A Novel Deuterium Effect on Dual Charge-Transfer and Ligand-Field Emission of the *cis*-Dichlorobis(2,2′-bipyridine)iridium(III) Ion

Sir:

Recent studies of the dual charge-transfer and ligand-field emissions of the $\mathrm{IrCl_2(phen)_2^+}$ ion[1,2] (phen = 1,10-phenanthroline) have been extended to the structurally similar $\mathrm{IrCl_2(bpy)_2^+}$ complex ion (bpy = 2,2′-bipyridine), which is also found to display two emissions. In the course of this study the perdeuterated analogue, $\mathrm{IrCl_2(bpy\text{-}}d_8\mathrm{)_2^+}$ was prepared, and several interesting deuterium effects on the luminescent properties have been observed. These include (i) a large increase in the lifetime for the ligand-field emission at 77 K; (ii) no change in the lifetime of the charge-transfer emission at 77 K; and (iii) a change in the ratio of the charge-transfer and ligand-field emission intensities in fluid DMF solutions.

The present study may be conveniently subdivided into two categories: (a) studies of the dual emissions under thermally nonequilibrated conditions (77 K, crystalline DMF solvent), and (b) studies under thermally equilibrated conditions (231–354 K, fluid DMF solvent). Under thermally nonequilibrated conditions both $\mathrm{IrCl_2(bpy)_2^+}$ and $\mathrm{IrCl_2(bpy\text{-}}d_8\mathrm{)_2^+}$ have nonexponential decay curves for broad-band (450–750 nm) emission measurements. When decay curves are measured for narrow-band emissions centered at 497 nm (~50-nm band width), exponential decays with lifetimes of 4.8 ± 0.1 μs are obtained for both the perprotonated and perdeuterated species. Both species also have exponential decay curves for narrow band emissions centered at 703 nm, lifetimes of 5.9 ± 0.2 and 12.2 ± 0.5 μs, respectively. Time-resolved emission spectra of the perdeuterated species at 1 and 30 μs after excitation (Figure 1) illustrate that the 4.8-μs green emission is structured. This emission has been previously assigned to a charge-transfer $(\mathrm{d}\pi^*)^3$ or a "delocalized molecular" [4] transition. The longer-lived red emission which is apparent in the 30-μs spectrum, is broad and structureless; this emission is analogous to the red emission observed in $\mathrm{IrCl_2(phen)_2^+}$,[1,2] and is assigned to a ligand-field (dd) transition.

In fluid DMF thermal equilibration is evidenced by identical lifetimes obtained for the charge-transfer and ligand-field emissions over the temperature range 231–354 K (Table I). At each temperature a substantial deuterium effect is observed which we believe to be due to contributions of radiationless decay between the ligand-field and ground states to the overall decay kinetics of the thermally equilibrated manifold of charge-transfer and ligand-field levels. Time-integrated emission spectra of both species as a function of temperature (Figure 2) indicate that the ratio of the charge-transfer emission intensity to the ligand-field emission intensity, I_g/I_r, as measured by the peak heights for the green and red emissions, is temperature dependent. In both species the ligand-field emission is favored at lower temperatures under thermally equilibrated conditions, indicating that this state lies below the charge-transfer state.

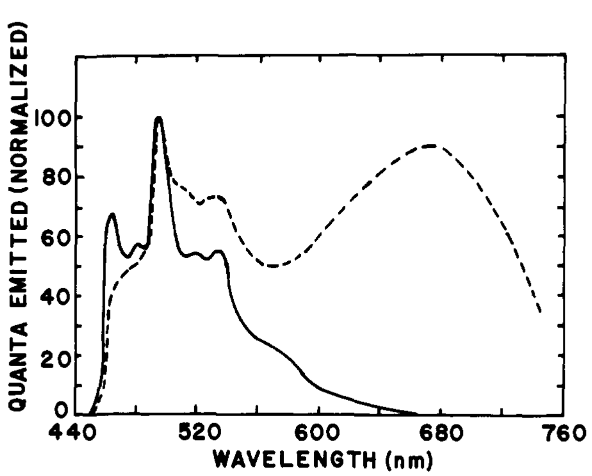


Figure 1. Time-resolved luminescence spectra of $\mathrm{IrCl_2(bpy\text{-}}d_8\mathrm{)_2^+}$ in dimethylformamide at 77 K excited at 337 nm: —, spectrum measured 1 μs after excitation; - - -, spectrum measured 30 μs after excitation.

