change reaction correspond to the achievement of nuclear configurations intermediate between those of chromium(III) and chromium(II), between half and all of the differences in ^{2}E and ^{4}A Franck–Condon parameters would contribute to the difference in reorganizational barriers of excited-state and ground-state electron-transfer reactions.[14,15] Thus the excited-state and ground-state self-exchange reactions are expected to differ by a factor of between 10 and 10^2. A factor of $\sim 10^3$ was inferred above from experimental observations.

Since there is always a Stokes shift between ground-state absorption and excited-state emission, there should always be a difference in the reorganizational barriers for the respective electron-transfer reactions. Thus the frequent assumption[3d] that the self-exchange rates of excited-state and ground-state polypyridyl-ruthenium(III)-ruthenium(II) reactions are the same cannot be correct unless these reactions are limited only by diffusion. In fact, the $Ru(bpy)_3^{2+}$ system exhibits a very large Stokes shift ($\sim 0.6\ \mu m^{-1}$),[2b] a part of which may be due to the configurational differences of the initially populated excited state and the emitting state.[16] The excited-state to ground-state decay in this system has some of the features of a unimolecular electron-transfer reaction with a 9 kcal mol^{-1} "activation barrier" ($k = 2 \times 10^6\ s^{-1}$).[14] This corresponds to a difference of $\sim 0.3\ \mu m^{-1}$ in excited-state and ground-state Franck–Condon parameters and about a 10^3 difference in excited-state and ground-state self-exchange rates. The observations of Sutin and co-workers[2] are consistent with slower excited-state than ground-state self-exchange rates.

In systems for which there is a greater barrier to excited-state than to ground-state electron transfer, as we find for $Cr(bpy)_3^{3+}$ and as probably is the case for $Ru(bpy)_3^{2+}$, this effect is another limitation on the utilization of these systems in such applications as the construction of photovoltaic cells since the degradative recombination reactions will tend to have smaller barriers than the excited-state redox reactions which produce the effect. On the other hand, there is no apparent reason that there should not be systems in which the reactivity order of ground and excited states is reversed from that found here.

Excited-state electron-transfer reactions of (^{2}E) $Cr(bpy)_3^{3+}$ have been followed using standard flash photolysis techniques[17] and monitoring the ^{2}E excited state absorbance at 445 nm.[4e]

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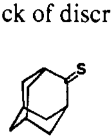
On Hydrogen Abstraction by the π,π^* Singlet State[1,2]

Sir:

The efficient reduction of the carbonyl group in its $^3(n,\pi^*)$ state by hydrocarbon hydrogen donors is well documented;[3] that in the $^1(n,\pi^*)$ is less so, but recent work suggests[4] that the expected intermolecular similarity[5,6] with the triplet obtains, as is probably the case intramolecularly also.[7] With the singlet (n,π^*) reaction the product formation is in competition with return to ground state via a common hypersurface. The corresponding $^3(\pi,\pi^*)$ state is, on the other hand, poorly reduced by hydrocarbon donors,[7,8] and such capacity as it has may be acquired by mixing with the n,π^* state.[7,9]

Recently we have reported that the second excited state of adamantanethione (**1**) is reduced by cyclohexane to give the sulfide **2** and the thiol **3** accompanied by the inevitable 1,3-dithietane dimer.[10] We now wish to report that the hydrogen abstraction is, at least in part, a radical process and that the S_2 thione is among the most indiscriminate hydrogen abstractors known.

The thione **1** (0.04 M) was irradiated at 254 nm to about 5% conversion in a number of hydrocarbons (Table I) in admixture with cyclohexane. The relative reactivities for both sulfide and thiol formation are expressed (per C–H bond) with respect to the formation of **2.** The relative total insertion per C–H bond with respect to cyclohexane as standard is also given. The process is much more indiscriminate than that of benzophenone triplet or *tert*-butoxy radical and surpasses the promiscuity of chlorine. Only fluorine and methylene are comparable.[11] The lack of discrimination in the abstraction is related in re-



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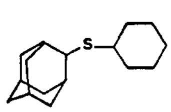

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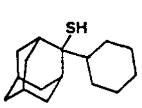

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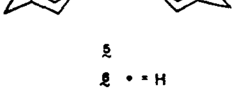

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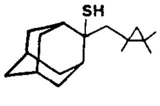

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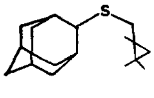

