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Ligand Field Photoaquation of *trans*-Dichlorotetrakis(amine)rhodium(III) Complexes[1]

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Photolysis at 410 nm of aqueous solutions of complexes of the type *trans*-$[RhA_4Cl_2]^+$, where A is a heterocyclic amine, gave both photoaquation of chloride and photoaquation of amine. The quantum yields for these two processes were found to depend strongly on the nature of the amine. The fraction of photoaquation that gave amine, $\phi_A/(\phi_A + \phi_{Cl})$, increased with increasing pK_b of the amine. The behavior of these complexes is in contrast to that observed for nonheterocyclic amine complexes of Rh(III), in which halide photoaquation is the predominant product. Both the photoaquation of halide and the photoaquation of amine occurred with stereoretention.

Introduction

Photochemical reactions of complexes of Rh(III) have received increasing attention in recent years.[3-17] Several approaches[18-21] have been used to predict the photolabilized ligand in d^6 six-coordinate complexes, and these agree well with most observations. Previous work from this laboratory[7] showed that of a variety of tetraamine complexes of Rh(III), only *trans*-$[Rh(py)_4X_2]^+$, (X = halide, py = pyridine) gave significant quantum yields for photoaquation of both amine and halide. The reaction predicted to be favored would be photoaquation of halide. Thus, it seemed of interest to study other amine complexes similar to *trans*-$[Rh(py)_4X_2]^+$ to see what factors determine whether amine or halide photoaquation is the major process.

Experimental Section

Physical Measurements. Absorption spectra in the visible–ultraviolet region were obtained with a Perkin-Elmer Model 202 or Model 200 spectrophotometer. Measurements of absorbance at selected wavelengths for determination of molar absorptivities were made with a Hitachi Perkin-Elmer 139 spectrophotometer. A Corning Model 12 pH meter was used for all potentiometric measurements.

Materials. Chemicals used were $RhCl_3 \cdot 3H_2O$ from PCR, Inc., or from Pfaltz and Bauer, Inc., 3-picoline (3pic) and 4-picoline (4pic) from Matheson Coleman and Bell, pyridine (py), 3-aminopyridine (3apy), 4-aminopyridine (4apy), and imidazole (im) from Aldrich Chemical Co., 3-chloropyridine (3cpy), 4-chloropyridine (4cpy), pyrazole (pzl), pyrazine (pzn), and *N*-methylimidazole (mim) from K & K Laboratories, and isoquinoline (iqn) and 3,5-lutidine (lut) from Eastman Co. The liquid amines, py, 3pic, 4pic, 3cpy, mim, lut, and iqn, were purified by distillation. For the solid amines, 3apy, 4apy, pzl, im, and pzn, the melting points were checked and recrystallization was deemed unnecessary. The hydrochloride salt of 4cpy was neutralized with dilute NaOH. Solvents were reagent grade thiophene-free benzene, glacial acetic acid, and water distilled from an all-glass still.

The complexes *trans*-$[RhA_4Cl_2]NO_3$, where A is the amine, were all prepared and purified by following methods from the literature[22,23] and characterized by their visible–UV spectra and elemental analyses. For A = py, 3pic, 4pic, pzl, and iqn, the method of Gillard and Wilkinson[22] was followed. For A = 3apy, 4apy, 3cpy, 4cpy, im, mim, lut, and pzn, the method of Addison[23] was used. Chloroaquo complexes of the type *trans*-$[RhA_4(H_2O)Cl](ClO_4)_2$ were prepared by the method of Addison.[23] Attempts to prepare complexes of the type *mer*-$[RhA_3(H_2O)Cl_2]^+$ from the very insoluble *mer*-$[RhA_3Cl_3]$ by refluxing with H_2O were not successful. A soluble product was eventually formed, but not enough could be obtained for purification and characterization.

