between typical C–S single and double bonds was also suggested. In addition it was reported that no evidence was found for $Cl^{\bullet}$ bonding at alternative sites.

It is beyond the scope of this investigation to determine the structural nature of the $Cl^{\bullet}/CS_2$ complex. It is, however, interesting to compare the UV–visible absorption spectra of the $Cl^{\bullet}$ benzene, CS_2, and pyridine complexes (Figure 7) and note the dramatic resemblance of the $Cl^{\bullet}/CS_2$ spectrum to that of the π-benzene complex. The equilibrium constants determined in this work[38] do confirm the strength of interaction of $Cl^{\bullet}$ with CS_2 to be intermediate between the π-benzene and σ-pyridine complexes, i.e., 200 M^{-1} > 1900 M^{-1} > 123 000 M^{-1}.

Conclusions

The reactivity of $Cl^{\bullet}$ toward CS_2 to form a reversible $Cl^{\bullet}/CS_2$ molecular complex has been investigated by time-resolved pulse radiolysis and LFP techniques. The equilibrium constant of the $Cl^{\bullet}/CS_2$ complex has been determined and is compared to that of the $Cl^{\bullet}$/benzene π-complex and a reevaluated K for the $Cl^{\bullet}$/pyridine σ-complex.

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[38] It should be noted that considerable error may still be associated with the absolute values of K determined by comparison with the 200 M^{-1} value for $Cl^{\bullet}$/benzene if k_{bi} for $Cl^{\bullet}$ + benzene determined in this work represents a more accurate measurement.

Determination of Metal–Hydride and Metal–Ligand (L = CO, N_2) Bond Energies Using Photoacoustic Calorimetry†

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Abstract: Photoacoustic calorimetry has been used to determine the M–H mean bond dissociation energies in $Ru(dmpe)_2H_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) and $H_2IrCl(CO)(PPh_3)_2$ (63.5 ± 2.0 and 64.0 ± 1.0 kcal mol^{-1}, respectively). The quantum yield for loss of H_2 from the ruthenium dihydride complex has been measured by transient actinometry as 0.85 ± 0.05. $Ru(dmpe)_2$ is an unsolvated intermediate and reacts with CO and N_2 to form $Ru(dmpe)_2CO$ and $Ru(dmpe)_2N_2$. By measuring the enthalpies of these reactions and utilizing the Ru–H mean bond dissociation energy, the Ru–CO and Ru–N_2 bond energies have been determined (43.0 ± 2.0 and 18.8 ± 2.0 kcal mol^{-1}, respectively).

Introduction

Transition metal hydride complexes represent an important class of organometallic compounds because of their ability to function in a variety of catalytic and stoichiometric processes.[1] For such processes to be considered in any detail, a knowledge of both kinetic and thermodynamic factors is desirable. Although kinetic studies regarding metal hydride forming/breaking processes have received constant attention,[2] there is a notable paucity of accurate values for M–H bond enthalpies in the literature, a fact which arises from the difficulty in making such measurements.[3] Isolated examples have employed kinetic measurements,[4] conventional solution calorimetry,[5] and, more recently, electrochemical cycles.[6]

Photoacoustic calorimetry (PAC) has received considerable attention and has been used to examine the energetics of a host of biochemical, organic, and organometallic reactions.[7] The PAC experiment detects, by way of the resulting thermal expansion of the solvent, the heat released into solution from reactions initiated by absorption of a laser pulse. Provided that the mechanism and the quantum yield for the photochemical reaction are well defined, the enthalpy changes due to assigned chemical processes can be evaluated. In many cases, this overall enthalpy change may be attributed to the cleavage and/or formation of specific bonds.

In the field of organometallic photochemistry, studies have concentrated on determining the metal–carbonyl bond energies in the group 6 hexacarbonyl complexes $M(CO)_6$ (M = Cr, Mo, W) and the energetics of the subsequent reaction between $M(CO)_5$ and alkane solvents.[8] The initial photodissociation of CO from $Cr(CO)_6$ and the ensuing solvent coordination to $Cr(CO)_5$ occurs in less than 25 ps.[9] The replacement of CO in $Cr(CO)_6$ by heptane is endothermic by 27 kcal mol^{-1} and yields a value for the chromium–solvent interaction of 9.8 kcal mol^{-1}.[10] In the case of a more coordinating medium (Et_3SiH), the chromium–solvent interaction was measured to be 21 kcal mol^{-1}.[11] Although this solvation effect is itself of primary significance, it is precisely this phenomenon which can be an underlying problem in evaluating not only the absolute bond energies of photolabile ligands, but also the energetics of subsequent reactions between organometallic fragments and an incoming ligand such as H_2 or CO. In this latter

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† Dedicated to the memory of Professor Jean-Louis Roustan.

