of $H_2Fe(CO)_4$ which is already present in the matrix. However, it is difficult to reconcile the loss of intensity in the bands assigned to $Fe(CO)_4$ without presuming that H_2 combines with $Fe(CO)_4$ by a thermal process.

These results are similar to the solution behavior of $H_2Ru(PPh_3)_3CO$ in that photolysis is presumed to lead to the formation of H_2 and $Ru(PPh_3)_3CO$.[16] The reverse process has not been demonstrated. It is intriguing to note that $Fe(CO)_4$ exhibited anomolous behavior in methane matrices.[13,14] In light of this report and recent reports of the chemistry of iron atoms, the data must be seriously reexamined in order to differentiate between CH_4 which has oxidatively added and that which has formed weak adducts.

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Direct Evidence for Exciplex Formation between a Triplet Alkanone and an Alkylbenzene

Thérèse Wilson*

The Biological Laboratories, Harvard University
Cambridge, Massachusetts 02138

Arthur M. Halpern

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

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Exciplexes are often postulated as intermediates in the quenching of triplet carbonyl compounds by olefinic and aromatic hydrocarbons.[1] Recently,[2] we presented new evidence for the reversible formation of a triplet exciplex of acetone and benzene on the basis of results obtained with 9,10-dibromoanthracene (DBA, at concentration $<10^{-3}$ M) as an acceptor of triplet energy.[3] Two triplet species were shown to act as energy donors, triplet acetone itself and its exciplex with benzene, the exciplex being the better donor.

When triplet cyclohexanone ($^3A^*$) is quenched by *o*-xylene (Xy) in a cyclohexane solution, the same sensitized DBA method now clearly reveals the formation of a relatively long-lived transient, $^3E^*$. Figure 1 shows a typical decay curve of the DBA fluorescence intensity, following ns pulse excitation at 305 nm, a wavelength at which both the alkanone and DBA absorb.[4] The first intensity peak, followed by fast decay, corresponds to the direct excitation and emission of DBA ($\tau_F \sim 2.4$ ns). The second peak, at $t_{max} \sim 100$ ns, reflects the buildup of the exciplex. Thus the fluorescence decay function comprises three components, of which the last two result from energy transfer to DBA.

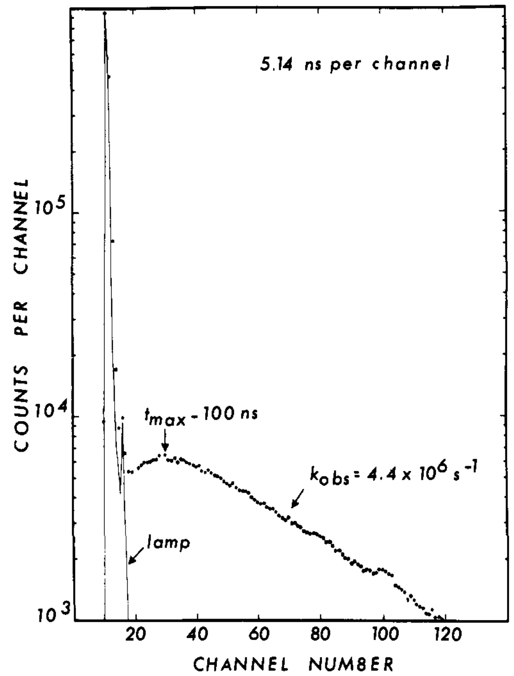


Figure 1. Fluorescence decay curve of a degassed *o*-xylene–cyclohexane (2:3 v/v) solution of DBA (1.1×10^{-4} M) and cyclohexanone (6.9×10^{-2} M) at 20 °C, with $\lambda_{exc} = 305$ nm. The full line is the lamp profile (the distortions around channels 77 and 100 in the DBA fluorescence curve are also present in the tail of the lamp curve). In the absence of cyclohexanone, the decay is strictly monoexponential ($1/\tau_F$).

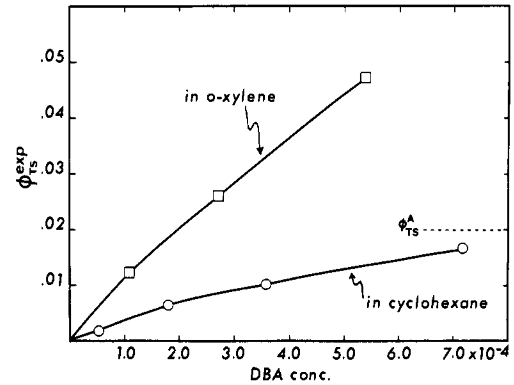
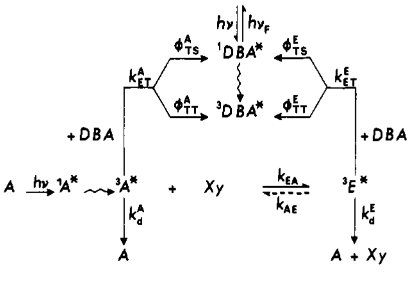


Figure 2. Efficiency of TS energy transfer as a function of DBA concentration in two solvents.