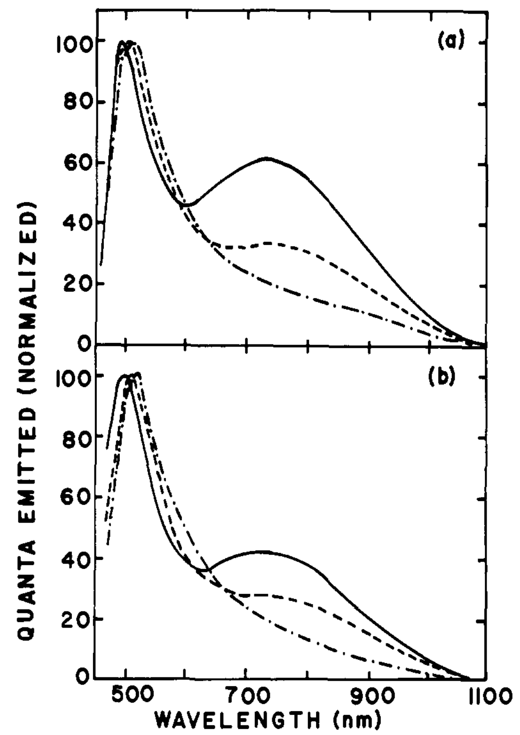


Figure 2. Time-integrated luminescence spectra of (a) $\mathrm{IrCl_2(bpy\text{-}}d_8\mathrm{)_2^+}$ and (b) $\mathrm{IrCl_2(bpy\text{-}}h_8\mathrm{)_2^+}$ in fluid dimethylformamide excited at 365 nm: —, spectra measured at 231 K; - - -, spectra measured at 298 K; -·-, spectra measured at 354 K.

Table I. Luminescence Lifetimes of $\mathrm{IrCl_2(bpy)_2^+}$ in Fluid Dimethylformamide

	perprotonated		perdeuterated	
temp K	$\tau^{a}{}_{\text{greens}}$ ns	$\tau_{\text{red}}{}^{b}$ ns	$\tau_{\text{green}}{}^{a}$ ns	$\tau_{\text{red}}{}^{b}$ ns
231	570± 25	545 ± 30	1190 ± 50	1120 ± 50
298	335 ± 15	330 ± 15	708 ± 25	720 ± 30
354	225 ± 20	260 ± 20	390 ± 25	390 ± 20

[a] Measured at 547 nm with 50-nm band pass. [b] Measured at 703 nm with 50-nm band pass.

Plots of log (I_g/I_r) vs. $1/T$ are linear for both species as expected for simultaneous emission from two thermally equilibrated excited states.[5] Analysis of the slopes of these plots to determine the energy gap between the charge-transfer and ligand-field manifolds, ΔE, yields a novel result; ΔE is found to be 0.037 ± 0.002 $\mu\mathrm{m}^{-1}$ for the perprotonated species and 0.054 ± 0.002 $\mu\mathrm{m}^{-1}$ for the perdeuterated species. *Thus, the energy gap between the two excited states is dependent upon isotopic substitution of the bpy ligands.*

This result suggests that the force constants and vibrational frequencies of the C–H modes are different in the charge-transfer and ligand-field excited states. Since the ligand-field state arises formally from localized excitation of the metal d orbitals, the C–H force constants in this state should be similar to those in the ground state. On the other hand, the charge-transfer state is characterized by a substantial enhancement of the π-electron density of the bpy rings, which is likely to bring about some alteration of the C–H stretching frequencies. As a rough approximation we assume that only the contribu-