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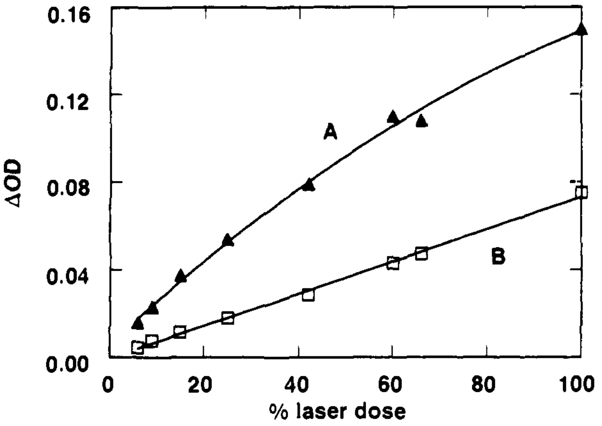

Figure 1. Changes in optical density as a function of 308-nm laser dose for triplet benzophenone in benzene (A, monitored at 525 nm) and Ru(dmpe)$_2$ in cyclohexane under argon (B, monitored at 470 nm).

case, the rate of reaction is often relatively slow and outside that of the response time of the apparatus, preventing accurate bond enthalpy determinations. If the energy of solvation is unknown or neglected, calculation of bond energies from enthalpy changes will lead to discrepancies.

The transient photochemistry of Ru(dmpe)$_2$H$_2$ (dmpe = 1,2-bis(dimethyl)phosphinoethane) has recently been reported.[12] Photodissociation of H$_2$ occurs rapidly (and reversibly) in cyclohexane to yield Ru(dmpe)$_2$ as a "naked" intermediate (eq 1).

$$\mathrm{Ru(dmpe)_2H_2} \overset{h\nu}{\rightleftharpoons} \mathrm{Ru(dmpe)_2 + H_2} \qquad (1)$$

In this study, we describe how photoacoustic calorimetry can be used to determine *directly* the Ru–H mean bond dissociation energy in Ru(dmpe)$_2$H$_2$, since solvation of Ru(dmpe)$_2$ is not a concern. Similarly, by employing CO and N$_2$ as traps for Ru(dmpe)$_2$ to form Ru(dmpe)$_2$CO and Ru(dmpe)$_2$N$_2$, we have measured the Ru–CO and Ru–N$_2$ bond strengths via secondary thermal reactions. To complement this study, we have also determined the mean M–H bond dissociation energy in the related complex H$_2$IrCl(CO)(PPh$_3$)$_2$. This value was first determined over 20 years ago by Vaska and Werneke[4] and, as such, is a good reference with which to compare our data.

Results

(a) Determination of the Quantum Yield for Loss of H$_2$ from Ru(dmpe)$_2$H$_2$. In order to apply the PAC technique for measuring the Ru–H bond energy in Ru(dmpe)$_2$H$_2$, the quantum yield for the elimination of H$_2$ needed to be established. To calculate this value, we have used time-resolved absorption methods using triplet benzophenone as an actinometer.[13] Solutions of Ru(dmpe)$_2$H$_2$ in cyclohexane and of benzophenone in benzene were prepared with matched optical densities (typically 0.3) at 308 nm. Determination of the quantum yield involved a series of transient absorption measurements in which the changes in optical density due to the formation of benzophenone triplet (at 525 nm) and Ru(dmpe)$_2$ (at 470 nm) were measured as a function of laser dose (Figure 1).

