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Outer-Sphere Charge-Transfer Photochemistry of Ruthenium(III) Complexes: Flash Photolysis of $Ru(NH_3)_5py^{3+}$/Halide Ion Pairs

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The $Ru(NH_3)_5py^{3+}$ complex in solution with various salts forms ion pairs characterized by outer-sphere ligand to metal charge-transfer (OSLMCT) absorptions. The photochemistries of these ion pairs with the halide ions Cl^-, Br^-, and I^- have been examined by using continuous and flash photolysis techniques. Continuous photolysis at wavelengths corresponding to the OSLMCT bands leads to low-yield photosubstitution of Ru(III) ligands as the only observable photoreaction. Quantum yields for photosubstitution were unaffected by added Cl^- or Br^- but were higher with I^- added. Under flash photolysis conditions, transient absorbance changes were observed for added Br^- or I^- consistent with the formation of photoredox products that decay back to starting species. When I^- is present, the transients (believed to be $Ru(NH_3)_5py^{2+}$ and I_3^-) were sufficiently long-lived to be observable by conventional microsecond flash photolysis; however, nanosecond laser flash techniques were necessary to observe Ru(II) transients from the Br^- ion pairs. No transient was observed by either technique for Cl^- ion pairs. These results are interpreted in terms of the possible reactivities of photoredox intermediates resulting from the OSLMCT transitions.

Introduction

Some years ago Beattie[2] demonstrated that the ruthenium(III) amine species $Ru(en)_3^{3+}$ (en = ethylenediamine) forms outer-sphere complexes with iodide in aqueous solution characterized by an outer-sphere ligand to metal charge-transfer (OSLMCT) absorption hand in the near-ultraviolet region. Later these observations were extended to $Ru(NH_3)_6^{3+}$ ion pairs with halides in a quantitative study by Navon.[3] Similar phenomena have long been noted in this laboratory for pentaammineruthenium(III) complexes of substituted pyridines $Ru(NH_3)_5(py\text{-}X)^{3+}$. Given the intensive activity in the study of thermal-redox and photoredox reactions of ruthenium(II) and -(III) complexes and especially the recent interest in the spectral and the photochemical properties of outer-sphere complexes, where both the cation and anion are metal complexes,[4-7] it is of interest to examine the photoreactivities of these "simpler" ion pairs. Reported here are the results of both continuous (CW) and flash photolysis studies of the $Ru(NH_3)_5py^{3+}$ ion in the presence and absence of added halide ion.

Experimental Section

Materials. The recrystallized $[Ru(NH_3)_5py](BF_4)_2$ and $[Ru(NH_3)_5py]_2(S_2O_6)_3$ salts were prepared from $[Ru(NH_3)_5Cl]Cl_2$ according to published procedures.[8,9] Photolysis solutions were prepared from redistilled water with $HClO_4$ used to adjust pH and were deaerated with chromous-scrubbed argon. Reagent grade NaCl, NaBr, and NaI were used as supplied. The photolysis solutions containing iodide were prepared by addition of NaI to a previously deaerated solution with the desired $Ru(NH_3)_5py^{3+}$ concentration. This solution was again deaerated. The I_3^- solutions used in the stopped-flow experiments were prepared by saturating an acidic solution of NaI with oxygen and leaving the solution in room light. The I_3^- concentration was determined spectroscopically. The solution was then deaerated with purified argon.

