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(21) This inability to decompose by a pathway other than bond disconnection might explain the high relative abundance of *m/e* 80 $[CH_3SSH]^{+\cdot}$ in the spectra of methyl alkyl disulfides studied.

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Triplet–Singlet Energy-Transfer Parameters from Tetramethyl-1,2-dioxetane Chemi-Energized 9,10-Dibromoanthracene Fluorescence in Polymer Matrices[1]

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The binary chemiluminescent system consisting of tetramethyl-1,2-dioxetane (TMD) and 9,10-dibromoanthracene (DBA) was investigated in polystyrene (PST) and poly(methyl methacrylate) (PMMA). Since collisional triplet–triplet energy transfer is negligible in rigid phases, our experimental results confirm that the main physical event is long-range triplet–singlet energy transfer from excited triplet acetone ($^3K^*$), thermally generated from TMD, to DBA affording singlet excited DBA, whose fluorescence is observed. From this enhanced chemiluminescence data the long-range triplet–singlet energy-transfer parameters $k_{K,DBA}{}^{TS} = (1.05 \pm 0.14) \times 10^9\ s^{-1}\ m^{-1}$ and $\phi_{K,DBA}{}^{TS} = 0.27 \pm 0.07$ were extrapolated. Furthermore, the activation energies for the enhanced DBA chemiluminescence are the same in the PST and PMMA matrices, i.e., $E_a \sim 18 \pm 1$ kcal/mol. These results are in good agreement with earlier data obtained in liquid phases or more complex solid-phase systems.

The biological function of the thyroid hormones has been speculated[3] to be an enhancement of the spin-forbidden triplet–singlet energy transfer between a chemigenerated triplet energy donor and a singlet energy acceptor by means of the heavy-atom effect of the iodine substituents of these hormones. As a chemical model system we may consider the TMD sensitized DBA fluorescence,[4] in which TMD is the excited state donor and DBA the triplet–singlet energy transfer mediator. For example, it is well established[5] that TMD is a selective and efficient source (ca. 50%) of triplet acetone since only 0.1% singlet acetone is formed.[6] Furthermore, it was recently shown[7] that in polymer matrices the rate of thermal decomposition of TMD remains unaltered. This represents a unique opportunity to isolate and elucidate the noncollisional, spin-forbidden, triplet–singlet energy-transfer process, since the collisional triplet–triplet energy transfer process should be inhibited due to immobilization of the excited states. Use of polymer matrices of different hardness, e.g., PST and PMMA, should enable us to assess how effectively triplet–triplet energy transfer is inhibited. Presently

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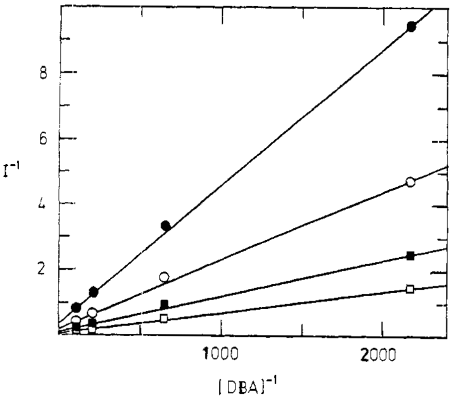

Figure 1. Inverse DBA intensities vs. inverse DBA concentration of the TMD/DBA chemiluminescent system in polystyrene matrices: (●) 313.0 K; (○) 320.3 K; (■) 327.3 K; and (■) 334.7 K.

Table I. DBA Emission Intensities as a Function of DBA Concentration and Temperature of the TMD[a]/DBA Chemiluminescent System in PST Matrix

$[\mathrm{DBA}]^b \times 10^4$	intensities, I,[c,d] at temperature = 313.0 K	320.3 K	327.3 K	334.7 K
4.61	0.106	0.213	0.405	0.704
15.3	0.303	0.570	1.140	1.952
46.1	0.816	1.546	2.939	6.075
91.9	1.259	2.456	4.539	7.917

[a] [TMD] = 1.75×10^{-3} molal. [b] Molality. [c] Arbitrary units. [d] Oxygen quenching of the DBA fluorescence was negligible (ca. 10–15%).

we communicate our findings on the binary TMD/DBA chemiluminescent system in PST and PMMA matrices and report the triplet–singlet energy-transfer parameters.

