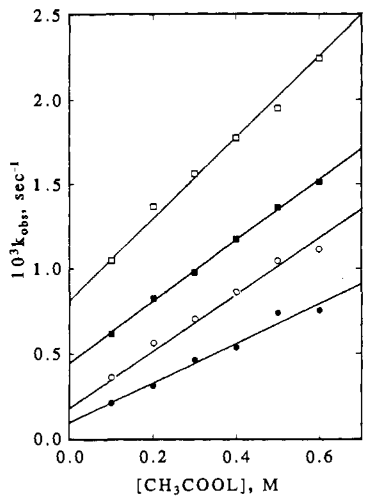

Figure 1. Dependence of the observed rate constants for reduction of 0.001 M *p*-benzoquinone by **1**-H (□, ■) and **1**-D (○, ●) on the concentration of acetic acid (fraction of acid = 0.75) in H_2O (open symbols) and D_2O (closed symbols).

conditions under which acid-catalyzed one-electron transfers can occur.

Figure 1 shows that the acetic acid catalyzed reduction of *p*-benzoquinone by **1**-L[19,20] shows small primary C–H isotope effects of $k_H/k_D = 1.48 \pm 0.11$ in H_2O and $k_H/k_D = 1.56 \pm 0.13$ in D_2O, as well as solvent isotope effects $k_{H_2O}/k_{D_2O} = 1.25 \pm 0.07$ for H transfer from **1**-H and $k_{H_2O}/k_{D_2O} = 1.32 \pm 0.13$ for D transfer from **1**-D.

The following evidence shows that the mechanism of eq 2 in which acid-catalyzed electron transfer, k_{cet}, and hydrogen atom transfer, $k_{L\bullet}$, are partially rate-limiting[1] cannot account for the experimental data. (1) General acid catalysis of electron transfer

$$\mathbf{1}\text{-L} + Q \underset{k_{cbl}[A^-]}{\overset{k_{cet}[AH]}{\rightleftharpoons}} (\mathbf{1}\text{-L}^{\bullet+}QH^\bullet) \xrightarrow{k_{L\bullet}} \mathbf{1}^+ + QH_2 \qquad (2)$$

is not expected because the hydron transfer from acetic acid to a transition state less basic than the semiquinone radical anion ($pK_a^{QH\bullet} = 4$)[14] is thermodynamically unfavorable.[15,22] (2) The C–H kinetic isotope effect (due to the second hydrogen transfer) is expected to *decrease* in D_2O, according to the multiple isotope effect criterion or concertedness developed by Hermes et al.[23] and Belasco et al.[24] This is because deuterium substitution of the acid catalyst selectively slows the initial hydron-transfer step thus partially "masking" the primary isotope effect for H atom transfer between **1**-$L^{\bullet+}$ and $QH^\bullet$. The C–H isotope effect that is independent of the isotopic solvent within experimental error is consistent with both hydrogen transfers occurring in a single transition state. (3) Deprotonation of **1**-$L^{\bullet+}$ by acetate ion with a second-order rate constant $\sim 10^7$ M^{-1} s^{-1} is expected to compete with the endothermic H atom transfer, in analogy to the e^-–H^+–e^- oxidation of **1**-H by $Fe(CN)_6^{3-}$, which shows a larger primary C–H isotope effect $k_H/k_D = 4.4$ for the kinetically unambiguous catalysis by acetate ion.[25]

The isotope effects indicate a small loss of both O–H and C–H zero-point energy in the transition state may reflect a reaction coordinate involving predominately heavy-atom motion[26] or hydrogen bonding to the catalyst,[27] or both. The Brønsted slope $\alpha = 0.85$ for catalysis by substituted acetic acids is consistent with a transition state resembling the protonated oxonium ion that is hydrogen bonded to the conjugate base of the catalyst.

These results show that even in cases where a Lewis acid complexed substrate has a favorable 1e$^-$ reduction potential,[11] direct hydride transfer will dominate if there is an unfavorable equilibrium for forming the Lewis acid complex.

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(19) Rate constants were determined as previously described[1] under pseudo-first-order conditions in substituted acetate/acetic acid buffers in H_2O and D_2O containing 3% CH_3CH_2OL (v/v) at 25 °C and ionic strength 1.0 (KCl). Compound **1**-D was >98.8% deuterium labeled as determined by 500-MHz ^{1}NMR spectroscopy in $CDCl_3$.