The data were then analyzed using eq 2, where ΔOD$_x$ and

$$\epsilon_x\Phi_x = \lim_{\mathrm{dose}\to 0}\left(\frac{\Delta \mathrm{OD_x}}{\Delta \mathrm{OD_a}}\epsilon_a\Phi_a\right) \qquad (2)$$

ΔOD$_a$ are the OD changes for sample and actinometer, Φ_a is the quantum yield for the actinometer (1 in benzene at 525 nm[14]), ϵ_a is the extinction coefficient of the actinometer (7800 dm^3 mol^{-1} cm^{-1} at 525 nm[13]), and ϵ_x is the extinction coefficient of Ru(dmpe)$_2$. The product $\epsilon_x\Phi_x$ was calculated for each pair of data points and then extrapolated to zero light dose (Figure 2). We note that the plot of Figure 2 should in principle give a horizontal line. The fact that it does not reflects a saturation effect due to the fact that at higher laser doses benzophenone triplet is sufficiently strongly absorbing to compete with the ground state for light absorption. Thus, the correct $\epsilon_x\Phi_x$ value is expected to be that obtained by extrapolation of the plot to zero laser dose.

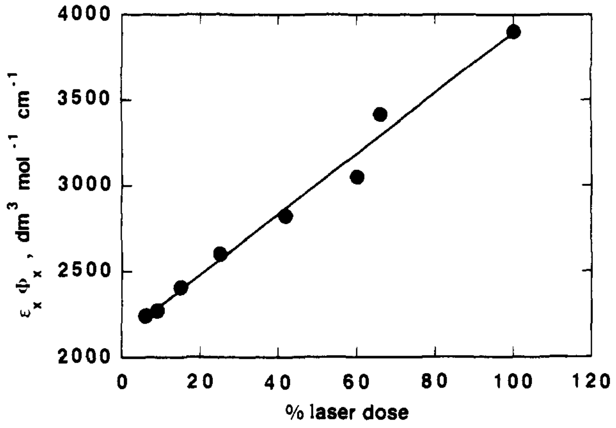

Figure 2. Plot of $\epsilon_x\Phi_x$ as a function of 308-nm laser dose for Ru(dmpe)$_2$ in cyclohexane under argon.

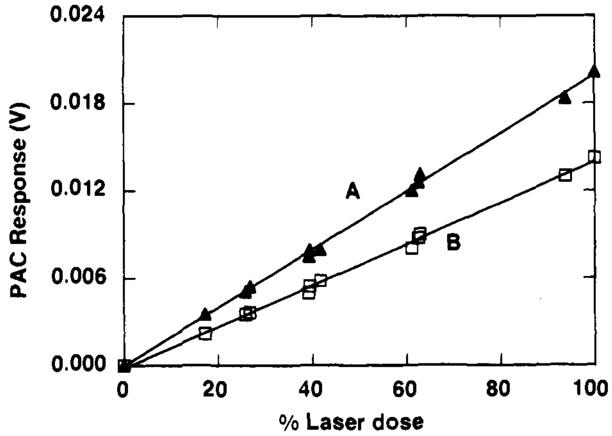

Figure 3. Photoacoustic response for the photodissociation of H$_2$ from Ru(dmpe)$_2$H$_2$ in cyclohexane under argon. The response for OHBP in cyclohexane is also shown for comparison: (A) OHBP and (B) Ru(dmpe)$_2$H$_2$ (100% laser dose corresponds typically to around 50 μJ).

An extinction coefficient of 2400 dm^3 mol^{-1} cm^{-1} at 470 nm for Ru(dmpe)$_2$ has been previously determined by laser flash photolysis.[12] Using this method, the quantum yield for photocleavage of Ru(dmpe)$_2$H$_2$ is 0.85 ± 0.05.

(b) Measurement of the Ru–H Bond Energy in Ru(dmpe)$_2$H$_2$. When Ru(dmpe)$_2$H$_2$ is irradiated (λ = 308 nm) in cyclohexane under an argon atmosphere, Ru(dmpe)$_2$ is formed within 30 ns.[12] More recent studies demonstrate that this H$_2$ elimination reaction occurs within a few picoseconds.[15] In the absence of an excess of hydrogen, the subsequent oxidative addition of photoeliminated H$_2$ to re-form the dihydride complex occurs over tens of microseconds. Therefore, when the PAC experiment is carried out under these conditions using a 0.5-MHz transducer (see Experimental Section), the enthalpy change corresponds to the difference between the mean bond dissociation energies (BDE) of Ru–H (×2) and H$_2$ (eq 3).

$$\Delta H_{\mathrm{obs}} = 2\mathrm{BDE(Ru{-}H)} - \mathrm{BDE(H{-}H)} \qquad (3)$$

