(unless the sample and stationary phase form an athermal solution), but the two quantities are related by the equation

$$\Delta H_v = \Delta H_s - \Delta H(v \rightarrow S).$$

where ΔH_s is the heat of solution of the sample in the solvent (DC-200) measured calorimetrically at 25 °C.

The ΔH_v values obtained in this way are not exactly identical with the correct values[10] but are linearly related. We have established the relationship by plotting the GC-calorimetry values of ΔH_v vs. a group of six ΔH_v values determined (mainly by direct vaporization calorimetry) with high accuracy (generally ±0.02 kcal/mol).[10] The compounds are *n*-octane, *n*-nonane, mesitylene, *n*-decane, *n*-dodecane, and 1-hexadecene. The plot has the slope 0.9696, an intercept of 0.8374, and a correlation coefficient (R) of 0.99990.

We have measured GC-calorimetry values for a number of other compounds and have calculated corrected ΔH_v values[11] by the equation

$$\Delta H_v(\text{cor}) = 0.9696\Delta H_v(\text{expl}) + 0.8374$$

Not surprisingly, values for some nonpolar aliphatic and aromatic hydrocarbons were in good agreement with literature values. More noteworthy is that measurements on polar compounds, mainly ketones, also gave excellent agreement with the best literature values (Table I). The determination with H-bonding 1-butanol is satisfactory, but slightly less accurate, owing in part to tailing of the GC peaks. We are investigating the use of more highly polar stationary phases to overcome this behavior.

Retention times were determined using capillary columns (30 m × 0.5 mm i.d.) at six temperatures over a 50 °C temperature range. The relationship of ln Δt vs. $1/T$ was deemed satisfactory when the correlation coefficient exceeded 0.9995. Essentially equivalent results were obtained for several samples using a lightly loaded column and a heavily loaded column, and using 10 or 5 psi pressure of nitrogen carrier gas. Because the flame ionization detector used does not respond to air, methane was used to measure t_a. DC-200 silicone fluid of 100 cSt viscosity was used both in column loading and as the calorimetric solvent. The use of less viscous (5 cSt) DC-200 in the calorimetric determinations gives somewhat different values of ΔH_s. The calorimetric procedure was essentially that previously described,[12] excepting that a somewhat reduced sensitivity was usually used (500 μV full-scale recorder deflection), and stronger magnetic stirring must be provided.

We believe that the present method offers substantial advantages over previous techniques, in that measurement of flow rate, w_t, and vapor pressure are avoided. Provided that measurements involve "infinitely dilute" solutions, a variety of liquid phases and a wide range of temperatures should be suitable.

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References and Notes

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Solar Energy Storage. Production of Hydrogen by 546-nm Irradiation of a Dinuclear Rhodium(I) Complex in Acidic Aqueous Solution

Sir:

We have reported[1] previously on the synthesis and characterization of a novel dinuclear rhodium(I) complex, $[Rh_2(bridge)_4]^{2+}$ (bridge = 1,3-diisocyanopropane). The orbital interactions between the directly coupled rhodium(I) centers give rise to striking electronic absorption spectral properties,[1,2] the most prominent being a low-lying system (λ_{max} 553 nm (ϵ 14 500), $[Rh_2(bridge)_4](BPh_4)_2$ in acetonitrile solution) attributable to the $^1A_{1g} \rightarrow {}^1A_{2u}$ ($1a_{2u} \rightarrow 2a_{1g}$) excitation. A logical avenue for exploratory research on $[Rh_2(bridge)_4]^{2+}$ involves its excited-state reactivity behavior, as a directly coupled dinuclear redox center might be able to channel charge-transfer excitation energy into redox-substrate chemical bond formation at rates that are competitive with back electron transfer. The purpose of the present communication is to report that we have achieved this goal in one important case, namely, in the reduction of protons to hydrogen through 546-nm irradiation of $[Rh_2(bridge)_4]^{2+}$ in aqueous HCl solution.

