action the more stable will be the singlet state (large negative J).[17] Further analysis of the spin exchange pathway will have to await the availability of additional experimental results for imidazolate bridged dicopper(II) complexes.

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(7) Analytical data. (a) Calcd for $C_{13}H_{15}N_5O_7Cu$: C, 37.46; H, 3.63; N, 16.80. Found: C, 37.35; H, 3.62; N, 16.51. (b) Calcd for $C_{29}H_{34}N_{11}O_{11.5}Cu_2$: C, 41.09; H, 4.04; N, 18.17; Cu, 14.99; O, 21.70. Found: C, 40.95; H, 3.92; N, 18.42; Cu, 15.4; O (by difference), 21.3. Heating the compound in vacuo at 90 °C for 16 h resulted in a 5.47% weight loss compared with the calculated value of 5.31%.

(8) X-ray data. The compound crystallizes in space group $P2_1/c$ with a = 17.531 (8) Å, b = 17.817 (10) Å, c = 23.582 (10) Å, and β = 105.80 (3)°. The density calculated for Z = 8, 1.589 (1) g cm^{-3}, agrees with the experimental value of 1.588 (1) g cm^{-3} determined by neutral buoyancy in CCl_4–$CHBr_3$ mixtures. Although single crystal x-ray diffraction data clearly reveal an imidazolate bridged dicopper(II) structure (Cu–Cu distance 5.93 Å), refinement has thus far been unsuccessful. Crystallographic work on this and other derivatives is continuing.

(9) The data were corrected for underlying diamagnetism using tabulated values of Pascal's constants. A value of 60×10^{-6} cm^3 g-atom^{-1} per copper was used for the temperature independent paramagnetism correction. Corrections for small amounts of paramagnetic impurities were made by fitting the low temperature data to a Curie–Weiss law and correcting all the data accordingly.[10]

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(12) The susceptibility may be calculated from the equation $\chi_A' = (g^2N\beta^2/kT)[(10W + 2X_1 + 2X_2 + 2Y)/(5W + 3X_1 + 3X_2 + 3Y + Z_1 + Z_2)] + \mathrm{TIP}$, where $W = \exp[(J_1 + J_2)/kT]$, $X_i = \exp\{[-(J_1 + J_2) + 2J_i]/kT\}$, $Y = \exp[-(J_1 + J_2)/kT]$, $Z_{1,2} = \exp\{[-(J_1 + J_2) \pm 2Q]/kT\}$, and $Q = (J_1^2 + J_2^2 - J_1J_2)^{1/2}$. The other symbols have their usual meaning.[11] Here it is assumed that copper atoms can spin exchange either through the bridging imidazolate ring of the bpim ligand or across the other im ring but not diagonally through space. An attempt to fit the data with the assumption that $J_1 = J_2$ gave statistically inferior results.

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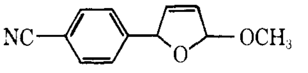
Photosensitized Electron-Transfer Reaction of Electron Donor–Acceptor Pairs by Aromatic Hydrocarbons[1]

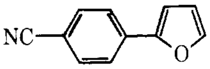
Sir:

Photosensitization is important in photochemistry, usually occurring in exothermic energy transfer.[2] Recently, photosensitized reactions which are endothermic in classical energy transfer have been discussed in terms of exciplexes.[3] In some photoreactions of electron donor–acceptor pairs, the final products arise only from the electron donor, showing a different type of "photosensitization" by the electron acceptor.[4-6] This reaction is shown to be initiated by photochemical electron transfer from the electron donor to the acceptor.[4-6] We wish to report here a novel type of photosensitization by aromatic hydrocarbons, in which excited singlet aromatic hydrocarbons catalyze electron transfer from an electron donor to an electron acceptor.

Irradiation of an acetonitrile–methanol solution containing furan (F), p-dicyanobenzene (p-DCNB), and phenanthrene (P) gave **1**, mp 50–51 °C, in 60–70% yield with 70% recovery of P.[7] Chromatography of **1** on silica gel or basic alumina gave **2**, mp 65–66 °C, in 20–40% yield with 30–50% recovery of **1**. Spectral properties of **1** and **2** accord with the structures assigned.



1



2

$(C_6H_5)_2CHCH_2OCH_3$

3

In control runs, it was confirmed that the recovery of P and yields of **1** were quantitative; irradiation at >300 nm in the absence of P did not give **1** at all. The quantum yield for the formation of **1** ([F] = 1.0 M) was 0.1 ± 0.01 at 313 nm.[8] Among aromatic hydrocarbons investigated, naphthalene can be effectively used in place of P.

