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LETTERS

Copper Catalysis of the Oxidation of Iodide by $[Fe^{III}(bpy)_2(CN)_2]^+$ in Acetonitrile

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Because of its potential relevance to the Grätzel photoelectrochemical cell, we have investigated the oxidation of iodide by $[Fe(bpy)_2(CN)_2]^+$ in acetonitrile solution at 25 °C. The reaction occurs on the stopped-flow time scale and is highly sensitive to catalysis by Cu^{2+}, to the degree that, under typical conditions, the impurity levels of Cu^{2+} are sufficient to dominate the reaction. 2,2′-Bipyridine is a very effective inhibitor of the Cu^{2+} catalysis, and 1 μM Cu^{2+} can accelerate the rates by as much as a factor of 280, relative to the bpy-inhibited reaction.

The general features of the kinetics and mechanisms of oxidation of excess iodide by typical outer-sphere oxidants in aqueous solution are well-understood.[1] These reactions generally have the form

$$2M_{ox} + 3I^- \rightarrow 2M_{red} + I_3^- \tag{1}$$

with the rate law being

$$-\frac{d[M_{ox}]}{dt} = 2(k_1[I^-] + k_2[I^-]^2)[M_{ox}] \tag{2}$$

The rates are usually insensitive to pH, and in no case has trace metal-ion catalysis been reported. The mechanisms of these reactions are sufficiently well-understood, such that one can predict the values of k_1 with exceptional accuracy and the values of k_2 can be predicted with good accuracy.

Similar remarks cannot be made about the kinetics of oxidation of iodide in nonaqueous media, because there are insufficient experimental data. Relevant studies are limited to three oxidants: $[Fe(phen)_3]^{3+}$, $[CoW_{12}O_{40}]^{5-}$, and $[IrCl_6]^{2-}$.[2-4] The reaction of $[Fe(phen)_3]^{3+}$ was studied in water/methanol and water/ethanol mixtures up to 20% alcohol; hence, little is revealed about the behavior in genuine nonaqueous media.[2] With $[CoW_{12}O_{40}]^{5-}$, aqueous solvent mixtures again were used—in this case, up to 40% methanol, 40% acetonitrile, and 60% dimethyl sulfoxide (DMSO).[4] With $[IrCl_6]^{2-}$, a variety of aqueous solvent mixtures were used, but the aqueous fraction was never <20%.[3] To our knowledge, there are no reports of kinetic data on such reactions in "pure" nonaqueous media.

Some knowledge of the kinetic features of iodide oxidation in nonaqueous media could be valuable, because of its relevance to the Grätzel photoelectrochemical cell.[5] These cells are typically fabricated with the two electrodes immersed in a nonaqueous solvent with an iodide/triiodide electrolyte that mediates the redox reaction.[6] One of the electrodes is composed of TiO_2 with a surface-adsorbed dye. It is generally believed that one function of the iodide is to reduce the photochemically oxidized dye back to its resting state.[7,8] A wide variety of dyes have been used; however, the classic example is a derivative of $[Ru^{II}(bpy)_2(SCN)_2]$.

Herein, we report on the homogeneous oxidation of iodide in acetonitrile by $[Fe^{III}(bpy)_2(CN)_2]^+$. This oxidant is well-known as a substitution-inert one-electron acceptor. It bears close similarity to the known Grätzel cell dye $[Fe(bpy\text{-}4,4'\text{-}COOH)_2(CN)_2]$,[9,10] and it has features that are typical of many other Grätzel cell dyes. We find that $[Fe^{III}(bpy)_2(CN)_2]^+$ reacts

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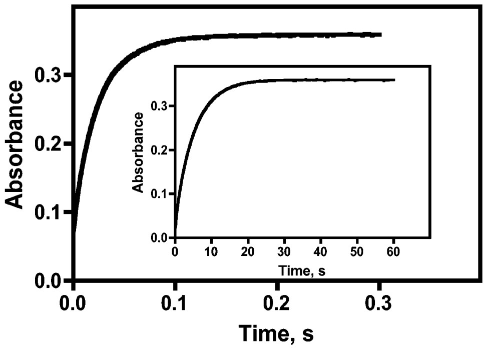

Figure 1. Kinetic traces for the oxidation of 2 mM NaI by 50 μM $[Fe(bpy)_2(CN)_2]^+$ in CH_3CN at 25 °C with 0.1 M et_4NBF_4. Data recorded at 605 nm. Main trace with 1 μM $Cu(NO_3)_2{\cdot}3H_2O$. Inset shows data with 1 mM bpy but no added Cu^{2+}. Note the vastly differing time scales for the two traces.

with iodide at rates that are easily monitored by conventional stopped-flow UV−vis spectrophotometry.

Our preliminary studies were plagued by irreproducibility; however, this effect was soon traced to catalysis by Cu ions at impurity levels of concentration. Thus, for a typical reaction of 2.0 mM NaI with 50 μM $[Fe^{III}(bpy)_2(CN)_2]NO_3$ in 0.1 M et_4NBF_4 at 25 °C, the half-life for formation of $[Fe^{II}(bpy)_2(CN)_2]$ is 0.81 s. With the addition of 5 μM $Cu(NO_3)_2{\cdot}3H_2O$, the half-life is too short to measure with our instruments (<3 ms); it is at least 270-fold shorter than in its absence. With the addition of 1 mM bpy as a Cu-ion scavenger, the half-life increases to 4.2 s and becomes highly reproducible. Essentially identical results were obtained with ethylenediamine as a Cu-ion scavenger, although this ligand is less reliable, because it undergoes slow direct oxidation by $[Fe(bpy)_2(CN)_2]^+$. Qualitative tests revealed that Fe^{3+} and Ni^{2+} have no comparable catalytic activity. The majority of our kinetic experiments were performed on a Hi-Tech SF-51 instrument; however, equivalent results were obtained with an Applied Photophysics stopped-flow instrument, which shows that the results are not a consequence of the instrument materials of construction.

