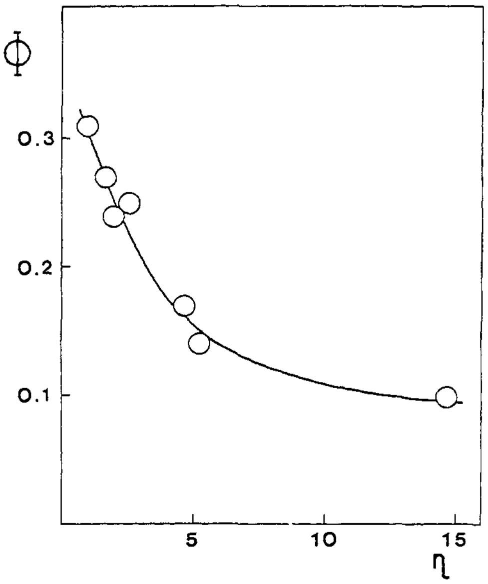

Figure 1. Dependence of the photoaquation quantum yield of $Co(CN)_6^{3-}$ on solvent viscosity.

with increasing solvent viscosity, while that of geminate recombination within the cage, k_5, should be essentially solvent independent. The possibility of calculating the primary quantum yield value from the experimental results is bound to our knowledge of the functional dependence of k_6 on solvent viscosity. Unfortunately, such a knowledge is highly uncertain, for a number of reasons. First, even in the best studied organic cage recombination processes, no general agreement has been reached on the exact dependence of the effect on solvent viscosity (with both $1/\eta$ and $(1/\eta)^{1/2}$ functions being commonly used).[2] Second, the accepted cage effect theories[2] do not explicitly allow for charge effects, which on the contrary are likely to be significant in this system. Third, a substantial degree of preferential solvation can be anticipated to occur in mixed solvent systems, which will certainly affect the dependence of diffusive cage escape on the bulk solvent viscosity.[17]

Empirically, both a visual extrapolation of the data in Figure 1 to zero viscosity, as well as an analytical curve fitting using $k_6 = A/\eta$, indicate a primary quantum yield of bond cleavage in the range 0.35-0.40. Thus, in the case of $Co(CN)_6^{3-}$, the cage effect seems to be quite efficient in the more viscous solvents while being relatively unimportant in pure aqueous solution.[19] It should be pointed out that this conclusion may not hold true for other ligand photosubstitution reactions, especially for those not involving geminate products of the same charge. Further experiments, in particular using positively charged complexes and solvents of low viscosity, will allow a test of this possibility.

The detection of cage recombination in the photoaquation of $Co(CN)_6^{3-}$ appears to be of some general interest. First of all, it shows that cage recombination can occur in ligand photosubstitution reactions following heterolytic bond splitting, and that this concept is not confined to radical reactions, as is usually understood. Second, this finding casts some doubt on the absolute meaning of photosubstitution quantum yields obtained in any particular solvent. In fact, depending on the extent of cage recombination occurring in the system, the measured quantum yield may deviate more or less from the primary quantum yield of bond cleavage. This point seems to be of particular relevance to a number of recently proposed theoretical models for substitutional photoreactivity of coordination compounds.[20,21] The experimental testing of these models is usually based on the comparison of experimental quantum yield values for the release of different ligands from the same complex, or even for photosubstitution reactions of different complexes. The possibility that such comparisons are affected by varying degrees of cage effect should be considered.

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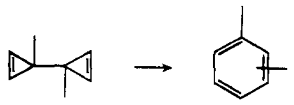
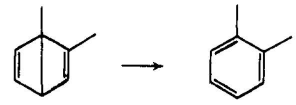
Mechanisms of Energy Storage and Release. Chemiluminescent Valence Isomerizations. Evidence for a Dewar Benzene Intermediate in a Biscyclopropenyl to Benzene Rearrangement

Sir:

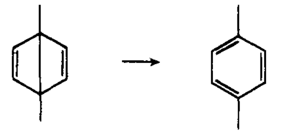
Valence isomers of high energy content play a dominant role in the interpretation of the photochemistry of aromatic compounds.[1] The rarely observed thermal interconversion of benzene valence isomers represents an exceptional rearrangement since, in order to be detected, such reactions must be competitive with the highly exothermic aromatization to benzene. On the other hand, recent theoretical calculations of the potential energy surfaces of benzene valence isomers suggest that *direct* conversion of the latter to benzenes is not likely in some cases, thereby favoring indirect pathways to benzene involving reactive intermediates.[2] The 3,3′-biscyclopropenyls are expected to possess the highest energy content of any of the benzene $(CH)_6$ isomers known. In fact, 3,3′-biscyclopropenyl to benzene thermal rearrangements have been viewed as proceeding via prismanes,[3a] benzvalenes[3b] and Dewar benzenes.[3c,d] Direct evidence for these intermediates has been difficult to obtain, presumably because of their low steady state concentrations. We report here (1) the first example (eq 1) of a chemiluminescent 3,3′-biscyclopropenyl to benzene rearrangement, (2) the use of chemiluminescence and kinetic techniques which allow identification of and elimination of reactive intermediates whose steady state concentrations are below the limit of detectability by conventional methods, and (3) the identification of a dimethyl Dewar benzene intermediate in reaction 1.



