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Photochemical reaction pathways of ruthenium(II) complexes. Evidence regarding the reactive excited state(s) from metal-to-ligand charge transfer excitation of pentaamine(pyridine)ruthenium(2+) and related complexes

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that the 4-31G \rightarrow 6-31G* energy lowering is about 7 kcal mol⁻¹ greater for the bridged form than for the classical form. This suggests that the energy of the H-bridged form at the 6-31G* level is about 11 kcal mol⁻¹ relative to 2-propyl, so that there may be a direct descent without activation from I to VIII.

Recent ion cyclotron resonance studies by McAdoo, McLafferty, and Bente³ suggest that the most stable form of C₃H₇⁺ is 2-propyl and that protonated cyclopropane either isomerizes to the 2-propyl cation or is higher in energy than the latter by *ca.* 7 kcal mol⁻¹. Similar conclusions have been reached by Chong and Franklin² on the basis of measurements of gas-phase ionic equilibrium constants. They demonstrated the existence of a second isomeric species of C₃H₇⁺ about 9 kcal mol⁻¹ less stable than the 2-propyl cation and identified this with protonated cyclopropane. According to our theoretical study, this is the corner-protonated form IV or V (with a theoretical energy of 13 kcal mol⁻¹ relative to 2-propyl). Lossing and Semeluk¹¹ obtain a heat of formation for the 1-propyl cation which is 16 kcal mol⁻¹ above that for the 2-propyl cation. This is obtained from the ionization potential of the 1-propyl radical and corresponds well with our relative energy of 17 kcal mol⁻¹ for structure I. However, it should be emphasized that I may not be a separate isomer and may rearrange directly to the corner-protonated form IV or V or to VIII. Finally, we may note that our results are consistent with the nuclear magnetic resonance data in superacid systems.¹ Saunders, *et al.*,¹ conclude that hydrogen and carbon scrambling in protonated cyclopropanes can best be interpreted in terms of a corner-protonated form a few kilocalories below an edge-protonated transition state. The lower energy barrier to 1,3-hydride shifts (now 6 kcal mol⁻¹ or less) is more consistent with experimental results on corner-to-corner hydrogen migration than the previous 4-31G barrier.⁴

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(11) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

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Photochemical Reaction Pathways of Ruthenium(II) Complexes. Evidence Regarding the Reactive Excited State(s) from Metal-to-Ligand Charge Transfer Excitation of Ru(NH₃)₅py²⁺ and Related Complexes

Sir:

Some strikingly contrasting photochemical behavior results from the irradiation of metal-to-ligand charge transfer (MLCT) absorption bands of ruthenium(II) complexes of nitrogen heterocycle ligands. In ambient

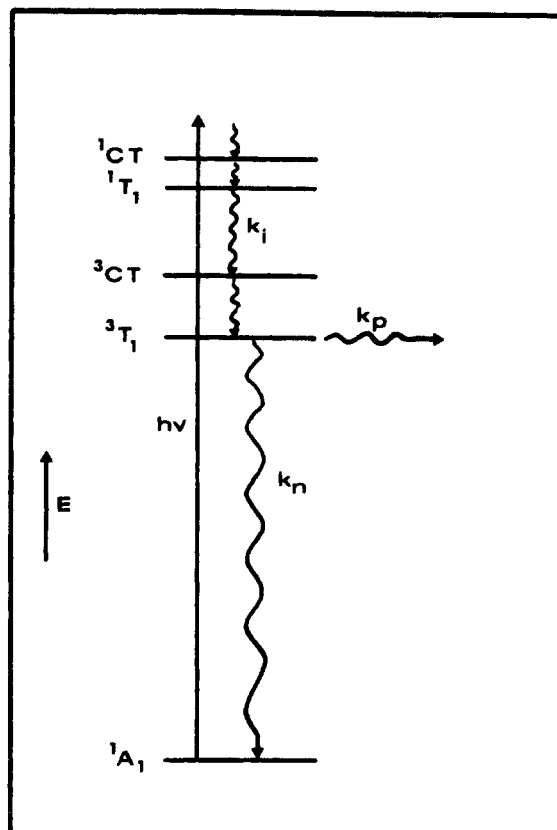


Figure 1. Excited-state diagram for the proposed mechanism for photoaquation of Ru(NH₃)₅py²⁺; *k_p* represents reactions leading to photoproducts.