Without the addition of ligands to scavenge metal ions, the reaction, as catalyzed by 1 μM Cu^{2+}, occurs rapidly but with observable rates ($t_{1/2} = 15$ ms), as shown in Figure 1. In this experiment, the Cu^{2+} cation was added to the I^- reactant solution for the Cu^{2+}/I^- reaction to be complete prior to mixing with the Fe(III) solution. The inset in Figure 1 shows the corresponding kinetic trace for the reaction when copper catalysis is inhibited by 1 mM bpy. In the presence of 1 mM bpy, the rate law is pseudo-first-order in Fe(III); however, significant deviations in the pseudo-first-order fits are observed for the copper-catalyzed reaction.

Spectrophotometric analysis of the product solutions of the copper-catalyzed reaction showed that the products are $[Fe(bpy)_2(CN)_2]$ and I_3^-, as revealed by their characteristic absorption features at 605 and 363 nm, respectively. Quantitative dual-wavelength analysis at 605 and 369 nm demonstrated that $[Fe(bpy)_2(CN)_2]$ is produced in 99% yield, whereas the product ratio is $\Delta[I_3^-]/\Delta[Fe(II)] = 0.48$ ($\epsilon_{605} = 7317$ M^{-1} cm^{-1} for Fe(II), $\epsilon_{605} \approx 0$ M^{-1} cm^{-1} for I_3^-, $\epsilon_{369} = 5731$ M^{-1} cm^{-1} for Fe(II), and $\epsilon_{369} = 25\,180$ M^{-1} cm^{-1} for I_3^-). These experiments were conducted with $[Fe(III)]_0 = 50$ μM, $[I^-] = 2.0$ mM, $[Cu^{2+}] = 1$ μM at 25 °C 0.1 M et_4NBF_4 in CH_3CN. Equation 1 evidently provides a good description of the copper-catalyzed reaction in acetonitrile.

The aforementioned experiments were conducted under nominally anhydrous conditions. ^{1}H NMR spectra of the product solutions showed that they typically contained ~0.1% water. When 1% water was deliberately added to reaction mixtures that contained 1 mM bpy, the rates were unaffected. In the absence of bpy but with 1 μM Cu^{2+} and 1% water, the half-life was similar to that without water. Thus, the 0.1% level of water present under nominally anhydrous conditions seems to have no significant effect on the reaction rates, either as catalyzed by 1 μM Cu^{2+} or with inhibition by 1 mM bpy.

When the reaction was conducted in 100% water, the rates were considerably slower. Thus, with 2 mM NaI, 50 μM $[Fe(bpy)_2(CN)_2]^+$ in 0.1 M $NaCF_3SO_3$, the half-life was 58 s, i.e., a factor of 72 longer than that observed in CH_3CN. Under the same conditions but with 5 μM Cu^{2+} added, the half-life was the same as that without added Cu^{2+}. Thus, the catalytic effect of Cu^{2+} is very strong in CH_3CN but insignificant in water.

In summary, the oxidation of I^- in acetonitrile solution by $[Fe(bpy)_2(CN)_2]^+$, which is a typical outer-sphere oxidant, is strongly catalyzed by Cu ions. The catalysis is so effective that trace impurities of copper are sufficient to dominate the reaction kinetics. These results come as a surprise, because similar catalysis has not been encountered in the extensive studies of iodide oxidations in aqueous media. Although our data are insufficient to probe the catalytic mechanism, it is notable that the solubility of CuI is quite high in CH_3CN but remarkably low in H_2O.[11] It remains to be determined whether trace copper catalysis is a significant factor under conditions that are more typical of those in operating Grätzel cells. There is also the possibility that copper catalysis of this type could be exploited in developing improved Grätzel cells.

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References and Notes

(1) Nord, G. *Comments Inorg. Chem.* **1992**, *13*, 221−239.
(2) Kimura, M.; Wada, G. *Inorg. Chem.* **1978**, *17*, 2239−2242.
(3) Blandamer, M. J.; Burgess, J.; Duce, P. P.; Haines, R. I.; McAuley, A. *Transition Met. Chem. (Dordrecht, Neth.)* **1982**, *7*, 10−13.
(4) Blandamer, M. J.; Burgess, J.; Hamshere, S. J.; White, C.; Haines, R. I.; McAuley, A. *Can. J. Chem.* **1983**, *61*, 1361−1370.
(5) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382−6390.
(6) Grätzel, M. *Nature* **2001**, *414*, 338−344.
(7) Nasr, C.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem. B* **1998**, *102*, 4944−4951.
(8) Kuciauskas, D.; Freund, M. S.; Gray, H. B.; Winkler, J. R.; Lewis, N. S. *J. Phys. Chem. B* **2001**, *105*, 392−403.
(9) Ferrere, S. *Chem. Mater.* **2000**, *12*, 1083−1089.
(10) Ferrere, S.; Gregg, B. A. *J. Am. Chem. Soc.* **1998**, *120*, 843−844.
(11) Ahrland, S. *Pure Appl. Chem.* **1990**, *62*, 2077−2082.