is known to be a much weaker reductant than the unprotonated AcrH<sub>2</sub>.<sup>18</sup>

With an increase in the HClO<sub>4</sub> concentration, the rate of reductive quenching of  $[Ru(bpy)_3]^{2+*}$  by AcrH<sub>2</sub> decreases as shown in Figure 3, while the rate of reduction of PhCOCH<sub>2</sub>X by [Ru- $(bpy)_{3}$  + may increase. In such a case, the rate-determining step may be changed from the reduction of PhCOCH<sub>2</sub>X by [Ru- $(bpy)_3]^+$  to the reductive quenching of  $[Ru(bpy)_3]^{2+\tilde{*}}$  by AcrH<sub>2</sub>. This may be the reason why the quantum yield decreases with an increase in the HClO<sub>4</sub> concentration  $(5.0 \times 10^{-3} - 4.0 \times 10^{-2})$ M in Figure 1). The reason why the  $\Phi$  value increases again with a further increase in the HClO<sub>4</sub> concentration (>4.0 ×  $10^{-2}$  M in Figure 1) is discussed next.

Oxidative Quenching Pathway. In the high concentrations of HClO<sub>4</sub>, the  $[\tilde{R}u(bpy)_3]^{2+}$ -sensitized reactions may be initiated by the reductive quenching of  $[Ru(bpy)_3]^{2+*}$ , instead of the oxidative quenching by AcrH<sub>2</sub>, as shown in Scheme II. No oxidative quenching of  $[Ru(bpy)_3]^{2+*}$  by PhCOCH<sub>2</sub>X occurs in the absence of HClO<sub>4</sub> in MeCN. However, the oxidative quenching occurs in the presence of HClO<sub>4</sub>, and the rate constant increases linearly with an increase in the  $HClO_4$  concentration. Since the rate constant of the reductive quenching of  $[Ru(bpy)_3]^{2+*}$  by AcrH<sub>2</sub> decreases with an increase in the HClO<sub>4</sub> concentration (Figure

3), the oxidative quenching of  $[Ru(bpy)_3]^{2+*}$  by phenacyl halides  $(PhCOCH_2X)$  may become a predominant pathway at the high HClO<sub>4</sub> concentration. This may be the reason why the  $\Phi$  value increases again in the high concentrations of  $HClO_4$  (Figure 1). The reductive quenching of  $[Ru(bpy)_3]^{2+*}$  by PhCOCH<sub>2</sub>X in the presence of high concentrations of HClO<sub>4</sub> produces PhC(OH)- $CH_2X$  and  $[Ru(bpy)_3]^{3+}$ , the latter of which is known to be a very strong oxidant (the reduction potential is 1.3 V vs SCE).<sup>8a</sup> Thus,  $[Ru(bpy)_3]^{3+}$  can oxidize AcrH<sub>2</sub> even in the presence of HClO<sub>4</sub> to produce  $AcrH_2^{*+}$ , accompanied by regeneration of [Ru-(bpy)<sub>3</sub>]<sup>2+,27</sup> The  $AcrH_2^{*+}$  may react with PhC(OH)CH<sub>2</sub>X after deprotonation to yield the same products as the case in Scheme

In Scheme II as well, the electron transfer step, the acid-catalyzed oxidative quenching of  $[Ru(bpy)_3]^{2+*}$  by PhCOCH<sub>2</sub>X, is rate-determining, and thus no kinetic isotope effect has been observed in the  $[Ru((bpy)_3]^{2+}$ -sensitized reduction of phenacyl bromide by  $AcrH_2$  in the presence of  $HClO_4$  (Table II).

# **Direct Rate Measurements of the Combination and Disproportionation of Vinyl Radicals**

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The rates of removal of vinyl radicals (C2H3) by means of combination and disproportionation reactions have been directly measured at room temperature. Vacuum-ultraviolet (vacuum-UV) flash photolysis of divinylmercury was used to generate vinyl radicals, and vacuum-UV absorption kinetic spectroscopy was used to monitor the time history of vinyl radicals through their absorption at 1647.1 Å. The absolute rate constant for vinyl radical decay was determined to be  $1.0 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ . A ratio of 4.7 for the combination/disproportionation rate constants was measured by gas chromatographic analysis of the final reaction products. Absorption coefficients for the vinyl radical absorption in the 1650-Å region were redetermined. The absolute rate constants for combination and disproportionation are then  $8.2 \times 10^{-11}$  and  $1.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively.