Experimental Section

Materials. Tetramethyl-1,2-dioxetane (TMD) was prepared according to the procedure of Kopecky et al.;[8] yellow needles, mp 75–76 °C (lit.[8] mp 78–79 °C). Dichloromethane was obtained from Baker and distilled prior to use. 9,10-Dibromoanthracene (DBA) was purchased from Fluka and recrystallized from ethanol, mp 220–221 °C. Polystyrene (PST) was prepared by the benzoyl peroxide-catalyzed polymerization of styrene and poly(methyl methacrylate) (PMMA) by peroxycarbonate-catalyzed polymerization of methyl methacrylate.

The polymer matrices were prepared by weighing the polymer into liquid scintillation vials and dissolving in the smallest possible amount (ca. 4 mL) of CH_2Cl_2. To this mixture the appropriate volumes of DBA stock solutions were added and dissolved by stirring with a glass rod. Finally, a convenient amount of TMD stock solution in CH_2Cl_2 was added, mixed thoroughly, placed into a chamber saturated with CH_2Cl_2 vapors, and covered with aluminum foil. The solutions were allowed to evaporate in the dark at room temperature until hard and clear matrices had formed (24–30 h). This method of matrix preparation afforded transparent matrices reproducibly, leading to reliable results.

Measurements. Emission intensities were measured with a Mitchell-Hastings[10,11] photometer equipped with a RCA 391A photomultiplier. The output signal was registered with the aid of a Perkin-Elmer 165 recorder. The sample temperature was kept constant (±1 °C) by means of a Colora constant temperature bath, circulating the heated bath fluid through a brass jacket which snuggly enclosed the liquid scintillation vial. The activation parameters were extrapolated from Arrhenius plots using the chemiluminescence decay rate constants.

Results and Discussion

The dependence on [DBA] of the TMD/DBA chemiluminescent system in PST and PMMA matrices is shown in Tables I and II, respectively. These data yield linear $1/I_0$ vs. 1/[DBA] plots for the temperature range 40–65 °C (Figure 1). To rationalize these observations, we propose the mechanism shown in Scheme I (eq 1–11). Since the triplet acetone yield (β) is ca. 500-fold greater than the singlet excited acetone yield (α), the steps k_2 to k_4 involving $^1K^*$ can be neglected in energy transfer processes involving $^3K^*$.

Table II. DBA Emission Intensities as a Function of DBA Concentration and Temperature of the TMD[a]/DBA Chemiluminescent System in PMMA Matrix

$[\mathrm{DBA}]^b \times 10^3$	intensities, I,[c,d] at temperature = 316.2 K	323.2 K	338.2 K
3.32	78	158	584
6.64	137	258	956
9.96	177	318	1230
13.23	198	358	1360
16.6	218	390	1470

[a] [TMD] = 5×10^{-4} molal. [b] Molality. [c] Arbitrary units. [d] Oxygen quenching of the DBA fluorescence was negligible (ca. 10–15%).

Scheme I

$$\mathrm{TMD} \xrightarrow{k_1} {}^1\mathrm{K}^* + {}^3\mathrm{K}^* + {}^1\mathrm{K}_0 \tag{1}$$

$${}^1\mathrm{K}^* \xrightarrow{k_2} {}^1\mathrm{K}_0 \tag{2}$$

$${}^1\mathrm{K}^* \xrightarrow{k_3} {}^1\mathrm{K}_0 + h\nu_f\,(400\ \mathrm{nm}) \tag{3}$$

$${}^1\mathrm{K}^* \xrightarrow{k_4} {}^3\mathrm{K}^* \tag{4}$$

$${}^3\mathrm{K}^* \xrightarrow{k_\mathrm{K}{}^\mathrm{d}} {}^1\mathrm{K}_0 \tag{5}$$

$${}^1\mathrm{K}^* + \mathrm{DBA} \xrightarrow{k_{\mathrm{K,DBA}}{}^{\mathrm{SS}}} {}^1\mathrm{DBA}^* + {}^1\mathrm{K}_0 \tag{6}$$

$${}^3\mathrm{K}^* + \mathrm{DBA} \xrightarrow{k_{\mathrm{K,DBA}}{}^{\mathrm{TS}}} {}^1\mathrm{DBA}^* + {}^1\mathrm{K}_0 \tag{7}$$

$${}^3\mathrm{K}^* + \mathrm{DBA} \xrightarrow{k_{\mathrm{K,DBA}}{}^{\mathrm{TT}}} {}^3\mathrm{DBA}^* + {}^1\mathrm{K}_0 \tag{8}$$