Since physical excitation transfer from excited P to either F or p-DCNB is highly endothermic (Table I), the classical energy-transfer mechanism is very unlikely for the photosensitization by P. In fact, the formation of **1** was not quenched even by 1.0 M isoprene, a triplet mechanism being thus discarded. The fluorescence of P was quenched by p-DCNB. In benzene or ethyl acetate, the fluorescence quenching was accompanied by the appearance of an exciplex emission with each isoemissive point at 387 or 393 nm, while exciplex emission could not be observed in acetonitrile or acetonitrile–methanol.[9] However, an exciplex mechanism is unlikely, since the photoreaction in benzene or ethyl acetate containing 10% methanol did not occur or was very slow.

In a variety of exciplex-forming systems, fluorescence quenching in very polar solvents has been established to occur via electron transfer between the fluorophor and the quencher.[10] In Table II are listed the fluorescence quenching rate constants and the calculated values of the free energy change (ΔG) associated with the electron-transfer process, using eq 1.[11]

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

The diffusion-controlled fluorescence quenching and the negative values of ΔG suggest that electron transfer from excited singlet P ($^1P^*$) to p-DCNB occurs to give P cation radical ($P^+\cdot$) and p-DCNB anion radical (p-DCNB$^-\cdot$).[12] From these results, therefore, a tentative mechanism for photosensitization by P is shown in Scheme I; a key mechanistic pathway is the hole transfer from $P^+\cdot$ to F, leading to the recovery of P and

Table I. Excited Singlet and Triplet Energies and Oxidation Potentials

Molecule	$E_{0\text{-}0}$ (kcal mol^{-1}) Singlet	$E_{0\text{-}0}$ (kcal mol^{-1}) Triplet	$E_{1/2}^{ox}$,[a] V
Naphthalene	92[b]	60.9[b]	1.34[c]
Phenanthrene	82.9[b]	62.0[b]	1.23[c]
Triphenylene	83.4[b]	66.5[b]	1.35[c]
Chrysene	79.2[b]	57.3[b]	1.22[c]
Furan	>120[d]	101[e]	1.45[f]
1,1-Diphenylethylene	>95[d]	54.5[g]	1.48[h]
Indene	>92[d]	59[i]	1.24[f] (1.25[c])
p-Dimethoxybenzene			1.04[c]
Isoprene		60.1[b]	
p-Dicyanobenzene	98.6[b]	70.5[b]	(−200)[j]

[a] Oxidation potentials vs. Ag|Ag$^+$ in acetonitrile. [b] Values compiled in S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973. [c] Values compiled in C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970. [d] Estimated from the onset of the UV absorption. [e] M. Orloff and D. D. Fitts, *J. Chem. Phys.*, **38**, 2334 (1963). [f] Determined in the present work. [g] E. F. Ullman and W. A. Henderson, *J. Am. Chem. Soc.*, **89**, 4390 (1967). [h] Reference 4c. [i] R. C. Heckman, *J. Mol. Spectros.*, **2**, 27 (1958). [j] Reduction potential.[4c]

Scheme I[a]

$$\begin{array}{rcl}
{}^1P^* + p\text{-DCNB} & \longrightarrow & P^{+\cdot} + p\text{-DCNB}^{-\cdot} \\
P^{+\cdot} + F & \longrightarrow & P + F^{+\cdot} \\
F^{+\cdot} + CH_3OH & \longrightarrow & \cdot F\text{-}OCH_3 + H^+ \\
\cdot F\text{-}OCH_3 + p\text{-DCNB}^{-\cdot} & \longrightarrow & \mathbf{1} + CN^- \\
P^{+\cdot} \text{ or } F^{+\cdot} + Q & \longrightarrow & P \text{ or } F + Q^{+\cdot} \\
Q^{+\cdot} + p\text{-DCNB}^{-\cdot} & \longrightarrow & Q + p\text{-DCNB}
\end{array}$$

[a] Q, *p*-dimethoxybenzene.

the formation of $F^{+\cdot}$ or its related species (vide infra). The final product **1** was thus formed by the nucleophilic attack of methanol on $F^{+\cdot}$ and the subsequent reaction of the intermediate radical with *p*-DCNB$^{-\cdot}$. Evidence for the intermediacy of cation radicals was provided by the efficient quenching of the reaction with *p*-dimethoxybenzene possessing a low oxidation potential.[13]

