p–p π overlap leads to a half-filled, folded-back π-band of total width 8.64 eV, with the Fermi level at −10.85 eV. This is for equal, nonalternating CC of 1.44 Å. When two such chains are brought together to 2.494 Å, as in **3**, they naturally repel each other. Paired polyene levels split by ~2 eV. Interestingly, the overlap of the bands results in a density of states that suggests metallic behavior even for this two-chain model. In **4** the band width due to interchain p–p σ overlap is ~4 eV, comparable to the dispersion due to p–p π overlap within one chain. In **5** and in the complete structure **1** it becomes difficult to separate the sources for the high dispersion, but clearly both inter- and intrachain overlaps contribute.

It is interesting to examine the nonbonded (2.494 Å) CC overlap population. It changes from −0.002 in **3** to +0.04 in **4**, to +0.06 in **5**, and to +0.013 in **1**. Note the positive values. Perhaps one way to think about this is that in some segments of the Brillouin zone one has gone past the repulsive region of interchain π-cloud interaction into the attractive regime of σ-bond formation between chains.

Further numerical experiments show that (1) the network in **1** resists the twisting deformation; (2) bond localization within the polyenes does not lead to an opening of a gap at the Fermi level or to net stabilization in **1**, **3**, **4**, or **5**; (3) from geometry optimization we expect the CC distance in **1** to be intermediate between graphite and diamond, and vertical nonconjugated bonds should be longer than the polyenic ones; (4) the computed total energy of **1** is −70.26 eV/C compared to −71.00 eV/C for graphite. These numbers are subject to the unreliability of the extended Hückel method. That the hypothetical structure **1** is unstable with respect to graphite is not a barrier to its existence—most molecules are thermodynamically unstable with respect to the elements but exist because of large kinetic barriers to geometrical transformation which break bonds. Many such bonds would have to be broken, at large cost in energy, in order to transform **1** to graphite.

Can this metallic form of elemental carbon, or other alternative structures, be synthesized?

Acknowledgment. Our work was generously supported by the National Science Foundation through research grants CHE 7828048 and DMR 7681083.

Registry No. Carbon, 7440-44-0.

Mechanisms of Water Oxidation to Oxygen: Cobalt(IV) as an Intermediate in the Aquocobalt(II)-Catalyzed Reaction

Bruce S. Brunschwig, Mei H. Chou, Carol Creutz,*
Pushpito Ghosh, and Norman Sutin*

Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

Received March 10, 1983

Both heterogeneous and homogeneous catalyses of water oxidation to O_2 have been recently reported for metal oxides[1] and aquo– or hydroxo–metal complexes.[2] One of the more efficient systems involves cobalt(II) catalysis of water oxidation by $Ru(bpy)_3^{3+}$ ($E°(Ru(bpy)_3^{3+/2+}) = 1.26$ V), which occurs above pH ~ 5[2a] (eq 1). We have studied the kinetics and product distribution of this system at pH ~7 (at pH 7, $E°(O_2/H_2O_2) = 0.27$ V, $E°(H_2O_2/H_2O) = 1.36$ V). Although the kinetic behavior is extremely complicated in both the absence[3] and presence[4] of Co(II), our results provide compelling evidence for rate-determining formation of a Co(IV) species that reacts with water or hydroxide ion to produce H_2O_2, with regeneration of the catalyst Co(II).

$$Ru(bpy)_3^{3+} + {}^1/_2H_2O = Ru(bpy)_3^{2+} + H^+ + {}^1/_4O_2 \quad (1)$$

As reported by Shafirovich et al.,[2a] O_2 formation according to eq 1 is stoichiometric at pH ~7 when the initial $[Ru(bpy)_3^{3+}]$ is $\sim 10[Co(II)]$.[5] Consistent with this we find that the rate of $Ru(bpy)_3^{2+}$ formation is greatly accelerated by the addition of Co(II). In the presence of Co(II), added Ru(II) markedly slows the rate,[6] establishing that product inhibition is a factor, and the absorbance–time behavior with excess Ru(II) manifests a second-order Ru(III) dependence. Over the range $[Ru(III)] = (0.01–1.5) \times 10^{-3}$ M, $[Co(II)] = (1–60) \times 10^{-6}$ M with added $Ru(II) \leq 10[Ru(III)]$ and $[Ru(III)] \geq 10[Co(II)]$, the fits to a second-order Ru(III) dependence are excellent and the second-order k_{obsd} is inversely proportional to [Ru(II)].

