comparable, but shorter than Li–H distances previously observed for organolithium compounds (e.g., 1.96 (1) Å for the shortest α-carbon hydrogen atom in cyclohexyllithium[5,19]). The puckering of the four-atom lithium rings shown in Figure 2 optimizes the close approach of C(1)–Li(1) (2.17 (2) Å) and Li(1)–D(1) (1.72 (2) Å). The observed D(1)–C(1)–D(2) angle is 100 (1)° with C–D distances of 1.09 (1) Å (C(1)–D(1)) and 1.18 (2) Å (C-(1)–D(2)).

The local geometry about the carbon atom (Figure 2) suggests two types of C–D coordination if one considers closest-neighbor interactions. The coordination to D(1) can be viewed as I, while that for D(2) is best represented by the semibridging model II
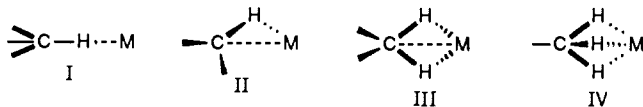
with coordination to the C–D bond (C–Li, 2.17 (2) Å; Li–D, 1.99 (3) Å). This configuration is also found in cyclohexyllithium[5,19] (C–Li, 2.184 (3) Å; Li–H, 2.00 (1) Å). III and IV have been previously described for the CH_3 groups in $LiB[CH_3]_4$[4] (C–Li, 2.207 (9) Å, Li–H, 2.115 (8) Å (III); C–Li, 2.359 (11) Å, Li–H, 2.231 (10) Å (IV)).

In the field of polylithium organic compounds, there have been extraordinary predictions of unusual geometries and, in particular, "hypervalent" polylithium compounds[20,21] which have forecast stabilities of such species as CLi_5,[22] CLi_6, and even CLi_8 neutral species. The environment of the carbon atom in the dilithio-methane structure could easily lead to such fragments, and indeed CLi_3H^+ has been observed by flash vaporization mass spectrometry.[23] Comparisons with previous theoretical models of molecular oligomeric groups made up of Li_2CD_2 units[9] are limited by the difficulty of appropriately including Li–H–C bonding interactions which are primarily responsible for the observed extended structure. The results obtained in this study clearly confirm the importance of metal··H–C bonding in the chemistry and structural properties[4,5,24] of early main group organometallics.

Supplementary Material Available: Structural parameters for CD_2Li_2 including the space group, Rietveld analysis fit of observed diffraction pattern, structural coordinates, and selected bond distances and angles (3 pages). Ordering information is given on any current masthead page.

(18) Another interesting comparison is with BeH₂, which has Be–H distances ranging from 1.38 (2) to 1.44 (2) Å (Smith, G. S.; Johnson, Q. C.; Smith, D. K.; Cox, D. E.; Snyder, R. L.; Zhou, R.-S.; Zalkin, A. Brookhaven National Synchrotron Light Source Annual Report; 1988, p 227.

(19) At 70 °C, cyclohexyllithium eliminates cyclohexene to give LiH. We find that, over a period of a year, dilithiomethane converts extensively to LiH at ambient temperatures. The average α-hydrogen–lithium atom distance in cyclohexyllithium (2.003 (7) Å) is also less than the Li–H distance in lithium hydride (2.043 Å) (Zintl, E.; Harder, A. *Z. Phys. Chem., Abt. B* **1935**, *28*, 478).

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Direct Evidence of the Triplet-State Origin of the Slow Reverse Proton Transfer Reaction of 3-Hydroxyflavone

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For many excited-state intramolecular proton transfer (ESIPT) molecules such as most of the derivatives of salicylic acid,[1–5] both experimental and theoretical results have concluded either the existence of a single minimum potential energy surface or a double minimum potential in which rapid tunneling is responsible for ultrafast proton transfer in the singlet excited state. However, the shape of the ground-state potential energy surface for several ESIPT molecules has raised many controversies. One prominent case is the study of 3-hydroxyflavone (3HF).