CW Photolysis Procedures. Solutions for photolysis and dark reactions were prepared and deaerated with purified argon in a Zwickel flask and transferred to the 2.0-cm path length quartz photolysis cells (V = 6.0 mL) in an all-glass apparatus. Samples were irradiated at 313, 334, 366, and 405 nm by using apparatus and procedures described previously.[10] Photolysis and thermally induced spectral changes were monitored by the periodic recording of the electronic spectra on a Cary 118C spectrophotometer. Dark reactions monitored under conditions identical with those of the photolysis experiments display no spectral changes. Ligand substitution quantum yields were determined via ion-exchange techniques similar to those described previously.[11] After photolysis, a 5.0-mL sample of the photolyzed solution was eluted on a Dowex 50W-X4 (200–400 mesh), Na^+-form, cation-exchange column. The reaction species were separated by an increasing ionic strength gradient of pH 2 NaCl solution eluent. Under these conditions, any aquoruthenium(III) complexes (e.g. $Ru(NH_3)_5H_2O^{3+}$) reacted with the Cl^- in solution to give the analogous chloro species (e.g. $Ru(NH_3)_5Cl^{2+}$). Therefore, the ion-exchange method easily separated the lower charged NH_3 or py labilized products from the tripositive starting material. The electronic absorption spectra of elution aliquots collected quantitatively were recorded on a Cary 118C spectrophotometer. Pyridine aquation quantum yields were calculated from the total pyridinium eluted as determined spectrally in these aliquots. The extent of NH_3 photoaquation was determined from the amounts of *cis*- and *trans*-$Ru(NH_3)_4pyX^{2+}$ (where X = Cl, Br, I, depending on the halide added) found in the product solutions as described before. Quantum yields determined in these manners had fairly large uncertainties (±~15% unless noted otherwise).

Conventional Flash Photolysis Procedures. Flash photolyses of solutions containing iodide were performed on a conventional kinetic flash photolysis apparatus described previously.[12] The sample cell was a concentric jacketed quartz cell 1 cm in diameter and 12 cm in length. A DMF cutoff filter solution was placed in an outer jacket to cut out light with wavelengths less than 270 nm. Halide solutions were between 1.0 and 0.1 M in NaX. The $Ru(NH_3)_5py^{3+}$ concentrations were approximately 10^{-4} M.

Laser Flash Photolysis Procedures. Laser flash photolysis was performed with a Quanta Ray DCR-1 Nd (YAG) laser or a PDL-1 pumped dye laser as an excitation source. A Varian 150-W Xe lamp was employed as a probe source. A 7-ns laser pulse was focused to a horizontal line on a 1-cm fluorescence sample cell by using a cylindrical focusing lens. The probe lamp was located at the far end of an optical bench orientated perpendicular to the direction of the laser pump beam. The probe beam was directed along the optical

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(1) (a) Reported in part at the 15th Western Regional Meeting of the American Chemical Society, Pasadena, CA, Oct 1979; taken in part from the Ph.D. dissertation of D.A.S., UCSB, 1982. (b) NSFURP student, Summer 1975.

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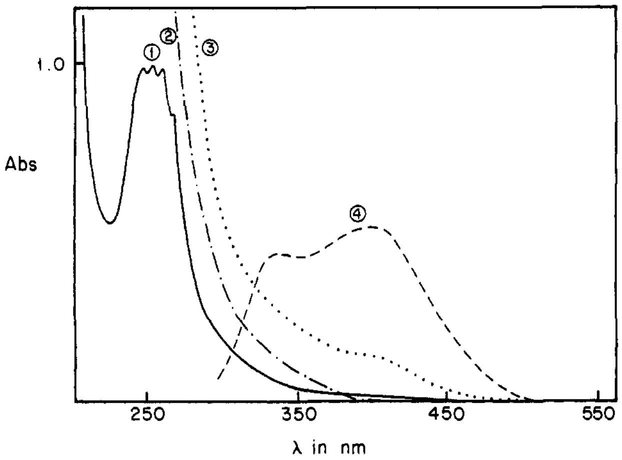

Figure 1. Spectra of aqueous $Ru(NH_3)_5py^{3+}$ in the presence and absence of iodide: (1) $[Ru(NH_3)_5py]_2(S_2O_6)_3$ (2.2×10^{-4} M) aqueous solution, pH 3; (2) 1.0 M NaI in pH 3 aqueous solution; (3) $[Ru(NH_3)_5py]_2(S_2O_6)_3$ (2.2×10^{-4} M) in 1.0 M NaI solution; (4) difference (vertical scale expanded ×5) of spectrum 3 minus spectrum 2 plus spectrum 1.

bench through a 10-cm water infrared filter, collimating lens, focusing lens, and variable horizontal slit, resulting in a plane of probe light passing through the sample cell. The probe light analyzed only that part of the solution that had been irradiated by the plane of laser light. The analyzing light was then collected and focused onto the slit of a $^1/_4$-m Jarell-Ash monochromator. Changes in probe light intensity with time were monitored with an EMI 9816A fast-response photomultiplier using a Tektronix 7904 oscilliscope as the recorder.