The rate exhibited a complex [Co(II)] dependence. With $(0.3–1.0) \times 10^{-3}$ M Ru(III) the value of $k_{obsd}[Ru(II)]$ decreased with increasing initial [Ru(III)] at a given [Co(II)] and plots of $k_{obsd}[Ru(II)]$ vs. [Co(II)] curved upward. Such behavior suggests catalyst deactivation. Since the initial [Ru(III)] was 10–100 times greater than the added [Co(II)], the diversion of a small fraction of the cobalt catalyst per catalytic cycle (to, for example, an inactive Co(III) dimer or polymer) could lower $k_{obsd}[Ru(II)]$ when [Ru(III)] is increased at constant [Co(II)]. In an attempt to simplify the behavior in the high Ru(III) region, the kinetics of the reaction of equimolar Ru(III) and Co(II) were studied by the stopped-flow technique. Drastically different absorbance–time profiles were, however, observed: the reaction exhibited triphasic behavior with most of the Ru(II) (450 nm) being produced in a rapid, apparently zero-order stage. Intense transient absorption at ~600 nm obscured the Ru(III) disappearance normally monitored at 675 nm, and a black solid containing >90% of the cobalt precipitated from the product solutions. Thus Co_2O_3 or a related solid is produced when [Ru(III)] and [Co(II)] are comparable and leads to the greatly diminished O_2 yield[2a,5] under these conditions.

Because of the complications described above, measurements were extended to lower Ru(III) and Co(II) concentrations. At pH 6.5–7.2 (0.025 M phosphate, 0.1 M ionic strength, 25 °C) with $(1–10) \times 10^{-5}$ M Ru(III), $(1–10) \times 10^{-4}$ M Ru(II), and $(1–6) \times 10^{-6}$ M Co(II),[7a] the rate law for disappearance of $Ru(bpy)_3^{3+}$ is given by $-d[Ru(III)]/dt = a[Ru(III)]^2[Co(II)]/[Ru(II)][H^+]^2$ with $a = (4 \pm 1) \times 10^{-10}$ M s^{-1}. The rate is first order in [Co(II)], inverse second-order in $[H^+]$, and, as before, second order in [Ru(III)] and inverse in [Ru(II)], but in this region, a is constant over a factor of 10 range in [Ru(III)], and Co_2O_3 formation is not observed.[7b] The rate law implicates a scheme such as eq 2–5

---

(1) Kiwi, J.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 860. Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 355. Kiwi, J.; Kalyanasundaram, K.; Grätzel, M. *Struct. Bonding (Berlin)* **1982**, *49*, 37.

(2) (a) Shafirovich, V. Ya.; Khannanov, N. K.; Strelets, V. V. *Nouv. J. Chim.* **1980**, *4*, 81. (b) Harriman, A.; Porter, G.; Walters, P. *J. Chem. Soc., Faraday Trans.* **1981**, *2*, 2373. (c) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1288.

(3) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A* **1975**, *72*, 2858.

(4) Ghosh, P.; Brunschwig, B. S.; Chou, M. H.; Creutz, C.; Sutin, N., manuscript in preparation.

(5) Oxygen yields were determined by gas chromatography (Ar or He carrier, 2 m × 0.3 cm molecular sieve 5A column) of the gas phase above $Ru(bpy)_3^{3+}$ solutions (pH 7, 0.025–0.25 M phosphate) reacted at ~22 °C. With 1.0×10^{-3} M Ru(III) the following yields were obtained (−log [Co(II)] added as $CoSO_4$, percent O_2 based on eq 1): 6.7, 10; 5.7, 28; 4.6, 68; 4.3, 95; 4.0, 95; 3.7, 66; 3.4, 55; 3.2, 18. The yield profile, which features a maximum O_2 yield between 5×10^{-5} and 3×10^{-4} M Co(II), is in excellent agreement with that reported in ref 2a. With lower initial [Ru(III)] the maximum yield shifts to lower [Co(II)]. At 2.0×10^{-4} M Ru(III) the maximum O_2 yield is near 1×10^{-5} M Co(II) (−log [Co(II)], percent O_2 in 0.025 M phosphate at pH 7): 6, 68; 5, 98;, 4.3, 83. In the absence of Co(II), ≪10% O_2 was found; instead, $Ru(bpy)_3^{2+}$ formation (in >90% yield) was accompanied by the formation of CO_2 and Ru(II) complexes containing partially oxidized bpy ligands.[4] In Co(II)-containing solutions the yields of these ligand-oxidized products dropped as the O_2 yield increased.

(6) Note that in the absence of Co(II), the Ru(III) decay *accelerates* in the presence of $Ru(bpy)_3^{2+}$ and with initial [Ru(III)].[3,4].

(7) (a) These data were determined for argon-saturated solutions. (b) After the completion of the kinetic runs, the solutions were subjected to Millipore filtration, and their cobalt content was determined by atomic absorption: >90% of the cobalt originally added was present in the filtrate.

