oxodiperoxomolybdenum(VI); the rate is sufficiently rapid under the experimental conditions in this study to maintain virtually all the Mo(VI) in the catalytic form. The corresponding kinetic data for the formation of oxodiperoxotungsten(VI) are not available, but the higher concentrations of hydrogen peroxide required to reach saturation kinetics for the tungsten(VI) systems suggest a slower formation rate.

The value of K_a for oxodiperoxochromium(VI) is apparently about 10^{-4} M.[30-32] Therefore, the acidities of the group 6 oxo diperoxo complexes stand in the order W(VI) > Mo(VI) > Cr(VI). The same ordering holds for the $MO_3(OH)^-$ ions.[33] This trend is opposite to that observed for oxoacids of the main-group elements. We are not aware of a satisfactory explanation for this reversal in periodic properties.

Acknowledgment. This research was supported by the U.S. Army Research Office. We are grateful to Professor R. K. Murmann for considerable assistance with the oxygen-18 tracer experiments.

Supplementary Material Available: Table S1 (variation of the extinction coefficient of oxodiperoxotungsten(VI) with acidity at 25 °C) (1 page). Ordering information is given on any current masthead page.

---

(30) Griffith, W. P. *J. Chem. Soc.* **1962**, 3948.

(31) Witt, S. N.; Hayes, D. M. *Inorg. Chem.* **1982**, *21*, 4014.

(32) Bartlett, B. L.; Quane, D. *Inorg. Chem.* **1973**, *12*, 1925.

(33) This comparison is valid since it has been shown that the $MO_3(OH)^-$ ions of group 6 are isostructural. See: (a) Cruywagen, J. J.; Rohwer, E. F. C. H. *Inorg. Chem.* **1975**, *14*, 3136. (b) Brown, P. L.; Shying, M. E.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1987**, 2149.

Notes

Contribution from Rocketdyne,
A Division of Rockwell International,
Canoga Park, California 91303

Formation of Chlorine–Fluorine and Nitrogen–Fluorine Bonds Using Carbonyl Difluoride as the Fluorinating Agent

Carl J. Schack and Karl O. Christe*

Received May 19, 1988

Previous studies by Shreeve and her co-workers have shown that carbonyl difluoride (COF_2) is a useful reagent for displacing either hydrogen by fluorine from P–H, N–H, and C–H bonds[1] or oxygen by fluorine from the oxides of V, Nb, Ta, Cr, Mo, W, B, Si, Ge, Sn, P, Se, Te, I, and U.[2] The latter study prompted us to examine whether COF_2 could also be used for the formation of Cl–F and N–F bonds from their oxides. The formation of Cl–F[3] and N–F[4] bonds usually requires relatively powerful fluorinating agents and previously has not been achieved with a fluorinating agent as mild as COF_2. Thermochemical calculations that were carried out by us revealed the feasibility of reaction 1 for M = Li and Na. It increases with decreasing atomic weight of M and

$$\begin{gathered} MNO_3 + COF_2 \rightarrow MF + FNO_2 + CO_2 \\ M = Li, Na, K, Rb, Cs \end{gathered} \tag{1}$$

for M = Li and Na results in ΔH values of −9.5 and −4.5 kcal mol^{-1}, respectively. Reaction 2 was found to be thermochemically feasible by comparable amounts with ΔH values of −20.6 and −11.2 kcal mol^{-1} for M = Li and Na, respectively.

$$\begin{gathered} MClO_3 + COF_2 \rightarrow MF + FClO_2 + CO_2 \\ M = Li, Na, K, Rb, Cs \end{gathered} \tag{2}$$

In view of the thermochemical results, reactions 1 and 2 were experimentally studied. It was found that $LiNO_3$, when heated with a slight excess of COF_2 in a steel cylinder at 45–90 °C, formed CO_2, N_2O_4, and O_2 in high yield. These products are best explained by reaction 3, followed by the attack of the steel cylinder

$$LiNO_3 + COF_2 \rightarrow LiF + FNO_2 + CO_2 \tag{3}$$

by FNO_2. Since HF generally promotes the attack of steel by oxidizers such as FNO_2, small amounts of CsF were added to the reaction as an HF getter (see reaction 4). In this manner, FNO_2

$$CsF + HF \rightarrow CsHF_2 \tag{4}$$

was isolable in essentially quantitative yield according to (3), with 12 mol % of CsF as an additive at 85 °C. For $NaNO_3$ with CsF addition, an 85% yield of FNO_2 was obtained under comparable conditions. For $CsNO_3$, either with or without CsF, no reaction was observed with COF_2, in agreement with the above thermochemical predictions.