The complexes *trans*-$[Rh(en)_2Cl_2]NO_3$,[24] *trans*-$[Rh(NH_3)_4Cl_2]NO_3$,[24] *mer*- and *fac*-$[RhA_3Cl_3]$[25] were prepared by methods reported in the literature. All elemental analyses for C, H, and N gave satisfactory agreement with the calculated values. Wavelengths corresponding to the absorption maxima and values of molar absorptivities agreed well with values in the literature.

Photolyses. A Bausch and Lomb mercury source (SP 200) and visible high-intensity grating monochromator were used. The exit slit of the monochromator was set at 3.00 mm to give an intensity suitable for the reactions. The sample, with a volume of 2.5 or 5.0 mL, was placed in a 1.00- or 2.00-cm Pyrex spectrophotometric cell. The cap of the cell was fitted with a septum so that N_2 could be bubbled through a syringe needle into the solution before photolysis. The intensity of the incident light was measured by means of the Reineckate[26] actinometer. The duration of photolysis of the samples was adjusted so that the maximum extent of reaction was 20%. At least three determinations were made for each complex. Little variation in quantum yield with variation in duration of photolysis was observed, so results were not extrapolated to zero time. Photolyses of all complexes were carried out at 410 ± 6 nm, which corresponds to the absorption maximum in the visible region for all the *trans*-$[RhA_4Cl_2]^+$ complexes. The temperature of the sample was 25 °C.

The concentration of chloride released during photolysis was measured with an Orion chloride electrode (94-17A) and an Orion double-junction reference electrode (90-02) and a Corning Model 12 pH meter. Standard halide solutions were used to prepare a calibration curve. The concentration of amine released during the photolysis was measured by a modification of the extraction and nonaqueous titration method of Fritz[27] as reported previously.[7] For the weaker bases, the following distribution ratios of amine in benzene and water were determined: py, 0.83; 3pic, 0.84; 4pic, 0.78; 3cpy, 0.87; 4cpy, 0.77; pzl, 0.11; iqn, 0.88; pzn, 0.58. For the stronger bases im, mim, NH_3, 3apy, 4apy, and lut, the concentration of free amine was determined by titration of the aqueous reaction mixture with HCl. A blank correction was made by extraction and titration of a sample of reaction

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mixture that had been kept in the dark.

Visible–UV spectra were obtained immediately after photolysis and compared with the spectrum of an aliquot kept in the dark. The sample solutions were from 1.00×10^{-3} to 5.00×10^{-3} M in complex. All the complexes used were isolated as nitrate salts, so no excess halide was present at the start of photolysis. No dark correction was necessary for any of the complexes studied. The photolysis of *trans*-$[Rh(en)_2Cl_2]NO_3$ in the presence of up to 0.001 M added chloride ion was studied. No effect of added chloride at this low concentration on the quantum yields could be detected.

A partial separation of the photolysis products was achieved by passing the photolyzed sample through a column of SP-Sephadex C-25 in the Na^+ form. Separation into two bands was achieved with 0.01 M $NaNO_3$. The first band contained the starting complex, *trans*-$[RhA_4Cl_2]^+$, in addition to another complex, found in a small amount at the front of the band. This could not be isolated in pure form. The visible spectrum of the portion of the band containing this complex was shifted about 10 nm toward longer wavelength compared to that of the starting complex. This would be reasonable for the expected product $[RhA_3(H_2O)Cl_2]^+$, in which the water molecule has replaced a slightly stronger field ligand, the amine.

The second band, eluted with 1 M $NaNO_3$, contained *trans*-$[RhA_4(H_2O)Cl]^{2+}$, which was isolated and characterized.

Although repeated attempts to separate the first band to obtain pure $[RhA_3(H_2O)Cl_2]^+$ were unsuccessful, additional evidence for the existence of this product was obtained. To several samples of *trans*-$[Rh(py)_4Cl_2]^+$ an aqueous solution of NaCl or NaI was added after the complex had been photolyzed. The solution was refluxed for 72 h, and the small amount of precipitate that formed was filtered off and dried. For samples to which NaCl was added, the spectrum in dichloromethane of the resulting precipitate corresponded to that of 1,2,6-$[Rh(py)_3Cl_3]$. The product obtained after the addition of NaI showed an absorption maximum at longer wavelength than the trichloro product. No such products were obtained upon refluxing $[Rh(py)_4Cl_2]^+$ or $[Rh(py)_4(H_2O)Cl]^{2+}$.