A plot of the photoacoustic response for Ru(dmpe)$_2$H$_2$ in cyclohexane under argon versus relative laser intensity is shown in Figure 3. The corresponding plot for the *o*-hydroxybenzophenone

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Table I. Enthalpy Changes and Metal–Ligand Bond Dissociation Energies Determined by Photoacoustic Calorimetry

reaction	ΔH_{obs} (kcal mol^{-1})	BDE (kcal mol^{-1})
$Ru(dmpe)_2H_2 \rightarrow Ru(dmpe)_2$	22.7	Ru–H = 63.5 ± 2.0
$Ru(dmpe)_2H_2 \rightarrow Ru(dmpe)_2CO$	−20.3	Ru–CO = 43.0 ± 2.0
$Ru(dmpe)_2H_2 \rightarrow Ru(dmpe)_2N_2$	3.9	$Ru–N_2$ = 18.8 ± 2.0
$H_2IrCl(CO)(PPh_3)_2 \rightarrow IrCl(CO)(PPh_3)_2$	24.0	Ir–H = 64.0 ± 1.0^{a,b}

[a] This work. [b] 60 kcal mol^{-1}, ref 4.

(OHBP) reference[16] is included for comparison. The observed heat deposition is related to the term α (defined as the ratio of the slopes of the sample and the reference sample) by eq 4, where

$$\Delta H_{obs} = E_\nu(1 - \alpha)/\Phi \qquad (4)$$

E_ν is the energy of a mole of photons (92.8 kcal mol^{-1} at 308 nm) and Φ is the quantum yield for the observed photoprocess.

From the slopes in Figure 3, $\alpha < 1$, demonstrating that the observed reaction is endothermic. Since the bond energy for hydrogen is accurately known (104.2 kcal mol^{-1}), the observed enthalpy change can be used to calculate the Ru–H mean bond dissociation energy using eq 3 and yields a value of 63.5 ± 2.0 kcal mol^{-1} (see Table I). The errors in the bond energy derive mainly from errors in Φ and α, although in these systems moderate errors in Φ do not introduce major differences into the bond energies. Thus, the extreme values for Φ of 0.80 and 0.90 (from 0.85 ± 0.05) would lead to mean bond dissociation energies of 64.0 and 63.1 kcal mol^{-1}.

In order to confirm that H_2 elimination from $Ru(dmpe)_2H_2$ occurs as a unique photochemical process, a PAC experiment was conducted under conditions in which both cleavage and re-formation of the two Ru–H bonds should occur; i.e., the observed enthalpy change is zero. Since the second-order rate constant for the reaction of $Ru(dmpe)_2$ with H_2 in cyclohexane is ca. 6×10^9 dm^3 mol^{-1} s^{-1},[12] it follows that the regeneration of $Ru(dmpe)_2H_2$ under 1 atm of hydrogen ($[H_2] = 3.8 \times 10^{-3}$ mol dm^{-1})[17] is complete in less than 50 ns and within the response time of the transducer. In accord with this lifetime, when the PAC experiment was carried out under these conditions, the observed enthalpy change was indeed equal to zero.

(c) Measurement of the Ru–CO Bond Strength in $Ru(dmpe)_2CO$. Previous laser flash photolysis experiments have shown that $Ru(dmpe)_2$ is readily trapped by CO in cyclohexane to form $Ru(dmpe)_2CO$ with a rate constant of ca. 5×10^9 dm^3 mol^{-1} s^{-1}.[12] Therefore, under 1 atm of CO ($[CO] = 9.3 \times 10^{-3}$ mol dm^{-3}),[18] the thermal reaction between $Ru(dmpe)_2$ and CO is complete within the response time of our transducer. Since the Ru–H bond energy has already been determined, the Ru–CO bond energy can be measured by the PAC technique according to:

$$Ru(dmpe)_2H_2 \xrightarrow{h\nu} Ru(dmpe)_2 \xrightarrow{CO} Ru(dmpe)_2CO$$

$$\Delta H_{obs} = 2BDE(Ru{-}H) - BDE(H{-}H) - BDE(Ru{-}CO) \qquad (5)$$

The representative PAC plot for the reaction is shown in Figure 4. In contrast to the endothermic enthalpy change observed in the absence of added substrates, the reaction in the presence of CO is exothermic by 20.3 kcal mol^{-1}. From eq 5, we derive a value of 43.0 ± 2.0 kcal mol^{-1} for the Ru–CO bond energy (see Table I).