### Introduction

Reactions of vinyl radicals and other unsaturated radicals may play an important chemical role in both the low temperatures of planetary atmospheres and the high temperatures involved in hydrocarbon pyrolysis and combustion. They also have been suggested to be important intermediates in processes involved in carbon growth and soot formation. Despite their perceived importance, relatively little is known about the chemistry of vinyl radicals. This has been due, in part, to the difficulties in generating cleanly these radicals and monitoring directly their behavior. Only in recent years has progress in understanding some aspects of the spectroscopy and gas-phase chemistry of vinyl radicals been reported. By use of either mass spectrometric detection or diode laser absorption techniques, gas-phase kinetic parameters for reactions of vinyl radicals with molecular and atomic oxygen, hydrogen, and HCl have been investigated at low temperatures.<sup>1-5</sup> In earlier work from our laboratory we reported the observation of two relatively strong vacuum-UV absorption features at 1647.1 and 1683.3 Å with extinction coefficients of 1650 and 1120 cm<sup>-1</sup> atm<sup>-1</sup> (base e), respectively, as well as kinetic data for the C<sub>2</sub>H<sub>3</sub>  $+ O_2$  reaction.<sup>6</sup> There it was suggested that the relatively strong vacuum-UV absorptions could provide an important new probe for the study of the reaction kinetics of vinyl radicals. The first use of these absorption bands in such a kinetic measurement is reported here.

In separate work by one of us (A.F.), rates of reactions of vinyl radicals with acetylene, ethylene, and benzene have been measured over the temperature range from 1000 to 1330 K using the very low pressure pyrolysis (VLPP) technique.<sup>7</sup> In these studies divinylmercury or phenyl vinyl sulfone were used as thermal radical initiators, and reaction products were monitored by mass spectroscopy. Assuming a vinyl radical combination rate constant of  $3.3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1100 K, then rate constants of  $(3.3 \pm 0.7) \times 10^{-13}$ ,  $(2.3 \pm 0.3) \times 10^{-13}$ , and  $(7.5 \pm 2.0) \times 10^{-14}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> were measured for vinylation of acetylene, ethylene, and benzene, respectively.

<sup>(27)</sup> The one-electron reduction potential of  $[Ru(bpy)_3]^{3+}$  is 1.29 V (vs SCE; ref 8a) is more positive than the one-electron oxidation potential of AcrH<sub>2</sub> ( $E_{ox}^0 = 0.80$  V vs SCE; ref 12), and thereby the electron transfer from AcrH<sub>2</sub> to [Ru(bpy)<sub>3</sub>]<sup>3+</sup> is highly exothermic.

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Several measurements have been reported on the gas-phase combination/disproportionation ratio of vinyl radicals. There are, however, very large discrepancies in the reported values varying from about 1 to 50 for the above ratio.<sup>8-13</sup> Most of the earlier studies have suffered from either complications regarding the cleanliness of the radical source or the presence of secondary reactions affecting the kinetic analysis. No direct measurements of the rate constants for vinyl combination or disproportionation have been reported. However, estimated values for these important processes have been widely used in combustion and atmospheric models. In the present work we have employed the vacuum-UV flash photolysis-absorption spectroscopy technique coupled with gas chromatographic product analysis to determine both the relative values for  $k_c/k_d$  and also the absolute values for vinyl combination and disproportionation rate constants. Divinylmercury  $(C_2H_3-Hg-C_2H_3)$  has been used again as the photolytic source of vinyl radicals.

