is largely thermally reversible. The thermal desorption studies clearly show there are two distinct chemisorption states. Neither was detected in the blank experiment. The more strongly bound state is ascribed to benzene on Pt(111) and the more weakly to benzene bound at or near imperfection sites.

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Energy and Electron-Transfer Processes of the Lowest Excited State of the Tris(phenanthroline)rhodium(III) Complex

Sir:

In the last few years it has been found that the excited states of complexes containing aromatic molecules such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) as ligands are particularly suitable for energy and electron-transfer processes.[1-5] These complexes are presently the focus of considerable interest because of their potential use in the conversion of light energy into chemical energy.[6-10] The best studied is certainly the Ru(bpy)$_3^{2+}$ ion, but other Ru(II), Cr(III), Os(II), and Ir(III) complexes have also been the object of photochemical and photophysical investigations.[1-5] We describe here the characteristics of $*$Rh(phen)$_3^{3+}$, which is the first excited rhodium complex whose energy and electron-transfer processes have been quantitatively investigated.[11] A rather striking aspect of this study is that energy and electron-transfer processes involving $*$Rh(phen)$_3^{3+}$ have been observed and their rate constants have been measured without relying on directly observable properties (such as absorption or emission spectra) of the excited state.[13]

In rigid matrix at 77 K Rh(phen)$_3^{3+}$ exhibits a well structured luminescence emission.[15-18] The emitting state is the lowest π,π^* triplet, with $E^{00} = 22.2$ kK and $\tau = 48$ ms.[15,16] In contrast to what happens for the analogous Cr(III), Ru(II), Os(II), and Ir(III) complexes,[2] no emission can be observed[19] in fluid solutions of Rh(phen)$_3^{3+}$ at room temperature. However, the presence of a relatively long-lived excited state upon irradiation (λ 290 nm) of aerated solutions of Rh(phen)$_3^{3+}$ in dimethylformamide (DMF) at room temperature is clearly shown by the occurrence of an energy-transfer process (reaction 1) which causes the sensitization of the well-known[20] Cr(CN)$_6^{3-}$ phosphorescence:

$$*\mathrm{Rh(phen)_3}^{3+} + \mathrm{Cr(CN)_6}^{3-} \rightarrow \mathrm{Rh(phen)_3}^{3+} + *\mathrm{Cr(CN)_6}^{3-} \quad (1)$$

A plot[1] of $1/I_{\mathrm{sens}}$ vs. $1/[\mathrm{Q}]$ (where I_{sens} is the intensity of the sensitized emission and [Q] is the Cr(CN)$_6^{3-}$ concentration) yielded a Stern–Volmer (SV) constant of 3.0×10^3 M^{-1}.[21] Assuming that the energy transfer occurs at diffusion-controlled rate ($\sim 10^{10}$ M^{-1} s^{-1}), the (lower limiting) value for the lifetime of $*$Rh(phen)$_3^{3+}$ is $\sim$0.30 μs. In a few experiments carried out by irradiating deaerated aqueous Rh(phen)$_3^{3+}$ solutions in the presence of biacetyl, the sensitized photophosphorescence of biacetyl was observed. As the emitting state of biacetyl lies at $\sim$20 kK,[22] the donor excited state of Rh(phen)$_3^{3+}$ has to be either the $^3\pi,\pi^*$ state which is seen in emission at 77 K ($E^{00} = 22.2$ kK) or some other excited state which lies not much lower than that state. Even in the first case, the lack of appreciable emission from the $^3\pi,\pi^*$ excited state at room temperature is not surprising in view of the five orders of magnitude decrease of τ, which causes a proportional decrease in the emission intensity.

