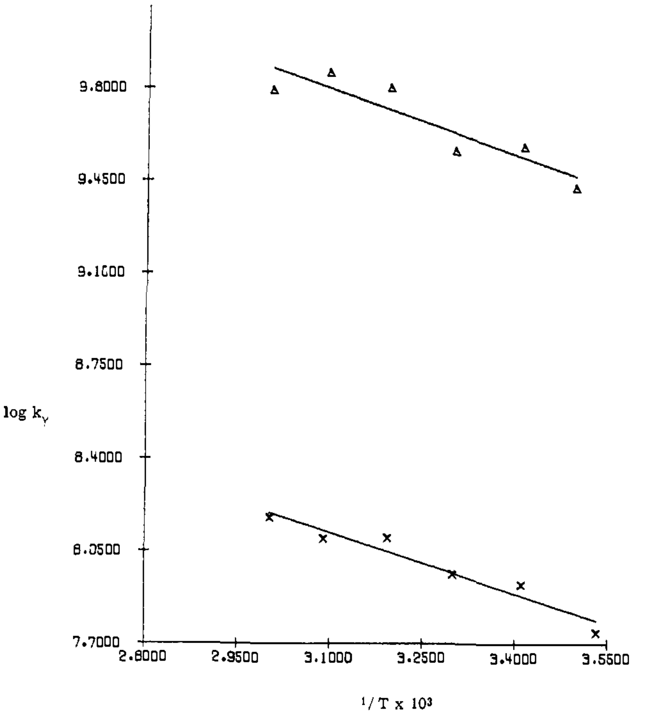

Figure 1. Plot of log k_γ *vs.* $1/T$ for valerophenone (I, ×) and *endo*-2-benzoylnorbornane (IV, Δ).

of the kinetic isotope effects indicates that the large difference in reactivity between I and IV cannot be due to differences in γ C–H bond strength or the geometry of the transition state. In addition, possible contributions of tunneling to the rate constant must be similar for I and IV.[22] The magnitude of the isotope effects indicates moderate C–H bond breaking in the transition state.[23]

The variation in rate constant with molecular structure for ketones I–VI suggests that the contributions of internal rotations to the entropies of activation may be responsible for the observed rate enhancements. The rate factors of 5–8 for each additional internal rotation which must be frozen out in the transition state is in good accord with recent predictions for strain-free six-membered transition states.[24] In order to evaluate the contributions of entropy to the transition state, Arrhenius parameters for I and IV were evaluated. Rate constants for γ-hydrogen abstraction were determined between 10 and 70° by Stern–Volmer quenching using 1,3-pentadiene in cyclooctane solvent.[25] The resulting Arrhenius plots are shown in Figure 1. The activation energies for I (3.5 ± 0.5 kcal/mol) and IV (3.7 ± 0.9 kcal/mol) are the same. However, the entropy of activation for I (−12.5 ± 1.5 eu) is much more negative than that for IV (−4.0 ± 2.8 eu).[26] Thus the large difference in reactivity between I and IV is primarily due to entropic contributions to the transition state which result from the two fewer rotational degrees of freedom which must be frozen out for IV.

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Direct Evidence for Charge Localization in Pyrazine-Bridged Mixed-Valence Ruthenium Complexes

Sir:

More than four years ago, Creutz and Taube[1] reported on the electronic spectra of binuclear pentaammine ruthenium complexes $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+,5+,6+}$ (pyr = pyrazine), in which an absorption band observed in the +5 mixed valence [Ru(II), Ru(III)] species and absent in the spectra of the +4 and +6 ions, was assigned as an intervalence charge-transfer transition corresponding to the process $[\text{Ru(II), Ru(III)}] \rightarrow [\text{Ru(III), Ru(II)}]^*$. Such an assignment, requiring essentially distinct valences localized on otherwise equivalent metal sites, has stimulated several theoretical analyses[2-4] and numerous experimental studies involving a variety of techniques, including nmr,[3] Raman,[5] Mössbauer,[6] and absorption[7] spectroscopies. The results of these investigations are either only suggestive or inconclusive and are, in some cases, in conflict. Further questions about the assignment have been introduced from the work of Adeymi, *et al.*,[8] in which an analogous charge-transfer band in the related systems $[Cl(bipy)_2Ru(pyr)Ru(bipy)_2Cl]^{2+,3+,4+}$ (bipy = bipyridine) was not observed. The implications of understanding both these systems in terms of electron exchange and metal–ligand interactions have been emphasized[7] and clearly warrant the elucidation of the charge distributions needed to explain the observed phenomena. In this communication we report direct evidence of the charge distributions in both the pentaammine and bipyridine ruthenium complexes using X-ray photoelectron spectroscopy. This technique is well suited for such an investigation because it monitors electron distributions rapidly ($\sim 10^{-17}$ sec) and unambiguously through inspection of so-called chemical shifts.[9]

All data were taken with a HP 5950A ESCA spectrometer which provides high-resolution low-background data by virtue of the relatively monochromatic Al Kα X-radiation used for photoejection. The working pressure in the sample analyzing region was no greater than 5×10^{-9} Torr, thus further simplifying data analysis through reduction of spurious sample

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contamination. The severe distortions of line shapes observed for these compounds as a result of inhomogeneous sample charging was effectively eliminated by scraping small quantities of the powdered materials into partially roughened surfaces of the gold covered sample holders.