#### **Experimental Section**

The vacuum-UV flash photolysis-kinetic spectroscopy apparatus used in the present experiments has been described in earlier publications from this laboratory.<sup>6,14,15</sup> Briefly, a 2200-J discharge, from a battery of six capacitors, through  $N_2$ , produced a flash with a 1/e decay time of about 5  $\mu$ s as monitored in the visible region. Spectroscopic analysis and direct observations of vinyl radicals were performed with a Garton-type flash of 350 J of apparent 2-µs pulse width monitored in the visible region but with less than 1  $\mu$ s measured fwhm in the vacuum-UV.<sup>6</sup> The analysis probe flash was trigged at preset delay times by means of a photomultiplier-oscilloscope circuit. The vacuum-UV output of the analysis flash was focused, through LiF optics, axially through a Suprasil<sup>21</sup> reaction vessel onto the entrance slit of a 2-m Eagle mount vacuum spectrograph with a dispersion of 2.77 Å/mm at the exit plane. Spectra were recorded on vacuum-UV sensitive (Kodak SWR<sup>21</sup>) plates and the data reduced via densitometric measurements in conjunction with previously determined characteristic curves of the plate response. The time history of the vinyl radicals, at room temperature, was monitored directly through their absorption at 1647.1 Å. Gas chromatographic separation and identification of photolysis products were carried out using a flame ionization detector. Immediately following the photolysis flash a sample of the photolyzed mixture was admitted to an evacuated volume that was subsequently pressurized and the sample injected onto the appropriate column by either a gas-tight syringe or directly from a vacuum-tight automatic sampling valve. The sampling valve was connected to both the gas chromatograph and the reaction cell. Two different columns, one with Suprasil<sup>21</sup> packing, 60 in. in length and 1/16-in. i.d., for separation of  $C_1$ - and  $C_2$ -containing hydrocarbons and a second column with Porapak N,<sup>21</sup> also 60 in. long and 1/16-in. i.d., for separating  $C_3$  and  $C_4$  hydrocarbons were used. Most of the chromatographic analyses were done at oven temperatures of 75 °C. The retention times and response of the gas chromatograph were calibrated by injection, through the reaction cell, of standard samples whose concentrations were comparable to these produced by flash photolysis of the substrate.

The radical initiator, divinylmercury, was obtained commercially (from ICN Pharmaceutical) and was purified by trap-to-trap distillation. Gas chromatographic analysis indicated the absence of lower molecular weight hydrocarbons or any detectable higher molecular weight impurities. The precursor was premixed with ultrahigh-purity He (99.99%) and expanded into the reaction vessel. If necessary, additional He or other reactant could be added to the reaction mixture prior to its photolysis. In certain experiments the concentration of precursor or the photolysis flash

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energy was varied. The latter was achieved by changing the number of engaged capacitors for the photolysis flash. In all cases, a single flash produced adequate plate darkening for densitometric analysis.

The concentration range over which the precursor could be varied was limited by the requirement of minimal absorption overlap between precursor molecule and the vinyl radical.

#### **Results and Discussion**

The hydrocarbon products resulting from photolysis of divinylmercury in the Suprasil<sup>21</sup> reaction cell are  $C_2H_2$ ,  $C_2H_4$ , and  $C_4H_6$  (1,3-butadiene). In the range of concentrations used in these experiments (20-60 mTorr of precursor in 400 Torr of He), no other measurable products were observed either spectroscopically or chromatographically. Under conditions of our experiments, that is, the high flash intensity with concomitant high radical concentration and low precursor concentration, the general reaction scheme that has been established<sup>9</sup> for divinylmercury decomposition is somewhat simplified. We may write the following generalized mechanism.

$$Hg-(C_2H_3)_2 = 2C_2H_3 + Hg$$
 (1)

$$Hg-(C_2H_3)_2 = C_2H_2 + C_2H_4 + Hg$$
 (2)

$$2C_2H_3 = C_2H_2 + C_2H_4 \tag{3}$$

$$2C_2H_3 = C_4H_6 (1,3-butadiene)$$
(4)

This mechanism was tested for adequacy in various ways, and several experiments were performed to investigate possible technical complications. As noted earlier, gas chromatographic analysis of photolyzed samples gave no evidence of either high molecular weight products or mercury-containing radicals. Reactions of vinyl radicals with either remaining parent molecule, product acetylene, or ethylene are insignificant. These have been discussed, in some detail, in an earlier publication.<sup>6</sup> In addition, it will be shown in the following section that the relative yield of butadiene to ethylene or acetylene, i.e., the ratio of  $C_4H_6/C_2H_4$ , appears to be independent of divinylmercury pressure and the flash energy. This indicates reaction of vinyl radicals with the divinylmercury remaining after the flash is insignificant. If a competition between vinyl-vinylmercury and vinyl-divinylmercury reactions were important, it might be expected that the relative yields of products would depend upon both the divinylmercury pressure and flash energy.