The postulate that CsF serves only as an HF getter and not as a catalyst was confirmed by carrying out reaction 3 in an all-Teflon reactor. In such a reactor, high yields of FNO_2 were obtainable without CsF addition.

For the reaction of $NaClO_3$ with COF_2, reaction conditions similar to those used for $NaNO_3$, i.e. 85 °C and CsF catalysis, were required. The best yield obtained for $FClO_2$ was about 44% based on the limiting reagent $NaClO_3$, but no systematic effort was undertaken to maximize this yield.

Attempts failed to prepare $FClO_3$ from $LiClO_4$ and COF_2. Although this reaction is thermochemically favored by 14.8 kcal mol^{-1}, no reaction was observed up to 120 °C. At 160 °C, a 30% conversion of $LiClO_4$ to LiF was obtained, but even in the presence of CsF only chlorine and oxygen and no $FClO_3$ were isolated.

In summary, the successful formation of N–F and Cl–F bonds from the corresponding oxides by the very mild fluorinating agent COF_2 was quite unexpected and significantly expands the utility of this fluorinating agent.

Experimental Section

Materials and Apparatus. $LiNO_3$ (J. T. Baker, 99.7%) and $NaNO_3$ (J. T. Baker, 99.5%) were dried in a vacuum oven at 120 °C for 1 day prior to their use. The $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. The CsF was dried by fusion in a platinum crucible, followed by immediate transfer of the hot clinker to the dry N_2 atmosphere of a glovebox. The $NaClO_3$ and $LiClO_4$ (Baker, Analyzed reagents) were used as received. The COF_2 (PCR Inc.) was used without further purification after removal of any volatile material at −196 °C.

Volatile materials were handled in a stainless steel–Teflon FEP vacuum line[5] and solids in the dry N_2 atmosphere of a glovebox.

Synthesis of FNO_2. In a typical experiment, $LiNO_3$ (2.10 mmol) and CsF (0.25 mmol) were loaded in the drybox into prepassivated (with ClF_3) 30-mL stainless steel cylinder, which was closed by a valve. On the vacuum line, COF_2 (2.38 mmol) was added to the cylinder at −196 °C. The cylinder was kept in an oven at 85 °C for 16 h and was then cooled again to −196 °C. It did not contain any significant amount of gas noncondensable at −196 °C. The material volatile at 25 °C was

---

(1) Gupta, O. D.; Shreeve, J. M. *J.* Chem. *Soc.*, *Chem. Commun.* **1984**, 416 and references therein. Williamson, S. M.; Gupta, O. D.; Shreeve, J. M. *Inorg. Synth.* **1986**, *24*, 62.

(2) Mallela, S. P.; Gupta, O. D.; Shreeve, J. M. *Inorg. Chem.* **1988**, *27*, 208.

(3) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 319.

(4) *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1987; Fluorine Supplement Vol. 5, Compounds with N.

(5) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

0020-1669/88/1327-4771$01.50/0

separated by fractional condensation, measured, and identified by infrared spectroscopy. It consisted of FNO_2 (2.09 mmol), CO_2 (2.1 mmol), and COF_2 (0.2 mmol). The white solid residue (91 mg, weight calculated for 2.10 mmol of LiF and 0.25 mmol of CsF 92.5 mg) consisted of LiF and CsF.