In Figure 1 we present the X-ray photoemission spectra of ruthenium 3d and carbon 1s electrons in both pentaammine and bipyridine systems. As shown, the electron binding energies of the C 1s peak in the *p*-toluenesulfonate (= tosyl) anion for the former system and the same peak as observed in bipyridine for the latter have been arbitrarily assigned a value of 284.4 eV for purposes of comparison (absolute binding energies are not meaningful quantities for irradiated insulators[10,11]). Superposed on the raw data we have indicated the Ru3d$_{5/2}$–Ru3d$_{3/2}$ spin-orbit components split by 4.1 ± 0.1 eV, as determined from analysis of $Ru(NH_3)_5Cl_3$ in which C 1s obstruction is not a problem.

Inspection of Figure 1 reveals conclusively that the valences of ruthenium in the [II, III] salts in both systems are, in spite of their molecular symmetry, inequivalent.[12] This, then, is the necessary (but not sufficient) evidence required for the assignment of the charge-transfer band in the pentaammine system. We should mention that this statement, although inferred from solid-state measurements, is applicable to those measurements made in solution for the pentaammine compounds since the spectral properties in both phases for that system are observed to be virtually identical.[7,13] For the bipyridine system, on the other hand, there is as yet no such firm evidence. It is therefore not inconceivable that the [II, III] bipyridine salt is simply a 50–50 mixture of the constituent [II, II] and [III, III] complexes in the solid phase. We may assume, however, that this is probably not the case based on its similarity to the pentaammine system and on the observation of no significant spectral changes concurrent with different phases for other, similar bridged mixed-valence ruthenium systems we have studied.[14] With this assumption, then, the possibility of not observing the charge-transfer band in solution as a result of electron delocalization is immediately ruled out. This, in turn, implies that the absence of a charge-transfer band in this class II mixed-valence salt[15] stems not from the Franck–Condon energy barrier being too low to observe the transition in the near-ir region but rather from the resonance stabilization in the individual ruthenium sites simply being too large. This resonance stabilization may be understood to result from the additional electron on the Ru(II) site being delocalized over the rather extended bipyridine π system. That we observe Ru(II) and Ru(III) 3d electron binding energies in the [II, III] salts that are slightly converged with respect to those in the [II, II] and [III, III] salts for the pentaammine case and not so converged for the bipyridine case may be interpreted as a reflection of the relative magnitudes of the square of the mixing coefficients coupling the ground and vibrationally excited states[4] and is thus supporting evidence for this explanation. Further discussion of these and other systems will be published in a separate work.

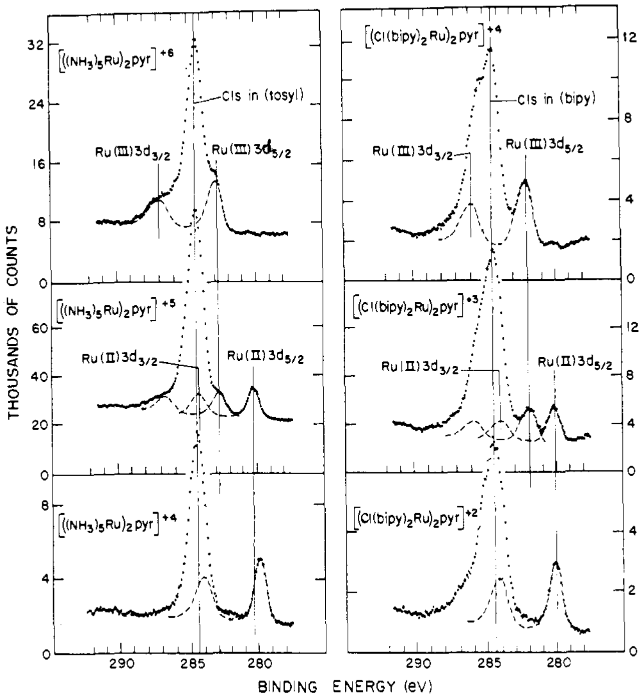

Figure 1. X-Ray photoemission spectra of $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+,5+,6+}$ and $[Cl(bipy)_2Ru(pyr)Ru(bipy)_2Cl]^{2+,3+,4+}$ salts. The C 1s electron binding energies in both systems have been arbitrarily assigned as 284.4 eV for purposes of comparison.

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Structure of Two Triterpenes. Application of Partially Relaxed Fourier Transform ^{13}C Nuclear Magnetic Resonance

Sir:

In the following we describe structural studies with extensive usage of partially relaxed Fourier transform[1] (PRFT) ^{13}C nmr on two triterpenes closely related to

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