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Photophysical Evidence for "d–d" Emissions from Homobischelated Complexes of Iridium(III)

Sir:

The pathways for energy transfer processes which begin with excitation and terminate with luminescence, photochemistry, and heat production in transition metal complexes have been explored by a variety of techniques. Photophysical evidence accumulated from studies of complexes of Rh(III), Ru(II), Ir(III), and Os(II) at 77 K has led to the formulation of the following postulate.[1,2] "In the absence of photochemistry from upper excited states, emission from a transition-metal complex with an unfilled d shell will occur from the lowest electronic excited state in the molecule or from those states which can achieve a significant Boltzmann population relative to the lowest excited state."[1] This postulate was formulated on the basis of the observation of luminescence quantum yields of Rh(III), Ru(II), and Os(II) complexes which were found to be independent of excitation wavelength.[1,2] However, in no case did the studies at 77 K include excitation of states of orbital parentage different from that of the emitting state (i.e., at all the excitation wavelengths employed in these studies the quantum yield for "d–d" emission from Rh(III) complexes was measured following excitation into higher "d–d" bands and the quantum yield for $d\pi^*$ emission from Ru(II) and Os(II) complexes was measured following excitation into higher $d\pi^*$ bands).

Recent photophysical evidence from studies of heterobischelated complexes of Ir(III)[3-5] and heterotrischelated complexes of Rh(III)[6] indicates that the emissions of these complexes originate from several thermally nonequilibrated levels at 77 K, contrary to the generalization quoted above. These results have led us to propose the following selection rules for radiationless transitions in Ir(III) complexes: $d\pi^* \leftrightsquigarrow d\pi^*$, $\pi\pi^* \leftrightsquigarrow \pi\pi^*$, $d\pi^* \not\leftrightsquigarrow \pi\pi^*$. These rules imply that there is a tendency for retention of orbital parentage in the radiationless pathways which lead from one electronically excited level to another in the charge-transfer and ligand-localized manifolds of levels. We have found these rules to be particularly rigid when the energy gaps between excited states of different orbital parentage are small (<300 cm^{-1}) and when these states are localized in different areas of the molecular framework.[7] For larger energy gaps the rules still appear to describe the preferred pathways for energy degradation in heterobischelated Ir(III) complexes,[4,5] though they may be somewhat less rigid.

Since no "d–d" emissions have been reported in these complexes, their role in the electronic energy transfer pathways in Ir(III) complexes has not been deduced from photophysical studies. However, studies of the photochemistry of iodoammine complexes of Rh(III) have led to the conclusion that the low lying charge-transfer-to-metal (CTTM) and "d–d" excited states do not interconvert efficiently.[8] Furthermore, recent photochemical results[9] indicate that chloride aquation of homobischelated Ir(III) complexes (e.g., $[IrCl_2(phen)_2]Cl$) takes place from a "d–d" level. These results suggest that a thermally controlled deactivation process of the emitting levels leads to population of the reactive "d–d" level in the temperature region between 8 and 65°C, although the emitting levels are presumed to be of the same orbital parentage as those observed at −196°C.

In order to investigate further the role of "d–d" levels in the deactivation pathways of Ir(III) complexes, we have undertaken a study of the time-resolved emission spectra of several homobischelated complexes of Ir(III) in the temperature region between −196 and 0°C. In this communication we report the results of this study for two homobischelated complexes of Ir(III) whose photochemistry in fluid solutions has been reported.[9]

The complexes, *cis*-dichlorobis(1,10-phenanthroline)iridium(III) chloride, $[IrCl_2(phen)_2]Cl$, and *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride, $[IrCl_2(5,6\text{-mephen})_2]Cl$, were prepared by the method of Broomhead and Grumley[10] and were purified by repeated recrystallization from dilute HCl followed by column chromatography on Sephadex LH-20. Solutions of the complexes (10^{-4} *M*) in glycerol (Matheson Coleman and Bell spectroquality) were prepared and stored in the dark at 0°C when not in use. Low temperature baths were used to attain temperatures between −196 and 0°C.[11] Time-resolved emission spectra were obtained with apparatus described in a previous publication[4] which utilizes a pulsed nitrogen laser for excitation at 337 nm. All spectra were corrected for the wavelength dependence of the photomultiplier-monochromator combination. Corrected steady-state luminescence spectra were recorded with a Hitachi MPF-3A spectrophotofluorimeter using 337-nm excitation. Photolysis of the complexes was found to lead to a luminescent product under prolonged laser excitation at 337 nm, particularly at temperatures above −41°C. However, the time-resolved