Scheme I



The main processes are presented in Scheme I, where exciplex dissociation is shown by a dashed arrow. It is in this respect that the quenching of $^3A^*$ by Xy differs most from that of triplet acetone by benzene. There, kinetic data implicated an exciplex in fast dynamic equilibrium with its components, such that triplet acetone and its benzene exciplex had the same decay rate.[2] At

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(3) In an energy-transfer process which results in the sensitized fluorescence of DBA. Although a higher triplet state of DBA (T_n, with $n \leq 2$) is probably populated before DBA (S_1), followed by $T_n \rightsquigarrow S_1$ or $T_n \rightsquigarrow T_1$, for simplicity the overall process is viewed here as a TS process. These alternatives are kinetically undistinguishable in the present work.

(4) At 20 °C in a degassed solution. The experimental method has been described.[2] Cyclohexanone (Eastman) was redistilled; *o*-xylene and cyclohexane (Burdick and Jackson "Distilled in Glass") were used without purification. The intensity decay curves were obtained by the single-photon counting method. The fluorescence was monitored at 430 nm.[2] The steady-state emission spectrum of the solution of Figure 1 is the same whether degassed or aerated; i.e., DBA fluorescence with a weak component of cyclohexanone fluorescence.

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all concentrations of benzene and DBA studied, the fluorescence decay curves could be described by the sum of two exponentials only. In contrast, a third exponential with a *negative* coefficient is *always* present in the quenching of $^3A^*$ by Xy (0.8–8.3 M). Thus in this case, dissociation of the exciplex is slow compared to its other modes of deactivation.

As expected, in neat cyclohexane (no Xy), the decay of DBA fluorescence sensitized by $^3A^*$ shows no second maximum. The subsequent slow exponential decay ($k_{obs} = k_d{}^A + k_{ET}{}^A[DBA]$) indicates that $k_d{}^A = 1.7 \times 10^6\ s^{-1}$ (compared to $2.0 \times 10^6\ s^{-1}$ in the case of acetone).

The buildup to a second maximum in the presence of Xy (even at 0.8 M, the lowest Xy concentration studied) requires (a) that $^3A^*$ and $^3E^*$ decay at different rates and (b) that $^3E^*$ be a sensitizer of DBA fluorescence. In fact, the S_1 state of DBA is populated *more efficiently* from $^3E^*$ than from $^3A^*$ (i.e., $\phi_{TS}{}^E > \phi_{TS}{}^A$, in Scheme I), as in the case of the acetone/benzene system.[2] This is shown in Figure 2, where $\phi_{TS}{}^{exp}$, the fraction of $^3A^*$ molecules which produce $^1DBA^*$ either directly or via an exciplex, is given by[5]

$$\phi_{TS}{}^{exp} = \left(\frac{N_s}{N_p}\right)\frac{\epsilon_{DBA}[DBA]}{\epsilon_A[A]}$$

N_p and N_s (in counts) are the integrated intensities of the prompt (the result of direct excitation of DBA) and slow emission (sensitized by $^3A^*$), respectively. $\epsilon_{DBA}[DBA]/\epsilon_A[A]$ is the ratio of the partial absorbances of DBA and A in the mixed solution. At $[DBA] = 5 \times 10^{-4}$ M (Figure 2), $\phi_{TS}{}^{exp}$ is ~3 times higher in *o*-xylene than in cyclohexane. Interestingly, this higher energy transfer efficiency is an intrinsic property of the exciplex, rather than a kinetic property of the system, since the lifetime of the exciplex is *shorter* than that of the uncomplexed triplet ketone in the same solution (i.e., ~*60* ns compared to ~200 ns, under the conditions of Figure 1). At a given concentration of Xy, the rate of decay of $^3A^*$ takes the form

$$k_{obs} = k + k_{ET}{}^A[DBA]$$

with $k = k_d{}^A + k_{EA}[Xy]$.[6] We have determined that $k_{EA} \lesssim 10^6\ M^{-1}\ s^{-1}$; thus the formation of $^3E^*$ is a slow process.

The contrast between the kinetics of the quenching of $^3A^*$ by Xy and that of triplet acetone by benzene illustrates the merits of using DBA as a tool for the characterization of nonemitting exciplexes. Interestingly, there is *no* evidence for a *long-lived* exciplex (i.e., no second peak) when $^3A^*$ is quenched by benzene instead of xylene. In fact, benzene is a less efficient "quencher" of $^3A^*$ than is *o*-xylene (smaller k_{obs} at the same DBA and quencher concentrations). The fluorescence decay curves are simple double-exponential functions, and $\phi_{TS}{}^{exp}$ appears to be no greater than it is in neat cyclohexane.