temperature fluid solution, the ions Ru(bipy)₃²⁺ and *cis*-Ru(bipy)₂(4-stilbazole)₂²⁺ are both essentially inert toward substitution, but the former ion displays significant phosphorescent emission¹ while MLCT excitation of the latter ion leads to very weak phosphorescence and primarily to *cis/trans* isomerization of the 4-stilbazole ligand.² A third behavior is observed with aqueous Ru(NH₃)₅py²⁺ where MLCT excitation results almost exclusively in substitution reactions.^{3,4} Substitutional behavior is not intuitively expected for the MLCT excited state⁴ of Ru(NH₃)₅py²⁺ given that Ru(III) amine complexes are relatively substitution inert.⁵ Thus, it has been argued⁴ that the substitution reactive state is ligand field in character, perhaps the triplet ³T₁. As charge transfer and ligand $\pi-\pi^*$ absorptions dominate the spectrum, the presence of such a state can only be inferred. Here, we present photochemical evidence that MLCT excited states are relatively unreactive toward substitution and that another, presumably ligand field, excited state is responsible for the photosubstitution reactions of Ru(NH₃)₅py²⁺.

Figure 1 is a simplified excited-state diagram for the proposed mechanism.⁴ Initial excitation is assumed to be followed by efficient intersystem crossing-internal

(1) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 2841 (1971).

(2) P. P. Zarnegar, C. R. Bock, and D. G. Whitten, *J. Amer. Chem. Soc.*, **95**, 4367 (1973).

(3) (a) P. C. Ford, D. H. Stuermer, and D. P. McDonald, *J. Amer. Chem. Soc.*, **91**, 6209 (1969); (b) P. C. Ford, D. A. Chaisson, and D. H. Stuermer, *Chem. Commun.*, 530 (1971).

(4) D. A. Chaisson, R. E. Hintze, D. H. Stuermer, J. D. Petersen, D. P. McDonald, and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 6665 (1972).

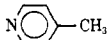


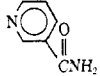
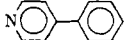

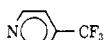
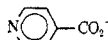

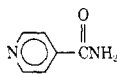
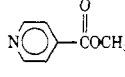
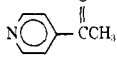
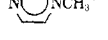
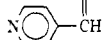
(5) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

conversion (k_i) to the lowest state in the triplet manifold,^{1,6} probably the 3T_1 ligand field triplet owing to proximity of the $^1A_1 \rightarrow ^1T_1$ and $^1A_1 \rightarrow ^1CT$ transitions in related Ru(II) complexes⁵ and to the greater Stokes shift and singlet/triplet energy differences observed for ligand field states of this type.⁷ That this state should be substitution labile is confirmed by the observation⁸ that the isoelectronic rhodium(III) complex $Rh(NH_3)_5py^{3+}$ undergoes pyridine aquation when its lowest energy band ($^1A_1 \rightarrow ^1T_1$) is irradiated. However, a complication in the photochemistry of $Ru(NH_3)_5py^{2+}$ is that the quantum yield for aquation of pyridine displays a competitive acid-dependent path. Ford and co-workers^{3,4} suggested that this path involves reversible formation of a ruthenium(II) intermediate complex probably by reaction of a ligand field excited state, while Natarajan and Endicott⁹ have made the alternate proposal that the path involves an intermediate formed by rehybridization and protonation of the pyridine nitrogen of the MLCT state to give a Ru(III) coordinated free radical species. Flash photolysis studies on aqueous $Ru(NH_3)_5py^{2+}$ have demonstrated the presence of an intermediate with an acid-dependent lifetime.⁹

