deep blue color in platinum complexes can arise for different reasons[18,19] in different cases.

Reactions of type **1** → **3** also occur when substituents in the phenyl ring are changed. We are examining the general applicability of this type of hydroxylation reaction in other palladium complexes having pendant phenyl rings close to a reactive bond (e.g. PdCl). The reaction **2** → **4** is only one example of a type of hydroxylation that also occurs in related molecules, e.g., where the ring substituent is C_6H_5 rather than CH_3. This entire class of (presumably intramolecular) redox transformations in metal complexes of oximes is under active study.

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Supplementary Material Available: Tables of atomic parameters, bond lengths and angles, and observed and calculated structure factors for complex **3** (18 pages). Ordering information is given on any current masthead page.

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(19) In our blue complex the color is undoubtedly due to charge-transfer transitions involving both ligand and metal orbitals.

(20) **Note Added in Proof:** The structure of **1** has now been accurately determined.

Mechanism of an Oscillating Organic Reaction: Oxidation of Benzaldehyde with O_2 Catalyzed by Co/Br

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The O_2 oxidation of benzaldehyde to benzoic acid, catalyzed by Co^{2+}/Br^-, was recently discovered to exhibit sustained oscillations.[2] Coincident variations in solution color and electrode potential were observed. We describe here the time dependence of dissolved oxygen, $[Co^{3+}]$, and PhCHO concentrations and suggest a mechanism to account for the oscillations. The mechanism postulates that in one stage of the reaction benzoyl radical reacts primarily with oxygen, while in the second, benzoyl is oxidized by Co^{3+}.

During stage I, the potential of the Pt electrode rises slowly and approximately linearly with the time until it reaches a maximum (Figure 1). (Note that the conditions are different in Figures 1a, 1b, and 2 to highlight pertinent features.) In stage II, the potential abruptly decreases to a minimum. At the maximum, the color of the solution is the dark green characteristic of Co^{3+} in acetic acid.[3,4] At the potential minimum, the solution exhibits the pale pink color of Co^{2+} in acetic acid. Under typical conditions (see caption, Figure 1), the amplitude of the oscillations is 50–80 mV with a period of 50–400 s.

The log $[Co^{3+}]$ parallels the potential in Figure 1a. Furthermore, $[Co^{3+}]$ increases approximately exponentially during stage I, indicating an autocatalytic production of Co^{3+}. Under some conditions, the maximum $[Co^{3+}]$ is less than 5% of the total amount of cobalt, and therefore, depletion of Co^{2+} is not required for oscillations.