0002-7863/83/1505-4832$01.50/0

$$\mathrm{Co^{2+} + 2H_2O \overset{K_2}{\rightleftharpoons} Co(OH)_2 + 2H^+} \quad (2)$$

$$\mathrm{Co(OH)_2 + Ru(III) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(OH)_2^+ + Ru(II)} \quad (3)$$

$$\mathrm{Co(OH)_2^+ + Ru(III) \xrightarrow[k_4]{slow} CoO^{2+} + Ru(II) + H_2O} \quad (4)$$

$$\mathrm{CoO^{2+} \xrightarrow[H_2O]{k_5} Co^{2+} + H_2O_2} \quad (5)$$

$$\mathrm{CoO^{2+} + Co(II) \xrightarrow{k_6} CoOCo^{4+} \rightarrow ppt.} \quad (6)$$

$$\mathrm{2Ru(III) + H_2O_2 \rightarrow 2Ru(II) + O_2 + 2H^+} \quad (7)$$

as part of the catalytic sequence.[2a,8] The net reaction, Ru(II) formation and Co(III) precipitation, found when [Ru(III)] and [Co(II)] are equal, results from eq 2–4 and 6 (or its equivalent).[9,10] The diminished catalyst activity at high Ru(III) is also ascribed to eq 6; this reaction converts part of the Co(IV) and Co(II) to an inactive Co(III) species each cycle. Thus the effective catalyst concentration is diminished at high [Co(II)] and high [Ru(III)]/[Co(II)] ratios. The production of peroxide in eq 5 is chemically reasonable and receives some support from electrochemical studies of Co(II).[11] The oxidation of H_2O_2 by Ru(bpy)$_3^{3+}$ (eq 7) is sufficiently rapid ($k_{\mathrm{eff}} = 5 \times 10^2$ M^{-1} s^{-1} at pH 7[3]) when [Ru(II)] > 5[Ru(III)] to quantitatively oxidize H_2O_2 to O_2.

The sequence eq 2–5 and 7 provides a mechanism for Co(II) catalysis of eq 1. It gives rise to a rate law of the observed form when reaction 4, oxidation of Co(III) to Co(IV), is the slow step preceded by equilibria 2 and 3. Provided that Co^{2+} and $Co(OH)_2^+$ are the dominant forms of Co(II) and Co(III), respectively, a is equal to $nK_2K_3k_4$ where n is 4 when reaction 7 is rapid. From the $Co(H_2O)_6^{3+/2+}$ reduction potential (1.86 V[12]) and estimated Co^{n+} hydrolysis constants,[13] $K_2K_3/[H^+]^2$ is ~1 × 10^{-2} at pH 7 (i.e., $K_2 = 10^{-18.8}$ and $E°(Co(OH)_2^+/Co(OH)_2) = 1.1$ V), giving k_4 ($=a/4K_2K_3$) ~1 × 10^6 M^{-1} s^{-1} and $k_5 \geq 100$ s^{-1}. The formation of Co(IV) is thus implicated to be rate determining in the Co(II) catalysis of eq 1 at pH ~7. At present the rate constant for the reaction of Co(IV) with water (hydroxide ion) can only be estimated as ≥100 s^{-1} at pH 7. Future experiments may provide greater insight into the details of O–O bond formation on Co(IV).

Acknowledgment. We thank E. Norton for performing the cobalt analyses. This work was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. H_2O, 7732-18-5; Co, 7440-48-4; Ru(bpy)$_3^{3+}$, 18955-01-6.

---

[8] Note that this mechanism is not unique. The following (and variants) are also consistent with the observed rate law:

$$\mathrm{2Ru(III) \rightleftharpoons Ru(IV) + Ru(II)}$$

$$\mathrm{Ru(IV) + Co(OH)_2 \rightarrow Ru(II) + Co(IV)\ etc.}$$

This interpretation seems less attractive than the scheme considered because of the very positive $E°$ for the Ru(IV)/Ru(III) couple. See: Gaudiello, J. G.; Sharp, P. R.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6373.

[9] The time profiles of high Ru(III) runs have been successfully simulated with $k_6 \sim (1 \times 10^4)\ k_5$. In addition, eq 6 finds precedent in the VO^{2+}/V^{2+}_{aq}[10a] and FeO^{2+}/Fe^{2+}_{aq}[10b] systems. Equation 6 is not, however, a unique "catalyst suicide" mechanism. Direct oligomerization also likely occurs at high Co(III) concentrations (as in the stopped-flow runs).

[10] (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1964**, *3*, 569. (b) Conochiolli, T. J.; Hamilton, E. J., Jr.; Sutin, N. *J. Am. Chem. Soc.* **1965**, *87*, 926.