Results

All the complexes of the type *trans*-$[RhA_4Cl_2]^+$ with A = heterocyclic amine gave ligand field photoaquation of both amine and chloride. The quantum yield for photoaquation of chloride, Φ_{Cl}, was calculated from the concentration of chloride ion in the photolyzed solution, and the quantum yield for photoaquation of amine, Φ_A, was calculated from the concentration of amine in the photolyzed solution. Values of Φ_{Cl} and Φ_A are listed in Table I for all the complexes.

The fraction of light absorbed by each sample was determined from the absorption spectrum, the concentration of the complex, and the path length of the reaction cell. No correction was made for internal filter effects. The incident intensity was determined immediately before each photolysis. The average value was 3.32×10^{16} quanta/s at 410 nm.

The quantum yields reported in Table I are averages of three or more determinations. The total observed quantum yields, $\Phi_{sum} = \Phi_{Cl} + \Phi_A$, were calculated from the average values. The ratios Φ_A/Φ_{sum} are listed in Table I, along with the values of pK_b for the amines.

The only complexes included in this work which did not show photoaquation of both amine and chloride were the complexes with NH_3 and ethylenediamine. Both gave photoaquation of chloride, but any free amine in solution had a concentration lower than the limits of detection. The results in Table I for these two complexes agree very closely with the values for these two complexes reported by Kutal and Adamson,[6] which are also listed in Table I.

Discussion

Table I. Quantum Yields for Photoaquation of Chloride and of Amine for *trans*-$[RhA_4Cl_2]^+$ at 410 nm

A	$10^2\Phi_{Cl}$, mol/einstein	$10^2\Phi_A$, mol/einstein	Φ_A/Φ_{sum}	pK_b
pyrazine	0.59 ± 0.01	9.42 ± 0.05	0.94	13.35[b]
pyrazole	0.40 ± 0.01	8.6 ± 0.1	0.96	11.52
3-chloropyridine	0.52 ± 0.01	8.2 ± 0.2	0.94	11.16
4-chloropyridine	0.62 ± 0.01	7.5 ± 0.2	0.92	10.16
pyridine	0.98 ± 0.01	4.12 ± 0.04	0.81	8.75
isoquinoline	0.87 ± 0.02	2.37 ± 0.05	0.73	8.58
3-picoline	2.51 ± 0.06	3.5 ± 0.3	0.58	8.32
3-aminopyridine	0.77 ± 0.03	0.9 ± 0.1	0.54	8.06
4-picoline	3.07 ± 0.07	1.36 ± 0.09	0.31	7.98
3,5-lutidine	3.08 ± 0.02	2.70 ± 0.03	0.46	7.85
imidazole	2.9 ± 0.1	1.4 ± 0.1	0.32	7.05
N-methylimidazole	3.42 ± 0.09	1.13 ± 0.02	0.25	6.48
4-aminopyridine	0.57 ± 0.05	0.29 ± 0.02	0.34	4.13
NH_3	15.2 ± 0.2	<0.2	<0.01	4.74
	13–17[a]	<0.2		
ethylenediamine	6.2 ± 0.2	<0.3	<0.05	3.29
	5.7	<0.3		

[a] Reference 6. [b] Perrin, D. D., Ed. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965.

Several experimental difficulties with the work reported previously from this laboratory[7] were eliminated in this work. Photolyses were done with more nearly monochromatic light, which permitted determination of absolute quantum yields. The complexes were obtained as nitrate salts, which eliminated the need to pass solutions through an ion-exchange column before photolysis in order to remove excess chloride ions. The addition of excess chloride ion did not affect the quantum yields. However, a large excess does affect the sensitivity of the method used for determining the chloride concentration after photolysis of the complex. Use of a meter with an expanded millivolt scale improved the determination of free chloride ion.