When a 4×10^{-5} M solution of Rh(phen)$_3^{3+}$ in acetonitrile was flashed at 347 nm with a ruby laser[23] in the presence of variable amounts (1.6×10^{-4} to 2.0×10^{-3} M) of diphenylamine (DPA), a transient spectrum was observed which practically coincided with the well-known spectrum of the DPA$^+$ radical cation (λ_{max} 680 nm).[24] This indicates that the reaction

$$*\mathrm{Rh(phen)_3}^{3+} + \mathrm{DPA} \rightarrow \mathrm{Rh(phen)_3}^{2+} + \mathrm{DPA}^+ \quad (2)$$

takes place and that Rh(phen)$_3^{2+}$ does not appreciably absorb in the 500–700-nm region.[25] A plot[1] of $1/A$ vs. $1/[\mathrm{Q}]$, where A is the absorbance at 660 nm and [Q] is the DPA concentration, yielded a SV constant of $\sim 2.5 \times 10^3$ M^{-1}. Assuming that reaction 2 takes place at diffusion-controlled rate ($\sim 10^{10}$ M^{-1} s^{-1}), the (lowest limiting) value for the $*$Rh(phen)$_3^{3+}$ lifetime in aerated acetonitrile is $\sim$0.25 μs, which is almost the same as that obtained from reaction 1 for aerated DMF solutions. A plot of $1/A$ vs. $1/[\mathrm{Q}]$ for the $*$Cr(bpy)$_3^{3+}$-DPA system yielded a value of 7×10^9 M^{-1} s^{-1} for the electron-transfer quenching constant; this value, which is close to the diffusion-controlled one, compares well with that previously obtained for the same system by luminescence quenching experiments.[27] This shows that the method of monitoring the absorbance of the electron-transfer products for obtaining the rate constant is reliable. Since $*$Rh(phen)$_3^{3+}$ is (as we will see later) a better oxidant than $*$Cr(bpy)$_3^{3+}$, there is no reason to believe that reaction 2 is not diffusion controlled. This means that the actual lifetime of $*$Rh(phen)$_3^{3+}$ in aerated acetonitrile at room temperature has to be $\sim$0.25 μs.

A few experiments carried out in acetonitrile solutions with 1,3,5-trimethoxybenzene (TMB) as a quencher showed that the TMB$^+$ radical cation (λ_{max} 590 nm)[28] was generated at a nearly diffusion-controlled rate. Since the reduction potential of the TMB$^+$/TMB couple is 1.49 V vs. SCE,[29] it follows that $*$Rh(phen)$_3^{3+}$ has to be a very powerful oxidant. This is not surprising because a value of 2.00 V vs. SCE is expected[2] for the $*$Rh(phen)$_3^{3+}$/Rh(phen)$_3^{2+}$ couple on the basis of the reduction potential of the Rh(phen)$_3^{3+}$/Rh(phen)$_3^{2+}$ couple (−0.75 V)[30] and the excited-state spectroscopic energy of the $^3\pi,\pi^*$ state (2.75 eV).[15] This means that $*$Rh(phen)$_3^{3+}$ is expected to be a much stronger oxidant than all the excited Ru(II), Cr(III), and Os(II) complexes and even than most of the excited Ir(III) complexes that have been studied up until now.[1,31] The availability of excited states which cover a wide range of redox potentials is, of course, important for both systematic studies (e.g., that one described in ref 32) and practical applications.

In view of the spectroscopic[15-18] and electrochemical[30] analogies between Rh(phen)$_3^{3+}$ and Rh(bpy)$_3^{3+}$, the results reported above contribute to the elucidation of some interesting results recently obtained by Lehn et al.[6,12] In the production of hydrogen upon ultraviolet irradiation of aqueous solutions containing Rh(bpy)$_3^{3+}$ and triethanolamine (TEOA),[12] the excited-state reaction has to be of the type of reaction 2. Secondary reactions of Rh(bpy)$_3^{2+}$ will then lead to hydrogen formation. On the other hand, in the production of hydrogen upon visible irradiation of aqueous solutions containing Ru(bpy)$_3^{2+}$, Rh(bpy)$_3^{3+}$, and TEOA,[6,10,12] the excited ruthenium complex ($E^{00} = 17.1$ kK)[2] cannot transfer electronic energy to the rhodium complex. Rather, electron transfer from $*$Ru(bpy)$_3^{2+}$ to Rh(bpy)$_3^{3+}$ has to occur with formation of Rh(bpy)$_3^{2+}$, which again leads to hydrogen generation, and Ru(bpy)$_3^{3+}$, which is then reduced by TEOA.