1 (1)



2 (2)



3 (3)

When **1** ($\sim 10^{-2}$ *M*, nitrogen purged acetonitrile solution) is heated (63°) in the presence of 9,10-dibromoanthracene (DBA), chemiluminescence (DBA fluorescence) is readily detected. The nature of the electronically excited state produced from **1** was established by an extrapolative Stern-Volmer analysis.[4,5] The results indicated that an electronically excited state whose lifetime was approximately 10 μsec is produced by thermolysis of **1**. Analogous analyses for the chemiluminescent reactions **2** and **3** also indicated that the key electronically excited states produced from **2** and **3** possess lifetimes of approximately 10 μsec. This lifetime value, coupled with previous work with Dewar benzenes[5] allows the conclusion that a *triplet xylene*[6] *is produced upon thermolysis of* **1**.

Chemielectronic formation of a xylene triplet from **1** was shown to involve an intermediate as follows. At 63° the intensity of indirect (DBA) chemiluminescence from **1** is *constant for hours* (area a, Figure 1). The constant intensity was a result of the high activation energy for the rearrangement of **1** ($E_a \sim 37$ kcal). The sample was then heated at 200° for ca. 50 sec and then quickly cooled back to 63°. The effect of this temperature jump on the chemiluminescent emission was dramatic (area b, Figure 1). The observed initial intensity of the emission clearly increased and, more importantly, *this increased initial intensity was no longer constant but decayed with a first-order rate constant of ca.* 2×10^{-4} *sec*$^{-1}$ *at 63°* (area c, Figure 1). Eventually, a steady chemiluminescent intensity was achieved which was much less than the intensity of the sample before heating to 200° (area d, Figure 1). We conclude that this thermal behavior is consistent only with the formation of a ground state intermediate during the thermolysis of **1**, and that this intermediate is responsible for the observed chemiluminescence. Furthermore, the activation energy for the thermolysis of the intermediate must be lower than that of **1**.

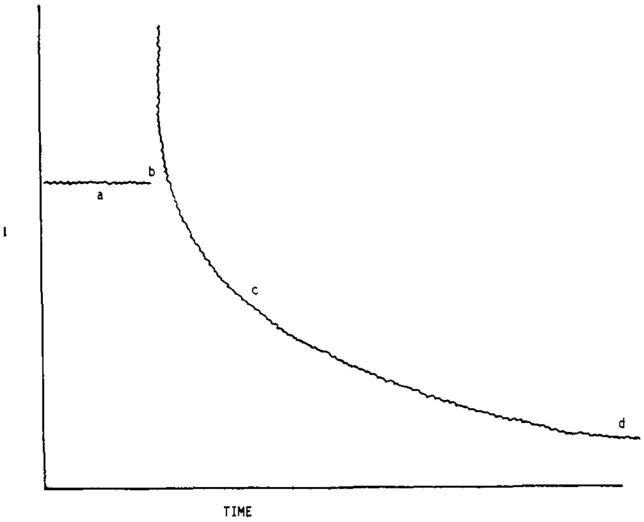


Figure 1. Detection of chemiluminescent intermediate in the thermolysis of **3**: area a, isothermal heating at 63°; b, sample heated to 200° for 50 sec; c, decay of chemiluminescence; d, final chemiluminescent intensity.

The nature of the intermediate responsible for chemiluminescence was established as follows. Three general types of compounds, Dewar benzenes, benzvalenes, or prismanes are considered potential intermediates. The activation energy for reaction 1 was measured by chemiluminescence step-analysis[4] and found to be 37 ± 2 kcal/mol. This value is much higher than that for the rearrangement of Dewar benzene,[7] benzvalene,[8] or prismane[9] to benzene. Valence isomerization of the latter compounds all possess activation energies in the range of 25-27 kcal/mol. It can thus be concluded that steady state concentrations and properties of benzene valence isomers derived from **1** will be too low to measure by most conventional techniques. Detection is possible, however, by chemiluminescence techniques. Of the three benzene isomers, we have found that *only Dewar benzene*[5b] *is capable of producing significant amounts of indirect chemiluminescence;* both benzvalene[10] and prismane[10] are insignificantly chemiluminescent under comparable conditions. By analogy we conclude that reaction 1 involves a dimethyl Dewar benzene intermediate. This conclusion is confirmed by qualitative measurement of the rate constant and activation energy for decay of the reactive intermediate (Figure 1) produced during thermolysis of **1**. We find that both the rate constant ($\sim 2 \times 10^{-4}$ sec^{-1}) and activation energy (~26 kcal/mol) for decay are comparable to the values found for Dewar benzenes **2** and **3**.