$${}^1\mathrm{DBA}^* \xrightarrow{k_6} {}^1\mathrm{DBA}_0 + h\nu_f\,(430\ \mathrm{nm}) \tag{9}$$

$${}^1\mathrm{DBA}^* \xrightarrow{k_7} {}^1\mathrm{DBA}_0 \tag{10}$$

$${}^3\mathrm{DBA}^* \xrightarrow{k_8} {}^1\mathrm{DBA}_0 \tag{11}$$

Turro and Steinmetzer[7] have presented evidence that the diffusion-controlled triplet–triplet energy transfer to DBA is strongly inhibited in PST, but not the triplet–singlet transfer since the latter is a long-ranged resonance type energy transfer. Thus step k_7 ($k_{\mathrm{K,DBA}}{}^{\mathrm{TS}}$) should be the principal mechanism of energy transfer in this chemiluminescent process.

With these considerations, our kinetic analysis yields the simplified expression shown below

$$1/I = \{1/P\beta^\mathrm{T}\phi^\mathrm{f}\}\{1 + (k_\mathrm{K}{}^\mathrm{d}/k_{\mathrm{K,DBA}}{}^{\mathrm{TS}})(1/[\mathrm{DBA}])\} \tag{12}$$

where P = instrumental parameter; $\beta^\mathrm{T} = k_1[\mathrm{TMD}]_0\beta$; $k_1[\mathrm{TMD}]_0$ = rate of TMD comsumption; β = triplet acetone yield; $k_\mathrm{K}{}^\mathrm{d} = k_5$, the triplet acetone decay rate constant; and $k_{\mathrm{K,DBA}}{}^{\mathrm{TS}}$ = triplet–singlet energy transfer rate constant from triplet acetone to give singlet DBA. It is predicted that the inverse intensity ($1/I$) depends linearly on the inverse DBA concentration (1/[DBA]), as confirmed by our experimental data (cf. Tables I and II, Figure 1). Extrapolation of this expression to infinite $[\mathrm{DBA}]_\infty$, i.e., all acetone triplets are being intercepted by DBA, affords $I_\infty = P\beta^\mathrm{T}\phi^\mathrm{f}$. Multiplication of

Table III. Slopes of I_∞/I vs. 1/[DBA] for the TMD/DBA Chemiluminescent System in PST and PMMA [b] Matrices as a Function of Temperatures

matrix	temp, K	slope × 10^2
PST[a]	313.0	1.06
	320.3	0.83
	327.3	0.90
	334.1	1.08
		av 0.97 ± 0.13
PMMA[b]	316.2	1.47
	323.2	0.98
	338.2	1.07
		av 1.17 ± 0.26

[a] Polystyrene. [b] Poly(methyl methacrylate).

eq 12 by I_∞ yields

$$I_\infty/I = 1 + \{k_K{}^d/k_{K,DBA}{}^{TS}\}(1/[DBA]) \quad (13)$$

The slope of the I_∞/I vs. 1/[DBA] plot gives the ratio $k_K{}^d/k_{K,DBA}{}^{TS}$. The slope values for the PST and PMMA matrices are identical within experimental error, as shown in Table III.

Thus, in the harder PMMA matrices, in which diffusion is more difficult, the ratios of the rate constants of triplet acetone decay and energy transfer are the same as in the softer PST matrices.[12] Furthermore, these ratios remain fairly constant up to the glass-transition temperature, where diffusion should increase and thereby augment the triplet–triplet vs. triplet–singlet energy transfer in these polymers. This suggests that the same energy transfer mechanisms, i.e., triplet–singlet energy transfer (Scheme I), operates in both matrices.

In the case of the PST results, the slope data from the I_∞/I vs. 1/[DBA] plot provide a unique opportunity of estimating $k_{K,DBA}{}^{TS}$, i.e., the triplet–singlet energy transfer rate constant. Although the required $k_K{}^d$ value in PST matrices is not presently available, a good estimate is the benzene solution value by Turro et al.,[4] i.e., $k_K{}^d = 10^7\ s^{-1}$. In defense of using the benzene value for PST we offer the facts that no phosphorescence has been observed for acetone triplets in either benzene solution or PST matrix, whereas acetophenone phosphorescence can be readily observed in PST matrices. Thus, the lifetime of triplet acetone in PST cannot be significantly longer than in benzene solution. On the other hand, the $k_K{}^d$ values in cumene solution are 1×10^7 and $7 \times 10^5\ s^{-1}$ for acetone and acetophenone triplets, respectively. Since in cumene solution acetophenone triplets are being quenched presumably via hydrogen abstraction, this process is by almost two orders of magnitude slower than quenching by phenyl groups. Consequently, the local environments felt by triplet acetone PST matrix and benzene solution are similar and $k_K{}^d = 10^7\ s^{-1}$ is a reasonable estimate for the acetone triplet decay rate constant.