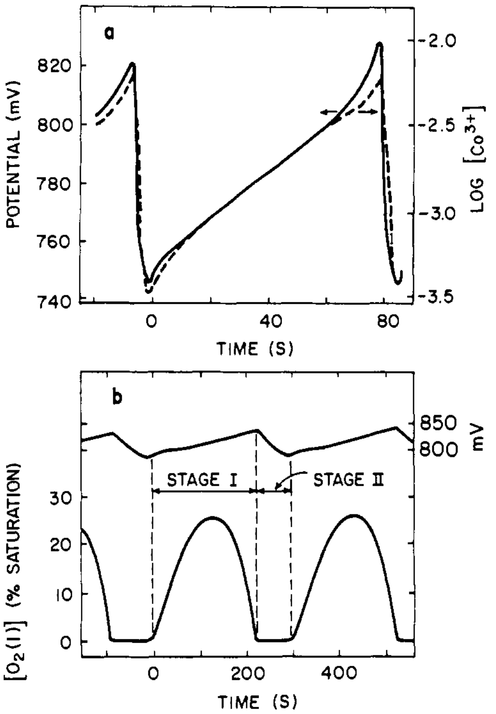

Figure 1. (a) Oscillations of the platinum electrode potential vs. Ag/AgCl reference electrode (—) and log $[Co^{3+}]$ determined by optical absorption at 620 nm (---). A 150-mL solution contained initially 500 nM PhCHO, 10 mM $Co(AcO)_2$, 5 mM NaBr, and 90/10 w/w $AcOH/H_2O$ as solvent. The temperature was 70 °C, an O_2 pressure of 580 torr was maintained above the solution, and the magnetic stirring speed was 400 rpm. (b) A comparison of the Pt electrode response (top trace) with the dissolved oxygen concentration (bottom trace) expressed in terms of the percentage of saturation with O_2 at a partial pressure of 580 torr. We estimate that 100% on this scale corresponds to $[O_2(l)] = 5 \pm 2$ mM. Conditions are as in (a), but the solution contained initially 750 mM PhCHO, 20 mM $Co(AcO)_2$, and 2 mM NaBr; O_2 was introduced at a flow rate of 20 mL/min through a frit immersed in the liquid.

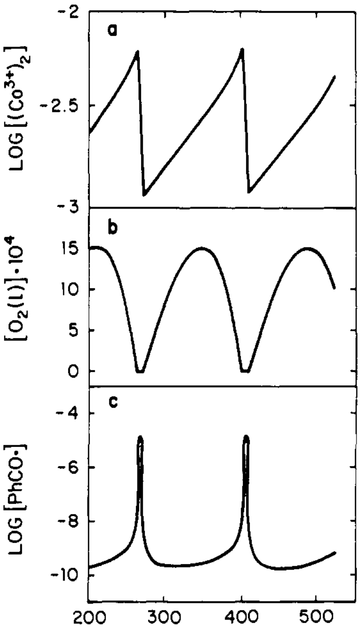

Figure 2. Calculated concentration oscillations in (a) $[(Co^{3+})_2]$, (b) $[O_2(l)]$, and (c) $[PhCO\cdot]$.

The dissolved oxygen concentration ($[O_2(l)]$) was followed with a Clark-type oxygen sensor (Altex) (Figure 1b). At the start of stage I, $[Co^{3+}]$ is low and $[O_2(l)]$ is less than our detection limit (1% of saturation). Initially, $[O_2(l)]$ rises as does $[Co^{3+}]$. About halfway through stage I, $[O_2(l)]$ begins to fall; i.e., the increasing

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rate of oxygen consumption, which we view as associated with the exponentially increasing [Co^{3+}] (see below), exceeds the constant rate at which O_2 is being supplied to the solution. When [$O_2(1)$] ≈ O, stage II begins (the potential begins to fall) and Co^{3+} is rapidly converted back to [Co^{2+}].

If [$O_2(1)$] is always appreciably less than saturation, then the rate of mass transfer of oxygen from the gas phase into the liquid determines the average rate of oxidation of PhCHO. The average rate of disappearance of PhCHO (measured by high-performance liquid chromatography) during a batch reaction is indeed zero order in [PhCHO]. Within a given oscillatory cycle, [PhCHO] shows a rapid decrease during stage II, suggesting that benzaldehyde reduces Co^{3+} in stage II.

Although oscillations did not occur without bromide ion under our conditions, [Br^-] (measured using a Br^--selective electrode, Orion) was essentially constant during oscillations. In the Belousov–Zhabotinsky and other bromate-driven oscillators, changes in [Br^-] of several orders of magnitude are an essential feature of the mechanism.[5]

To account for these observations, we propose the following mechanism for the oxidation:

$$(Co^{3+})_2 + Br^- \rightleftarrows (Co^{3+})_2Br^- \qquad (R1)$$

$$(Co^{3+})_2Br^- + PhCHO \rightarrow PhCO\cdot + Br^- + Co^{3+} + Co^{2+} + H^+ \qquad (R2)$$

$$PhCO\cdot + O_2(1) \rightarrow PhCO_3\cdot \qquad (R3)$$

$$PhCO\cdot + (Co^{3+})_2 + H_2O \rightarrow PhCO_2\cdot + 2Co^{2+} + 2H^+ \qquad (R4)$$