Synthesis of $FClO_2$. The reaction was carried out as described above for $LiNO_3$ and COF_2, with use of $NaClO_3$ (1.41 mmol), COF_2 (2.00 mmol), and CsF (0.3 mmol) at 85 °C for 46 h. The products consisted of $FClO_2$ (0.62 mmol, 44% of theory), CO_2 (0.64 mmol), unreacted COF_2, and smaller amounts of Cl_2 and material noncondensable at −196 °C.

Acknowledgment. We are grateful to R. D. Wilson for help with some of the experiments and to the U.S. Army Research Office for financial support of this work.

Registry No. COF_2, 353-50-4; CsF, 13400-13-0; FNO_2, 10022-50-1; $LiNO_3$, 7790-69-4; $FClO_2$, 13637-83-7; $NaClO_3$, 7775-09-9; $NaNO_3$, 7631-99-4; $CsNO_3$, 7789-18-6; $LiClO_4$, 7791-03-9.

Contribution from the Chemistry Department,
The University of North Carolina,
Chapel Hill, North Carolina 27514

Electrocatalytic Reduction of Nitrite Using Simple Coordination Complexes of Iron and Ruthenium

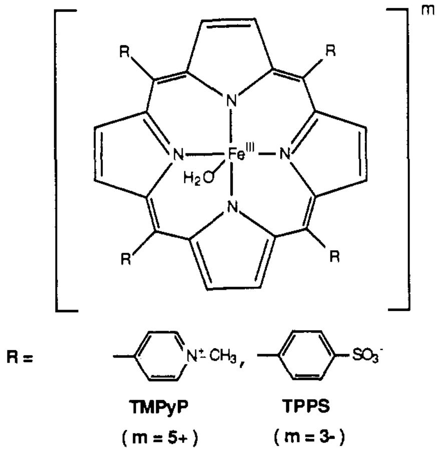
Matthew R. Rhodes and Thomas J. Meyer*

Received April 22, 1988

The reduction of nitrite to ammonia is an important metabolic reaction that is catalyzed by the nitrite reductase enzymes.[1] The reduction is a complex multielectron process

$$NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O \qquad (1)$$

which, by inference, presents formidable mechanistic demands. Given the implied mechanistic complexity, it might have been expected that the facile reduction of NO_2^- would be restricted to enzymatic systems and not be a property shared by simple coordination complexes. However, we showed earlier that the water-soluble iron porphines $[Fe(TPPS)(H_2O)_n]^{3-}$ and $[Fe(TMPyP)(H_2O)_n]^{5+}$ (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine, TMPyP = *meso*-tetrakis(1-methyl-4-pyridiniumyl)porphine) are effective electrocatalysts for this reduction.[2,3]



Mechanistic studies have shown that the initial stages in the catalyzed reactions involve reduction of nitrite bound to Fe(II) as NO^+. The stoichiometric reduction of nitrite bound as NO^+ has also been shown to occur in polypyridyl complexes of ruthenium and osmium. Mechanistic studies based on these complexes have helped to elucidate the steps involved in the overall reductions,[4,5] steps that may occur in the enzymatic reactions as well.

Table I. Current Efficiencies for Controlled-Potential Electrolyses[a]

catalyst	pH	E_{app}, V[b]	current efficiency, %[c] N$_2$O	N$_2$	NH$_3$OH$^+$	NH$_4^+$
$[Ru^{II}(Hedta)(NO^+)]$	5.0	−0.75	16 ± 1	14 ± 2	20 ± 6	54 ± 5
$[Fe^{II}(Hedta)(NO^\bullet)]^-$ [d]	5.0	−0.90	22	13	30	31
$[Fe(H_2O)_6]^{2+}$	2.1	−0.70	74	9	0	23

[a] At room temperature with $[NO_2^-]$ = 10 mM and [catalyst] = 0.1 mM except where noted. The working electrode was a Hg pool with an area of 12.6 cm². In all cases the electrolyses were taken to completion. [b] The potential applied. [c] The current efficiency percentage for each of the products was calculated from the following formula: current efficiency (%) = $100(m_i n_i \mathfrak{F})Q_f$. m_i is moles of product formed, n_i is the n value for its formation (n = 4 for N_2O, n = 6 for N_2, n = 4 for NH_3OH^+, and n = 6 for NH_4^+), $\mathfrak{F}$ is the Faraday constant, and Q_f is the total charge passed during the electrolysis. Hydrazine was not observed in any experiment within the limit of our detection (<10% current efficiency). Typical uncertainties are given for the first electrolysis. [d] 0.5 mM.