(d) Measurement of the $Ru–N_2$ Bond Strength in $Ru(dmpe)_2N_2$. Preliminary laser flash photolysis experiments have shown that $Ru(dmpe)_2$ is readily trapped by N_2 to form $Ru(dmpe)_2N_2$ with a rate constant of ca. 10^9 dm^3 mol^{-1} s^{-1}. Thus, under 1 atm of nitrogen ($[N_2] = 7.6 \times 10^{-3}$ mol dm^{-3}),[18] the $Ru–N_2$ bond energy can be measured using a method analogous to that described for CO. The representative PAC plot is shown in Figure 5. The reaction in the presence of N_2 is endothermic by 4 kcal mol^{-1} (see Table I) and yields a $Ru–N_2$ bond strength of 18.8 ± 2.0 kcal mol^{-1} (eq 6).

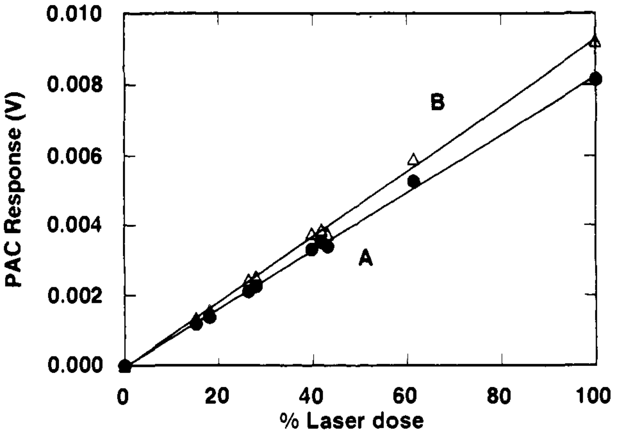

Figure 4. Photoacoustic response for reaction of $Ru(dmpe)_2$ with CO in cyclohexane. The response for OHBP in cyclohexane is shown for comparison: (A) OHBP and (B) $Ru(dmpe)_2H_2$ (100% laser dose corresponds typically to around 50 μJ).

$$Ru(dmpe)_2H_2 \xrightarrow{h\nu} Ru(dmpe)_2 \xrightarrow{N_2} Ru(dmpe)_2N_2$$

$$\Delta H_{obs} = 2BDE(Ru{-}H) - BDE(H{-}H) - BDE(Ru{-}N_2) \qquad (6)$$

(e) Measurement of the M–H Mean Bond Dissociation Energy in $H_2IrCl(CO)(PPh_3)_2$. Following the determination of the Ru–H mean bond dissociation energy in $Ru(dmpe)_2H_2$, we have measured the metal hydride bond strengths in the related compound $H_2IrCl(CO)(PPh_3)_2$ for comparison. Photoelimination of H_2 from $H_2IrCl(CO)(PPh_3)_2$[19] occurs with a quantum yield of 0.56.[20] In contrast to $Ru(dmpe)_2$, the corresponding square-planar complex $IrCl(CO)(PPh_3)_2$ reacts with H_2 less rapidly[20] and well outside the response time of the transducer. Irradiation of $H_2IrCl(CO)(PPh_3)_2$ in benzene solution under 1 atm of hydrogen results in an endothermic enthalpy change of 24.0 kcal mol^{-1}. Using eq 3, we calculate the Ir–H mean bond dissociation energy to be 64.0 ± 1.0 kcal mol^{-1}.

Discussion

In this report we have determined the M–H mean bond dissociation energies in $Ru(dmpe)_2H_2$ and $H_2IrCl(CO)(PPh_3)_2$ using photoacoustic calorimetry. The validity of our results is borne out by the value of 64 kcal mol^{-1} found for $H_2IrCl(CO)(PPh_3)_2$, which is in excellent agreement with the bond energy (60 kcal mol^{-1}) derived from earlier kinetic studies.[4] We believe that these values represent the first application of PAC to the determination of M–H mean bond dissociation energies via a *direct method*. In a previous report, Nolan et al.[21] used the photoacoustic technique to measure the Ir–H bond strength in $Cp^*Ir(PMe_3)H_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), although their value was determined by a hydrogen abstraction reaction using *tert*-butoxyl radicals generated by photochemical cleavage of *tert*-butyl peroxide.