The first dynamic study of the ground-state reverse proton transfer of 3HF was reported by Itoh et al. By using transient absorption and two-step laser-induced fluorescence (TSLIF) measurements, they demonstrated that an unexpectedly long-lived ground-state tautomer (∼microseconds) is involved in the reverse proton transfer at room temperature.[6,7] Consequently, Aartsma and co-workers reexamined the ground-state reverse proton transfer by means of picosecond time-resolved absorption spectroscopy coupled with a stimulated emission pumping technique.[8] Contradictory to the results of Itoh et al., they put a lower limit of 3 × 10¹⁰ s⁻¹ on the rate of the ground-state reverse proton transfer. Shortly after Aartsma's report, Itoh et al. published detailed transient absorption and TSLIF studies to reconfirm the existence of the long-lived ground-state tautomer.[9,10] However, in the meantime, from the observation of the gain spectrum profile of the amplified spontaneous emission of 3HF, Chou et al. suggested that the energy barrier for the ground-state reverse proton transfer was negligibly small.[11] In addition, Brucker and Kelley, by analysis of the homogeneous bandwidth for matrix-isolated 3HF at 30 K, proposed a lower limit of 60 fs for the ground-state reverse proton transfer reaction.[12]

Most recently we have conducted transient absorption and TSLIF measurements for 3HF in combination with a photo-oxygenation study in order to resolve these controversies.[13–15] Although our kinetic results are qualitatively in agreement with those obtained by Itoh et al., several detailed quantitative analyses discount the assignment of the long-lived species to the ground-state tautomer singlet state. We summarize the key results as follows:

(1) The yield of tautomer emission from the TSLIF measurement (probed at 437 nm) is only ∼0.013 of the non-time-resolved tautomer emission at room temperature.

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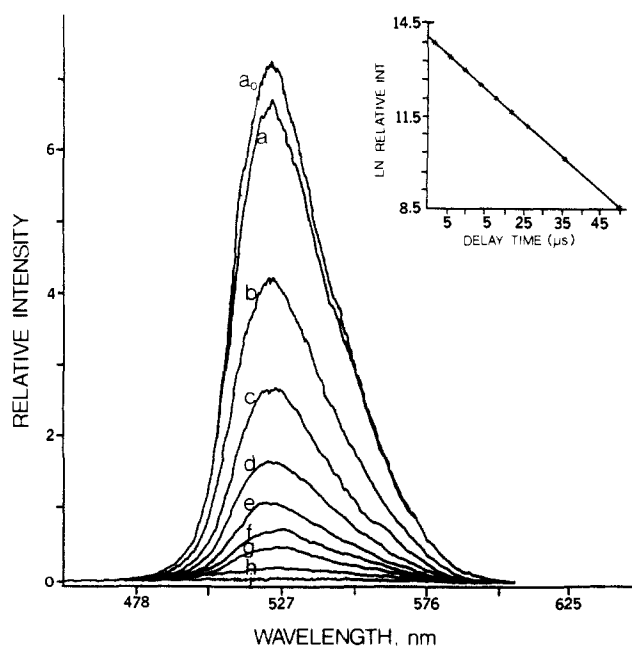
Figure 1. Steady state and TSLIF of 3HF in *n*-heptane at room temperature. The concentration of 3HF is 5.0×10^{-5} M. The pump pulse energy is 4 mJ cm^{-2} at 355 nm, and the probe pulse energy is 3 mJ cm^{-2} at 610 nm. (a$_0$) Steady-state tautomer emission; (a) 1.5-μs delay time; (b) 7.5 μs; (c) 11.5 μs; (d) 15.5 μs; (e) 19.5 μs; (f) 23.5 μs; (g) 27.5 μs; (h) 37.5 μs; (i) 52.5 μs. The emission profile is distorted at >600 nm due to the cut-off filter (Corning 4-96) which is used to block the probe laser. Inset: decay of TSLIF, with first-order fit yielding a 7.58×10^4 s^{-1} (13.2 μs) decay constant.

(2) By the TSLIF measurement, the bimolecular quenching rate constant of the long-lived species by ground-state oxygen is measured to be $\sim 3.2 \times 10^9$ M^{-1} s^{-1}, while the yield of the oxygenation products is only ~ 0.001, indicating that physical quenching by oxygen is the major deactivation process for the long-lived tautomer species.