A systematic investigation on the photochemical and photophysical properties of Rh(phen)$_3^{3+}$ and other Rh(III) complexes is in progress in our laboratories.

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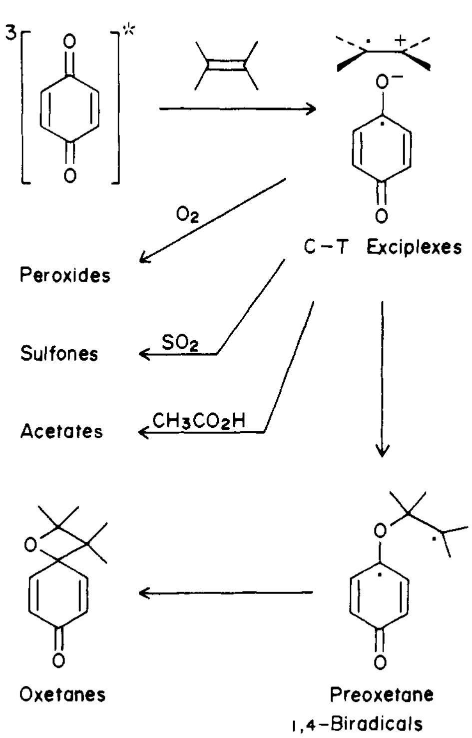
Photocyclizations Involving Quinone–Olefin Charge-Transfer Exciplexes

Sir:

The photocycloaddition of $^3n,\pi^*$ *p*-benzoquinone (*p*Bq) to various olefins to form oxetanes (Scheme I) has received a great deal of attention in recent years.[1] It has been well established that this reaction proceeds through an intermediate with biradical character that can be trapped by oxygen or sulfur dioxide.[2] This intermediate was at first thought to be the traditional preoxetane 1,4 biradical (Scheme I). However, the following results seem to indicate that this is not always the case: (1) experiments with simple unsymmetrical olefins demonstrate that the intermediate which is trapped by oxygen occurs on the reaction pathway *before* the branching into the two possible preoxetane 1,4 biradicals;[2f] (2) in the *p*Bq-cyclooctatetraene system this intermediate apparently is a very polar species as it can also be trapped by acetic acid;[2b] (3) furthermore, CNDO calculations for the triplet *p*Bq-ethylene system indicate that quite stable charge-transfer (C-T) exciplexes might be expected to exist,[2f] and that these could be the "intermediates" being trapped in the aforementioned experiments as summarized in Scheme I. To determine the extent to which triplet C-T exciplexes influence the photochemistry of *p*Bq with simple olefins, a series of olefins specifically designed to maximize the probability of intramolecular trapping of C-T exciplexes has been studied.

Scheme I



Argon ion laser irradiation[3] of *p*Bq in the presence of either 4-pentenoic acid[4] or *trans*-5-phenyl-4-pentenoic acid[4] afforded the δ-lactones **1a** and **1b**,[5] respectively (Scheme II). That these products were the δ-lactones **1a** and **1b** and not the γ-lactones was firmly established by the carbonyl stretching frequencies at 1735–1730 cm^{-1}. The stereochemistry of **1b** is most probably trans, although the coupling between the methinyl hydrogens (4.0 Hz) is smaller than expected. Distortion of the half-chair conformation of the δ-lactone ring in **1b**[6] by the two adjacent, bulky equatorial substituents might account for this decrease in the coupling constant. *cis*-5-Phenyl-4-pentonoic acid was studied also and found to undergo rapid isomerization to the trans acid followed by formation of **1b** as the only lactone product. The possibility that the lactones arise from the acid-catalyzed rearrangement of the corresponding oxetanes, which also occur in these reaction mixtures, has been excluded by control studies with the oxetanes. Therefore, this novel photolactonization seems to be most easily rationalized as the result of C-T exciplex trapping by a carboxylic acid functional group as outlined in Scheme II. The events depicted in Scheme II are intended to illustrate the electronic reorganization necessary to transform the exciplexes into the products, rather than the actual timing of these events. In fact collapse of the quinone-olefin C-T complexes probably proceeds without the localization of charge or spin density at either of the olefin-derived carbon atoms. Under these circumstances one would

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