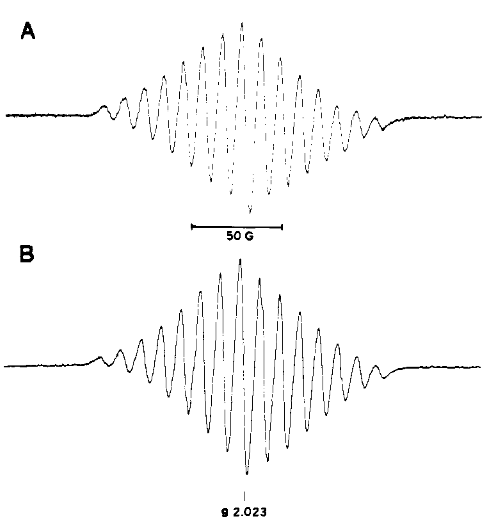

Figure 1. EPR spectra of μ-superoxo complexes of **1b** (A) and **2b** (B). Spectra was obtained by reacting the bis Co^{II} dimers with dioxygen at 23 °C in CH_2Cl_2 containing 0.1 M *N*-tritylimidazole and a trace amount of iodine.

Table I. Electrocatalytic Properties of Cobalt Porphyrin-Adsorbed Electrodes

Co porphyrins	E_f^s, V[a]	$E_{1/2}$, V[b]	% H_2O_2[c]
Co–Co–4[d]	0.69, 0.36	0.45	<5
1b	0.63, 0.33	0.43	<8 (4)
2b	0.64, 0.34	0.46	<8 (4)
Co_2FTF4[e]	0.61, 0.27	0.47	<1
CoTPP[f]	0.66	0.27	>60

[a] Formal potential for surface-confined redox couple, obtained from CV in 0.5 M HTFA (vs. SCE). [b] Half-wave potential for oxygen reduction at rotating disk electrode, evaluated at rotation rate of 100 rpm (vs. SCE). [c] Percentage of formation of hydrogen peroxide evaluated from % $H_2O_2 = -i_R/(Ni_D)$ where i_R and i_D are ring and disk limiting current, respectively, and N (=0.182) is the collection coefficient. At a fixed potential, e.g., +0.3 V, the current ratios yield % H_2O_2 given in the parenthesis. The number of electrons involved during the reduction of dioxygen for **1b** and **2b** is ca. 3.7–3.8, as calculated from the Levich equation. [d] Present study; these data deviate slightly from those in ref 4 due to different procedures used for the pretreatment of graphite electrode.[11] [e] See ref 3. [f] Liu, H. Y. Ph.D. Dissertation, Michigan State University, East Lansing, 1982.

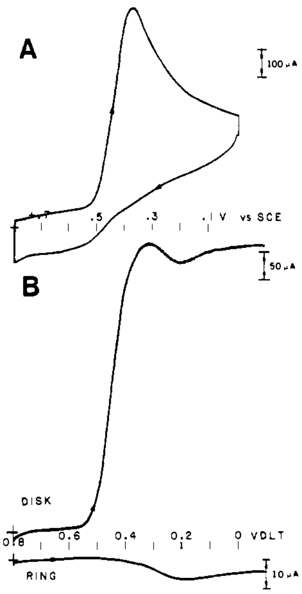

Figure 2. (A) Cyclic voltammogram obtained for an oxygen-saturated solution in 0.5 M trifluoroacetic acid at pyrolytic graphite disk (area = 0.47 cm^2) coated with **1b**. (B) Rotating ring–disk voltammograms in the same solution, using the same electrode; rotating speed = 100 rpm; disk current shown above, and ring current below, the *x* axis. All potentials are referenced against SCE.

have two compounds whose interplanar distance can differ as much as 1 Å,[13] yet both are effective catalysts for the 4-e reduction of O_2. It is perhaps the inherent flexibility of the pillard system that allows the complex to assume the optimum metal–metal distance as well as an overall conformation best suited for the reduction. We previously proposed that protonation and cleavage of the O–O bond of the Co–O–O–Co complex would be facilitated if it is in a cis configuration.[4,14] Considering the steric constraints in the pillared system and the dimers' "chomping" action, it seems highly probable that the peroxo complex is indeed in a cis configuration. Another difference between the pillared dimers and the previous amide system is the ease with which intramolecular bis Fe–(μ-oxo) complexes can be obtained: the Fe–Fe-5 or longer amide-linked diporphyrins preferentially form *intermolecular* Fe–O–Fe whereas the pillared analogues yield the internal oxo bonds easily. If one assumes that during O_2 reduction a protonated Co–O–OH^+–Co would have to rearrange to Co–O^+(OH)–Co according to well-studied binuclear peroxo Co^{III} examples,[15] then the flexibility of the pillared system is clearly of great importance. It remains to be seen as to what effect a polar group (e.g., the amide bond in Co–Co–4) near the edge of porphyrin may have in facilitating the protonation and reductive cleavage of Co–O_2–Co.

Acknowledgment. We thank Professor Fred Anson for discussion. This work was supported by NSF. C.K.C. is an Alfred P. Sloan Fellow, 1980–1984, and a recipient of the Camille and Henry Dreyfus Teacher-Scholar Award.

