Title
Photochemical Reaction Pathways of Ruthenium(II) Complexes. Evidence Regarding the Reactive Excited State(s) from Metal-to-Ligand Charge Transfer Excitation of Ru(NH2)5Py2+ and Related Complexes

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that the 4-31G → 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 Bente 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 Franklin 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 Semeluk 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. Saunders, et al., 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.

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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 temperature fluid solution, the ions Ru(bipy)₅²⁺ and cis-Ru(bipy)₅(4-stilbazole)²⁺ are both essentially inert toward substitution, but the former ion displays significant phosphorescent emission while MLCT excitation of the latter ion leads to very weak phosphorescence and primarily cis/trans isomerization of the 4-stilbazole ligand. A third behavior is observed with aqueous Ru(NH₃)₅py²⁺ where MLCT excitation results almost exclusively in substitution reactions. Substitutional behavior is not intuitively expected for the MLCT excited state of Ru(NH₃)₅py²⁺ given that Ru(III) amine complexes are relatively substitution inert. Thus, it has been argued that the substitution reactive state is ligand field in character, perhaps the triplet 3T₁. As charge transfer and ligand π-π* 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 photostimulation reactions of Ru(NH₃)₅py²⁺.

Figure 1 is a simplified excited-state diagram for the proposed mechanism for photosaquation of Ru(NH₃)₅py²⁺. kₚ represents reactions leading to photoproducts.

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conversion ($k_r$) to the lowest state in the triplet manifold, probably the $^3T_1$ ligand field triplet owing to proximity of the $^3T_1 \rightarrow ^3T_1$ and $^3A_1 \rightarrow ^3C_T$ transitions in related Ru(II) complexes and to the greater shift and singlet/triplet energy differences observed for ligand field states of this type. That this state should be substitution labile is confirmed by the observation that the isoelectronic rhodium(II) complex Rh(NH$_3$)$_5$py$^2+$ undergoes pyridine aquation when its lowest energy band ($^3A_1 \rightarrow ^3T_1$) is irradiated. However, a proposal that the path involves an intermediate formed by rehybridization and protonation of the pyridine while Natarajan and Endicott have made the alternate suggestion that this path involves reversible formation of a ruthenium(II) intermediate complex probably by reaction of a ligand field excited state, nitrogen of the MLCT state to give a Ru(II) coordinated free radical species. Flash photolysis studies on aqueous Ru(NH$_3$)$_5$py$^2+$ have demonstrated the presence of an intermediate with an acid-dependent lifetime.

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 X$^+$ (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., $E(T_1) < E(CT))$ for the pyridine complex, it should be possible by appropriate choice of substituents to "tune" 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 yields$^{10}$ 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 $\sim$460 nm, $\Phi_\lambda$ is dramatically lower than for those complexes having $\lambda_{max}(CT)$ of higher energy. For example, the relative quantum yields of the pyridine ($\Phi_{\lambda}_{max}$ 24.5 K), p-trifluoromethylpyridine (22.0 K), pyrazine (21.2 K), methylysonicotinate (20.2 K), and N-methylpyrazinium (18.5 K) complexes are 1.00, 0.49, 0.033, 0.062, and < 0.0009, respectively, a range spanning 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 $\Phi_\lambda$ for the methylysonicotinate 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$_3$)$_5$py$^{2+}$ and related species under the influence of

<table>
<thead>
<tr>
<th>L</th>
<th>$\lambda_{max}^{CT}$ (nm)</th>
<th>$\nu_{max}^{CT}$ (kK)</th>
<th>$\lambda_{tr}^{CT}$</th>
<th>$\Phi_{\lambda} \times 10^4$ (mole/einstein)</th>
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</thead>
<tbody>
<tr>
<td>N</td>
<td>398</td>
<td>25.1</td>
<td>405</td>
<td>37 ± 3 (2)</td>
</tr>
<tr>
<td>N</td>
<td>408</td>
<td>24.5</td>
<td>405</td>
<td>45 ± 2 (3)</td>
</tr>
<tr>
<td>N</td>
<td>426</td>
<td>23.5</td>
<td>436</td>
<td>48 ± 2 (2)</td>
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<tr>
<td>N</td>
<td>427</td>
<td>23.4</td>
<td>430</td>
<td>3.6 ± 0.9 (2)</td>
</tr>
<tr>
<td>N</td>
<td>446</td>
<td>22.4</td>
<td>450</td>
<td>39 (1)</td>
</tr>
<tr>
<td>N</td>
<td>447</td>
<td>22.4</td>
<td>450</td>
<td>28 ± 3 (3)</td>
</tr>
<tr>
<td>N</td>
<td>454</td>
<td>22.0</td>
<td>455</td>
<td>22 ± 5 (2)</td>
</tr>
<tr>
<td>N</td>
<td>457</td>
<td>21.9</td>
<td>460</td>
<td>20 ± 10$^a$ (2)</td>
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<tr>
<td>N</td>
<td>472</td>
<td>21.2</td>
<td>475</td>
<td>1.5 ± 0.6 (2)</td>
</tr>
<tr>
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<td>479</td>
<td>20.9</td>
<td>480</td>
<td>0.5 ± 0.2 (2)</td>
</tr>
<tr>
<td>N</td>
<td>495</td>
<td>20.2</td>
<td>500</td>
<td>0.28 ± 0.04 (3)</td>
</tr>
<tr>
<td>N</td>
<td>523</td>
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<td>0.25 ± 0.1 (2)</td>
</tr>
<tr>
<td>N</td>
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<td>&lt; 0.04 (2)</td>
</tr>
<tr>
<td>N</td>
<td>545</td>
<td>18.3</td>
<td>546</td>
<td>&lt; 0.1 (1)</td>
</tr>
</tbody>
</table>

$^a$ At 25°C. 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. $^d$ In 1.0 M HCl.

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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 photoactive complexes to unreactive complexes as a function of the MLCT energy occurs rapidly when \( \lambda_{\text{max}} \) exceeds \( \sim 460 \text{ nm} \) but not instantaneously. \(^{(11)} \) The observation of an intermediate \( \Phi_t \) value for the pyrazine complex \( \lambda_{\text{max}} \) (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.

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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, Eu(FOD)\(_3\)\(^{+} \)

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 transition of the metal offers another probe of degree of association, \(^{(3)} \) conformation, and (in the present case) absolute configuration. \(^{(4)} \)

Present methods for determining the absolute configuration of a hydroxylated center typically involve formation of diastereomeric derivatives followed by spectroscopic measurements \(^{(5)} \) or indirect determination of \( \Delta \Delta G^\circ \) of diastereomeric transition states. \(^{(6)} \) We wish to present a direct spectroscopic method based on the sign of the induced CD of the 525-nm transition of Eu(FOD)\(_3\) on complexing ligands in which the donor is a chiral center.

The common nmr shift reagents offer an ideal electrophilic component for complexes with chiral donors. The bulky dionato 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 Eu(FOD)\(_3\) during studies of LSR-substrate stoichiometry. \(^{(7)} \) Studies of 2-alkanols, menthol, 2-aryl-cyclohexanols, \( \alpha \)-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 (where a steric bulk sequence rule is employed) produces a positive CD for the 2:1 complex with Eu(FOD)\(_3\). Such a determination of configuration, in contrast to previous methods, \(^{(6, 7)} \) 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 \( \Delta \Delta G^\circ \) are small so that measurements require solutions

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