[11] Shafirovich, V. Ya.; Strelets, V. V. *Nouv. J. Chim.* **1978**, *2*, 199, footnote 10.

[12] Warnquist, B. *Inorg. Chem.* **1970**, *9*, 682.

[13] Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976; p 238. K_{nh} is defined as the equilibrium constant for $M^+ + nH_2O \rightleftharpoons M(OH)_n^{(1-n)+} + nH^+$. The following log K_{nh} values were used here: Co(II) −9.65 (n = 1), −18.8 (n = 2); Co(III) −2.5 (n = 1), −5.9 (n = 2). The Fe(III) values (p 230) were used for Co(III). Note that the potential complication of phosphate complexing has been neglected.

1,3-Asymmetric Induction in Addition Reactions of Chiral β-Alkoxy Aldehydes: Efficient Chelation Control via Lewis Acidic Titanium Reagents

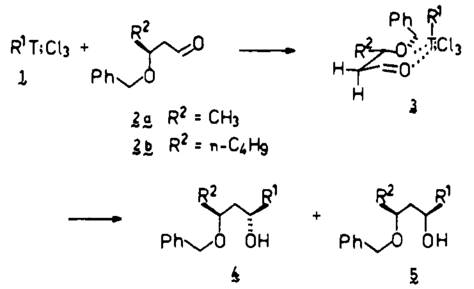
M. T. Reetz* and A. Jung

Fachbereich Chemie der Universität
3550 Marburg, Federal Republic of Germany

Received March 21, 1983

Controlling 1,3 asymmetric induction in Grignard- and aldol-types of additions to acyclic carbonyl compounds remains a challenge.[1] Since ketones and aldehydes devoid of additional heteroatoms generally show poor degrees of diastereofacial selectivity in stereochemically relevant cases,[1] chiral β-alkoxy derivatives have been tested in hope of potential chelation control. However, such reagents as RMgX,[2] RLi,[2] and R_2CuLi[3] failed to perform well, in spite of the fact that they chelate efficiently in systems involving 1,2 asymmetric induction.[3,4] We report that Lewis acidic titanium reagents[5] provide a solution to this long-pending problem.

Since compounds of the type $RTiCl_3$ (**1**) are known to form bis-etherates as well as other octahedral six-coordinate adducts,[6] we speculated that they might react with chiral β-alkoxy aldehydes **2** to form the chelation-controlled products **4** via intermediates **3**.[7] We also thought that $TiCl_4$ could interact similarly, so that addition of proper carbon nucleophiles that do not destroy chelation should likewise afford **4** preferentially.



Indeed, the reaction of **2a** and **b** with CH_3TiCl_3[8] in CH_2Cl_2 at −78 °C yielded compounds **4** with unprecedented levels of 1,3 asymmetric induction (Table I). Furthermore, complexation of **2a** and **b** using $TiCl_4$ followed by addition of allylsilanes[9] or dibutylzinc[10] at −78 °C also resulted in stereoselectivities of ≥90% (Table I).[11] In these cases we are not certain whether the or-

---

[1] (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3. (b) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice Hall: Englewood Cliffs, NJ, 1971.

[2] Leitereg, T. J.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 4011, 4019.

[3] Still, W. C.; Schneider, J. A. *Tetrahedron Lett.* **1980**, *21*, 1035.

[4] (a) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. (b) Wolfrom, M. L.; Hanessian, S. *J. Org. Chem.* **1962**, *27*, 1800. (c) Nakati, T.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2745. (d) Eliel, E. L.; Koskimies, J. K.; Lohri, B. *J. Am. Chem. Soc.* **1978**, *100*, 1615. (e) Still, W. C.; McDonald, J. H. *Tetrahedron Lett.* **1980**, *21*, 1031. (f) Bernardi, R. *Ibid.* **1981**, *22*, 4021.

[5] Reviews of organotitanium reagents in organic synthesis: (a) Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1. (b) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31.

[6] Reetz, M. T.; Westermann, J. *Synth. Commun.* **1981**, 647 and references therein.

[7] **3** is simply an operation model. Half-chair conformations lead to the same results. Also, the benzyl group may be axial.

[8] CH_3TiCl_3 was prepared by reacting $Zn(CH_3)_2$ with $TiCl_4$ in CH_2Cl_2: Reetz, M. T.; Westermann, J.; Steinbach, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 900.

[9] Allylsilanes are known to add to aldehydes in the presence of $TiCl_4$: (a) Hosomi, A.; Sakurai, M. *Tetrahedron Lett.* **1976**, 1295. (b) Trost, B. M.; Coppola, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 6879.

[10] Aldehydes react smoothly with ZnR_2 in the presence of $TiCl_4$: Reetz, M. T.; Steinbach, R.; Wenderoth, B. *Synth. Commun.* **1981**, 261.