The energy of the MLCT band ($\lambda_{max}(CT)$) of $Ru(NH_3)_5(py-X)^{2+}$, (where py-X is a substituted pyridine or related aromatic nitrogen heterocycle) is very sensitive to the nature of the substituent X⁵ (Table I). Although it is uncertain how ligand field excited-state energies are affected by ligand substituents, they should be much less sensitive to this perturbation than are the MLCT states. Therefore, if Figure 1 is correct (*i.e.*, $E(^3T_1) < E(^3CT)$) for the pyridine complex, it should be possible by appropriate choice of substituents to "tune"^{6b} the order of excited states so that the lowest triplet is 3CT . If so, and if photochemistry can be attributed to the lowest triplet, then a change in the nature of the lowest state should be reflected as a significant perturbation in the photoreactivity. Such a modification of reactivity is the purpose of the experiments described here.

Quantum yields¹⁰ for photoaquation of py-X from the complexes $Ru(NH_3)_5(py-X)^{2+}$, when irradiated at or near $\lambda_{max}(CT)$, are listed in Table I. Most of the photolyses were carried out in pH 3 aqueous solution, conditions where contributions of the acid-dependent paths are at most very minor. The crucial observation is that for complexes where $\lambda_{max}(CT)$ exceeds ~ 460 nm, Φ_L is dramatically lower than for those complexes having $\lambda_{max}(CT)$ of higher energy. For examples, the relative quantum yields of the pyridine (ν_{max} 24.5 kK), *p*-trifluoromethylpyridine (22.0 kK), pyrazine (21.2 kK), methylisonicotinate (20.2 kK), and *N*-methylpyrazinium (18.5 kK) complexes are 1.00, 0.49, 0.033, 0.0062, and < 0.0009 , respectively, a range spanning

Table I. Spectroscopic Quantum Yields for the Photoaquations of $Ru(NH_3)_5L^{2+}$ in Aqueous Solution^a

$Ru(NH_3)_5L^{2+} + H_2O \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{2+} + L$				
L	λ_{max}^- (CT), nm	ν_{max}^- (CT), kK	λ_{irr} , nm	$\Phi_L \times 10^3$ (mole/einstein)
	398	25.1	405	37 ± 3 (2) ^b
	408	24.5	405	45 ± 2 (3)
	426	23.5	436	48 ± 2 (2)
	427	23.4	430	3.6 ± 0.9 (2)
	446	22.4	450	39 (1)
	447	22.4	450	28 ± 3 (3)
	454	22.0	455	22 ± 5 (2)
	457	21.9	460	20 ± 10 ^c (2)
	472	21.2	475	1.5 ± 0.6 ^d (2)
	479	20.9	480	0.5 ± 0.2 (2)
	495	20.2	500	0.28 ± 0.04 (3) 0.2 ± 0.1 (2) ^e
	523	19.1	520	0.25 ± 0.1 (2)
	540	18.5	540	<0.04 (2)
	545	18.3	546	<0.1 (1)

^a At 25°. In pH 3 aqueous NaCl solution (0.2 M) except where noted. New results reported here were obtained with 150-W xenon short arc lamp as light source with interference filters for wavelength selection. See ref 10. ^b Reference 3. ^c pH 10. ^d pH 7. ^e In 1.0 M HCl.

more than 3 orders of magnitude. These observations provide convincing evidence that modification of the MLCT energy with appropriate electron-withdrawing substituents leads to a reversal in the order of the triplet excited states to give a substitution unreactive charge transfer state with the lowest energy. In addition, the observation that Φ_L for the methylisonicotinate complex in 1 M aqueous HCl is indistinguishable from the value measured at pH 3 (Table I) indicates that an acid-dependent aquation of the MLCT state is not occurring under these conditions. Thus we are led to the conclusion that the substitution reactions of the ion $Ru(NH_3)_5py^{2+}$ and related species under the influence of

(6) (a) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **92**, 7262 (1970); (b) R. J. Watts and G. A. Crosby, *ibid.*, **94**, 2606 (1972).