Spectral Measurements. UV–visible spectra were recorded at 25 °C on a Cary 118 spectrophotometer equipped with a thermostated cell compartment. Difference spectra were obtained as follows: A 2-cm path length cylindrical quartz cell containing a solution with particular concentrations of the Ru(III) complex and of halide was placed in the sample compartment. A matched tandem cell (consisting of two 1-cm path length cylindrical cuvettes fused together) with one compartment containing a solution of the Ru(III) complex and the other containing a solution of the halide, each solution at concentrations exactly double those in the sample solution, was placed in the reference compartment. The spectrum thus obtained indicated the spectral differences resulting from interaction between the Ru(II) complex and the halide in the sample solution.

Results and Discussion

Spectra. When the colorless acidic aqueous solutions of $[Ru(NH_3)_5py]_2(S_2O_6)_3$ and NaI were combined, the resulting brownish yellow solution displayed absorption in the near-UV region not seen in spectra of solutions containing only Ru(III) or I^-. Difference spectra (Figure 1) demonstrated the presence of bands at 350 and 410 nm, which are apparently the result of ion-pair formation as seen previously for other Ru(III) complexes. Difference spectra of $Ru(NH_3)_5py^{3+}$ solutions containing added Cl^-, Br^-, SCN^-, or $C_2O_4^{2-}$ (oxalate) display similar bands (Table I). It is noteworthy that the energies of these broad bands follows a qualitative inverse relationship to the ease of oxidizing the anions. A similar relationship to anion electronegativities is seen (Table I). Accordingly, these bands are assigned as outer-sphere ligand to metal charge-transfer (OSLMCT) absorptions of the $Ru(NH_3)_5py^{3+}/X^{n-}$ ion pairs, in agreement with similar assignments for the hexaammine- and tris(ethylenediamine)ruthenium(III) complexes.[2,3] The energies of the absorption maxima of the ion pairs of $Ru(NH_3)_5py^{3+}$ with the same halide are lower than for the analogous ion pair of $Ru(NH_3)_6^{3+}$. This effect parallels the larger reduction potential for the former in water (0.30 V) than for the hexaammine (0.05 V),[13] consistent with assignment of the transition as OSLMCT. Ion-pairing constants with $Ru(NH_3)_5py^{3+}$ were not determined; however, K_{ip} values with the halide ions were assumed to be comparable to the 10–15 M^{-1} (25 °C, zero ionic strength) values estimated for ion pairing of $Ru(NH_3)_6^{3+}$ with X^- (X = Cl, Br, I).[3]

Table I. Absorption Maxima of the OSLMCT Bands Observed by Difference-Spectra Techniques for Ruthenium(III) Pentaammine Complexes $Ru(NH_3)_5L^{3+}$ in Aqueous Solution

added	λ_{max}, nm					
anion[a]	L = py	L = NH_3[b]	L = CH_3CN	$E°$,[c] V	$E°$,[d] V	χ_{opt}[e]
Cl^-	312	294	318	1.358	2.60	3.0
Br^-	338	306	334	1.087	2.07	2.8
SCN^-	400			0.77		2.6
I^-	410 (1.0)[f] 350 (1.6)	402 (1.0)[f] 318 (1.0)	*g*	0.536	1.42	2.5
$C_2O_4^{2-}$	409		*g*	0.49		

[a] Sodium salt in each case. [b] Reference 3. [c] Standard reduction reduction potential for the process $^1/_2X_2 + e^- \rightarrow X^-$ in aqueous solution. [d] Standard reduction potential for the process $\dot{X} + H^+ + e^- \rightarrow HX$ in aqueous solution. [e] Optical electronegativity of anions X^- as reported by: Jϕrgensen, C. K. "Modern Aspects of Ligand Field Theory"; American Elsevier: New York, 1971; pp 362–3. [f] Relative peak heights are shown in parentheses. The splitting of the charge-transfer bands involving iodide can be attributed to the formation of I· in both the $^2P_{3/2}$ and $^2P_{1/2}$ states upon OSLMCT. [g] Thermal-redox reaction.