The Ru–H bond energy is comparable to literature values for other complexes of the iron triad. Tilset and Parker[22] have recently reported corrected values of 57 and 65 kcal mol^{-1} for $CpFe(CO)_2H$ and $CpRu(CO)_2H$ ($Cp = \eta^5\text{-}C_5H_5$), respectively,[22] as well as a value of 67 kcal mol^{-1} for $Fe(CO)_4H_2$, which is marginally higher than the previously determined value.[3] Calderazzo[23] has proposed a lower limit of 78 kcal mol^{-1} for the Os–H mean bond dissociation energy in $Os(CO)_4H_2$, although it is generally accepted that third-row transition metal hydride bonds are stronger than either

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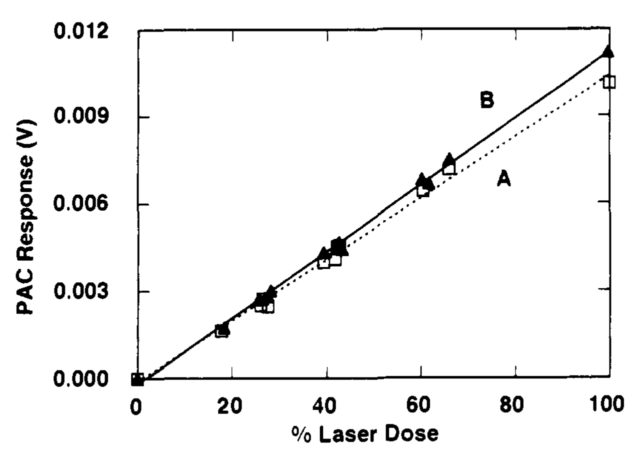

Figure 5. Photoacoustic response for the reaction of $Ru(dmpe)_2$ with N_2 in cyclohexane. The response for OHBP in cyclohexane is shown for comparison: (A) OHBP and (B) $Ru(dmpe)_2H_2$ (100% laser dose corresponds typically to around 50 μJ).

first- or second-row complexes. We might have expected to find a difference between our value and those given above arising from the significant change in the nature of the ancilliary ligands about the metal. However, a quantitative analysis correlating geometric and electronic factors with bond energy data is absent at the present time. Interestingly, guided ion beam mass spectrometry studies on singly ligated metal hydride ions have pointed to an "intrinsic" transition metal hydride bond enthalpy of ca. 59 kcal mol^{-1} for second-row metals.[24]

In discussing the accuracy of our measurements, it is pertinent to note that, although the photoacoustic technique utilizes the quantum yield for the reaction, the dependence of the Ru-H bond strength on its error in Φ is only ± 0.6 kcal mol^{-1}.

The absence of solvation combined with the high reactivity that $Ru(dmpe)_2$ exhibits toward added substrates has allowed the measurement of both Ru-CO and $Ru-N_2$ bond energies. The Ru-CO binding energy in $Ru(dmpe)_2CO$ is within the range of 24-43 kcal mol^{-1} found for other M-CO complexes[25] and is close to the estimates for the bond dissociation energy of the first CO ligand from both $Fe(CO)_5$[26] and $Ru(CO)_5$.[27] Our determination of the Ru-CO bond energy via a secondary thermal process represents a complementary approach to previous PAC studies in which dissociation of the M-CO bond has been employed.

In contrast to the overall exothermic change upon going from $Ru(dmpe)_2H_2$ to $Ru(dmpe)_2CO$, the reaction with N_2 to give $Ru(dmpe)_2N_2$ results in an endothermic change. Since there are very few reports of $M-N_2$ bond energies in the literature,[28] it is difficult to discuss in detail the value that we obtain. However, a bond energy of 19 kcal mol^{-1} demonstrates a weak coordination of N_2 to the metal center.

Experimental Section

Materials. All materials were obtained from Aldrich unless otherwise stated. $Ru(dmpe)_2H_2$ was a gift from Professor R. N. Perutz. $H_2IrCl(CO)(PPh_3)_2$ was prepared from $IrCl(CO)(PPh_3)_2$ as described in the literature.[29] Cyclohexane (BDH Omnisolve) was distilled over CaH_2 under argon prior to use. Benzene (BDH Omnisolve) was used as received. Benzophenone (99.9%) was recrystallized twice from ethanol before use. The standard for PAC experiments, o-hydroxybenzophenone (OHBP), was recrystallized from ethanol. Argon, hydrogen, carbon monoxide, and nitrogen were obtained from Air Products and were >99.9%. UV-visible absorption spectra were recorded using a Hewlett-Packard 8451A diode array spectrophotometer.