The quantum yields for chloro complexes for photoaquation of amine and chloride listed in Table I show a variation of 1 order of magnitude as the amine is varied. Since the complexes were all of the same trans geometry and all had chloride ions in the starting complex, it is necessary to consider properties of the amines, which did vary. There was no correlation with polarographic half-wave potentials, $E_{1/2}$, of the complexes.[28] There were not enough values of nucleophilicity constants such as n_{Pt}[29,30] available in the literature for that parameter to be used. However, values of pK_b were available and are listed in Table I. These were taken to give an estimate of σ-bonding ability.

The values of Φ_{Cl} show little correlation with the pK_b values of the amines, but the values of Φ_A and of Φ_{sum} tend to decrease as the basicity of the amine increases. A better correlation with pK_b is found, however, for the fraction of the total observed photoaquation yield that is due to photoaquation of amine, Φ_A/Φ_{sum}. This is shown in Figure 1. For the weakest bases, a limiting fractional yield of about 0.95 seems to be reached. In other words, even for the amines with highest pK_b, which probably form the weakest σ bonds between Rh and N and which would therefore be the best leaving groups, there remains a small but significant fraction of the yield that represents photoaquation of chloride. The one point that falls completely off the curve in Figure 1 is for 4-aminopyridine, for which the pK_b value is not indicative of σ bonding by the heterocyclic nitrogen. The value for 4-picoline is also off the curve but not by such a large amount.

A dependence on the pK_b of the amine when amine is a leaving group has been observed previously for both thermal and photochemical systems. The rates of substitution reactions of $[AuACl_3]$ in which an amine A is replaced by various nucleophiles have shown a linear free energy relation between the basicity of the amine and the rate of substitution.[31,32] A

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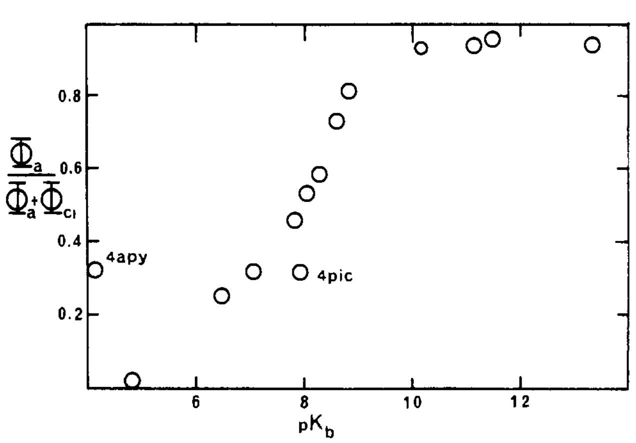

Figure 1. Ratio of the quantum yield for photoaquation of amine to the total photoaquation quantum yield, $\Phi_A/(\Phi_{Cl} + \Phi_A)$, as a function of p$K_b$ of the amine for *trans*-$[RhA_4Cl_2]^+$.

dependence of quantum yield on the basicity of an amine leaving group has been reported for the series of complexes $[Rh(NH_3)_5A]^{3+}$.[33,34]

It is not possible, for the series of complexes studied here, to predict the relative quantum yields Φ_{Cl} and Φ_A by considering the ligand field strengths. All the complexes have ligand field absorption bands very near 410 nm. What seems to vary is not the energy of the Franck–Condon state but the relative labilities of the ligands in the thermally equilibrated excited state. The relative bond energies of the Rh–N bonds in the excited state must be similar to the relative bond energies in the ground state, as indicated by the amine basicities.

The apparent difference in photochemical behavior between *trans*-$[Rh(NH_3)_4Cl_2]^+$, which gives little or no amine photoaquation, and *trans*-$[Rh(py)_4Cl_2]^+$, which gives more amine than halide photoaquation, may simply result from the difference in base strength between NH_3 and pyridine. Clearly, many complexes share the characteristics of the pyridine complex in producing both chloride and amine on ligand field photoaquation. The mechanism by which the photolysis occurs requires further study.