Continuous Photolysis. The continuous photolysis (CW) experiments were carried out in deoxygenated acidic aqueous solution (10^{-4} M $HClO_4$). In the absence of added salts, photolysis of $Ru(NH_3)_5py^{3+}$ solutions led to minor spectral changes. After long-term photolysis, these solutions were analyzed by chromatography to give products attributed to the photolabilization of NH_3 or pyridine:

$$\begin{aligned} Ru(NH_3)_5py^{3+} &\xrightarrow[H_2O]{h\nu} Ru(NH_3)_5(H_2O)^{3+} + py \\ &\text{or} \xrightarrow[H_2O]{h\nu} Ru(NH_3)_4(H_2O)py^{3+} + NH_3 \end{aligned} \qquad (1)$$

For 313-nm photolysis, quantum yields for pyridine (ϕ_{py}) and ammonia (ϕ_{NH_3}) labilization were respectively 0.008 (2) and 0.012 (4) mol/einstein. These values are about the same magnitude as reported earlier for the acidic aqueous solution photolysis of $Ru(NH_3)_6^{3+}$ at similar wavelengths.[13] Although the photochemistry of ruthenium(III) amine complexes has not been subjected to a thorough analysis, it appears likely that these photolabilizations reflect the reactivities of ligand field (LF) excited states (es) having the $(t_{2g})^4(e_g)^1$ configuration. Overall the quantum yields are somewhat smaller than seen for the analogous d^6 ruthenium(II) complex, for which the photochemistry has been attributed largely to reactions of the lowest energy LF state.[11,14].

Photolysis of $Ru(NH_3)_5py^{3+}$ in the presence of added halide led to much larger spectral changes owing to the formation of Ru(III) inner-sphere halide complexes, which display strong ligand to metal charge-transfer (LMCT) band in their absorption spectra. The photolabilization quantum yields for 313-nm irradiation in 1 m NaCl and for 334- and 405-nm irradiations in 1 M NaBr solutions were indistinguishable from those measured in the absence of halide but at the same pH. In contrast, photolysis of this complex in 1 M NaI solution at a wavelength (405 nm) corresponding to the λ_{max} of the OSLMCT band gave significantly larger values for both ϕ_{py} (0.012) and ϕ_{NH_3} (0.025).[15] Thus, iodide enhances the 405-nm photosubstitution chemistry, both by dramatically increasing

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the absorptivity of the solutions at this wavelength and by giving a larger quantum yield for reaction.

Photolysis of the $Ru(NH_3)_5py^{3+}/C_2O_4^{2-}$ ion pair ($\lambda_{irr} = 405$ nm) led to far more dramatic consequences, i.e. the reduction of Ru(III) to the Ru(II) complex $Ru(NH_3)_5py^{2+}$ with a large quantum yield (0.35 mol/eistein). Although such photoreactivity may indeed be reflective of the OSLMCT es (see below), it is worth the cautionary note that even the LF es should also be an oxidant capable of undergoing electron transfer to a strong, irreversible reductant such as $C_2O_4^{2-}$ present in the second coordination sphere.[16] Net photoreduction of $Ru(NH_3)_5py^{3+}$ to $Ru(NH_3)_5py^{2+}$ with a small quantum yield (0.0035) was also found for 313-nm photolysis of the Ru(III) complex in 1 M aqueous NaCl solution when 2-propanol (1 M) was added. Given the absence of photoreduction when the alcohol was not present, we interpret this result as indicating the irreversible trapping by alcohol of the OSLMCT excited state or some oxidizing intermediate derived from this state.

