nm were calculated; these are very similar to the values found for the $Ru(acac)_3$ complexes and are similar to those found in acetonitrile solutions.[20] This complex was not investigated further.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research. Helpful discussions with other members of our research group and with Prof Charles Hussey are also acknowledged.

---

(37) Nanjundiah, C.; Shimizu, K.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474.

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo Bunkyo-Ku, Tokyo 113, Japan, Engineering Research Institute, The University of Tokyo, Yayoi, Bunkyo-Ku,
Tokyo 113, Japan, Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-Ku, Kyoto 606, Japan,
and Department of Chemistry, Faculty of Science, Nara Women's University, Nara-City, Nara 630, Japan

Observation of Radical Intermediates for Unusual C–N Bond Formation of α-Aminomalonate To Give an α-Diamine Linkage. ESR Studies on Electron Transfer Reactions in Cobalt(III)–Polyamine Complexes

Takahiko Kojima,[*,†,‡] Jun-ichi Tsuchiya,[§] Satoru Nakashima,[∥] Hiroaki Ohya-Nishiguchi,[∥]
Shigenobu Yano,[⊥] and Masanobu Hidai[†]

Received December 20, 1991

The reactions of α-aminomalonate anion (AM^{2-}) with complexes *trans*-$[Co^{III}Cl_2(N_4)]^+$ (N_4 = $(en)_2$, 2,3,2-tet, 3,2,3-tet; en = ethylenediamine, 2,3,2-tet = 3,7-diaza-1,9-diaminononane, 3,2,3-tet = 4,7-diaza-1,10-diaminodecane) were investigated by spin trapping and low-temperature electron spin resonance (ESR) spectroscopy. In the thermal C–N bond formation between the α-carbon of AM^{2-} and a coordinated amino group of polyamine ligands, pathways for oxidation of AM^{2-} to an iminomalonato intermediate depend on polyamine systems. Spin-trap ESR spectroscopy showed that the oxidation of AM^{2-} proceeds via the radical formation at the α-carbon in the en and 2,3,2-tet systems. In both systems, MeOH plays an indispensable role in the α-diamine formation. Especially in the en system, the radicalization of MeOH took place upon heating prior to that of AM^{2-} accompanying electron transfer (ET) to give a d^7 high-spin ($S = {}^3/_2$) Co(II) species from a d^6 low-spin Co(III) ion. This change of the spin state at the cobalt center is required when a Co(III) complex acts as an oxidant for AM^{2-}. In contrast, in the 2,3,2-tet system, the Co(III) center was reduced upon heating toward a low spin ($S = {}^1/_2$) Co(II) species which readily reacted with dioxygen in the air to give a Co^{III}–O_2^- complex. EHMO calculation suggested that the superoxo ligand can perform intramolecular deprotonation of the α-proton of AM^{2-} ligand and ET can occur from the α-carbon of the AM^{2-} ligand to the Co(III) center. In the 3,2,3-tet system, formation of a high-spin Co(II) species was observed like the en system under conditions where the α-diamine formation occurs via ET from AM^{2-} to a Co(III) ion. For the oxidation of substrates by Co(III) complexes via ET, the change of the spin state at the cobalt center is important and it is controlled by the polyamine ligands.

Introduction

The oxidation of organic compounds by transition-metal complexes has been intensively investigated in the light of not only industrial benefits but also modeling metalloenzymatic systems for elucidation of their functions and mechanisms, in which radical intermediates are often involved.[1] The oxidation processes catalyzed by transition-metal complexes include activation of substrates and/or reactants and often involve electron transfer (ET) reactions from the substrates to the metal centers.[2]

The oxido-reductases which contain metal ions in their active sites or flavin adenine dinucleotide (FAD) as a cofactor require dioxygen for the oxidation of substrates. In those reactions radical intermediates have been detected and proposed.[3b,4c,d] Thus, the action of these enzymes brings attention to dioxygen activation. For example, the well-reported observations of dioxygen activation in cytochrome P-450 systems have been integrated and the reaction mechanism has become the subject of much interest in chemistry.[5] For the reaction catalyzed by cytochrome P-450 systems and their models, radical intermediates have been also proposed and detected.[6] In addition, Nishinaga and Drago and their co-workers

---

[†] Department of Synthetic Chemistry, The University of Tokyo.

[‡] Present address: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

[§] Engineering Research Institute, The University of Tokyo.

[∥] Kyoto University.

[⊥] Nara Women's University.

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.

(2) Bäckvall, J. K.; Hopkins, R. B.; Grennberg, H.; Mader, M. M.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 5160, and references cited therein.

(3) (a) Ibers, J. A.; Holm, R. H. *Science* **1980**, *209*, and references cited therein. (b) Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8085.

(4) (a) Flashner, M. S.; Massey, V. In *Molecular Mechanisms of Oxygen Activation*; Hayaishi, O., Ed.; Academic Press: New York, 1974; Chapter 7. (b) Bruice, T. C. *Acc. Chem. Res.* **1980**, *13*, 256. (c) Yelekci, K.; Lu, X.; Silverman, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 1138. (d) Gates, K. S.; Silverman, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 8891.

(5) (a) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759. (b) Dawson, J. H.; Sono, M. *Chem. Rev.* **1987**, *87*, 1255. (c) Ortiz de Montellano, P. R., Ed. *Cytochrome P-450 Structure, Mechanism, and Biochemistry*; Plenum Press: New York, 1986. (d) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

0020-1669/92/1331-2333$03.00/0