---

(13) X-ray crystallographic studies have been carried out on a Ni–Ni anthryldiporphyrin and a Cu–Cu biphenylene diporphyrin. While the structures are in final refinements, it is unmistaken that the two porphyrins lay perfectly parallel to each other, with interring distances of roughly 4.6 and 3.7 Å, respectively (Reidel, T.; Fillers, J. A.; Tulinsky, A.; Chang, C. K., unpublished results).

(14) Chang, C. K.; Wang, C.-B. In "Electron Transport and Oxygen Utilization"; Ho, C., Eaton, W. A., Collman, J. P., Gibson, Q. H., Leigh, J. S., Margoliash, E., Moffat, K., Scheidt, W. R., Eds.; Elsevier: Amsterdam, 1982; p 237.

(15) For a general discussion, see: Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 44–50 and references therein.

Low-Temperature Synthesis of Plutonium Hexafluoride Using Dioxygen Difluoride

J. G. Malm, P. G. Eller,* and L. B. Asprey

Los Alamos National Laboratory, University of California
Los Alamos, New Mexico 87545

Received January 9, 1984

We report the unprecedented low-temperature synthesis of plutonium hexafluoride by the action of dioxygen difluoride (O_2F_2) on plutonium fluorides, oxides, and oxyfluorides at room temperature and below. This development has technological significance because direct synthesis of PuF_6 has only been achieved previously by high-temperature fluorination[1] (typically >300 °C, at which temperature PuF_6 decomposition is extremely rapid) and by microwave or photolytic generation of fluorine atoms (a low-efficiency process).[2] The potency of O_2F_2 is illustrated by the following experiments:

(1) A sample of plutonium hexafluoride was photolyzed in a quartz U-tube using a 450W Hg lamp to form plutonium tetrafluoride (98 mg, 0.31 mmol). O_2F_2 (3.7 mmol) was condensed

---

(1) Cleveland, J. M. "The Chemistry of Plutonium"; Gordon and Breach Science Publishers, London, 1970; p 339 FF.

(2) Unpublished results, INC, CHM, and MST Divisions, Los Alamos National Laboratory: Trevorrow, L. E.; Gerding, T. J.; Steindler, M. J. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 837.

0002-7863/84/1506-2726$01.50/0 © 1984 American Chemical Society

into the tube and allowed to warm to room temperature. The condensable gaseous products were collected after a few minutes and found to contain 99 mg of PuF_6 (90% yield) as the only infrared-detectable product. All visible amounts of PuF_4 in the reaction flask had disappeared. (O_2F_2 is readily prepared by UV irradiation of an equimolar mixture of oxygen and fluorine at liquid nitrogen temperature.)[3]

(2) A small amount of water was placed in a quartz U-tube and allowed to stand for 30 min to saturate the glass surface. The excess water was pumped off. Plutonium hexafluoride (0.26 mmol) was condensed in the U-tube and was completely converted to PuO_2F_2 during the course of 3 h. O_2F_2 (3.5 mmol) was condensed in and the tube was allowed to warm to 25 °C. We recovered 0.044 mmol of PuF_6 (17% of starting material). The reaction with O_2F_2 was repeated, and additional PuF_6 (12%) was recovered.

(3) In a prefluorinated Monel metal U-tube, 0.850 mmol of PuF_6 was decomposed to PuF_4 by heating at 250 °C for 16 h. Only 0.020 mmol of PuF_6 remained; this was pumped away and the U-tube was pumped to a good vacuum. O_2F_2 (5.5 mmol) was condensed in the U-tube and then warmed to room temperature. About 0.062 mmol of PuF_6 (7% yield) was recovered. In a second experiment, O_2F_2 gas was passed through the U-tube at 25 °C for 15 min. An additional 0.074 mmol (8%) of PuF_6 was collected.

The low yields observed in (2) and (3) above reflect the slower reaction rates observed as one proceeds from the very finely divided reactive photoproduct, PuF_4, to the less reactive solid forms such as PuO_2F_2 and the highly crystalline PuF_4 obtained by thermal decomposition of PuF_6. In general, with O_2F_2 higher reaction yields can be obtained by *lowering* the reaction temperature, which gives longer contact time with the decomposing O_2F_2. In experiments (2) and (3) above, we did not attempt to optimize the PuF_6 yield.

(4) A 10-mg sample of PuO_2 (previously fired at 450–500 °C) was treated at room temperature with a stream of O_2F_2 gas for about 30 min (total gas pressure at the sample was maintained $\leq$10 torr). Analysis of the residue in the reaction tube showed that only 15% of the original plutonium remained unvolatilized.

(5) A 54-mg sample of highly impure incinerator ash containing 39 wt % Pu was treated with an O_2F_2 gas stream for about 1 h at room temperature, with modest Pu volatilization. However, when a second ash sample was given ClF_3 pretreatment followed by exposure to an HF/O_2F_2 solution at −78 °C for about 40 min, only 31% of the plutonium remained in the residue after removal of volatiles. Also of significance is the fact that the unvolatilized plutonium had been rendered readily soluble in 8 M nitric acid.