(3) Both the energy barrier (0.85 kcal/mol) and the preexponential factor ($\sim 2.3 \times 10^5$ s^{-1}) determined by the temperature-dependent study are remarkably small. In addition, the tautomer species cannot be trapped either in 77 K hydrocarbon glass or in a 12 K argon matrix.

Result (3) is very intriguing. On the basis of the previous assignment of the long-lived ground-state tautomer, the exceedingly small preexponential factor indicates that among numerous vibrational states accessible by thermal excitation only a few specific ones compatible with the required geometrical change result in the proton-transfer reaction. This concept is difficult to accept for a coplanar, intramolecularly hydrogen bonded system. However, since the above results conflict with the assignment of the long-lived ground-state tautomer indirectly, definitive spectroscopic evidence is necessary in order to unambiguously assign the long-lived tautomer species.

In this communication, we report the first direct spectroscopic evidence that the long-lived species of 3HF observed from TSLIF and transient absorption measurements is ascribed to a triplet state rather than a singlet ground state. Furthermore, on the basis of the expected dynamics of a triplet state, previous controversies and several unexplained results can be resolved.

In this study we extend our TSLIF study to a longer probe wavelength. When the probe laser is tuned to 610 nm, a transient emission maximum at 526 nm (Figure 1) is observed at various delay times. This emission is concluded to be the tautomer florescence due to complete identity with the non-time-resolved tautomer emission. The decay of the TSLIF is also plotted (inset in Figure 1), and the fit by first-order decay yields a decay constant calculated at 7.58×10^4 s^{-1} (13.2 μs). The TSLIF was also observed when the probe laser was tuned to 690 and 710 nm, yielding 15.1- and 14.1-μs decay constants, respectively. Within experimental error, these results are consistent with those obtained
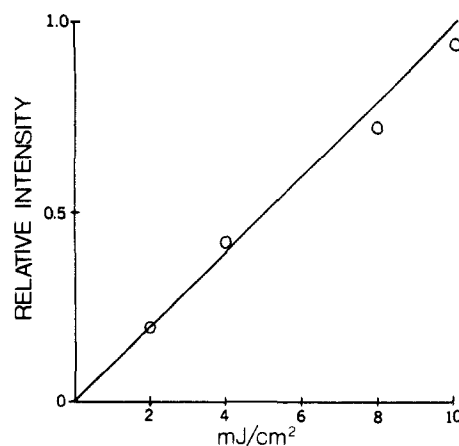

Figure 2. The plot of TSLIF intensity monitored at 525 nm versus the probe pulse energy (610 nm) for 3HF in *n*-heptane at room temperature.

in a probe wavelength of 435 nm.[9,15] Since tuning the probe wavelength in a broad range is accompanied by a change in the overlapping area between pump and probe pulses, the excitation spectrum was not obtained at this stage. A detailed study will be published elsewhere.

The definitive conclusion that a triplet state is responsible for the observed slow reverse proton transfer process of 3HF results from the following evidence:

(1) Since the 0–0 onset of the tautomer emission is ~ 485 nm in the condensed phase, the probe wavelength at >610 nm definitely cannot be ascribed to the tautomer absorption in the singlet-state manifold.

(2) The quenching rate by ground-state oxygen for the TSLIF is determined to be $\sim (2.7 \pm 0.3) \times 10^9$ M^{-1} s^{-1} for the three probe wavelengths, indicating a triplet-O$_2$ energy-transfer process.

(3) Biexponential decay of the TSLIF was observed at higher concentrations of the excited 3HF, indicating that triplet–triplet annihilation takes place.

(4) A power-dependent study shows that the TSLIF is caused by a single photon event (Figure 2), thus eliminating the possibility of a multiphoton process.

Accordingly, the observed TSLIF[9,15] results from triplet–singlet intersystem crossing in the highly excited triplet state. Several controversial results, as well as some of our own perplexing data, can be rationalized by the above mechanisms:

(1) The low yield of the TSLIF emission for 3HF is due to T–S intersystem crossing, which competes with T–T internal conversion in the condensed phase.

(2) The small preexponential factor for the reverse proton transfer in the case of 3HF can be rationalized by the spin–orbit coupling factor and the density of the state mixing between T$_1$ and S$_0$ or T'$_1$ and S'$_0$ (the unprimed and primed states denote the normal and tautomer species, respectively).