$$PhCO\cdot + PhCO_3\cdot \rightarrow 2PhCO_2\cdot \qquad (R5)$$

$$PhCO_3\cdot + PhCHO \rightarrow PhCO_3H + PhCO\cdot \qquad (R6)$$

$$PhCO_3\cdot + Co^{2+} + H^+ \rightarrow PhCO_3H + Co^{3+} \qquad (R7)$$

$$PhCO_2\cdot + PhCHO \rightarrow PhCO_2H + PhCO\cdot \qquad (R8)$$

$$PhCO_3H + 2Co^{2+} + 2H^+ \rightarrow PhCO_2H + (Co^{3+})_2 + H_2O \qquad (R9)$$

$$Co^{3+} + Co^{3+} \rightarrow (Co^{3+})_2 \qquad (R10)$$

$$O_2(g) \rightleftarrows O_2(1) \qquad (R11)$$

Although the radicals have been written here in the standard form, they may exist in solution complexed with Co ion, leading to unusual chemical behavior, e.g., (R5).

Initiation steps R1 and R2 use a Co^{3+} dimer, $(Co^{3+})_2$, to produce a benzoyl radical at a rate proportional to the product of [PhCHO], [Br^-], and [$(Co^{3+})_2$]. During stage I, benzoyl radical is rapidly intercepted by oxygen in (R3) to form the perbenzoxy radical. (R6) continues the radical chain, while (R7) terminates it. (R3), (R6), and (R7) are well established.[6,7] The rapid oxidation of Co^{2+} by perbenzoic acid, (R9), then completes the autocatalytic generation of $(Co^{3+})_2$.[8]

It is only when oxygen becomes severely depleted that stage II begins, the benzoyl radical lifetime increases, and its concentration rises sharply. During stage II, $(Co^{3+})_2$ is reduced by benzaldehyde through the intermediacy of benzoyl radicals in R4 + R8. The sequence (R5) followed by 2 × (R8) provides an alternate fate for perbenzoxy radicals during stage II which does not generate more Co^{3+}.

The rate equations[9] for (R1)–(R11) were integrated using a Gear algorithm,[10] with the results shown in Figure 2. The qualitative agreement with the experimentally measured [Co^{3+}] and [$O_2(l)$] oscillations of Figure 1 is encouraging.

In conclusion, we propose that the Co^{2+}/Br^--catalyzed O_2 oxidation of benzaldehyde differs from oxyhalogen-driven oscillators, in that an organic radical is one of the oscillatory, phase-determining intermediates. An essential feature of the oscillations is a periodic depletion of dissolved oxygen, allowing for the alternative pathway of Co^{3+} oxidation of benzoyl radicals.

Acknowledgment. We thank A. P. Berry for excellent experimental assistance.

Registry No. Benzaldehyde, 100-52-7; cobaltous acetate, 71-48-7; sodium bromide, 7647-15-6.

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(8) The rate of oxidation of Co^{2+} by *m*-chloroperbenzoic acid is reported to be second order in [Co^{2+}] and first order in peracid.[3] Addition of perbenzoic acid ([$PhCO_3H$]/[total Co] = 0.05) during the middle of stage I results in a rapid (<1 s) increase in both potential and [Co^{3+}]. This indicates that (R9) is rapid and that perbenzoic acid does not accumulate from cycle to cycle. Possible variations involving thermal rearrangements[3] of $(Co^{3+})_2$, ligand variation on Co, and other Co-containing oligomers have not been considered here.