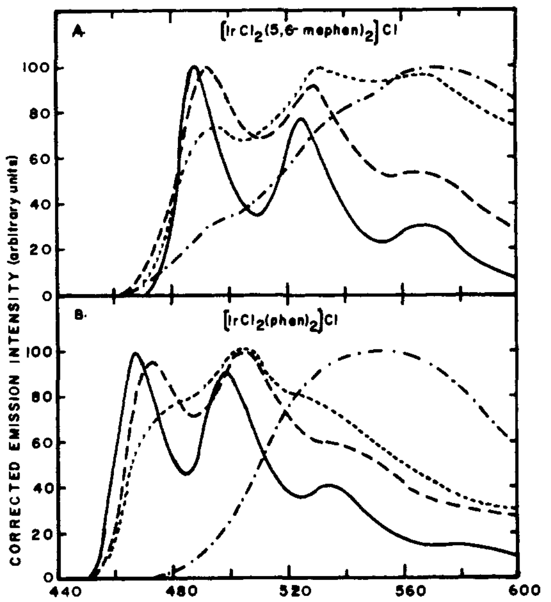

Figure 1. Steady-state luminescence spectra in glycerol at several different temperatures: (A) [IrCl$_2$(5,6-Mephen)$_2$]Cl (—) −196°C, (- -) −41°C, (- - -) −23°C, (- · -) 0°C; (B) [IrCl$_2$(phen)$_2$]Cl (—) −196°C, (- -) −130°C, (- - -) −95°C, (- · -) 0°C.

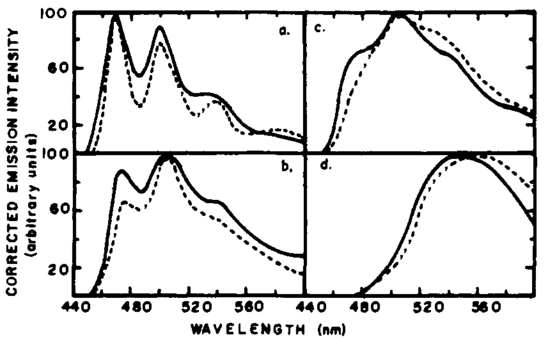

Figure 2. Time resolved spectra of [IrCl$_2$(phen)$_2$]Cl in glycerol at several different temperatures: (a) at −196°C (—) 0.5 μsec delay time, (- - -) 100 μsec delay time; (b) at −130°C (—) 0.5 μsec delay time, (- - -) 10 μsec delay time; (c) at −95°C (—) 0.5 μsec delay time, (- - -) 10 μsec delay time; (d) at 0°C (—) 0.5 μsec delay time, (- - -) 5 μsec delay time.

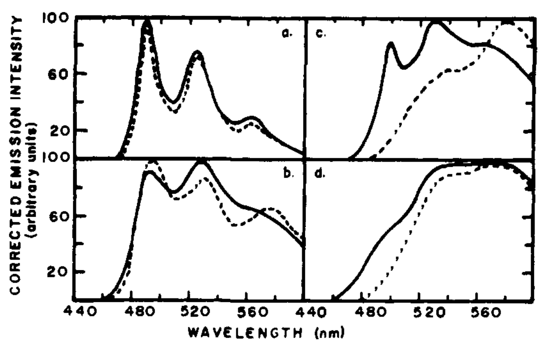

Figure 3. Time resolved spectra of [IrCl$_2$(5,6-Mephen)$_2$]Cl in glycerol at several different temperatures: (a) at −196°C (—) 0.5 μsec delay time, (- - -) 250 μsec delay time; (b) at −41°C (—) 0.3 μsec delay time, (- - -) 25 μsec delay time; (c) at −23°C (—) 0.5 μsec delay time, (- - -) 10 μsec delay time; (d) At 0°C (—) 0.3 μsec delay time, (- - -) 5 μsec delay time.

spectra were all recorded on freshly prepared samples and were found to be reproducible and in good agreement with the steady state spectra measured under low-intensity illumination. Furthermore, freshly prepared samples, which were exposed to the laser above −41°C for a time long enough to determine a time-resolved spectrum (~300 laser pulses) and then cooled to −196°C, were found to have spectra identical with those of freshly prepared samples irradiated only at −196°C.

The steady-state luminescence spectra of the two complexes at several temperatures between −196 and 0°C are shown in Figure 1. The glycerol solutions were rigid glasses at temperatures as high as −41°C and gradually turned to viscous, supercooled fluids above this temperature. In glycerol at −196°C the emission of the [IrCl$_2$(phen)$_2$]Cl complex is from a $d\pi^*$ excited state with a lifetime of 12.8 μsec, whereas the [IrCl$_2$(5,6-Mephen)$_2$]Cl emission originates from a $\pi\pi^*$ state with a lifetime of 158 μsec.[12] Figure 1 indicates that emission spectra of both complexes broaden and red-shift as the temperature is raised above −196°C.