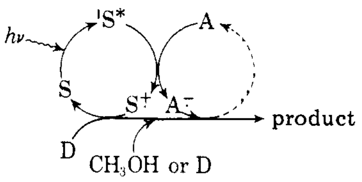
This mechanism is further supported by the observation that P can sensitize the photochemical anti-Markownikoff addition of methanol to 1,1-diphenylethylene (DPE) in the presence of *p*-DCNB; DPE$^{+\cdot}$ is known to be a key intermediate in the photoreaction of DPE with an electron acceptor in acetonitrile.[4a] The photosensitized reaction gave **3** in 70% yield with the recovery of 70% P and 95% *p*-DCNB.[7] The quantum yield for the formation of **3** ([DPE] = 0.1 M) was 0.32 ± 0.01 at 313 nm.[8] In the absence of P, the formation of **3** occurred less than one-tenth as efficiently as in the presence of P. Naphthalene and triphenylene also sensitized this reaction. In place of *p*-DCNB, *o*- and *m*-DCNB can be used. In a similar way, the photodimerization of indene was sensitized by P, triphenylene, and chrysene to give syn and anti head-to-head cyclobutane dimers in ~5:95 ratio, in accord with the cation radical mechanism.[5] In the presence of 10% methanol, the photoreaction gave 2-methoxyindane in 50% yield at the expense of the dimers.

Table II. Rate Constants and Calculated ΔG Values for Fluorescence Quenching by *p*-Dicyanobenzene

Fluorophor	τ,[a] ns	$k_q \times 10^{-10}$,[a] s^{-1} M^{-1}	ΔG,[b] kcal mol^{-1}
Naphthalene	118[c,d]	1.2[d]	−16.3
Phenanthrene	60 ± 1[d]	2.0[d]	−10.7
	17 ± 1[e]	1.5[e]	
Triphenylene	34 ± 0.5[e]	1.4[e]	−7.4
Chrysene	48 ± 0.5[e]	1.2[e]	−6.2

[a] For degassed solutions; concentration, 10^{-3}–10^{-4} M. [b] Calculated values in acetonitrile, using eq 1 and the thermodynamic data in Table I. Coulombic term is estimated to be 1.3 kcal mol^{-1}. [c] N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965). [d] In acetonitrile. [e] In 3:1 acetonitrile–methanol.

Scheme II[a]



[a] S, sensitizer; A, electron acceptor; D, electron donor.

In these photosensitized reactions, therefore, the sensitizer can be considered to act as a redox carrier as shown in Scheme II.[14] In the case of indene, the formation of indene cation radical can occur since the hole transfer process is isothermal or only slightly endothermic. However, the complete hole transfer from $S^{+\cdot}$ to F and DPE is unfavorable since this process is highly endothermic. This requires an alternative mechanism. A reasonable interpretation would be provided by assuming the intervention of the π complex $(S\cdot D)^{+\cdot}$;[15] methanol attacks the partially developed positive charge on D side of the π complex.

$$S^{+\cdot} + D \rightleftarrows (S\cdot D)^{+\cdot} \xrightarrow[A^{-\cdot}]{CH_3OH} S + \text{product} \tag{2}$$

However, detailed discussion requires the exact values of the oxidation potentials determined under identical conditions, since the values listed in Table II are obtained from a variety of sources. Further work is in progress.

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(7) A 3:1 acetonitrile–methanol solution containing P (0.2 g), *p*-DCNB (1.0 g), and F (10 g) or DPE (1.0 g) was irradiated with a high-pressure mercury arc using a glass filter (>300 nm) at ambient temperature. For all the products, sufficient analytical data were obtained.

(8) Quantum yields were determined for 3:1 acetonitrile–methanol solutions containing 0.01 M P, 0.1 M *p*-DCNB, and 1.0 M F or 0.1 M DPE. Under these conditions, P absorbs >90% incident light at 313 nm.

(9) From UV spectra, no indication of formation of charge-transfer complexes in the ground state was obtained.

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(13) The photoreaction of 0.01 M P, 0.1 M *p*-DCNB, and 1.0 M F was completely

quenched by 0.05 M *p*-dimethoxybenzene, while the fluorescence of P was not quenched by *p*-dimethoxybenzene.

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Organic Chemistry by Infrared Lasers.[1] 1. Isomerization of Allene and Methylacetylene in the Presence of Silicon Tetrafluoride

Sir:

We wish to report here on the isomerization of allene and methylacetylene in the presence of SiF_4 as induced by a pulsed CO_2 megawatt infrared laser, demonstrating that under controlled conditions isomerizations can be carried out by this method and that competitive thermal decomposition of methylacetylene can be minimized.

Thermal isomerization of allene to methylacetylene in the temperature range of 900-1150 K has been studied by Levush et al.[2] who demonstrated that the reaction proceeds unimolecularly with an activation energy of ~55 kcal/mol. Though no rate constants were calculated, Sakakibara[3] demonstrated that structural isomerization was considerably faster than decompositions. Recently, Lifshitz et al.[4] studied this isomerization using a single-pulse shock tube technique in the temperature range of 1030-1220 K and found the isomerization to be "clean" and unimolecular with an activation energy of 61.2 ± 7.5 kcal/mol. They also found that the rate of the reverse action, methylacetylene to allene, was smaller than that of the forward reaction.