0002-7863/79/1501-2742$01.00/0

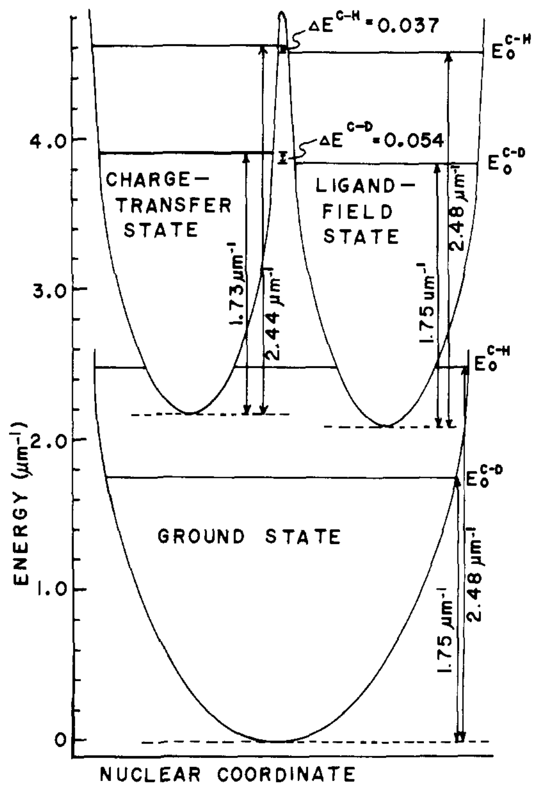


Figure 3. Interpretation of the deuterium effect on the energy gap between charge-transfer and ligand-field states. Symbols in the diagram are defined as follows: $E_0{}^{C-H}$, contribution of C-H vibrational modes to the zero-point energy; $E_0{}^{C-D}$, contribution of C-D vibrational modes to the zero-point energy; ΔE^{C-H}, difference in energy of zeroth vibrational levels of the charge-transfer and ligand-field states for the perprotonated complex; ΔE^{C-D}, difference in energy of zeroth vibrational levels of the charge-transfer and ligand-field states for the perdeuterated complex.

tions of C-H or C-D stretching modes to the zero-point energy need be considered to interpret the observed deuterium effect. Furthermore, we use the assumption (substantiated, for other cases, both experimentally[6] and theoretically[7]) that the C-H or C-D stretching motions are not coupled to each other. Thus, the vibrational contribution to the energy from the C-H or C-D bonds is roughly that of 16 independent oscillators. Using a vibrational frequency of 0.310 μm^{-1} for a C-H stretching mode and 0.219 μm^{-1} for a C-D stretching mode in the ground- and ligand-field states, the contribution of 16 C-H stretches to the zero-point energy is estimated to be 2.48 μm^{-1} while that of 16 C-D stretches is estimated to be 1.75 μm^{-1}. If the C-H stretching frequency decreases to 0.305 μm^{-1} in the charge-transfer state, then the C-D frequency should decrease to 0.216 μm^{-1}; the contributions of these modes to the zero-point energies would be 2.44 and 1.73 μm^{-1}, respectively. This would lead to an increase of 0.02 μm^{-1} in ΔE on deuteration, compared with the observed increase of 0.017 μm^{-1} (see Figure 3). Thus, a decrease of 1% in the C-H stretching frequency in the charge-transfer state is sufficient to account for the observed deuterium effect. This calculation suggests that the 0-0 band of the charge-transfer emission should lie at ~0.02 μm^{-1} higher for the deuterated species than for the protonated species compared with the difference of 0.01 ± 0.05 μm^{-1} which we observe in DMF at 77 K under high resolution.

Acknowledgment is made by R.J.W. to the Committee on Research of the University of California, Santa Barbara, for support of this research.