(20) The product 4-hydroxycyclohexa-2,5-dienone should enolize rapidly to the hydroquinone product. Similar cyclohexa-2,5-dienone intermediates have been observed spectroscopically on the millisecond time scale in the bromination of phenol.[21] A mechanism involving hydride transfer to the carbonyl oxygen with hydron transfer to the second oxygen to yield the hydroquinone product QH_2 directly cannot be excluded.[6]

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Direct Evidence for Intersystem Crossing Involving Higher Excited States of Acenaphthylene

Anunay Samanta†

School of Chemistry, University of Hyderabad
Hyderabad 500134, India
Radiation Laboratory, University of Notre Dame
Notre Dame, Indiana 46556

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Despite the fact that higher excited states of aromatics in condensed media play a minor role in dictating the overall photophysics and photochemistry, studies in recent years show that photoprocesses involving higher excited states are not uncommon. Fluorescence from S_2 (abnormal fluorescence) has been found to be a general feature in systems with a large S_1–S_2 gap.[1-3] In systems with a very low S_1–S_2 gap, abnormal fluorescence is the result of thermal excitation of the S_1 state.[4] On the other hand, when T_2 is above S_1 by only a few kcals, a similar mechanism leads to emission from T_2 as well.[5] Under such a situation T_2 can participate in a variety of photophysical processes.[6] T_2 is shown

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† Correspondence should be addressed to the University of Hyderabad.

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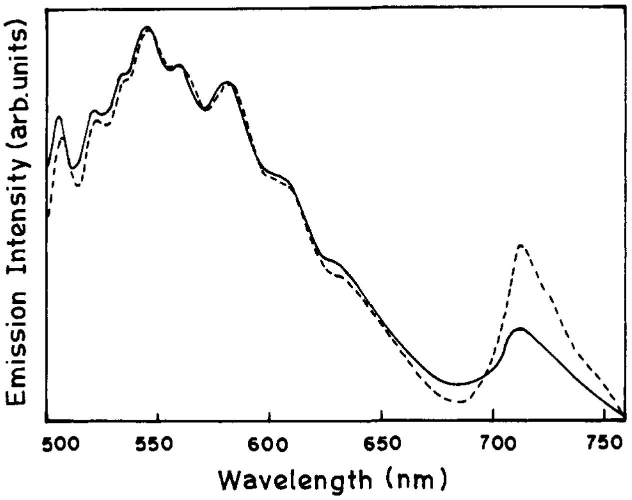

Figure 1. The emission spectra obtained on 266-nm laser excitation of a nondegassed (continuous line) and a degassed (dashed line) solution of acenaphthylene.

to be populated via intersystem crossing (ISC) from S_1 when it is located below S_1.[7] A novel two-laser technique has been recently used by Scaiano and co-workers for a detailed study of the T_2 state.[8] The photochemical reactions from higher excited states have been discussed in an excellent review article by Turro and co-workers.[9]

It is important to note that despite a large number of such studies, ISC from a higher excited singlet state (e.g., from S_2) is yet to be demonstrated. Though speculated in some systems,[10] no direct proof of this process exists in the literature. It is for this purpose we have undertaken this investigation. Acenaphthylene is selected as the system because it has a comparatively long lifetime for the S_2 state,[2] and this may allow the ISC process to compete with the internal conversion of this state. Another good reason for selecting acenaphthylene as a candidate is the fact that direct excitation of S_1 does not populate T_1.[11] Thus, if T_1 is seen (either by laser flash photolysis or by phosphorescence emission) on higher excitation, it must be due to the $S_2 \rightsquigarrow T_1$ process.

Though no transient is seen in the range 300–500 nm on flash photolysis of a solution of acenaphthylene at 355 nm (excitation below S_2), when excited at 266 nm by the fourth harmonic of the laser a transient is seen with a maximum at around 350 nm.[12] The absorption is rather weak and has a lifetime in the microsecond range. The transient is sensitive to oxygen and quenched by low-energy triplet quenchers. The spectral characteristics of the transient are similar to those of acenaphthylene triplet, as characterized by us in an earlier communication through heavy atom perturbation and sensitization techniques.[11] Thus we are led to conclude that ISC involving a higher singlet state is operative in this system. It is likely that this process may be mediated by T_2 or a higher triplet. As of now, since the higher triplet states of this molecule have not been characterized, it is not possible to predict whether T_2 or a higher triplet is involved. The quantum yield of this triplet formation is measured under 266-nm excitation following procedures described elsewhere,[11] and a value of 0.03 is obtained.