(9) The simulation is for a batch mode, except for the flow of O_2. Rate constants used were $(k_1k_2)/k_{-1} = 2.5 \times 10^{-1}\ M^{-2}\ s^{-1}$, $k_{-1} >> k_2$, $k_3 = 1 \times 10^8\ M^{-1}\ s^{-1}$, $k_4 = 2 \times 10^4\ M^{-1}\ s^{-1}$, $k_5 = 2 \times 10^8\ M^{-1}\ s^{-1}$, $k_6 = 1 \times 10^4\ M^{-1}\ s^{-1}$, $k_7 = 8 \times 10^4\ M^{-1}\ s^{-1}$, $k_8 = 1 \times 10^5\ M^{-1}\ s^{-1}$, $k_9 = 1 \times 10^9\ M^{-2}\ s^{-1}$, $k_{10} = 1 \times 10^6\ M^{-1}\ s^{-1}$, $k_{-11} = 1 \times 10^{-2}\ s^{-1}$, and $k_{11}/k_{-11} = 6 \times 10^{-3}$ M (atm $O_2)^{-1}$. Initial concentrations were [PhCHO] = 750 mM, [total Co] = 20 mM, [Br^-] = 10 mM. O_2(g) pressure was held constant at 580 torr, and [H^+] is incorporated in the rate constants.

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Syntheses and Structures of a Novel Series of Tetrathiolene Clusters: $(\eta^5\text{-}C_5H_5)_2Fe_2(C_{10}Cl_4S_4)(C_{10}Cl_4S_3)$, $(\eta^5\text{-}C_5H_5)_2Co_2(C_{10}Cl_4S_4)$, and $(\eta^5\text{-}C_5H_5)_2Ni_2(C_{10}Cl_4S_4)$

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Recently we reported the synthesis and characterization of a novel series of metal tetrathiolene complexes containing 1, 2, 2, 3, and 4 metals and corresponding to 2, 4, 6, 8, and 12 electron-donating ligand systems, respectively.[1] In an attempt to prepare the "six-electron" systems $(\eta^5\text{-}C_5H_5)_2M_2(C_{10}Cl_4S_4)$ where M = Fe, Co, and Ni, which span the metal–metal bond orders of 2 (Fe═Fe), 1 (Co—Co), and 0 (Ni···Ni), the ligand $C_{10}Cl_4S_4$ (TCTTN)[2] was reacted with $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, $(\eta^5\text{-}C_5H_5)$-$Co(CO)_2$, and $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$, respectively. To our surprise, the iron complex reacts differently from the cobalt and the nickel analogues. Instead of forming the anticipated Fe═Fe bond it yielded $(\eta^5\text{-}C_5H_5)_2Fe_2(C_{10}Cl_4S_4)(C_{10}Cl_4S_3)$ via a *facile desulfurization* reaction of one of the TCTTN ligands under very mild conditions. The corresponding cobalt and nickel reactions gave rise to $(\eta^5\text{-}C_5H_5)_2Co_2(C_{10}Cl_4S_4)$ with a Co–Co single bond and $(\eta^5\text{-}C_5H_5)_2Ni_2(C_{10}Cl_4S_4)$ with no Ni···Ni bond.

The title compounds $(\eta^5\text{-}C_5H_5)_2Fe_2(C_{10}Cl_4S_4)(C_{10}Cl_4S_3)$ (**1**), $(\eta^5\text{-}C_5H_5)_2Co_2(C_{10}Cl_4S_4)$ (**2**), and $(\eta^5\text{-}C_5H_5)_2Ni_2(C_{10}Cl_4S_4)$ (**3**) were prepared by reacting $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, $(\eta^5\text{-}C_5H_5)Co$-$(CO)_2$, and $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$, respectively, with $C_{10}Cl_4S_4$(TCTTN)[2] in a metal:TCTTN = 2:1 molar ratio in refluxing benzene for ca 12–24 h. The dark brown or dark red precipitates thus formed were filtered, washed with benzene and acetonitrile, and vacuum dried. The yields were 40, 65, and 77% for **1**, **2**, and **3**, respectively. The crude products were recrystallized from either $CHCl_3/CH_3CN$ or $CHCl_3$/toluene. All three compounds gave satisfactory elemental analyses.

The molecular architecture of the title compounds are depicted in Figures 1–3. Crystallographic details are summarized in the supplementary material.

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