The spectrographic observations of  $C_2H_2$  and  $C_2H_4$  formation at the shortest delay times following the photolysis flash (5  $\mu$ s) indicate that they are produced, partially, through a primary photolytic process (reaction 2). The contribution of this channel to the total yield of acetylene and ethylene was established by adding oxygen to the reaction mixture. Reaction of vinyl radical with  $O_2$  is now a well-characterized, rapid process with a rate constant of about  $7 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> <sup>1,5,6</sup> Addition of sufficient oxygen would remove vinyl radicals in a sensible time scale and block the radical channels leading to disproportionation and combination. In our experiments, all the butadiene product and also about half of the total acetylene and ethylene products were scavenged by addition of up to 1.5 Torr of oxygen to the photolysis mixtures. The scavenged products, therefore, were formed from radical precursors and not through the molecular detachment process (2). The percent contribution of the direct molecular process (2) on the total yield of acetylene and ethylene was independent of flash intensity. Within the experimental error the yields of acetylene and ethylene, from the direct molecular detachment press, are identical. Further the total yield of products formed by the flash was proportional to the divinylmercury concentration and also to the flash intensity. In general, less than 10% of the divinylmercury is photodissociated by the photolysis flash

Relative Rate Constants. Several gas-phase relative rate measurements for combination versus disproportionation of vinyl radicals have been reported. A large discrepancy exists in the reported values.<sup>8-10</sup> Here, we have used the gas chromatographic data, obtained from the photolyzed samples of divinylmercury,

<sup>(8)</sup> Ibuki, T.; Takezaki, Y. Proc. Chem. Soc. Jpn. 1975, 48, 769.

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 TABLE I: Yield of Products from Combination and

 Disproportionation of Vinyl Radicals from the Photolysis of DVM

 (Divinylmercury) in 400 Torr of He

P, mTorr				flash energ	v
DV	M C <sub>2</sub> H	2 C <sub>2</sub> H <sub>4</sub>	C₄H <sub>6</sub>	(relative)	$k_{\rm c}/k_{\rm d}$
60	3.30	0.90	4.1	6	4.6
50	0.96	0.81	3.3	6	4.1
50	0.64	0.90	4.4	6	4.9
50	) 1.31	0.40	2.2	4	5.5
40	0.85	0.67	3.1	6	4.6
40	) 1.05	1.04	3.5	4	3.4
40	) 0.44	0.30	1.7	3	5.7
25	0.43	0.31	1.5	6	4.8

to measure the relative value of the combination/disproportionation rate constants. Since vinyl radicals, in the present study, are produced relatively cleanly and secondary reactions are not significant, we expect less error and fewer complications in our measurements than in previous studies.

As is shown by the above mechanism, the ratio of rate constants for combination and disproportionation could be derived from the ratio of the final yields of vinyl combination product, 1,3-butadiene, and radical precursor disproportionation products, acetylene and/or ethylene, i.e.

$$k_{\rm c}/k_{\rm d} = [C_4H_6]_{\rm f}/([C_2H_4]_{\rm f} \text{ or } [C_2H_2]_{\rm f})$$
 (A)

The yields of products from the combination and disproportionation of  $C_2H_3$ , after correction of the  $C_2H_2$  and  $C_2H_4$  yields for contributions from the primary molecular photolytic process (2), are listed in Table I. The chromatographic analyses of calibration mixtures, with known concentration of reaction products, showed significantly larger error for measurements of acetylene than those for either ethylene or butadiene. Therefore, for the reported relative rate measurements we have used the yield of  $C_2H_4$  as the indicator for the importance of the disproportionation process. From these data we derive a value of  $4.7 \pm 0.7$  for  $k_c/k_d$ . This value agrees, at least in the order of magnitude, to  $k_c/k_d = 11$ as reported by Ibuki et al.<sup>8</sup> However, agreement is not as good between other reported literature values and our measurements. In most of the earlier work, the measurements are less direct and there are large uncertainties in the analysis of the data or the techniques used.