References and Notes

(1) R. J. Watts, T. P. White, and B. G. Griffith, *J. Am. Chem. Soc.*, **97**, 6914 (1975).
(2) R. J. Watts and D. Missimer, *J. Am. Chem. Soc.*, **100**, 5350 (1978).
(3) R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 3184 (1971).
(4) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).
(5) G. D. Hager and G. A. Crosby, *J. Am. Chem. Soc.*, **97**, 7031 (1975).
(6) See, for example, R. L. Swafford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.*, **65**, 179 (1976).
(7) W. Siebrand, *J. Chem. Phys.*, **46**, 330 (1967); **47**, 2411 (1967). C. Guttman and S. A. Rice, *ibid.*, **61**, 651 (1974). B. R. Henry and W. Siebrand, *ibid.*, **49**, 5369 (1968). B. R. Henry, *J. Phys. Chem.*, **80**, 2160 (1976). R. Wallace, *Chem. Phys.*, **11**, 189 (1975). M. L. Elert, P. R. Stannard, and W. M. Gelbart, *J. Chem. Phys.*, **67**, 5395 (1977).

Richard J. Watts,* Shlomo Efrima, Horia Metiu
Department of Chemistry, University of California
Santa Barbara, California 93106

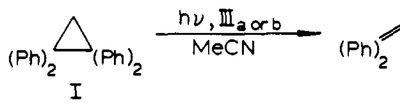
Received August 3, 1978

Radical Ions in Photochemistry. 9. Reactions of the 1,1,2,2-Tetraphenylcyclopropane Radical Cation[1]

Sir:

The photosensitized (electron transfer) reactions of cyclopropanes are particularly interesting because of the unusual intermediates, 1,3 radical ions, that are involved. The direct irradiation of 1,1,2,2-tetraphenylcyclopropane (I) leads to ring fragmentation to give 1,1-diphenylethylene and products derived from diphenylcarbene.[2] In contrast, we find that the sensitized (electron transfer) irradiation of I, using 1-cyanonaphthalene (IIIa) or 1,4-dicyanonaphthalene (IIIb) as electron-accepting sensitizers, gives good yields of the ring-cleaved product, 1,1,3,3-tetraphenylpropene[3] (II) (reaction 1). The

REACTION 1



irradiations were carried out in argon-purged acetonitrile solutions under conditions such that only the sensitizer (IIIa or IIIb) absorbed light. In the time required to complete the conversion of I, little if any of the sensitizer was consumed.

This reaction can be discussed in terms of electron transfer from I to the excited sensitizer. The free-energy (ΔG) change for such a process, leading to the formation of a radical-ion pair, can be calculated from the Weller equation.[4] Reliable values were available in the literature[5] for all of the required quantities except for the oxidation potential of I; this we have determined.

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06[E(D/D^+) - E(A/A^-) - (e_0{}^2/\epsilon\alpha)] - \Delta E_{0\text{-}0}$$

Analysis of the oxidative process (irreversible) of I by cyclic voltametry gives $E_{ox}^{1/2} = 1.22$ V ($Ag/AgNO_3$ (0.1 M) in acetonitrile). Since the oxidative process was irreversible, the potential derived from the voltamagram does not have thermodynamic significance. Even though it has been demonstrated that meaningful correlations can be obtained using such data,[6,7b] the value was obtained by another method. There is a known relationship between the maximum in the absorption spectra of the charge-transfer complex between tetracyanoethylene (TCNE) and various donors and the $E_{ox}^{1/2}$ of the donor.[7] The cyclopropane I forms a charge-transfer complex with TCNE which exhibits an absorption maximum at 404 nm and a shoulder at 510 nm (methylene chloride solution). The position of the maximum (540 ± 10 nm) giving rise to the long wavelength shoulder is that expected from a donor having $E_{ox}^{1/2} = 1.28 \pm 0.04$ V, in good agreement with the value obtained by cyclic voltametry. Substitution of the appropriate values into the Weller equation leads to the conclusion that the elec-

0002-7863/79/1501-2743$01.00/0