The time-resolved spectra of both complexes at two times in their decay and several different temperatures are shown in Figures 2 and 3. Although the dominant emission from both complexes arises from one set of thermally equilibrated $d\pi^*$ or $\pi\pi^*$ levels at −196°C, the time-resolved spectra reveal a small contribution from a shorter-lived set of levels which are not in thermal equilibrium with the $d\pi^*$ or $\pi\pi^*$ levels, respectively. In both complexes, the lifetime of the set of levels primarily responsible for emission at −196°C shortens as the temperature is raised to 0°C and eventually becomes shorter than the lifetime of the other set of levels, which dominate the emission spectra at higher temperatures. The luminescence decay curves of both complexes deviate strongly from exponential behavior in this temperature region, and the time-resolved spectra clearly show that the emissions come from at least two sets of nonequilibrated levels in each complex.

On the basis of these results, we propose the following tentative interpretation. (1) At −196°C in glycerol, the emission of each of these complexes comes primarily from a set of thermally equilibrated levels of either $d\pi^*$\{[IrCl$_2$(phen)$_2$]Cl\} or $\pi\pi^*$\{[IrCl$_2$(5,6-Mephen)$_2$]Cl\} orbital parentage. *A small contribution from a shorter lived set of levels which are not in thermal equilibrium with the $d\pi^*$ or $\pi\pi^*$ levels is also present in the emission spectra.* (2) As the temperature is raised, the life-times and intensities of the $d\pi^*$ and $\pi\pi^*$ emissions diminish, and another set of levels begin to dominate the emission spectra. The new emissions are broad and maximize at much lower energy than the −196°C emissions. *We believe these emissions arise from a set of levels of "d-d" orbital parentage in both complexes.* (3) Our results indicate that these "d-d" levels are populated via a thermally activated radiationless process from the $d\pi^*$ or $\pi\pi^*$ levels. *The emission spectra in the region around 0°C are not due to $d\pi^*$ or $\pi\pi^*$ sets of levels as previously assumed[9] but are due to a set of "d-d" excited levels.* (4) The dominance of the emission spectrum of each complex by the "d-d" levels at temperatures around 0°C in spite of their lifetimes, which are *longer* than the $d\pi^*$ or $\pi\pi^*$ levels, suggest that *the "d-d" levels are the lowest excited state of each complex,* i.e., that thermally activated radiationless processes lead to population of the lower energy "d-d" levels between −196 and 0°C, but back-population of the $d\pi^*$ or $\pi\pi^*$ levels is unimportant.

These results indicate that the postulate quoted above, which has been widely used to link spectroscopic observations at −196°C and photochemical results near room temperature,[9] is not applicable to these complexes. We suggest that in rigid glasses radiationless transitions between low-lying excited states of different orbital parentage are severely hindered in these complexes, and that our previous selection rules may be expanded to include the forbidden character of transitions between "d-d" levels and those of

$d\pi^*$ or $\pi\pi^*$ parentage. As a result, photochemical processes in fluid solutions above 0°C cannot be anticipated from low temperature spectroscopic results. The determination of the range of applicability of these selection rules for radiationless transitions to other transition metal complexes awaits more definitive studies of the wavelength dependence of photoluminescence quantum yields and lifetimes (vide supra). Studies of this type, when coupled with time-resolved spectroscopy throughout the temperature region between −196 and 25°C, will help to determine whether efficient population of the lowest set of thermally equilibrated excited levels regardless of orbital parentage is general, as previously postulated,[1,2] or whether the selection rules we have proposed are generally applicable. A firm experimental substantiation of the general pathways for radiationless deactivation in metal complexes is fundamental to understanding the photophysics and photochemistry of these molecules.