Flash Photolysis. Flash photolysis experiments were performed using both microsecond "conventional" xenon lamp and pulse laser excitation. The two systems gave different kinetic results, which can be attributed to the different spectral and temporal properties of the excitation sources and photoactive nature of the reactants and chemical transients produced upon excitation.

Flash photolysis ($\lambda_{irr} > 270$ nm) of $Ru(NH_3)_5py^{3+}$ in aqueous 10^{-4} M $HClO_4$ or 1.0 M NaCl or NaBr solution did not lead to the formation of transients within the time frame accessible with the xenon lamp flash apparatus (>30 μs). In contrast, flash photolysis in 1.0 M NaI solution led to the following spectral changes: A strong transient absorbance with a λ_{max} ~400 nm is generated within the flash duration, and there is additional growth on a millisecond time scale in this absorbance subsequent to the flash. The transient absorbance decays on a longer time scale (seconds); however, there is a net optical density increase in the 600-nm region consistent with the formation of some inner-sphere iodoruthenium(III) products.

The initial increase in absorbance subsequent to the flash follows first-order kinetics with a markedly pH-dependent rate constant ($k = 60 + 6.2[H^+]^{-1}$). The strongly absorbing transient is indicative of the formation of the Ru(II) ion $Ru(NH_3)_5py^{2+}$ ($\lambda_{max} = 407$ nm, $\epsilon = 7800$ M^{-1} cm^{-1} in H_2O). Furthermore, the dynamic absorbance increases immediately subsequent to the flash correspond closely to those seen upon the flash photolysis of this Ru(II) complex in dilute aqueous solution. Thus we conclude that flash irradiation of the $Ru(NH_3)_5py^{3+}/I^-$ ion pair leads initially to the formation of $Ru(NH_3)_5py^{2+}$, which is subject to secondary photolysis in the duration of the flash to give the short-lived bleached transient observed earlier and proposed to be a π-bonded pyridine complex of Ru(II)[12] (eq 2, 3). The pyridine of this intermediate is oriented in a manner that permits the nitrogen lone pair to be reversibly protonated, thus accounting for the pH dependence of k_3. The much slower decay of the 400-nm transient absorbance can be attributed to the reoxidation of Ru(II) to Ru(III) by I_3^- (see below).

$$Ru(NH_3)_5py^{2+} \xrightarrow{h\nu} Ru(NH_3)_5(\pi\text{-}py)^{2+} \qquad (2)$$

$$Ru(NH_3)_5(\pi\text{-}py)^{2+} \xrightarrow{k_3} Ru(NH_3)_5py^{2+} \qquad (3)$$

A very different pattern is observed when the flash excitation of the $Ru(NH_3)_5py^{3+}/I^-$ solutions is initiated by using the laser flash photolysis system. Transient absorption at 400 nm was the immediate result of the laser pulse (70 mJ, 15-ns duration at 355 nm), but the subsequent further increase in absorption on the millisecond time scale was not seen. The laser pulse is apparently short enough to diminish the significance of secondary photoreactions of the initially formed transients. The slower decay of these transients back to starting reactants was observed as before.

The relatively slow decay of the transient absorbances (λ_{max} ~ 400 nm) generated by the flash photolysis of the $Ru(III)/I^-$ solutions follows second-order kinetics when studied on either the conventional or laser flash photolysis apparatus. In the present configurations, the apparatus employ high-intensity CW probe lamps, which can also generate modest photochemistry and more importantly can photocatalyze the slow decay, attributed to the reoxidation of $Ru(NH_3)_5py^{2+}$ by I_3^- (see below). Use of a 401-nm interference filter to attenuate the probe lamp intensity and to limit the wave-lengths of the analyzing beam gave reproducible data that, when plotted as $(A - A_\infty)^{-1}$ vs. t, gave linear second-order rates of 4×10^4 M^{-1} s^{-1}. However, nonreproducible decay rates up to an order of magnitude faster were noted when the filter was removed.