The order of quenching efficiency is reversed in the case of triplet acetone, which is more effectively quenched by benzene than by *o*-xylene. No second maximum is observed with either quencher nor in the quenching of 2-hexanone by *o*-xylene (3.2 M, as in the experiment of Figure 1), all at 20 °C. On the other hand, 3-pentanone and DBA in mixed cyclohexane/*o*-xylene produced a fluorescence intensity profile very similar to that of Figure 1, thus clearly indicative of a relatively stable exciplex.

The rate of formation and the stability of such triplet exciplexes seem therefore to be quite subtly dependent on the electronic and structural properties of both the aromatic quencher and alkanone quenchee. DBA, with its ability to scavenge triplet excitation energy and reemit it (with a ~2-ns lifetime) will help us assess the factors involved, in cases where the overall TS energy transfer is exergonic.

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(5) If exciplex dissociation is indeed unimportant, Scheme I leads to the following expression for [DBA]-dependent $\phi_{TS}{}^{exp}$ as a kinetic average of $\phi_{TS}{}^A$ and $\phi_{TS}{}^E$:

$$\phi_{TS}{}^{exp} = \phi_{EA}\phi_{ET}{}^E\phi_{TS}{}^E + \phi_{ET}{}^A\phi_{TS}{}^A$$

where $\phi_{ET}{}^E$ $\phi_{ET}{}^A$ are the efficiencies of scavenging $^3A^*$ and $^3E^*$ by DBA and ϕ_{EA} is the efficiency of exciplex formation over all other modes of deactivation of $^3A^*$.

(6) Experimentally, plots of *k* vs. [Xy] are not linear but curve upwards. This curvature may reflect the inadequacy of the kinetic treatment based on Scheme I, at the high Xy concentrations used here, where Xy is becoming the solvent. Also, a three-component exciplex AXy_2 may possibly play a role.

Carbenic Philicity: 6,6-Dimethylfulvene as an Indicator Substrate

Robert A. Moss,* Claire M. Young,[†] Leon A. Perez, and Karsten Krogh-Jespersen*

Wright and Rieman Laboratories, Deparment of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

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Singlet carbenes have been characterized as electrophilic,[1] ambiphilic,[2] or nucleophilic[3] on the basis of their selectivities[4] toward electron-rich and electron-poor alkenes. The variation of carbenic "philicity" with carbenic structure (i.e., X and Y in CXY) has been experimentally probed by linear free-energy analysis of carbenic relative reactivities with various series of olefinic substrates[1,4,5] and theoretically treated by molecular orbital techniques.[6-8] In previous experimental philicity determinations, subject carbenes were each studied with at least 4 or 5 olefinic substrates of varying π-electronic properties.[1,4] Consequently, one seeks a single "indicator" alkene which, by itself, could furnish an initial classification of carbenic philicity upon reaction with a given carbene.

In this vein is the observation that the regiochemistry of cyclopropanation of 1,1-dimethylallene by various ring-substituted phenylcarbenes rationally parallels the electronic properties of the phenyl substituents.[9] However, 1,1-dimethylallene is unable to differentiate ambiphilic from electrophilic carbenes[10] and is unlikely to react at all with strongly nucleophilic carbenes. A more promising candidate is 6,6-dimethylfulvene (**1**),[14] which reacts with nucleophilic lithium dichloromethide (THF, −75 °C) exclusively at its exocyclic double bond but reacts with electrophilic chlorocarbenoid (CH_2Cl_2, CH_3Li, Et_2O, −20 °C) only at an in-

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[†] Special Graduate School Fellow, Rutgers University.

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(10) CH_3OCCl, a bona fide ambiphile,[2] adds exclusively to the most substituted double bond of 1,1-dimethylallene,[11] as do the archetypal electrophiles CCl_2[12] and CBr_2.[12,13]

(11) Thermal decomposition (25 °C) of methoxychlorodiazirine in 1,1-dimethylallene gave 23% of 1-chloro-1-methoxy-2,2-dimethyl-3-methylenecyclopropane [bp 52 °C (25 mmHg)]. The structure was established by mass spectroscopy (*m*/*e*, 146, 148, *M*$^+$) and a definitive proton NMR spectrum, $\delta_{CCl_4}{}^{Me_4Si}$ 1.23, 1.35 (2 s, 6 H, CH_3's), 3.52 (s, 3 H, CH_3O), 5.43, 5.77 (2 s, 2 H, $=CH_2$). No trace of the isomeric adduct resulting from CH_3OCCl addition at $C{=}CH_2$ was observed in the NMR spectrum of the crude reaction product.

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