(6) We have repeatedly observed complete Pu removal from contaminated metal surfaces after treatment with O_2F_2 gas.

These experiments strongly suggest the feasibility of O_2F_2 utilization in the recovery of Pu from refractory and highly impure oxides and its usefulness in Pu decontamination of difficult-to-access surfaces. *No other known chemical* is capable of PuF_6 generation at temperatures even approaching the low temperatures used here. The potency of O_2F_2 as an oxidative fluorinating agent allows reaction at low temperature and thus avoids many of the problems associated with the fluoride volatility process for plutonium recovery from oxide fuels. Also, despite its short lifetime at ambient temperature, O_2F_2 can be delivered effectively to relatively remote locations[4] and thus has important applications for plutonium decontamination. It has been suggested that the great potency of O_2F_2 is attributable to its rapid thermal decomposition to fluorine atoms.[5] Our results are consistent with this hypothesis.

The reagent O_2F_2 has obvious potential for many applications in the nuclear industry. This reagent also has shown great potential for low-temperature synthesis of other difficulty prepared high-valent fluorides. These results will be the subject of forthcoming papers.[6]

Acknowledgment. We thank W. Carnall of Argonne National Laboratory for the use of facilities of the Heavy Element Group during the initial portion of these studies. We gratefully acknowledge many valuable discussions throughout the course of this work with B. I. Swanson and especially with R. A. Penneman who initiated this work.

Registry No. PuF_6, 13693-06-6; O_2F_2, 7783-44-0; PuF_4, 13709-56-3; PuO_2, 12059-95-9; Pu, 7440-07-5; PuO_2F_2, 13778-20-6.

---

(3) Smalc, A.; Lutar, K.; Slivnik, J. *J. Fluorine Chem.* **1975**, *6*, 287.
(4) Streng, A. G. *Chem. Rev.* **1963**, *63*, 607.
(5) Solomon, I. J.; Kacmarek, A. J.; Raney, J. *Inorg. Chem.* **1968**, *7*, 1221.
(6) Eller, P. G.; Asprey, L. B., manuscripts in preparation.

Subnanosecond Transients in the Spectra of Cobalt(III) Amine Complexes

Cooper H. Langford,* Aramice Y. S. Malkhasian, and
Devendra K. Sharma

Department of Chemistry and
Canadian Centre for Picosecond Flash Photolysis
Concordia University
Montreal, Quebec, Canada H3G 1M8

Received December 8, 1983

We have recently described wavelength dependence of photosubstitution yield for Co(III) amines over the envelope of the lowest spin allowed ligand field band.[1] Unfortunately, no explicit information on excited-state lifetimes has been available against which to test hypotheses concerning very fast processes. This circumstance stands in contrast to that for the analogous low-spin d^6 complexes of Rh(III) or hexacyanocobaltate(III) where weak emission with lifetime in the range 10–40 ns has been described.[2] The emitting state has been assigned as the lowest LF triplet. It would appear that the corresponding lifetime in Co(III) complexes may be too short. We have now sought evidence for excited-state lifetimes in Co(III) amines by means of transient-excited-state absorption following excitation with the 355-nm third-harmonic pulse of a Nd/YAG mode locked laser system where the pulse width is 30 ps.[3] This system uses two amplifiers to deliver a pulse energy of 2.5 mJ and has a continuum probe pulse in the range 400–650 nm.

Complexes examined were $Co(NH_3)_5Cl^{2+}$, *cis*- and *trans*-$Co(en)_2Cl_2^+$, *trans*-$Co(en)_2(NO_2)_2^+$, and *cis*-$Co(en)_2NCSCl^+$. In all these cases, 355-nm excitation initially populates a ligand to metal charge-transfer state. In no case was transient-ground-state bleaching observable, presumably because absorbance changes for weak LF bands are too small. In the three chloroamine complexes with only ligand π to metal charge transfer possible, no excited-state absorption was found in the visible. However, for both of the complexes containing ligands with π^* acceptor orbitals, transient absorption was found in the visible in the subnanosecond time domain.

Curve A of Figure 1 shows the excited-state absorption spectrum of the trans dinitro compound at a probe pulse delay of 44 ps. The curve is the average of 10 records with a standard deviation of <0.02 absorbance units. Curves B, C, and D show the spectrum of the cis isothicyanato complex at three delay times ($\sigma = \pm 0.01$ Å). In this second case, there is clear evidence for an initial excited-state absorbance in the near-UV which appears with the pulse and rapidly decays in favor of a lower energy band centered near 605 nm and decaying with a lifetime of 40 ± 20 ps. In the spectrum of the dinitro complex, the evidence for a preliminary transient is less well defined but there is again a longer lived transient in the visible with a lifetime of 150 ± 30 ps.

---

(1) Langford, C. H.; Malkhasian, A. Y. S. *J. Chem. Soc., Chem. Commun.* **1982**, 1210.
(2) Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61.
(3) Serpone, N.; Sharma, D. K.; Langford, C. H., unpublished results.