The electronic absorption spectrum of $[Rh_2(bridge)_4](BF_4)_2$[3] in aqueous 12 M HCl solution exhibits an intense band at 578 nm (ϵ 52 700) that may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition in the blue protonated species, $[Rh_2(bridge)_4H]^{3+}{\cdot}Cl^-$.[4] The proton stoichiometry was determined by measuring the change in pH upon dissolution of a known quantity of $[Rh_2(bridge)_4](BF_4)_2$ in each of six standard aqueous HCl solutions. Initial pH values varied from 3.77 to 3.88. In all six experiments the pH increased as predicted for the binding of 1.05 ± 0.10 protons to $[Rh_2(bridge)_4]^{2+}$. The fact that the principal absorption maximum in the spectrum of $[Rh_2(bridge)_4H]^{3+}{\cdot}Cl^-$ is very near that of $[Rh_2(bridge)_4]^{2+}$ shows that a relatively small electronic perturbation has occurred upon protonation. In contrast, a related oxidative-addition product, $[Rh_2(bridge)_4(CH_3)(I)]^{2+}$, exhibits an intense absorption band at much higher energy (397 nm in acetonitrile solution; assigned to the $\sigma \rightarrow \sigma^*$ transition $1a_{1g} \rightarrow 1a_{2u}$ in a $[I\text{-}Rh^{II}\text{-}Rh^{II}\text{-}CH_3]^{2+}$ species).[1] Thus we prefer to formulate the ground state of $[Rh_2(bridge)_4H]^{3+}{\cdot}Cl^-$ as a protonated dinuclear Rh^I complex, $[(Cl^-)Rh^I\text{---}Rh^I(H^+)]^{2+}$, rather than the hydrido Rh^{II} oxidative-addition product, $[Cl\text{-}Rh^{II}\text{-}Rh^{II}\text{-}H]^{2+}$.

Irradiation of $[Rh_2(bridge)_4H]^{3+}{\cdot}Cl^-$ in 12 M HCl solution at 546 nm leads to clean conversion to a yellow product (Figure 1) and a gas. The absorption spectrum of the yellow product (λ_{max} 338 nm (ϵ 56 200)) is identical with that of a sample of $[Rh_2(bridge)_4Cl_2]^{2+}$ prepared by Cl_2 oxidation of $[Rh_2(bridge)_4]^{2+}$ in 12 M HCl solution. Characterization of several oxidative-addition products of the type $[Rh_2(bridge)_4X_2]^{2+}$ has been reported previously.[1] The gas was identified as H_2 both by mass spectroscopic analysis and by

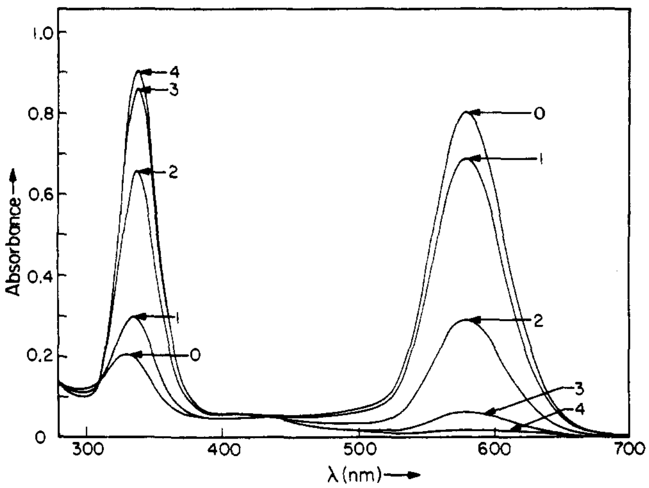

Figure 1. Irradiation (546 nm) of 1.6 × 10^{-4} M $[Rh_2(bridge)_4](BF_4)_2$ in degassed 12 M HCl solution. The four scans after t = 0 were taken at intervals of ~2 min.

collecting (Toepler pumping) and burning a sample over CuO. In a typical experiment in which some O_2 was present, conversion of 0.0567 mmol of $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ in 12 M HCl solution by irradiation at $\lambda > 530$ nm yielded 0.0466 mmol of H_2.[5] The photoreaction is therefore

$$\underset{\text{blue}}{[Rh_2(bridge)_4H]^{3+}\cdot Cl^-} + H^+ + Cl^- \xrightarrow[12\ M\ HCl]{546\ nm} \underset{\text{yellow}}{[Rh_2(bridge)_4Cl_2]^{2+}} + H_2 \qquad (1)$$

The appearance quantum yield of $[Rh_2(bridge)_4Cl_2]^{2+}$ in rigorously degassed 12 M HCl is 0.0040 ± 0.002 (λ_{irradn} 546 nm). The photoreaction is not inhibited by the presence of 1 atm of H_2 at 28 °C. Under such conditions the thermal back-reaction between $[Rh_2(bridge)_4Cl_2]^{2+}$ and H_2 to yield $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ requires several days to go to completion. Thus there is reason to believe that the photochemical/thermal kinetic properties of this type of system may be adjusted (a_{H^+}, added anions) such that it could be used to produce H_2 in solar energy conversion schemes.

