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]

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**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.

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

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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 $\pi$ to metal charge transfer possible, no excited-state absorption was found in the visible. However, for both of the complexes containing ligands with $\pi^*$ 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.

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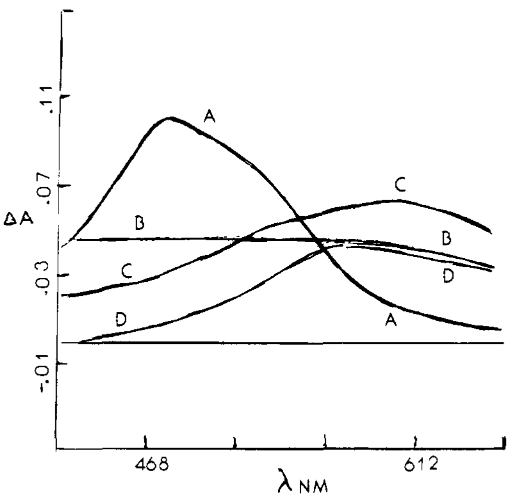

**Figure 1.** Curve A, the transient spectrum of *trans*-Co(en)($NO_2$) at a pulse delay of 44 ps. Curves B, C, and D, transient spectra of *cis*-Co-(en)NCSCl at 0-, 20-, and 50-ps probe pulse delays, respectively. Note that in the 420–550-nm region the transient appears with the pulse (0 delay) and decays monotonically. In contrast, the 0- and 50-ps curves are nearly coincident in the 550–650 region, but the intermediate-time 20-ps curve shows higher absorbance. Curves represent smoothed average of 10 records. Standard deviation is 0.01 A with a shape following the average curve.

Two possibilities susceptible of interpretation suggest themselves as assignments for the visible transients: (1) a transition from the halogen or pseudo-halogen formed by homolytic fission of the Co–X bond to the Co(II) species produced by the same fission event or (2) a transition from the lowest ligand field triplet ($^3T_{2g}$ in $O_h$ symmetry and analogous to the nanosecond emitting state in Rh(III)) to a ligand based acceptor orbital ($\pi^*$).

The assignment based on homolytic fission offers no reason for the apparent requirement for a nitro or –NCS ligand with a low-lying acceptor orbital. Furthermore, the optical electronegativity of Co(III) is given[4] as 1.6–1.9, whereas the lower subshell of Co(II) is given as 1.9. There is no clear basis for predicting a large red shift of ligand to metal charge transfer on homolytic fission. The other assignment may be more attractive.

The assignment, ligand field triplet to ligand $\pi^*$ is the one most consistent with discussions of Rh(III) and $Co(CN)_6^{3-}$ luminescence. It also provides a rationale for the apparent requirement for ligands like $-NO_2$ and –NCS. It can be evaluated energetically by using standard LF parameters[5] and vibronic relaxation estimates derived from Rh(III) Stokes shift data.[2] Using $O_h$ symmetry labels, the $^3T_{2g}$ LF triplet states are estimated to lie, after relaxation, between 4.00 and 10 kK below the $^1T_{2g}$ absorption positions. Spectral assignments of Yamasaki et al.[6] place the first LF singlet at 23.4 kK for the dinitro complex and at 19.9 kK for the isothiocyanato. (This difference of 3.5 kK compares to the difference of 3.7 for the transients!) The relaxed triplet of the dinitro complex should lie between 13.5 and 19.5 kK. We take 16.5 as a "trial" value. On this basis, the 488-nm transient corresponds to excitation to a state at 37 kK above the ground state. In ground-state spectra,[6] a band that is unique to nitro, –NCS, and $-N_3$ complexes among Co(III) amines appears near 40 kK in the *trans*-$Co(en)_2(NO_2)_2^+$ case. This band may identify the ligand $\pi^*$ level. If so, the LF triplet to ligand $\pi^*$ assignment for the transient is possible.

Following the kinetic analysis developed by Ford for the Rh(III) amines,[2] we find that a lifetime that is 100 times shorter than the 10–40 ns characteristic of Rh(III) can account for the difference in substitution quantum yields between Rh(III) and Co(III) amines. If triplet formation yields and rate constants for the reactive pathway were chosen very close to values for the Rh(III) amines, the shorter triplet lifetime would account for the overall reduction in quantum yield.

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## Photohydration via Intramolecular Proton Transfer to Carbon in Electronically Excited States

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We wish to report that (*o*-hydroxyphenyl)acetylene (**1**) and *o*-hydroxystyrene (**2**) photohydrate cleanly and efficiently in both neutral aqueous and dilute acid solution, to give *o*-hydroxyacetophenone and 1-(*o*-hydroxphenyl)ethanol, respectively.[1] We believe these to be the first clear[2] examples of excited-state intramolecular proton transfer leading to irreversible[3] photochemical reaction. Quantum yield dependence[5] on pH has been measured for these two substrates, as well as for the corresponding *o*-methoxy derivatives, which also photohydrate but show quite different dependence on acidity.

The acid-catalyzed photohydrations of substituted phenylacetylenes,[6] styrenes,[6] and related compounds[7] opened up the possibility that such processes could be catalyzed by intramolecular proton transfer in the excited state. Although intramolecular proton transfer in electronically excited aromatic systems has been a well-studied phenomenon[4,8] since the classic work of Weller[9] on salicylic acid derivatives, this has dealt almost exclusively with proton transfers between heteroatoms, and emphasis has been on possible equilibria involved and the importance of proton transfer as a mechanism for electronic deactivation of excited states.[10]

The quantum yield dependence on pH is shown in Figure 1a for the reaction of **1** (irradiated at 300 nm), with that of several other substituted phenylacetylenes for comparison. The *o*-hydroxy derivative attains its maximum quantum yield[11] for product

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(1) Products were identified by comparison of their UV, IR, and NMR spectra with those of authentic samples.

(2) Ferris and Antonucci (Ferris, J. P.; Antonucci, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 2010) have investigated the photochemical reactions of **1** in acetonitrile and in neutral and basic aqueous solution. The major product observed in all cases was 2,3-benzofuran, and only in 0.01 M $OH^-$ was any 2-hydroxyacetophenone found, as a minor product. However, they irradiated (Rayonet reactor) at 254 nm for up to 13 h, whereas in the present work irradiations (Rayonet reactor) were carried out at 300 nm for only 20–40 min. Only traces of 2,3-benzofuran were found under the latter conditions, and it may be that under Ferris and Antonucci's reaction conditions this is a secondary photochemical product. It is doubtful whether the formation of 2,3-benzofuran, even as a primary photochemical product, would meet Wubbels' (Wubbels, G. *Acc. Chem. Res.* **1983**, *16*, 285) definition of an acid-catalyzed photochemical reaction.

(3) Photochromism[4] caused by intramolecular proton transfer is excluded, since such color changes are easily reversible, thermally or photochemically.

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(5) Reactions of **1–4** were followed by changes in UV absorption, which showed sharp isosbestic points in every case, indicating that there are only two interconvertible absorbing species present, reactant and product. Reactions were followed to at least 50% completion, except for **1** and **2** above pH 7 where the photoreactions are inefficient.

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(10) Many substances capable of intramolecular proton transfer in the first singlet excited state are used as photochemical stabilizers.[4]

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