(7) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

(8) J. D. Petersen and P. C. Ford, Abstracts of the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, INOR 39.

(9) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 5909 (1972).

(10) The quantum yield for aquation of py-X is based on the decrease in the charge transfer absorbance at $\lambda_{max}(CT)$ as a function of light absorbed. Complexes having very small values of Φ_L also displayed no shifts in $\lambda_{max}(CT)$, thus indicating that quantum yields for NH_3 aquation are comparably small (ref 3).

MLCT excitation are due to the presence of lowest lying, substitution reactive, ligand field excited states, not MLCT states such as those which dominate the visible absorption spectrum.

The progression from relatively photoreactive complexes to unreactive complexes as a function of the MLCT energy occurs rapidly when $\lambda_{\text{max}}(\text{CT})$ exceeds ~ 460 nm but not instantaneously.¹¹⁻¹³ The observation of an intermediate Φ_{L} value for the pyrazine complex ($\lambda_{\text{max}}(\text{CT})$ 472 nm) may have several explanations, one being that the lowest energy triplet state may have character and reactivity intermediate between the pure charge transfer and pure ligand field state owing to mixing of these two states when they are close in energy.

Acknowledgment. This research was supported by the National Science Foundation (GP-26199 and GP-36634X).

(11) The lone exception to the relatively smooth progression of Φ_{L} as a function of $\lambda_{\text{max}}(\text{CT})$ is the nicotinamide complex, which displays an intermediate value for Φ_{L} despite a $\lambda_{\text{max}}(\text{CT})$ of 427 nm. However, it has been pointed out (ref 12) that these complexes may have several MLCT states of comparable energy, but the absorption band is especially sensitive to para substituents and much less to meta substituents. Consequently $\lambda_{\text{max}}(\text{CT})$ may place the nicotinamide complex in an anomalous position, as the strongly delocalizing amide group in the meta site may lower a spectrally unobservable MLCT state to an energy comparable to the lowest ligand field state.

(12) (a) P. C. Ford, D. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968); (b) A. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).

(13) Irradiation of the substitution unreactive isonicotinamide and 4-acetylpyridine complexes with 405-nm light (corresponding to an absorption minimum in the spectra) shows quantum yields of $(4 \pm 1) \times 10^{-3}$ mol/einstein for each. These values represent enhancements of about 1 order of magnitude over the $\lambda_{\text{max}}(\text{CT})$ values but are still 1 order of magnitude below the reactivity of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ at the same wavelength. This result indicates both the presence of a reactive excited state at higher energy (presumably LF in character) and that interconversion of upper to lower states though apparently efficient is not the only significant path of the reactive upper state(s).

(14) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1971-1976.

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Metal Ion Probes of Molecular Geometry. II. A Direct Spectroscopic Determination of the Absolute Configuration of Hydroxyl Bearing Asymmetric Centers Based on the Shift Reagent, $\text{Eu}(\text{FOD})_3$ ¹

Sir:

Increasingly subtle probes of molecular geometry are required in order to define the configuration of complex natural products and to determine their conformation in solution. Thus far nmr and CD have been the major spectroscopic tools in such studies, and each can be used with metal ion probes by virtue of the magnetic or electronic properties of transition and lanthanide metals.² In the study of chiral molecules the circular dichroism induced in the electronic transitions of the metal offers another probe of degree of

(1) For part I of this series, see N. H. Andersen, B. J. Bottino, and S. E. Smith, *J. Chem. Soc., Chem. Commun.*, 1193 (1973). This work is taken in part from the Masters Thesis of B. J. B. (University of Washington, 1972).

(2) The application of lanthanide shift reagents (LSR) in nmr conformational studies is an example of the former.

association,³ conformation, and (in the present case) absolute configuration.⁴

Present methods for determining the absolute configuration of a hydroxylated center typically⁵ involve formation of diastereomeric derivatives followed by spectroscopic measurements⁶ or indirect determination of $\Delta\Delta G^\ddagger$ of diastereomeric transition states.⁷ We wish to present a direct spectroscopic method based on the sign of the induced CD of the 525-nm transition of $\text{Eu}(\text{FOD})_3$ on complexing ligands in which the donor is at a chiral center.