Quantum Yield Measurements. Samples of $Ru(dmpe)_2H_2$ in cyclohexane were prepared using standard Schlenk techniques and transferred via cannula under argon to 7 × 7 mm Suprasil cells capped by septa. The absorbance of a solution was typically 0.3 at 308 nm. The flash photolysis apparatus was similar to that previously described[30] with the laser dose at 308 nm being attenuated by a series of calibrated neutral density filters. For the actinometer, samples of benzophenone in benzene with the same absorbance as the ruthenium sample (to within 0.01 absorbance unit) were then irradiated immediately afterward to avoid any drift in the apparatus. The quantum yield for $Ru(dmpe)_2H_2$ was determined three times. In every experiment, eight shots were recorded at each laser dose both for the sample and actinometer.

PAC Experiments. Photoacoustic experiments were carried out using an apparatus similar to that described previously.[31] Attenuated pulses from a Lumonics EX-510 excimer laser (λ = 308 nm, 5-ns pulse, 30 mJ per pulse) were used for excitation of samples contained in a 10 × 10 mm path length quartz cuvette. The bottom face of the cuvette was placed into contact with a Panametrics A101, 0.5-MHz transducer. A thin layer of silicone grease was applied between the cell and the transducer to ensure efficient transmission of the photoacoustic signals. In addition, the cell was clamped into place with a brass mount to prevent any movement of the arrangement during the course of the experiment. Signals from the transducer were amplified by a Panametrics 5670 preamplifier and then fed to a Tektronix 2440 digital oscilloscope. The system was interfaced to a Macintosh IIci computer using National Instruments interfaces and LabVIEW-2.2 software. The magnitude of the photoacoustic signal was measured from the amplitude of the first wave. The excitation beam from the laser was attentuated by a series of calibrated neutral density filters allowing for 100% to 5% transmission before passing through a pinhole (diameter ca. 1 mm). Thus, laser energies at the sample were in the range 10-50 μJ. To account for variations in laser beam intensity, a fraction of the beam (ca. 10%) was diverted using a quartz plate beam splitter onto a photodiode arrangement.

In order to verify that all of the chemical processes in our experiments give rise to "prompt" heat, we use an analysis which correlates the appropriate chemical kinetics with the effective response time of the transducer. The latter parameter has been determined in two ways. The first method, which utilizes the calculated transit time for a 1-mm acoustic wave in benzene, yields a response time of ca. 500 ns. A second value, determined experimentally, was established using the hydrogen abstraction reaction from phenol by *tert*-butoxyl radicals which occurs with a rate constant of 3.3×10^8 dm^3 mol^{-1} s^{-1} in benzene.[32] Briefly, solutions of *tert*-butyl peroxide in benzene were irradiated in the presence of increasing phenol concentrations until the amplitude of the photoacoustic signal became invariant of phenol concentration. From these data, we conclude that contributions to the acoustic wave (i.e., "prompt" heat) arise from heat-evolving processes which occur within ca. 200 ns of the laser pulse. Since both photochemical and subsequent thermal reactions in this study have been shown to occur on a timescale <30 ns, the corresponding enthalpy changes all take place well within the shortest calculated response time of the transducer. We note that the response time determined in this way does not reflect a true "time constant" or "bandwidth" for the system, but, rather, it identifies the longest time in which processes can lead to prompt heat without any detectable effect on the shape of the photoacoustic wave. Processes with lifetimes above 200 ns may be faster than the time constant for the system, but are sufficiently long to introduce detectable changes in the shape/amplitude of the photoacoustic response.

Samples of $Ru(dmpe)_2H_2$ in cyclohexane were prepared using standard Schlenk techniques and then transferred via canula to the 10 × 10 mm quartz cell capped with a septum used in the PAC apparatus. The absorbance of the sample was typically 0.13-0.16.

OHBP in cyclohexane was prepared in a separate cuvette to the same absorbance (to within 0.01 absorbance unit) and then carefully transferred to the 10 × 10 mm cell without altering the PAC arrangement. At the end of the experiment, the PAC cell was removed, and the absorbance of the OHBP sample was remeasured so that any corrections for differences in absorbance could be made.