In our previous paper on the spectroscopy of vinyl radicals,<sup>6</sup> we reported extinction coefficients of  $1650 \pm 500$  and  $1120 \pm 500$  cm<sup>-1</sup> atm<sup>-1</sup> for the absorptions of vinyl radical at 1647.1 and 1683.3 Å, respectively. To obtain a value for the extinction coefficient, a determination of the absolute concentration of the vinyl radical was required. In those determinations, due to the lack of sufficient information on the extent of a disproportionation reaction, the initial concentration of vinyl radical was determined primarily from the final yield of butadiene. In the present studies we have shown that the contribution of the disproportionation reaction to the decay of  $C_2H_3$  is about 20% of the combination reaction. The initial concentration of vinyl radical, therefore, should be derived as

$$[C_2H_3]_0 = 2[C_4H_6]_f + 2[C_2H_4]_f$$
(B)

again following corrections for molecular versus radical yields. The correction suggests about 20% higher initial concentration of vinyl radical than those used in our previous work. As a result, the corrected values for the extinction coefficients of vinyl absorption at 1647.1 and 1683.3 Å are 1320 and 896 cm<sup>-1</sup> atm<sup>-1</sup>, well within the error limits expressed earlier.<sup>6</sup>

Absolute Rate Constants. It is clear that information about absolute rates of radical-radical reactions will ultimately be necessary before an understanding of the factors affecting the fate of radicals will be really possible. For only a few radicals has the rate of combination been directly studied. The combination of methyl radicals is probably the most extensively studied system, both theoretically<sup>16</sup> and experimentally.<sup>17</sup>



Figure 1. Observed second-order decay of vinyl radicals (40 mTorr of

 $(C_2H_3)_2Hg$  in 400 Torr of He). Typical measurement error is indicated.

In the present study we have monitored the temporal profile of the vinyl radical via its absorption at 1647.1 Å in the vacuum-UV. The time history of the radical decay was plotted in second-order fashion as shown in Figure 1. Within the error of our measurements, the slope retained its linearity to about 160  $\mu$ s, the maximum time delay probed. In all cases time, measured from a photograph of the oscilloscope trace, was determined from the peak of the photolysis flash to the onset of the analysis flash. At t = 0 [C<sub>2</sub>H<sub>3</sub>] was calculated from chromatically determined products, as in eq B, and provided a redundant measure of the extinction coefficient. At all other times, [C<sub>2</sub>H<sub>3</sub>] was calculated by using the Lambert-Beer law and the extinction coefficient of 1320 cm<sup>-1</sup> atm<sup>-1</sup> for the transition at 1647 Å used in these measurements. The decay of vinyl radicals with time, shown in Figure 1, was obtained from mixtures of 40 mTorr of divinylmercury in 400 Torr of He. Both combination and disproportionation processes contribute to the observed decay (eq A) with combination being the dominant component.

$$-d[C_{2}H_{3}]/dt = 2[k_{c}(C_{2}H_{3})^{2} + k_{d}(C_{2}H_{3})^{2}]$$
$$= 2[k_{obs}(C_{2}H_{3})^{2}]$$
(C)

Within the error of our measurements, we cannot distinguish and separate each component of the decay. The slope derived from the least-squares fit of the second-order plot of decay of vinyl yields an observed decay rate constant of  $(1.0 \pm 0.15) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This observed rate constant is the sum of the rate constants for the disproportionation and combination processes. By use of the relative value of  $k_c/k_d = 4.7$ , absolute rate constants of  $8.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for disproportionation and  $1.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for disproportionation are derived. The experimental error in the slope of vinyl decay, shown in Figure 1, is 15%. A detailed error analysis of the flash photolysis-kinetic spectroscopy technique done previously suggests that an error of 25% is expected for rate measurements of this kind, if all sources of errors are correctly identified and evaluated.<sup>18</sup> Therefore, the total rate constant should be expressed, preferably, as  $(1.0 \pm 0.25) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

In another direct measurement of reaction 3, although at lower pressures in the subTorr region, MacFadden and Currie<sup>19</sup> observed exclusively a disproportionation process in the dimerization reaction of  $C_2H_3$ . The temperature of their system may have been quite high as well so that the value they obtained for the dimerization reaction,  $5.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is probably well into the falloff region and within a factor of 3 of the present value for the disproportionation process.