Recently[5] we demonstrated the usefulness of the inert sensitizer, SiF_4, for inducing chemical reaction of substrates which do not themselves absorb in the 9.2-11-μ region of the CO_2 laser. After absorption of laser energy at 1025 cm^{-1} the vibrational energy of the highly excited SiF_4 is sufficient, if converted adiabatically into random thermal energy, to produce temperatures in excess of 1000 K while the reaction vessel remains at ambient temperature. Although we do not know the detailed molecular dynamics[6] of energy transfer to the reactive substrate, reactions very similar to those in normal thermal decompositions take place. The effective reaction temperatures can be controlled by varying the concentration of SiF_4 or of reactant, or by varying the dose per flash of the laser beam.

In our studies, using the method described previously by Olszyna et al.,[5] various mixtures of allene and SiF_4 were irradiated at 1025 cm^{-1} using a pulsed megawatt CO_2 laser. The reactions were carried out in Monel cells (17-cm^3 volume) with KCl windows using two different dose levels. The results are given in Table I. It is obvious that at the lower dose (0.40 J/cm^2) the thermal decomposition of methylacetylene to methane and acetylene is minimized. At the higher dose, on the other hand, pyrolysis is favored even with fewer pulses. Thus, in run 7, after 25 pulses, all the allene has been isomerized and the presence of large quantities of CH_4 and C_2H_2 indicates the extensive secondary thermal decomposition of the methylacetylene. This is to be contrasted with run 1 where, after 50 pulses, the amount of methylacetylene is approximately the same, yet the presence of CH_4 and C_2H_2 is ~100 and 160 times less than that observed in run 7. This is probably due to the fact that the final temperature in run 1 is lower than that in run 7. Thermal decomposition of methylacetylene can also be minimized by decreasing the SiF_4 pressure. Runs 8-11 demonstrate that, even at the higher dose levels, isomerization can be controlled with a minimum of thermal decomposition. When these are compared with runs 1 and 2, it is obvious that the efficiency of the thermal isomerization is greater at the higher dose and low SiF_4 pressure.

Interestingly, in runs 1-4 and 8-11, the disappearance of allene per flash is greater in the earlier stages of the reaction. The results follow a pattern resembling the kinetics of reversible approach to a photostationary state[7] or an equilibrium state. That reversibility is indeed present, was demonstrated by the following experiments. (1) A mixture of SiF_4 (5 Torr) and methylacetylene (20 Torr) was irradiated at 0.73 J/cm^2. After 250 pulses the composition of the mixture was 10.0% allene, 80.0% methylacetylene, 0.3% methane, and 9.6% acetylene. This experiment, when compared with run 8, qualitatively implies that, by this method, the rate of isomerization of methylacetylene to allene is several times slower than the rate of isomerization of allene to methylacetylene. (2) Irradiation of a 17:16-Torr mixture of allene and methylacetylene in the presence of 16 Torr of SiF_4 at low dose (0.4 J/cm^2) showed no significant changes in the ratio of allene and methylacetylene even after 400 pulses.

It should finally be pointed out that this isomerization has

Table I

Run[a]	SiF_4 (Torr)	Allene (Torr)	Dose (J/cm^2) per flash	No. of pulses	% rxn[b]	% CH_4[c]	% $HC{\equiv}CH$[c]	% $CH_2{=}C{=}CH_2$[c]	% $H_3C{-}C{\equiv}CH$[c]
1	20	20	0.40	50	14.6	0.1	0.5	85.8	12.5
2	20	20	0.40	100	57.9	1.2	3.8	42.7	51.4
3	20	20	0.40	150	60.2	1.2	3.6	40.1	53.0
4[d]	20	20	0.40	400	72.9	8.4	23.4	20.7	45.5
5	20	20	0.73	1	13.9	0.8	4.6	92.1	2.5
6	20	20	0.73	5	54.5	4.2	25.6	54.0	16.3
7	20	20	0.73	25	99.5	8.7	79.6	<0.1	11.8
8	5	20	0.73	25	9.2	<0.1	0.4	87.3	12.3
9	5	20	0.73	50	42.6	0.5	1.7	55.7	41.2
10	5	20	0.73	75	46.3	0.9	2.7	45.6	49.8
11[d]	5	20	0.73	400	64.5	3.8	10.4	31.2	51.5

[a] Bright flashes of light are frequently observed during irradiation and a black sooty material (elemental carbon) is seen in the reaction vessel after irradiation. [b] Percent reaction is calculated by following the decrease in absorption of the allene 1970-cm^{-1} band in the infrared spectrum after a given number of pulses. [c] Identifications were made by IR and GC (flame ionization) analysis and percent composition of the mixtures after irradiation were calculated from integrated GC traces. [d] In these reactions ethylene is also observed by GC and IR analysis (0.5% in run 4 and 0.6% in run 11).