A more detailed analysis of these photoreactions, including photochemical kinetic studies, would be very helpful in interpreting these observations. It is possible that the variations in quantum yield depend to a greater extent on variations of the rates of various processes than on ground-state basicity differences. In the absence of kinetic data, however, the correlation of fractional yield with amine basicity is the only useful relationship found.

These results provide a clear deviation from the theoretical model of Vanquickenborne and Ceulemans.[20] The value of I^*_{M-Cl} will always be smaller than I^*_{M-A} for the complexes *trans*-$[RhA_4Cl_2]^+$. From the parameters[35] $e_\sigma(Cl) = 8.3$, $e_\pi(Cl) = 1.0$, $e_\sigma(py) = 11.0$, $e_\pi(py) = -1.5$, and $B = 0.4\ 10^3 \times cm^{-1}$, $I^*_{M-Cl} = 9.4$ and $I^*_{M-py} = 24.7$. Thus, the theory clearly fails to predict the significant labilization of amine.

The model provides predictions of the stereochemistry of these reactions. For photolabilization of Cl, retention of geometry is expected. When amine is the leaving ligand, the expected product is 1,2,6-$[RhA_3(H_2O)Cl_2]^+$. Rearrangement to give the 1,2,3-isomer would require the initial SP to pass through two TBP excited states before reaching the SP state, which would give the 1,2,3-isomer on addition of H_2O. The easier path can produce the 1,2,6-isomer in more than one way.

The photoproducts *trans*-$[Rh(py)_4(H_2O)Cl]^{2+}$ and *trans*-$[Rh(4pic)_4(H_2O)Cl]^{2+}$ were isolated as the perchlorate salts. The visible–UV spectra of these complexes clearly indicate that they have trans geometry, since they are very similar[14] to the spectrum of *trans*-$[Rh(en)_2(H_2O)Cl]^{2+}$. These differ markedly from known spectra of cis complexes. The protons on the pyridine rings give proton NMR spectra that are nearly identical for the dihalo and chloroaquo complexes of pyridine. This supports the retention of trans geometry on photoaquation of the halide.

On the basis of spectral data it is possible to conclude that the photoproduct resulting from loss of amine, $[RhA_3(H_2O)Cl_2]^+$, gave 1,2,6-$[RhA_3Cl_3]$ after refluxing with NaCl. This is the isomer that would be formed if no rearrangement occurred subsequent to loss of the amine. However, given the small amount of product obtained, it is possible that some 1,2,3-$[RhA_3Cl_3]$ was also present but not detected in the spectrum.

A more detailed analysis of the predictive power of the Vanquickenborne–Ceulemans model in this system will be possible when work in progress on the stereochemistry of reactions of complexes of the type *trans*-$[RhA_4XY]^+$ is completed.

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Registry No. *trans*-$[Rh(pzn)_4Cl_2]^+$, 82265-62-1; *trans*-$[Rh(pzl)_4Cl_2]^+$, 42829-96-9; *trans*-$[Rh(3cpy)_4Cl_2]^+$, 42829-95-8; *trans*-$[Rh(4cpy)_4Cl_2]^+$, 82265-71-2; *trans*-$[Rh(py)_4Cl_2]^+$, 47515-30-0; *trans*-$[Rh(iqn)_4Cl_2]^+$, 42904-03-0; *trans*-$[Rh(3pic)_4Cl_2]^+$, 33395-30-1; *trans*-$[Rh(3apy)_4Cl_2]^+$, 42813-28-5; *trans*-$[Rh(4pic)_4Cl_2]^+$, 33395-31-2; *trans*-$[Rh(lut)_4Cl_2]^+$, 82265-72-3; *trans*-$[Rh(im)_4Cl_2]^+$, 82310-78-9; *trans*-$[Rh(mim)_4Cl_2]^+$, 42830-00-2; *trans*-$[Rh(4apy)_4Cl_2]^+$, 42813-27-4; *trans*-$[Rh(NH_3)_4Cl_2]^+$, 38781-29-1; *trans*-$[Rh(en)_2Cl_2]^+$, 18539-17-8.

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