A final question remains as to what fraction of the rearrangement of **1** to xylene proceeds via Dewar xylene. This question was answered by quantitatively measuring the indirect chemiluminescence yields from **1**, **2**, and **3** under comparable conditions (Table I). The total chemiluminescent intensity was then compared to that of tetramethyldioxetane under similar conditions.[11] The results are shown in Table I. Several different acceptors were used in the determination. 9,10-Dibromoanthracene (DBA) accepts energy via *triplet-singlet* energy transfer and fluorescence is observed, 1,4-dibromonaphthalene (DBN) accepts energy via *triplet-triplet* energy transfer and phosphorescence is observed, and biacetyl is capable of accepting energy via both *triplet-triplet* and *singlet-singlet* energy transfer.[12] Spectral analysis of the biacetyl emission showed essentially pure phosphorescence, consistent with the previous determi-

Table I. Yield of Excited States from the Thermolysis of 1, 2, and 3 under Various Conditions

Compound	Solvent	Acceptor	Triplet yield, %
2	CH_3CN	DBA	0.07[a]
2	CH_3CN	DBN	0.06
2	CH_3CN	Biacetyl	0.04
3	CH_3CN	DBA[b]	0.08
3	CH_3CN	DBA[c]	0.06
1	CH_3CN	DBA	0.08
2	Hexane	DBA	0.06

[a] Yields calculated assuming tetramethyldioxetane efficiency is 50%. Estimated error ±50% of the reported value. [b] Compared to **2**. [c] Compared to tetramethyldioxetane.

nation of the triplet multiplicity of the chemiproduced excited xylene. From the near identity of these yields we can conclude that (1) the yields of excited xylenes are comparable from **2** and **3** and (2) the yield of Dewar xylene(s) from **1** is very high and rearrangement of **1** to Dewar xylene possibly occurs with unit efficiency.

In conclusion we provide evidence that identifies Dewar xylene as the key chemiluminescent intermediate in the thermolysis of biscyclopropenyls to benzenes.[13] It is, of course, possible that **1** passes inefficiently through a highly efficient chemiluminescent species that exhibits the exact same chemielectronic characteristics as Dewar xylenes. The thermolysis of **2** represents the first clear cut case of an energy sufficient Dewar benzene rearrangement; i.e., one in which the sum of reaction enthalpy and activation enthalpy (~60 + 28 = 88 kcal/mol) is greater than the energy of the final excited state (E_T of xylene ~82 kcal/mol). The observation that the excited state yield from **2** is no higher than from the parent system lays to rest the idea that the low yield of excited states results from unfavorable energetics.

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Isotopically Selective Photochemistry in Molecular Crystals

Sir:

We wish to report here the first low temperature (1.6-10 K) *isotopically selective photochemical reaction* performed in a molecular crystal. We in addition document the feasibility of selective optical excitation of molecules rich in naturally abundant isotopes, in this example ^{13}C, ^{15}N, and ^{2}H, using available tunable dye lasers, and demonstrate that such excitations can be readily used for (a) the total enrichment of isotopes, (b) the exploration of photoprocesses and their intermediates, and (c) the study of the optical emission spectra of specific isotopically substituted molecules.

In molecular crystals at low temperature it is invariably possible to discern optical transitions corresponding to organic molecules containing ^{13}C and ^{15}N atoms in natural abundance because the zeropoint or vibronic isotope shifts are in the range 1-10 cm^{-1} whereas the inhomogeneous zerophonon optical line widths[1] are usually between 0.1 and 3 cm^{-1}. However, in the gas phase[2,3] isotopic selectivity in moderate size molecules is not so clear cut because of overlapping rotation envelopes. The isotopic processes resulting from selective excitation depend on the effectiveness of energy transfer, but isotopic scrambling can be eliminated (or studied!) in suitably dilute mixed crystals. In systems where a photochemical process occurs faster than the excitation energy is channeled into the various photophysical pathways, one can perform isotopically selective photochemistry. In this communication we present a resumé of our results on the dye laser induced photochemical decomposition of *sym*-tetrazine ($C_2N_4H_2$) in neat and mixed crystals at low temperature.

Two excited states of *sym*-tetrazine known[4-10] to have transitions in the 5000-7000 Å region are $^1B_{3u}$ and $^3B_{3u}$. Both states correspond to $n \rightarrow \pi^*$ electronic promotions but are unusual in that the observed lifetimes are very short ($\tau_S \lesssim 500$ psec, $\tau_T \simeq 80$ μsec[8,9]) compared with other heteroaromatic $n\pi^*$ transitions, and substantially no intersystem crossing $^1B_{3u} \rightsquigarrow {}^3B_{3u}$ occurs in this molecule. Phosphorescence can be studied by directly exciting the triplet state.[8-10] In a neat or in mixed crystal at 1.6 K *sym*-tetrazine undergoes efficient photochemical decomposition following excitation into either $^1B_{3u}$ or the $^3B_{3u}$ states. The $^1B_{3u} \leftarrow {}^1Ag$ radiative transition displays mainly a progression in ν_{6a} (ca. 700 cm^{-1}) and each vibronic transition in the spectrum shows naturally abundant isotopic side bands that can be selectively excited using a dye laser. The fol-