Both the electrocatalysts and the enzymes have as their active sites the iron heme group. Given the "magic" of iron heme sites in biological systems, where they play a role in such diverse processes as oxygen transport, catalytic oxidations, and electron transfer, the question arises as to whether the catalytic reduction of nitrite is a property unique to the porphyrin ligand environment. We demonstrate here that the essential features of nitrite reduction are maintained in simple coordination complexes, that the key is the metal–NO interaction, and that, as shown earlier for the reduction of NO,[6,7] the electrocatalysis is a general phenomenon.

Experimental Section

Chemicals. $FeSO_4{\cdot}7H_2O$, $Na_2H_2edta{\cdot}2H_2O$, phthalic acid, tetraethylammonium hydroxide, and hexafluorophosphoric acid (60 wt %) were purchased from Aldrich Chemical Co. KH_2PO_4, Na_2SO_4, and concentrated H_3PO_4 were obtained from Fisher Scientific. All chemicals were used without further purification. $[Ru^{III}(Hedta)(H_2O)]$ and $[Fe^{II}(Hedta)(H_2O)]^-$ were prepared by using methods previously published.[8,9] $[Fe^{II}(Hedta)(NO^\bullet)]^-$ was generated by the in situ reaction between $Fe^{II}SO_4{\cdot}7H_2O$, $Na_2H_2edta{\cdot}2H_2O$, and NO gas as described earlier.[7,10] $[Ru^{II}(Hedta)NO]$ was isolated after the direct reaction between $[Ru^{III}(Hedta)(H_2O)]$ and NO gas.[11]

Electrochemical Apparatus. Differential pulse voltammetric experiments were performed on a PAR 174 apparatus, while cyclic voltammetry and bulk electrolyses utilized a PAR 173 potentiostat coupled with a PAR 179 digital readout and an in-house-designed super cycle. Simple one-compartment cells consisting of an SSCE reference electrode and a platinum auxiliary electrode were used for routine cyclic voltammetry and differential pulse experiments. The cell used for bulk electrolyses was a two-compartment gastight cell in which there was a porous Vycor divider between the Pt auxiliary electrode and the working electrode. The working electrode was a Hg pool. The cell design allowed for a gas inlet and outlet, a separate working electrode for obtaining cyclic voltammograms during electrolyses, and a manometer, which was used for

---

(1) Losada, M. *J. Mol. Catal.* **1975**, *1*, 245–264.
(2) (a) Barley, M. H.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 5876. (b) Barley, M. H.; Takeuchi, K. J.; Murphy, W. R., Jr.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 507.
(3) Barley, M. H.; Rhodes, M. R.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1746.
(4) Murphy, W. R., Jr.; Takeuchi, K. J.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1041.
(5) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 5577.
(6) Uchiyama, S.; Muto, G. *J. Electroanal. Chem.* **1981**, *127*, 275–279.
(7) Ogura, K.; Ishikowa, H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2243–2253.
(8) (a) Mukaida, M.; Okuno, H.; Ishimore, T. *Nippon Kagaku Zasshi* **1965**, *86*, 598. (b) Baar, R. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *187*, 265–282.
(9) (a) Gustafson, R. L.; Martell, A. E. *J. Phys. Chem.* **1963**, *67*, 576. (b) Schwarzenbach, G.; Heller, J. *Helv. Chim. Acta* **1951**, *34*, 576.
(10) Hishinuma, Y.; Kaji, R.; Akimoto, H.; Nakajima, F.; Mori, T.; Kamo, T.; Arikawa, Y.; Nozawa, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2863–2865.
(11) Rhodes, M. R.; Barley, M. H.; Meyer, T. J., manuscript in preparation.
(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; p 505.

0020-1669/88/1327-4772$01.50/0