For the photoacoustic experiments carried out in the presence of H_2, CO, or N_2, the 10 × 10 mm septum-capped cell was purged with the appropriate gas for 20 min prior to being clamped in place for the experiment. The absorbance of the sample was remeasured after purging

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so that any evaporation of the solvent was accounted for.

Each photoacoustic experiment was recorded at least twice. The transducer signals and energy meter readings were the average of eight shots.

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Electrolyte Effects on the Photophysical Properties of Intramolecularly Hydrogen-Bonded Molecules

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Abstract: Salt effects on the photophysics of the intramolecular hydrogen-bonded solute molecule 1-aminofluoren-9-one (1-AF) are examined in acetonitrile solution. Unlike previous studies on the related molecule 3-aminofluoren-9-one (3-AF), combined steady-state and time-resolved studies show that 1-AF forms ground-state complexes with dissolved cations. The association between 1-AF and the dissolved electrolytes is dependent on the size of the cation. No complexes are observed between 1-AF and the molecular cations Bu_4N^+ and Me_4N^+. The differences between the photophysics of 1-AF and 3-AF in acetonitrile–salt solutions are discussed in terms of the molecular properties arising from the intramolecular hydrogen bond between the amino nitrogen and the carbonyl group present in 1-AF.

Introduction

Medium effects on the energetics of charge-transfer transitions have played a central role in developing solvation scales for solute molecules in both neat solvents[1] and binary solvent mixtures.[2] In binary mixtures, observed changes in absorption spectra are used to evaluate the importance of specific solvation. In some cases, molecular solutes are solvated by solvent molecules in the same proportion as the bulk concentrations of the mixture components. In other cases, specific solvation by one of the components occurs. In this later limit, it is the degree of specific solvation that plays an important role in determining chemical reactivity of the solute, not the composition of the mixed solvent system. Similar to solvent mixtures, electrolyte solutions have the potential of affecting molecular reactivity through bulk and specific interactions.[3–5] Added salts affect bulk solution properties such as polarity, polarizability, viscosity, and dielectric constant. The solvation of ions also impacts the intermolecular solvent structure and dynamical motion of individual solvent molecules.[6,7] Similar to the cases of specific solvation in mixed liquids, electrolytes also have the potential to form specific interactions with solute molecules, thereby altering both the photophysics and the photochemistry. Isolating the effects of these different types of interactions between electrolyte and solute molecules is a challenging and important problem.

In this paper, electrolyte effects on the solution photophysics of 1-aminofluoren-9-one (1-AF) and 3-aminofluoren-9-one (3-AF) are compared. We recently reported a study of salt effects on the photophysics of 3-AF in acetonitrile solution.[8] That study reported three significant observations that arise from bulk interactions between dissolved salts and molecular solutes. First, the maxima of both the absorption and emission spectra red-shifted with increasing salt concentration. This was interpreted in terms of the salt effects on solution polarity. Second, changes in the radiative rate of 3-AF upon addition of salt were quantitatively accounted for by the Strickler–Berg equation. Third, electrolyte effects on the nonradiative decay rate of 3-AF were quantitatively accounted for in terms of the energy gap law. In this previous report we focused on the inability of current theoretical models to describe these general observations. Comparison between the experimental data and theory was justified as there was no evidence of any specific interactions between the salts and the solute molecule. This enabled us to study the ability of current models to describe bulk effects (both static and dynamic) of electrolyte solutions on solute photophysics. While no current theoretical model could account for the observed dynamics, the experimental results for 3-AF in salt solutions serve as a model case for anticipated effects that electrolyte solutions have on nonreactive "spectator" probe molecules.

Unlike 3-AF, 1-AF can form an intramolecular hydrogen bond between the amino and carbonyl moieties of the molecule. This intramolecular interaction influences the nonradiative dynamics of the electronically excited molecule in protic and aprotic solvents. In particular, a systematic study of the photophysics of 1-AF in neat solvents suggested that the intramolecular hydrogen bond provides a more efficient deactivation pathway than intermolecular hydrogen bonds to protic solvents.[9] This effect was quantified by examining the photodynamics of 1-AF in a mixed solvent system. Addition of small amounts of a strong hydrogen-bond-donating solvent, e.g., 2,2,2-trifluoroethanol (TFE), to a dilute solution of 1-AF in heptane revealed an isosbestic point in the

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