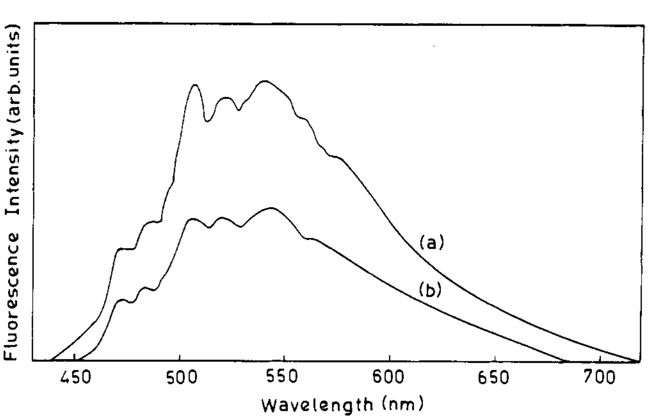

Figure 2. The excitation wavelength dependence of the normal fluorescence spectra of acenaphthylene: (a) 355-nm excitation and (b) 320-nm excitation.

Further proof of ISC from S_2 is obtained from emission studies. In view of the very low quantum yield of emission a picosecond laser source with a sensitive detection system was used for most of the emission studies.[13] When excited at 355 nm, $S_1 \rightarrow S_0$ fluorescence with maximum at around 540 nm is observed as the sole emission. On 266-nm excitation of a degassed solution of acenaphthylene one more emission band, apart from the normal and $S_2 \rightarrow S_0$ fluorescence, is observed at 715 nm (Figure 1). The emission is extremely weak but could be observed readily in the highly sensitive setup. As seen from the figure, while the normal fluorescence is insensitive to oxygen, the weaker band is not. The emission enhancement on degassing is indicative of a long-lived component associated with this emission. The origin of this emission band corresponds very closely to the origin of the T_1 state as determined by us and by others.[11,14] These point to the fact that the emission is phosphorescence from T_1, which is evidently populated from S_2.

The evidence for the $S_2 \rightsquigarrow T_1$ process has also been obtained from a comparison of the intensity of the normal fluorescence band on two different excitations under matched condition; one over S_1 and the other over S_2. The fluorescence quantum yield is expected to be independent of excitation wavelength if internal conversion is the only decay mode of S_2. However, as evident from Figure 2 there is nearly a 50% decrease in ϕ_f on excitation over S_2. This result further corroborates that S_2 decays by some other channel.

The triplet yield, as measured here, is 0.03, and therefore the normal fluorescence intensity is expected to decrease by only 3%. Although the decrease can be partly due to some emission from S_2, $\phi_f(S_2)$ is too low to account for this large difference. The following arguments can be put forth to explain this anomaly. The weakness of the first absorption band, large Stokes shift between absorption and fluorescence, and extremely low fluorescence quantum yield of acenaphthylene have led to the idea that the S_1 state is highly distorted with respect to S_0,[3a] and this may result in crossing of S_1 and S_0 energy surfaces. Excitation at S_2 will result in the formation of S_1 via a nonradiative process with a large excess of vibrational energy. Thus, if the molecule is energetically above the crossing point, the probability of it crossing over to S_0 without emitting from S_1 is enhanced considerably. Our result, therefore, conforms with the present idea of the distorted S_1 state of the molecule and a decrease in ϕ_f by more than 3% is fully

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justified by the existing data on this system. In summary, this is the first direct evidence of ISC from the S_2 state.

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Registry No. Acenaphthylene, 208-96-8.

Rapid Intermolecular Ligand Exchange between Square-Planar Iridium(I) Complexes: *trans*-Ir(CO)L_2X (X = Cl or Me, L = P(*p*-tolyl)$_3$ or $PMePh_2$)

Jeffrey S. Thompson and Jim D. Atwood*

Department of Chemistry, University at Buffalo
State University of New York, Buffalo, New York 14214

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Square-planar complexes provide one of the foundations of inorganic and organometallic chemistry.[1] Reactivity studies of square-planar complexes have centered on substitution[1] and oxidative addition reactions.[1,2] In the course of our studies of iridium(I) complexes,[3] we have discovered an extremely facile ligand-exchange process for the complexes *trans*-Ir(CO)L_2X (L = P(*p*-tolyl)$_3$ and $PMePh_2$, X = Cl, Me, or OMe).

The compounds *trans*-Ir(CO)(P(*p*-tolyl)$_3$)$_2$X, X = Cl, Me, and OMe, have been previously reported.[3,4] The characterizations are consistent with those previously reported.[4] *trans*-Ir(CO)(Cl)($PMePh_2$)$_2$ was prepared by ligand exchange on *trans*-Ir(CO)(Cl)(PPh_3)$_2$.[5] The methyl complex *trans*-Ir(CO)(Me)($PMePh_2$)$_2$ was prepared from the chloride by the same procedure as for *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$.[6] The main technique used in this study is ^{31}P NMR spectroscopy; Table I contains the ^{31}P resonances of the complexes and free ligands.