The key observations from these experiments are that flash photolysis of the iodide ion pair generates a transient absorbance with a maximum at about 400 nm, consistent with the formation of the ruthenium(II) pyridine complex, and that this absorption decays by an apparently second-order pathway. Although photocatalysis cannot be confidently excluded as a contributor to the decay kinetics, a maximum rate constant of 4×10^4 M^{-1} s^{-1} can be assigned to this relaxation process under the reaction conditions.

Laser flash photolysis at 355 nm of a solution of $Ru(NH_3)_5py^{3+}$ in 1 M NaBr also produced a transient absorption with a λ_{max} at ~400 nm. However, in this case the absorption disappeared within 30 μs via second-order kinetics ($k_{obsd} \cong 5 \times 10^{10}$ M^{-1} s^{-1}). In contrast, a solution of the complex in 1 M NaCl produced no detectable transient upon flash photolysis with a 40-mJ, 309-nm laser pulse.

For the laser flash photolysis experiment ($\lambda_{irr} = 355$ nm) with the $Ru(NH_3)_5py^{3+}/1$ M I^- solutions an attempt was made to estimate the photoredox quantum yield of Ru(II) formation. This required evaluating the energy of the laser pulse by measuring the laser power with a Scientech power meter, estimating the volume of the solution actually subjected to the excitation pulse, and determining the Ru(II) concentration from the absorbance changes immediately subsequent to the pulse. From these data, a lower limit for this quantum yield was estimated as 0.02 mol/einstein of light absorbed.

The transients generated by laser flash photolysis of the $Ru(III)/I^-$ ion-pair solutions can be rationalized in terms of reactions 4–8. Given that the observed photochemistry is the result of OSLMCT excitation, it is assumed that A is a species such as $Ru(NH_3)_5py^{2+}/I\cdot$ produced upon relaxation of the initially formed OSLMCT state. However, as noted earlier, such redox intermediates could be formed from a LF state of the metal center generated in the field of a reductant such as I^-. The I_3^- ion can be produced either by reaction of I^- with A or by dissociation of A to give $I\cdot$, which then reacts with

$$Ru(NH_3)_5py^{3+}/I^- \underset{k_{-4}}{\overset{h\nu}{\rightleftharpoons}} A \qquad (4)$$

$$A + I^- \rightarrow Ru(NH_3)_5py^{2+} + I_2^- \qquad (5)$$

$$2I_2^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} I^- + I_3^- \qquad (6)$$

$$Ru(NH_3)_5py^{2+} + I_3^- \xrightarrow{k_7} Ru(NH_3)_5py^{3+} + I^- + I_2^- \qquad (7)$$

$$Ru(NH_3)_5py^{2+} + I_2^- \xrightarrow{k_8} Ru(NH_3)_5py^{3+} + 2I^- \qquad (8)$$

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I^-. Disproportionation of I_2^- (eq 6) occurs with a rate constant of 8×10^9 M^{-1} s^{-1}; thus, the metastable products of flash irradiation would be $Ru(NH_3)_5py^{2+}$ plus I_3^-. The slow second-order relaxation of these species apparently reflects the relatively small rate constant of eq 7. Preliminary stopped-flow experiments of this redox reaction confirmed the approximate rate of this reaction although, as in the case of the flash experiments, the relatively intense light source used in the stopped-flow spectrometer led to photocatalysis and precluded an accurate measurement of the rate constant. Such photocatalysis probably involves the light-driven reverse of eq 6 since I_3^- absorbs at the monitoring wavelengths 400 nm. Preliminary pulse radiolysis experiments have demonstrated a second-order rate constant of 2.3×10^9 M^{-1} s^{-1} for eq 8.[17]

The strongly absorbing transients observed in the laser flash photolysis of the Ru(III)/Br^- solutions very likely are the result of the formation of Ru(II) plus Br_2^-. The very fast ($k_9 = 5 \times 10^{10}$ M^{-1} s^{-1}) relaxation of these solutions back to starting materials apparently reflects eq 9, which has a driving force

$$Ru(NH_3)_5py^{2+} + Br_2^- \xrightarrow{k} Ru(NH_3)_5py^{3+} + 2Br^- \quad (9)$$

even larger than that of eq 8. The failure to see any transients for the analogous laser flash photolysis with the $Ru(NH_3)_5py^{3+}/Cl^-$ solutions is the probable result of two factors. One would be the lower sensitivity of this experiment resulting from the necessity to use a less intense pulse of shorter wavelength; the second would be the even faster rates in this case for relaxation processes such as the analogues of k_{-4} and k_8.