(3) The lower limit of 60 fs for the ground-state reverse proton transfer rate[12] proposed by Brucker and Kelley may be valid. Hence, there is a negligible energy barrier for the ground-state reverse proton transfer.

Recent studies by Scaiano et al.[16] claim the observation of fluorescence through T$_1$ $\rightarrow$ T$_n$ excitation of 9,10-dibromoanthracene. On the basis of the dynamics of the T$_1$ $\rightarrow$ T$_n$ transient absorption, they conclude that the T–S intersystem crossing originates from the T$_2$ state which has lifetimes as long as 200 ps. However, the T$_n$ $\rightarrow$ S$_m$ ($n \geq 2$, $m \geq 1$) efficiency in the condensed phase is normally $\sim 10^{-5}$ in aromatic compounds.[17,18]

In the case of 3HF, since the TSLIF is still observed when probed at >700 nm, it is very likely that the intersystem crossing originates from the T$_2$ or T'$_2$ state. For 3HF due to the 7.7 $\times$ 10^{11} s^{-1} rate at ESIPT[19] and the risetime of $\ll 50$ ns for the

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TSLIF,[20] we tentatively ascribe the precursor of the TSLIF to the tautomer triplet state. For this case, at this stage, whether the rate of $T'_2 \rightarrow T'_1$ internal conversion is exceptionally slow (e.g., several hundred picoseconds) due to the large T'_2–T'_1 energy gap or the rate of $T'_2 \rightarrow S'_1$ intersystem crossing is remarkably fast cannot be determined. Research focused on the study of the dynamics of the triplet state is currently in progress.

(20) The TSLIF reaches a maximum intensity at a delay time of 50 ns, which is the response time of our TSLIF measurement.

Unprecedented Example of Four Coordination at a Vanadium(II) Center. Synthesis, Structure, and Properties of a Reactive, Nearly Planar V(II) Phenolate Complex, [V(DIPP)₄{Li(THF)}₂] (DIPP = 2,6-Diisopropylphenolate)

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Received October 3, 1989

Characterization of the coordination chemistry of divalent vanadium, particularly for nonorganometallic complexes, has lagged well behind that of most of the other first-row transition elements.[1] For example, the first V^{II} porphyrin complex was reported quite recently.[2] Presumably, this situation is a consequence of the tendency for many such complexes to be oxidized to V^{IV} and V^V oxo species in the presence of even traces of oxygen and/or water. While a considerable number of V^{II} complexes are known,[1] they are invariably six-coordinate and their reaction chemistry is often dominated by outer-sphere electron-transfer processes.[1,3] As a part of our ongoing effort to obtain very reactive, low-valent, coordinatively unsaturated vanadium complexes, it was discovered that reduction of the four-coordinate V^{III} phenolate species [V(DIPP)₄{Li(THF)}][4] was not a fruitful pathway to the desired V^{II} analogue.[5] However, by using V^{II} starting materials we were successful in isolating a V^{II}–phenolate complex, [V(DIPP)₄{Li(THF)}₂] (1), the subject of this report. This species represents the first example of a four-coordinate V^{II} complex and displays remarkable reactivity properties.