In a typical reaction (represented for the methyl compounds), 25 mg of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ and 25 mg of *trans*-Ir(CO)(Me)($PMePh_2$)$_2$ were placed in an NMR tube equipped with a vacuum adaptor, which was then removed from the inert-atmosphere glovebox and placed on a high-vacuum line. The solids were evacuated and cooled to N_2(l) temperature, and 1.0 mL of CD_2Cl_2 was added by vacuum distillation. The sample was placed frozen in the NMR instrument (Varian VXR-400) and monitored from −70 °C to room temperature by ^{31}P NMR spectroscopy. Figure 1 shows spectra for a typical reaction. Proton spectra were also recorded but were quite complicated, and we did not attempt assignment.

Table I. ^{31}P NMR Resonances in CD_2Cl_2 for Various Complexes

reagents	^{31}P NMR, ppm
Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$	22.5 (s)
Ir(CO)Me(P(*p*-tolyl)$_3$)$_2$	28.2 (s)
Ir(CO)(Cl)($PMePh_2$)$_2$	9.4 (s)
Ir(CO)Me($PMePh_2$)$_2$	10.2 (s)
$PMePh_2$	−26.85 (s)
P(*p*-tolyl)$_3$	−7.96 (s)

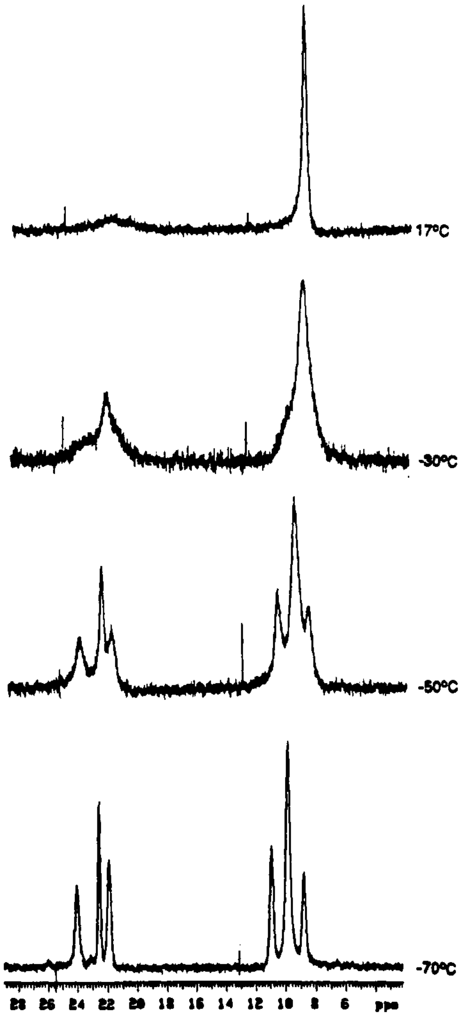

Figure 1. ^{31}P NMR spectra recorded at four temperatures for a mixture of *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ (22.4 (s) ppm) and *trans*-Ir(CO)(Cl)($PMePh_2$)$_2$ (10.0 (s) ppm). Even at −70 °C, these are fully exchanged with formation of *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)($PMePh_2$) (2 d, 23 and 10 ppm). As the temperature is warmed, the exchange becomes rapid.

For each reaction of *trans*-Ir(CO)(P(*p*-tolyl)$_3$)$_2$X with *trans*-Ir(CO)($PMePh_2$)$_2$X, three species are present in approximately statistical amounts at −70 °C: *trans*-Ir(CO)(P(*p*-tolyl)$_3$)$_2$X, *trans*-Ir(CO)($PMePh_2$)$_2$X, and *trans*-Ir(CO)($PMePh_2$)(P(*p*-tolyl)$_3$)X.[7] The mixed phosphine complex shows two doublets with coupling ($J_{P-P} \cong 300$ Hz) typical for trans phosphines.[8]

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[6] *trans*-Ir(CO)(Cl)($PMePh_2$)$_2$: IR (KBr) ν_{CO} = 1950 cm^{-1}; ^{31}P NMR 9.5 (s) ppm. *trans*-Ir(CO)(Me)($PMePh_2$)$_2$: IR (KBr) ν_{CO} = 1925 cm^{-1}; ^{31}P NMR (C_6D_6) 10.6 (s) ppm; ^{1}H NMR (C_6D_6) 0.42 (t), J_{P-H} = 9.5 Hz, 2.0 (s), 2.3 (t), J_{P-H} = 3.2 Hz, 6.9 (m), 7.6 (m).

[7] Integration of the −70 °C ^{31}P NMR spectrum for reaction of *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ with *trans*-Ir(CO)(Cl)($PMePh_2$)$_2$ in a 1:2 ratio results in a 1:3:4 ratio of *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$, *trans*-Ir(CO)(Cl)($PMePh_2$), and *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)($PMePh_2$).

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