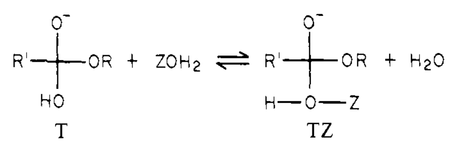


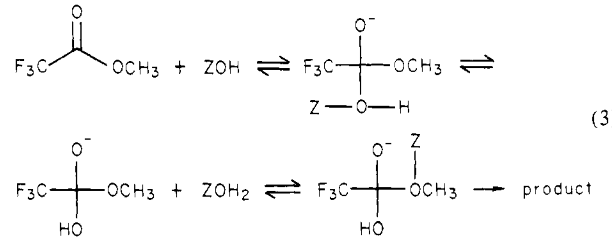
$$\mathrm{R'}-\overset{\displaystyle O^-}{\underset{\displaystyle HO}{|}}-\mathrm{OR} + \mathrm{ZOH_2} \rightleftharpoons \mathrm{R'}-\overset{\displaystyle O^-}{\underset{\displaystyle H-O-Z}{|}}-\mathrm{OR} + \mathrm{H_2O} \qquad (2)$$

T TZ

the C–O bond in T can also be used to predict the efficiency of the catalyst. In accordance with the principle of microscopic reversibility, if the metal hydroxide can catalyze the formation of T from the substrate, it should also catalyze the formation of the substrate from T. There will be no catalysis if T in eq 2 is so short lived that the metal–oxygen exchange cannot take place. At 10 mM catalyst concentration, the formation of TZ from T should have a pseudo-first-order rate constant of about 10^4 s^{-1}. In order to have any chance at catalysis, T must be long lived (lifetime > 10^{-4} s).

Table I shows the relationship between the lifetime of the anionic intermediate in various reactions and the catalytic efficiency of ZOH with respect to hydroxide. All of the anions live long enough to bind with the catalyst except the anion formed from methyl acetate. Knowing the tetrahedral intermediate stability is important in understanding the mechanism of these reactions, and there has been much progress in measuring and estimating the lifetimes of these species.[13-15]

At equilibrium, the ratio TZ/T (eq 2) is equal to $\mathrm{ZOH_2/H_2O}$ if it is assumed that the Z–O bond strengths are the same.[16-18] At 10 mM ZOH, TZ/T is about 10^{-4}. In order to account for the observed ZOH-catalyzed hydrolysis of methyl trifluoroacetate (sixfold rate enhancement under these conditions) the lifetime of T must be longer than the lifetime of TZ by a factor of 10^4–10^5. Since the lifetime of T is 10^{-1} s (Table I), the lifetime of the C–O bond in TZ is about 10^{-5} to 10^{-6} s. The basicity of the leaving group in T is higher than that in TZ by a factor of 10^7. The metal hydroxide not only catalyzes the formation T but also the breakdown of T to form the products (eq 3) since the expulsion



(3)

of methoxide should be at least partially rate determining for the uncatalyzed process.[19,20]

In conclusion, a weakly basic nucleophile has been shown, for the first time, to be highly effective in catalyzing the hydrolysis of an ester with a poor leaving group. This catalysis is effected by rapid metal–oxygen ligand exchange processes. The effectiveness of the catalyst is related to the lifetime of the tetrahedral intermediate involved and can be estimated. We are currently investigating the reactions of other esters and metal hydrates.

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Registry No. ZOH, 90065-64-8; methyl trifluoroacetate, 431-47-0; methyl acetate, 79-20-9.

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Resonance Raman Spectra of the First Three Reduction Products of Tris(bipyridyl)ruthenium(II)

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The extent of localization in the emitting state of the tris(bipyridyl)ruthenium(II) ion, Ru(bpy)$_3^{2+}$, has been of considerable interest. Photoselection,[1] absorption,[2] and resonance Raman[3,4] studies have all been interpreted in terms of a metal ligand charge-transfer (MLCT) excited state in which the promoted electron is localized on one of the bipyridines rather than delocalized over all three. Electrochemical[5] and absorption spectra[6] investigations of the reduced species have been interpreted in a similar manner. We have initiated a study of the resonance Raman spectra (RRS) of various reduction products of a series of metal di- and triimmine complexes. We report here our preliminary results for complexes, Ru(bpy)$_3^n$, where n = 2, 1, 0, −1. Our results are consistant with a localized redox orbital which appears to be similar in nature to the optical orbital.

As an electron is added to the redox orbital, one of two possibilities exists: the electron will be delocalized over all three bipyridine rings with a net increase of $^1/_3$ of an electron per bipyridine or the electron will be localized on one ring thus forming one bpy$^-$ anion and two neutral bipyridines on the resulting +1 cation. The addition of a second electron will then result in a neutral molecule in which there are either three bipyridines with $-^2/_3$ charge each or two bipyridine anions and one neutral bipyridine. In the case of the three-electron reduction product both models predict three equivalent bipyridine anions on the resulting −1 anion. Since these electrons are being added to π^* orbitals of the bipyridine, one would expect a decrease in energy of most of the bipyridine skeletal modes as the number of electrons in these orbitals increases. Thus in the delocalized model, one would expect to see only one set of bipyridine vibrations whose frequencies would decrease with the addition of each electron. In the localized model, both bpy and bpy$^-$ modes would be expected in the cases of [Ru(bpy)$_3$]$^{1+}$ and Ru(bpy)$_3$ depending on the nature of the excited state in resonance with the resonance Raman excitation. The frequencies of the bipyridine vibrations should be essentially the same as in the [Ru(bpy)$_3$]$^{2+}$ species and the bipyridine anion frequencies should be those observed for the [Ru(bpy)$_3$]$^{1-}$ species. Thus the resonance Raman spectra of this series of complexes should allow for a clear distinction between these two models.