The charge-transfer excited state involved in the photoreaction must be $^1A_{2u}$ or $^3A_{2u}$. In either case, the MO configuration is $(1a_{1g})^2(1a_{2u})^1(2a_{1g})^1$. If we assume, as seems reasonable, that the $2a_{1g}$ level possesses substantial 1s(H) character, then the excited state may be formulated as $[(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*}$. Attack either by H_2O or H_3O^+ could induce a second electron transfer ($1a_{2u} \rightarrow H\cdot$), yielding H_2 and the two-electron oxidative-addition product, $[Rh_2(bridge)_4Cl_2]^{2+}$.

$$[(Cl^-)Rh^I\text{- - -}Rh^I(H^+)]^{2+} \xrightarrow{546\ nm} [(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*} \qquad (2)$$

$$[(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*} \xrightarrow[HCl(aq)]{fast} [Cl\text{-}Rh^{II}\text{-}Rh^{II}\text{-}Cl]^{2+} + H_2 \qquad (3)$$

It is attractive to propose that axial ligand–metal interactions may operate in such a way as to reduce the fraction of excited species returning to the Rh^I–Rh^I ground state by back electron transfer. The σ-binding interactions along the internuclear axis Cl- -Rh- -Rh- -H in a $(1a_{1g})^2(1a_{2u})^1(2a_{1g})^1$ excited state are predicted[1,6] to be larger than in the ground state $[(1a_{1g})^2(1a_{2u})^2]$; therefore, these interactions favor the H_2-producing pathway ($1a_{2u} \rightarrow H\cdot$) over back-transfer ($1a_{2u} \leftarrow H\cdot$), as the energy of the $1a_{2u}$ σ^* level increases sharply as the extent of Cl- -Rh- -Rh- -H coupling increases. Further elucidation of the role of axial interactions must await the completion of mechanistic studies of the photoreaction that are now in progress.

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(4) The visible absorption maximum of $[Rh_2(bridge)_4H]^{3+}$ is both solvent and anion sensitive, shifting from 549 nm in acetonitrile solution (0.1 M in *p*-toluenesulfonic acid) to 596 nm in concentrated aqueous HBr. Detailed studies of the dependence of the absorption spectra of $[Rh_2(bridge)_4H]^{3+}$ on $[Cl]^-$ indicate that the principal species in 1 M HCl is $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$. It should be noted here that we have not been able to locate a band in the IR spectrum of $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ attributable to Rh–H stretching, nor have we observed an NMR peak for the bound H^+.

(5) The amount of H_2 obtained in any given experiment depends strongly on $[O_2]$, as the excited state reacts with O_2 to give $[Rh_2(bridge)_4Cl_2]^{2+}$. In rigorously degassed 12 M HCl solutions the molar ratio of H_2:$[Rh_2(bridge)_4Cl_2]^{2+}$ was found to be 0.96 ± 0.04.

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Allylic Oxidation of Olefins by Catalytic and Stoichiometric Selenium Dioxide with *tert*-Butyl Hydroperoxide

Sir:

Selenium dioxide remains the most reliable and predictable reagent for the direct insertion of oxygen into an allylic carbon-hydrogen bond.[1] A serious complication in this reaction is the inevitable production of reduced forms of selenium. The frequent difficulty of removing colloidal selenium from the products is well known. Another drawback of these oxidations is the formation of organoselenium by-products. We have recently shown that one of the principal selenium containing by-products arises from addition of intermediate selenium(II) electrophilic species across the olefinic bond.[2] We reasoned that an oxidant which would rapidly and selectively reoxidize the reduced selenium species to SeO_2 would circumvent these