In our initial synthetic procedure, 1 was prepared from [V₂Cl₃(THF)₆](PF₆) (2), which can be obtained in turn from the corresponding (Zn₂Cl₆)²⁻ salt by metathesis with [(n-Bu)₄N](PF₆) in THF solution.[6] To 1.51 g (1.92 mmol) of 2 and 3.89 g (21.14 mmol) of Li(DIPP) was added 45 mL of dry hexanes, and the reaction mixture was stirred for 2 days and then filtered. Cooling
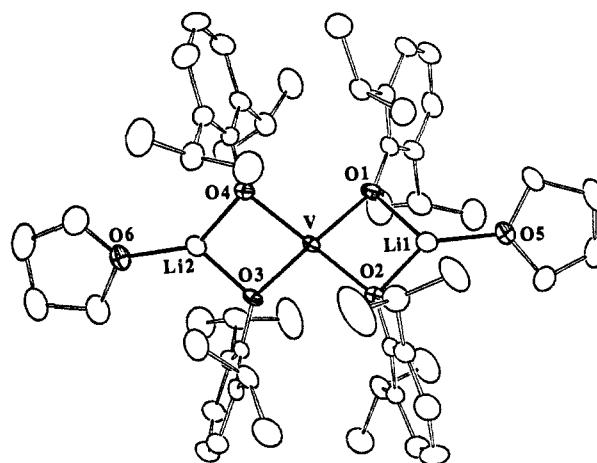
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Figure 1. Structure of [V(DIPP)₄{Li(THF)}₂] (1) showing the anisotropic thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (degrees), are as follows: V–O(1), 2.007 (2); V–O(2), 2.034 (3); V–O(3), 2.010 (2); V–O(4), 2.034 (2); Li(1)–O(1), 1.835 (6); Li(1)–O(2), 1.811 (7); Li(1)–O(5), 1.888 (7); Li(2)–O(3), 1.830 (7); Li(2)–O(4), 1.835 (7); Li(2)–O(6), 1.875 (7); O(1)–V–O(2), 79.4 (1); O(1)–V–O(3), 162.9 (1); O(1)–V–O(4), 103.2 (1); O(2)–V–O(3), 104.3 (1); O(2)–V–O(4), 161.9 (1); O(3)–V–O(4), 78.6 (1); V–O(1)–C(11), 145.8 (2); V–O(2)–C(21), 145.7 (2); V–O(3)–C(31), 147.3 (2); V–O(4)–C(41), 140.0 (2).
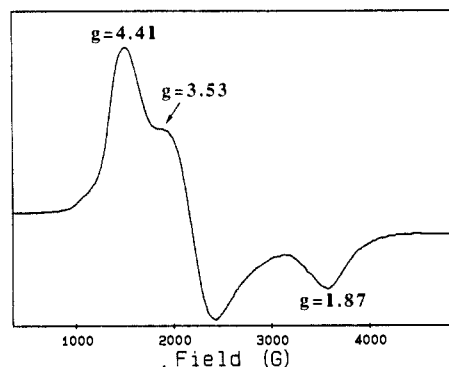

Figure 2. X-band (ν = 9.33 GHz) EPR spectrum of 1 in cyclohexane at 77 K obtained by using the following instrument settings: microwave power, 12.6 mW; field modulation amplitude, 10 G; modulation frequency, 100 kHz.

of the filtrate at –30 °C for 2 days afforded a crop of PF₂(DIPP)₃.[7] The yellow-green solution was decanted away and cooled for an additional 2 days, after which time a crop of 1 was collected (0.540 g, 30% yield). Crystals suitable for elemental analysis,[8] X-ray crystallography,[9] and magnetic and spectroscopic measurements were obtained by recrystallization from hexanes. Because it was found that the PF₆⁻ anion was not innocent in the aforementioned reaction, another V^{II} starting material was sought. Recently we have prepared compound 1 from [V(THF)₄(CF₃SO₃)₂][10] in 77% yield by a procedure similar to that described above. Judging from UV–vis–near IR spectra, it is difficult to obtain 1 with less than approximately 3% of [V(DIPP)₄{Li(THF)}] (3) present as an impurity.

(7) The identity of this product was confirmed by X-ray crystallography.

(8) Elemental analysis for 1. Calcd for C₅₆H₈₄O₆Li₂V: C, 73.26; H, 9.22. Found: C, 72.73; H, 9.34.

(9) Compound 1 crystallizes in the monoclinic space group *Pn*, with a = 13.103 (3) Å, b = 12.150 (5) Å, c = 17.109 (4) Å, β = 97.63 (2)°, V = 2701 (3) Å³, Z = 2, and ρ_{calcd} = 1.129 g cm⁻³. X-ray diffraction data were collected at 183 K by using Mo Kα radiation out to 2θ = 45°, yielding 3163 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS 86) and refined by using 584 parameters to final R (R_w) values of 3.87% (4.69%).

(10) The novel V^{II} starting material, [V(THF)₄(CF₃SO₃)₂], was prepared by reduction of V(CF₃SO₃)₃[11] using metallic zinc. Full details of the synthesis and structure will be reported elsewhere.

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