In summary, the flash photolysis studies described here demonstrate that the principal photochemical result of OSLMCT excitation of the ion pairs $Ru(NH_3)_5py^{3+}/X^-$ (X = I or Br) is the formation of ruthenium(II) transients that relax to starting materials via second-order reactions with the resulting oxidized halogen species. If the counterion is an irreversible reductant (e.g. $C_2O_4^{2-}$), such photolysis can lead to substantial net photoreduction of the metal center under continuous photolysis. For the halides, CW photolysis of the OSLMCT absorptions leads only to modest photosubstitution of the Ru(III) coordination sphere with quantum yields comparable to those for $Ru(NH_3)_5py^{3+}$ in dilute perchlorate solutions. However, for X = I substantially higher ϕ_{NH_3} and ϕ_{py} values are noted, a result that suggests some special reactivity of the OSLMCT state in this case. In this context, we consider an attractive speculation to be that relaxation of species A via the k_{-4} pathway might occur in part via an "inner-sphere" reaction between the electrophile I· and the electron-rich $Ru(NH_3)_5py^{2+}$ ion, giving a seven-coordinate Ru(II) intermediate $[Ru(NH_3)_5(py)I]^{2+}$, which can relax to the normal six-coordinate state by loss of I^-, NH_3, or py.

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Registry No. $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5py^{2+}$, 21360-09-8; $Ru(NH_3)_5(H_2O)^{3+}$, 25590-52-7; $Ru(NH_3)_4(H_2O)py^{3+}$, 88034-44-0; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; $C_2O_4^{2-}$, 338-70-5; I_3^-, 14900-04-0.

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Intrazeolite Rhodium Carbonyl and Rhodium Carbonyl Phosphine Complexes

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Intrazeolite rhodium carbonyl complexes are readily synthesized by carbon monoxide reduction of rhodium(III)-exchanged zeolites. Although a variety of rhodium carbonyls can be formed within and on the zeolite, the dicarbonyl, $Rh(CO)_2^+$, is the best characterized and easiest to synthesize reproducibly. The reactions of this species with phosphines (P(2-cyanoethyl)$_3$, PPh_3, PMe_2Ph, and $Ph_2PCH_2PPh_2$) over a range of temperatures give insight into the location and mobility of $Rh(CO)_2^+$.

Rhodium-exchanged zeolites have received a great deal of attention in the literature.[1-12] These materials have been studied by infrared spectroscopy,[1-4,8-11] X-ray photoelectron spectroscopy,[5] solution- and gas-phase hydroformylation,[6,7] methanol and ethanol carbonylation,[8-11] and transmission electron microscopy.[12] Although it is difficult to compare independent studies directly owing to different sample preparation and handling techniques, the following general themes seem to be fairly well accepted.

(1) Reduction of Rh(III) to Rh(I) occurs readily at ambient temperatures under low pressures of CO in the presence of water.[3] The most likely process is

$$Rh(III) + CO + H_2O \rightarrow Rh(I) + CO_2 + 2H^+ \quad (1)$$

At very low temperatures, a Rh(III)–CO species has been observed.[3]

(2) The rhodium(I) species formed is usually postulated to be a dicarbonyl complex, $Rh(CO)_2^+$, with the anion not specified (perhaps a framework oxygen). It is speculated that the state of aggregation of rhodium varies from atomic dispersion to rhodium rafts.[11] By analogy to homogeneous systems, $[Rh(CO)_2X]_2$ and $Rh(CO)_2LX$ (L = ligand, X = anion) are likely possibilities. Infrared data for the intrazeolite $Rh(CO)_2^+$ complexes vary according to preparation, with two

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