The common nmr shift reagents offer an ideal electrophilic component for complexes with chiral donors. The bulky didonate ligands associated with large paramagnetic shifts should also produce complexes of distinctly dissymmetric polarization for, as an example, ligand geometry I, (which corresponds to an S center in most cases) particularly when two such ligands are incorporated in the complex. With this in mind we have examined the sign of the CD induced at the 525-nm line of $\text{Eu}(\text{FOD})_3$ during studies of LSR-substrate stoichiometry.³ Studies of 2-alkanols, menthol, 2-aryl-cyclohexanols, α -phenethylamine, amphetamine, and a series of sesquiterpene-derived alcohols (II, III, IV, V, and VII) established that a correlation of sign and chirality at the donor-bearing carbon exists. The full results appear in the table. See paragraph at end of paper regarding supplementary material.

We consider this initial data sufficient to conclude that *ligand geometry I* (S, where a steric bulk sequence rule is employed) produces a positive CD for the 2:1 complex with $\text{Eu}(\text{FOD})_3$. Such a determination of configuration, in contrast to previous methods,⁵⁻⁷ does not require derivatization and allows simple recovery of the alcohol tested.⁸ Further, the method appears to be applicable to tertiary alcohols as well. Before proceeding with the analysis of the data and a consideration of the apparent exceptions, some warning concerning potential pitfalls in the application of the method will be discussed. First, the absolute values of $[\theta]$ are small so that measurements require solutions

(3) This technique was used in our studies demonstrating that $\text{Eu}(\text{FOD})_3$ gives octacoordinate complexes, $(\text{ROH})_2\text{Eu}(\text{FOD})_3$, with chiral alcohols when $C_{\text{ROH}}/C_{\text{Eu}} > 2$: ref 1.

(4) LSR complexes of *vic*-glycols display CD couplets that can be used to assign chirality in much the same way as application of the aromatic exciton method: K. Nakanishi and J. Dillon, *J. Amer. Chem. Soc.*, **93**, 4058 (1971); N. Harada and K. Nakanishi, *Accounts Chem. Res.*, **5**, 257 (1972). The major bands in the uv region are employed for this assignment. Monohydroxylic substances also give CD couplets in this region (ca. 300 nm for Eu). The $\Delta\Delta\epsilon$ values are too low for easy determination. Our use of LSR complexes is by analogy related to the benzoate rule.⁵

(5) Application of the benzoate rule still requires an examination of a derivative which must be obtained in pure state: J. H. Brewster, *Tetrahedron*, **13**, 106 (1961); *J. Amer. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959). See also the benzoate sector rule: N. Harada, M. Ohashi, and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 7349 (1968); N. Harada and K. Nakanishi, *ibid.*, **90**, 7351 (1968).

(6) Differences in ¹⁹F shifts correlate with configuration of diastereomeric α -methoxy- α -trifluoromethylphenylacetic esters (MTPA esters): (a) J. A. Dale and H. S. Mosher, *J. Amer. Chem. Soc.*, **95**, 512 (1973); (b) G. R. Sullivan, J. A. Dale, and H. Mosher, *J. Org. Chem.*, **38**, 2143 (1973).

(7) The method of Horeau and its recent modifications: A. Horeau, *Tetrahedron Lett.*, 506 (1961); A. Horeau and H. B. Kagan, *Tetrahedron*, **20**, 2431 (1964); R. Weidmann and A. Horeau, *Tetrahedron Lett.*, 2979 (1973); C. J. W. Brooks and J. D. Gilbert, *J. Chem. Soc., Chem. Commun.*, 194 (1973).

(8) The alcohols are recovered from the CCl_4 solution of the $\text{Eu}(\text{FOD})_3$ by addition of 3 equiv (related to Eu) of *n*-hexylamine. The resulting mixture is applied to a short column of silica. Elution with benzene yields alcohol completely free of shift reagent by nmr.