Figure 1 shows the Raman spectra of the four complexes in the region of 980 to 1630 cm^{-1} and Table I gives the frequencies of these complexes as well as those for the MLCT excited state and the bipyridine anion reported by Woodruff et al.[3] and by Forster and Hester.[4] The resonance Raman spectrum of the ground state of the +2 ion has been reported previously[3,4] but has been included for comparison. The spectrum of the −1 species is predicted to be that of a bipyridine anion in either a localized or delocalized model. That this is the case can readily be seen by referring to Table I. With the exception of the bipyridine peaks at 1090 and 1429 cm^{-1}, which are covered by solvent peaks in the −1 species, there is a one to one correlation of every peak in the region studied. Thus, the top spectrum (n = 2) is the bipyridine limit whereas the bottom spectrum (n = −1) is the bipyridine anion limit. The peaks at 1174 and 1273 cm^{-1} in the +2 species are

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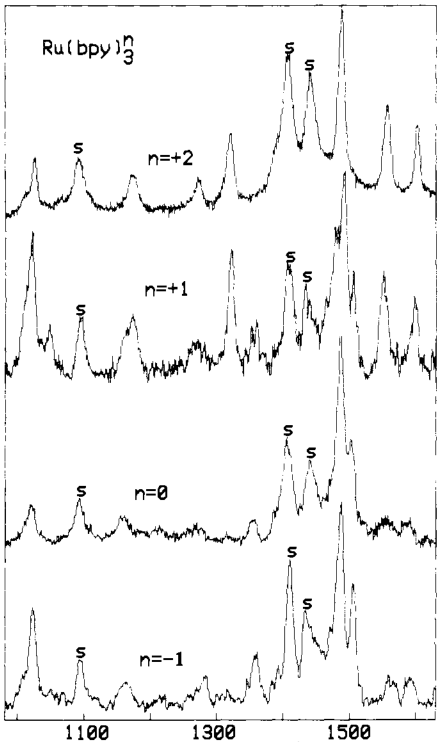

Figure 1. Raman spectra of the Ru(bpy)$_3{}^n$ recorded as 1.5 mM solutions in dimethylformamide recorded with a 5-cm^{-1} slit. The solvent peaks are indicated by "s". The value of n is indicated on each spectrum. The spectrum of the +2 ion was recorded with ~100 mW of 457.9-nm excitation. All others were recorded with ~250 mW of the 514.5-nm line. The +2 and 0 species are at room temperature while the others were recorded at 77 K.

Table I. Raman Frequencies for [Ru(bpy)$_3$]^n Compared with Those of the Excited State and the Bipyridyl Anion from Ref 3 and 4

n					
+2	+1	0	−1	+2*	bpy$^-$
1009	1012	1010	1007	1016	982
1025	1025	1021	1022	1035	1033
1040	1044			1044	
1107	1105	s	s	1101	1090
1174	1173				
	1166	1158	1163		1151
	1220	1213	1220	1214	1205
1273	1270	1268	1269		1273
	1287		1282	1288	
1321	1322			1324	
	1361	1354	1358	1370	1357
	s	s	s	1429	1429
1488	1486			1482	
	1497	1486	1486	1496	1478
	1509	1502	1505		1497
1558	1556	1558	1558	1550	1558
1603	1605	1590	1595	1609	1598

[a] s is solvent interference.

found at 1163 and 1282 cm^{-1} in the −1 ion. A stronger and more easily characterized peak at 1320 cm^{-1} in the +2 sample is missing in the anion but a new peak at 1358 cm^{-1} is observed. The most pronounced difference is found around 1500 cm^{-1}. In the parent ion, one very strong peak is observed (1488) but two peaks are observed in the three-electron reduced species (1487 and 1506). Finally, the intensities and frequencies of the two peaks around 1550 and 1600 cm^{-1} are different.

The RRS of the n = +1 species is a composite of the n = −1 and n = 2 spectra (see Figure 1 and Table I). Thus there are both types of bipyridine present in this ion and the first electron is definitely localized yielding a bipyridyl anion and neutral bipyridines. Comparison of this spectrum with that obtained for the RRS of the excited state (Table I) reveals that they are quite similar and thus the redox and optical orbitals are probably very similar in nature.

Evidence for localization in the neutral compound (n = 0) is not nearly so definitive as only one set of bipyridine modes is observed (essentially those of the bpy$^-$). However, the intensities of the Raman lines in RRS are dependent upon the extent to which the excited state is displaced along each normal coordinate, thus only those modes along which the excited state distorts should show enhancement. If the electronic transition is localized on a bipyridine anion (Heath[6] has assigned this region to a localized π to π^* of the bpy$^-$), then it is to be expected that only the bpy$^-$ modes should be enhanced since it is not expected that a neutral bipyridine would be distorted in this excited state. However, the frequencies of the vibrations in the neutral compound are so similar to those of the n = −1 ion that localization is still the likely rationale since, in the delocalized limit, we would expect three rings with a $-^2/_3$ charge on each with frequencies higher in energy than those observed in the anion limit.

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Synthesis and Crystallographic Characterization of a Gallium Salicylaldimine Complex of Radiopharmaceutical Interest

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The application of modern chemical techniques to the study of compounds of interest in diagnostic nuclear medicine has greatly increased the knowledge of technetium radiopharmaceutical chemistry and led to the systematic development of new γ-emitting ^{99m}Tc ($t_{1/2}$ = 6 h)[1] radiopharmaceuticals.[2-11] Positron emission

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