With this $k_K{}^d$ estimate and the slope data in Table III we find that $k_{K,DBA}{}^{TS} = (1.05 \pm 0.14) \times 10^9\ s^{-1}\ M^{-1}$ in the PST matrix. This value is in reasonable agreement with the value $2 \times 10^9\ s^{-1}\ M^{-1}$ reported by Turro et al.[4] for the TMD/DBA system in benzene, with the value $1.5 \times 10^9\ s^{-1}\ M^{-1}$ reported by Berenfeld et al.[13] for the acetophenone/DBA system, and the value $(1.4 \pm 0.4) \times 10^9\ s^{-1}\ M^{-1}$ obtained by us[14] from the more complex TMD/DBA/rubrene system.

The fact that this $k_{K,DBA}{}^{TS}$ value derives from long-range triplet–singlet energy transfer is corroborated by the critical quenching radius value $R_0 = 35$ Å calculated from our data.[15] This value is in reasonable agreement with other long-range triplet–singlet energy-transfer data.[16]

By combining the polystyrene results with benzene solution data, the triplet–singlet energy-transfer efficiency $\phi_{K,DBA}{}^{TS}$ can be evaluated. Thus, in solution the dependence of $1/I$ on 1/[DBA] is shown in eq 14, in which all terms have already been defined, except $k_{K,DBA}{}^{TT}$, the collisional triplet–triplet energy-transfer rate constant, which competes with the triplet–singlet energy-transfer efficiency.

$$1/I = \{1/P\beta^T\phi_{DBA}{}^f\} \times \{1 + k_{K,DBA}{}^{TT}/k_{K,DBA}{}^{TS} + (k_K{}^d/k_{K,DBA}{}^{TS}) \times (1/[DBA])\} \quad (14)$$

Multiplication of eq 14 by I_∞ leads to an expression analogous to eq 13 but for solutions. The slope of the I_∞/I vs. 1/[DBA] plot was independently measured by Turro et al.[17] and by us. The values are 1.9×10^{-3} and 2.75×10^{-3}, respectively, giving an averaged value $(2.4 \pm 0.5) \times 10^{-3}$. Since the slope is given by $(k_K{}^d/k_{K,DBA}{}^{TS})\phi_{K,DBA}{}^{TS}$, substituting for $k_K{}^d/k_{K,DBA}{}^{TS} = (9.7 \pm 1.3) \times 10^{-3}$ (Table III) and the averaged slope value above affords a limiting $\phi_{K,DBA}{}^{TS} = 0.27 \pm 0.07$. This approximate triplet–singlet energy transfer efficiency falls within the established 0.3 ± 0.1 range.[14]

Another point of interest about the TMD/DBA chemiluminescent system is the observation that the activation energy of enhanced chemiluminescence (DBA fluorescence) in PST and PMMA matrices is $E_a = 18 \pm 1$ kcal/mol, compared to $E_a = 23 \pm 1$ kcal/mol for the direct chemiluminescence (acetone fluorescence) in PST matrices.[14] The 4-kcal difference is ascribed to the negative activation energy exhibited by DBA fluorescence.[18] Consequently, the activation energies for energy transfer from triplet acetone to give singlet excited DBA are the same. This also suggests that the energy-transfer mechanism must be the same, i.e., long-range triplet–singlet energy transfer.