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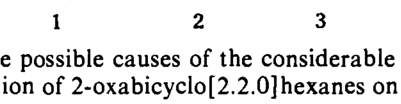
Mechanistic Photochemistry of γ,δ-Unsaturated Ketones. Discovery of a Photo-Cope Reaction of β-Oxa-γ,δ-enones and Its Implications for the Mechanism of Intramolecular Photocycloaddition

Sir:

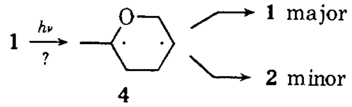
Irradiation of γ,δ-unsaturated ketones and aldehydes most often results in formation of 2-oxabicyclo[2.2.0]hexanes and/or 5-oxabicyclo[2.1.1]hexanes (eq 1).[1] The quantum yields for these intramolecular photocycloaddition reactions are usually low, particularly for acyclic γ,δ-enones.[1a,b,l] Srinivasan has reported, for example, a quantum yield of 0.006 for formation of oxetane **2** on irradiation of ketone **1**.[1a]



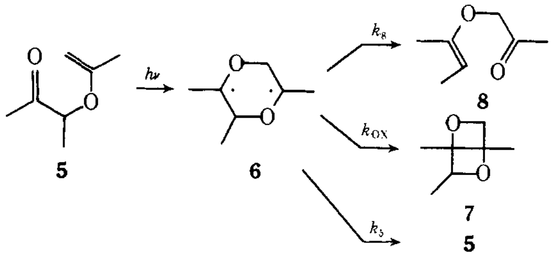
(1)

1 **2** **3**

One of the possible causes of the considerable inefficiency in formation of 2-oxabicyclo[2.2.0]hexanes on photolysis of γ,δ-enones is the intermediacy of a cyclic 1,4-biradical, e.g., **4**, which undergoes β-cleavage to regenerate the starting γ,δ-enone more efficiently than closure to the 2-oxabicyclo[2.2.0]hexane (see eq 2).[1,2] If such biradical partitioning does occur, then irradiation of a suitably labeled β-oxa-γ,δ-enone such as **5** should yield photo-Cope products, e.g., **8**,[3] since in this case the cyclic 1,4-biradical, **6**, is "symmetrical" and has two possible β-cleavage pathways to yield γ,δ-enones (see eq 3).[4] By measuring the quantum yields for intramolecular photocycloaddition (**5** → **7** and **8** → **7**) and for photo-Cope reactions in both directions, i.e., **5** → **8** and **8** → **5**, the relative values of k_8, k_5, and k_{ox} can be determined. This establishes an upper limit on the extent to which cyclic 1,4-biradical **6** undergoes β-cleavage and allows the role of β-cleavage from **6** in contributing to the inefficiency of intramolecular photocycloaddition of β-oxa-γ,δ-enones to be evaluated.[5]



(2)



(3)

With these thoughts in mind, we have studied the photochemistry of γ,δ-enones **5**[6] and **8**.[7] Irradiation of a pentane solution (0.08 *M*) of 3,5-dimethyl-4-oxa-5-hexen-2-one (**5**) at 313 nm for 5 hr results in 32% loss of **5** and a 27% yield of two new compounds, an intramolecular photocycloaddition product, **7**,[8] and the photo-Cope product, **8**, in a ratio of 2.5:1 (eq 4).[9] Prolonged irradiation leads to disappearance of both the starting γ,δ-enone **5** and the photo-Cope product **8**, and formation of 1,4,6-trimethyl-2,5-dioxabicyclo[2.2.0]hexane (**7**) as the major product. Quantum yields for formation of **7** and **8** from photolysis of **5** in hexane to less than 5% conversion are found to be 0.12 and 0.04, respectively.[10] Similar irradiation of a pentane solution (0.08 *M*) of 5,6-dimethyl-4-oxa-5-hexen-2-one, **8**, for 4 hr leads to a 27% loss of **8** and a 20% yield of oxetane **7** and photo-Cope product **5** formed in a 3.1:1 ratio (see eq 5).[11]

$$\mathbf{5} \xrightarrow[\text{pentane}]{h\nu} \underset{\Phi = 0.12}{\mathbf{7}} + \underset{\Phi = 0.04}{\mathbf{8}} \tag{4}$$

$$\mathbf{8} \xrightarrow[\text{pentane}]{h\nu} \underset{\Phi = 0.13}{\mathbf{7}} + \underset{\Phi = 0.05}{\mathbf{5}} \tag{5}$$

Quantum yields for formation of **7** and **5** from photolysis of **8** in hexane to less than 5% conversion are measured to be 0.13 and 0.05, respectively.[10] Thus we note that β-oxa-γ,δ-enones **5** and **8** undergo competitive intramolecular photocycloaddition and photo-Cope reactions. Although still overall an inefficient process, the efficiencies of intramolecular photocycloaddition for **5** and **8** are considerably greater than the efficiencies reported for other acyclic γ,δ-enones.[1a,b,l]

The formation of photo-Cope products upon irradiation of β-oxa-γ,δ-enones **5** and **8** is consistent with the intermediacy in these photolyses of 1,4-biradical **6**, which partitions between closure to bicyclo[2.2.0]hexane **7** and cleavage to β-oxa-γ,δ-enones **5** and **8** in a ratio of approximately