In addition, the transition states for combination and disproportionation are probably not comparable. For example, in the H + HCO radical-radical reaction, calculations indicate that there

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are two processes: one is a direct bimolecular abstraction to produce  $H_2$  + CO and a second process to produce the excited adduct, H<sub>2</sub>CO\*, followed by molecular elimination yielding the same  $H_2$  + CO or stabilization.<sup>20</sup>

(21) Certain commercial instruments and materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

In our experiments we could not approach the low pressures required to observe the falloff in 1,3-butadiene formation that might provide firm evidence for two separate transition states for the reaction. We plan on studies at higher temperature to examine this question.

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**Registry No.** C<sub>2</sub>H<sub>3</sub>, 2669-89-8; C<sub>2</sub>H<sub>3</sub>-Hg-C<sub>2</sub>H<sub>3</sub>, 1119-20-6.

# Picosecond Raman Measurements of Electron Transfer in the Metal-to-Ligand Charge-Transfer Excited States of 1,10-Phenanthroline-Ruthenium(II) Complexes

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Picosecond time-resolved resonance Raman spectroscopy has been utilized to investigate the metal-to-ligand charge-transfer (MLCT) excited states of Ru(II) mixed ligand complexes of 1,10-phenanthroline and 2,2'-bipyridine. A two-color pump and probe technique is shown to provide a powerful method for separating the highly congested spectra of these complexes. The first pure excited-state spectrum of  $[Ru(phen)_3]^{2+}$  has been obtained. It is clearly demonstrated by using this approach that the interpretation of previous nanosecond Raman results on similar complexes is incorrect with respect to the assignments of the electronic-state parentage of the observed vibrational bands. The implications of these results are discussed with respect to the dynamics of interligand electron transfer in the excited MLCT state.

### 1. Introduction

Transition-metal complexes with polypyridyl ligands have attracted a great deal of attention due to their interesting photochemical properties.<sup>1</sup> Ruthenium complexes containing 2,2'bipyridine (bpy) and 1,10-phenanthroline (phen) have been particularly well studied.<sup>2-4</sup> In the visible and near-ultraviolet regions of the spectrum these complexes1 exhibit intense metalto-ligand charge-transfer (MLCT) absorptions, and much of the research has focused on the photophysics of these low-lying electronic states. Resonance Raman spectroscopy (RR) has been highly successful in determining the vibrational structure of the excited MLCT states of bpy-substituted complexes.<sup>5,6</sup> For the phen-substituted complexes, however, the excited state is not as well understood. Several theoretical<sup>7-10</sup> attempts have been made to calculate the molecular structure of the [Fe(phen)<sub>3</sub>]<sup>2+</sup> MLCT state. The lowest  $\pi^*$  orbital of H<sub>2</sub> phen<sup>2+</sup> has also been modeled<sup>11</sup> to investigate the chromophoric differences between the phen and bpy ligands from a molecular orbital perspective. Yet, no real structural information exists to supplement these studies.

This paper is one of a series<sup>12-14</sup> that investigates the mechanisms resulting in electron localization and, in addition, the factors controlling the rates of interligand electron transfer in the MLCT state. In particular, we report the picosecond RR spectra of the complexes  $[Ru(bpy)_{3-n}(phen)_n]^{2+}$  where n = 0-3. Turro et al.<sup>15</sup> have published the RR spectrum of [Ru(phen)<sub>3</sub>]<sup>2+</sup> and have recently published<sup>16</sup> results on the same mixed ligand bpy complexes discussed in this paper. The authors have concluded<sup>16</sup> that several excited-state bands in  $[Ru(phen)_3]^{2+}$  can be identified and that these same excited-state bands persisted in tandem with excited bpy bands in the mixed ligand complex [Ru(bpy)<sub>2</sub>-(phen)]<sup>2+</sup>. We have reanalyzed the spectroscopy of these complexes and have determined that it is much more complicated than originally thought. A new interpretation is found for the population of electron density on the phen and bpy ligands following MLCT excitation of mixed ligand complexes.

#### 2. Experimental Section

 $[Ru(phen)_3]^{2+}$ ,  $[Ru(bpy)(phen)_2]^{2+}$ , and  $[Ru(bpy)_2(phen)]^{2+}$ were synthesized and purified according to the methods reported in the literature.<sup>17</sup> All products were analyzed by mass spectroscopy. [Ru(bpy)<sub>3</sub>]<sup>2+</sup> was purchased from Aldrich Chemical Co. and was used without further purification. Solvents used in the spectroscopic studies were HPLC grade acetonitrile from

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