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References and Notes

(1) Paper No. 55 in the Cyclic Peroxide Series.
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Rearrangement of Cycloheptatrienylidenes in Solution

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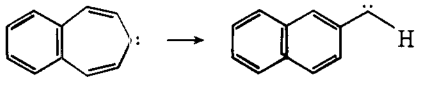
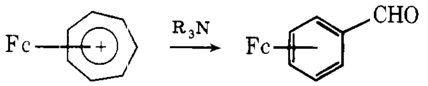
Factors that could promote the rearrangement of cycloheptatrienylidene to phenylcarbene in solution were studied. Simple dilution and increase of the temperature to 240 °C were not sufficient for the rearrangement of the parent cycloheptatrienylidene to be competitive with dimerization to heptafulvalene. Rearrangement did appear when dimerization was retarded by 2,7-disubstitution. 2,7-Diphenylcycloheptatrienylidene was thermally and photolytically generated from the corresponding tosylhydrazone salt and gave exclusively 9-phenylfluorene, the product expected from carbene–carbene rearrangement. 2,7-Dimethyltropone was synthesized next, but could not be converted to its tosylhydrazone. 2,7-Dimethylcycloheptatrienylidene was therefore generated by dehydrochlorination of 2-chloro-1,3-dimethylcycloheptatriene. At 100 °C, tetramethylheptafulvalene was exclusively formed, but at 150–160 °C, in addition to 37% of dimer, 31% of *o*-methylstyrene (from the rearrangement) was isolated. Finally, attempts were made to generate 2,7-diethylcycloheptatrienylidene by dehydrochlorination of 2-chloro-1,3-diethylcycloheptatriene. Conditions could not be found in which base-induced elimination was competitive with thermal aromatization.

The conversion of aromatic carbenes to aryl carbenes has been found in the gas phase,[1] but in solution confirmed examples[2] have been limited to the rearrangement of benzannelated cycloheptatrienylidenes such as **1**.



1 2

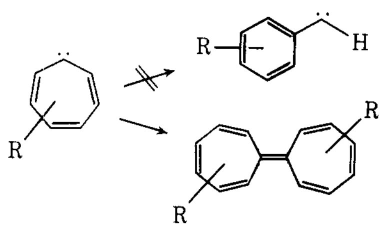
The first reported example of a reaction that might involve this type of rearrangement in solution is the base-induced contraction of the ferrocenyl substituted tropylium salt **3** to



3 4

give benzaldehyde products.[3] Carbene involvement in this reaction remains to be confirmed.

In the absence of reactive substrates either the parent or simple substituted cycloheptatrienylidenes[4] give only heptafulvalenes.[1] If it is assumed that the heptafulvalenes arise



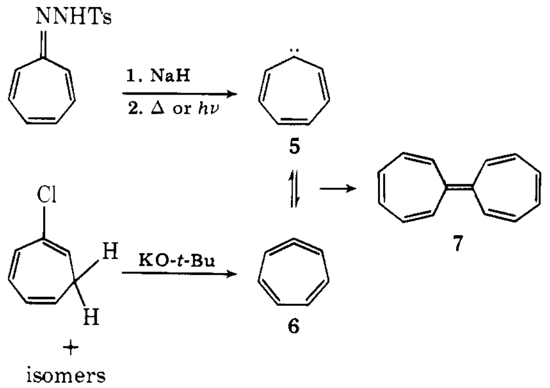
from simple dimerization of the aromatic carbenes (or allenes) by a mechanism of low activation energy, then it should be possible to promote the rearrangement over the dimerization by: (a) reducing the concentration of the reactive intermediate (and probably also by increasing the temperature); and (b) substituting the cycloheptatrienylidene with groups that would retard dimerization.

In view of the ease of detection of rearrangement from the known reaction of phenylcarbene with solvent,[1c,5] we undertook a study of the chemistry of cycloheptatrienylidene in solution under the conditions of (a). A series of 2,7-disubstituted tropone tosylhydrazones were also prepared in order to study aromatic carbenes under the conditions of (b).

Results and Discussion

(1) Effect of Concentration and Temperature on the Carbene–Carbene Rearrangement of Cycloheptatrienylidene. Initially cycloheptatrienylidene (**5**) was generated at low concentration by slowly adding solid tropone tosylhydrazone salt to refluxing dioxane. Careful analysis of the reaction mixture showed only heptafulvalene (**7**). Since the sodium salt is only slightly soluble in dioxane, a Soxhlet thimble was charged with the salt and extracted over a 48-h period. During this time only a fraction of the salt was extracted, but again only the dimer was formed (11% isolated); no dioxane–phenylcarbene insertion product could be detected.

As the rates of dimerization and rearrangement could have different temperature dependencies, the effect of increasing the temperature of the reaction was studied. At 150–160 °C, generation of cycloheptatrienylidene either by slowly adding a mixutre of 1-, 2-, and 3-chlorocycloheptatrienes to potassium *tert*-butoxide in refluxing diglyme[6] or by the Bamford–Stevens reaction[7] led exclusively to the formation of heptafulvalene (**7**).



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