8

Table I. Reactivity (per C–H) of Excited (S_2) **1** and Other Species

Hydrocarbon		Adamantanethione[a]			Other species		
		2	**3**	**2 + 3**	Cl·[c]	$Bu^tO\cdot$[d]	$^3[\phi_2(C{=}O)]$[e]
Cyclohexane	(II)	(1.00)[b]	0.82	(1.00)[b]	(1.0)[b]	(1.0)[b]	(1.0)[b]
Neopentane	(I)	0.35	0.50	0.47			
n-Butane	(I)	0.64	0.46	0.60	0.36[f]		
	(II)	0.77	0.58	0.74	1.4[f]		
2,3-Dimethylbutane	(I)	0.44	0.44	0.48	0.37	0.07	0.03
	(III)	0.40	0.40	0.44	1.6	2.9	8.6

[a] Estimated error < ±6%. [b] Assumed to be unity. [c] See ref 32. [d] See ref 33. [e] See ref 15. [f] For *n*-pentane assuming all II-H are equivalent.

actions of similar type to the thermicity of the process. The reactions of *tert*-butoxy radical and benzophenone triplet, which are very similar overall, with a secondary hydrogen are exothermic by about 10 kcal/mol,[15] that of chlorine by 9 kcal/mol, and that of fluorine by about 40 kcal/mol. There is a lack of thermodynamic data for thiones, but we estimate that a figure of >25 kcal/mol for the reaction from S_2 is probable.[14] Under these conditions the activation energy, as in the case of fluorine, is likely to be very small and the preexponential term becomes dominant,[17] and steric hindrance to approach of the large short-lived excited thione will be more important than relative bond strength, especially with regard to tertiary hydrogen.

To ascertain whether the reaction involved radical intermediates or was the consequence of a $2_{\pi_s} + 2_{\sigma_s}$ addition, **1** (0.035 M) was irradiated in a 1:1.8 molar mixture of perdeuteriocyclohexane[18] and cyclohexane. The products **2** and **3** were separated chromatographically and analyzed mass spectroscopically. The occurrence of a radical process was unambiguously required by the presence, in the **2** and **3** obtained, of "crossed" products containing the $C_6H_{11}^-$ and $C_6D_{11}^-$ moieties. From the relative amounts of deuterated and protiated cyclohexyl residues, the values of k_H/k_D could be obtained; they were 1.0 and 1.2 for the sulfide and thiol, respectively. A further check on the isotope effect was possible in the case of the thiol which displayed a prominent (M − SH) ion. The precision here is not quite so good because of very minor extraneous peak overlap but was in the range 1.3 ± 0.1. These values are much smaller than those found for triplet ketone abstraction both inter-[19] and intramolecularly,[20] where they appear in the range 3.8–7.0 for abstraction from a hydrocarbon, but is in keeping with the expected low activation energy.

Escape from the cage by the (perdeuterio) cyclohexyl radical leads to its rapid trapping by the ground-state thione[21] to give the radical **4** which further abstracts hydrogen (deuterium). The protium incorporated into the deuterated sulfide was 11.8%, and the deuterium into protiated sulfide was 3.1%. Since escape from the solvent cage should be equal for deuterated and protiated molecules, it is possible to compute the isotope effect for the abstraction by **4** and the total escape: $k_H'/k_D' = 2.1$; escape ~14.4%. No other product derived from the cyclohexyl radical has so far been detected.[22]

The counter radical must escape in equivalent amount, and its most probable fate is trapping by ground-state thione[21b,24] to give **5** and ultimately the corresponding **6**. The amount of this[25] may also be taken as a measure of escape. At 21 ± 0.5° in cyclohexane this amounts to ~11.2 ± 0.6%, a reasonable agreement. A similar investigation in the cyclic hydrocarbons (C_5–C_8) at 24 ± 0.5° showed a decrease in the formation of **6** from 23.9 to 18.8 to 18.5 to 12.1% as the viscosity increased from 0.43 to 2.29 cP. Although the correlation is subject to some error, the trend is real.[26,27]

The rate of diffusion k_{diff} out of the solvent cage is given by[28] $6D/\sigma^2$. If $\sigma \sim 0.6$ nm,[29] with typical values of D, the lifetime in the cage is $\sim 2 \times 10^{-11}$ s. Only about 10% escapes so the lifetime of the singlet radical pair is of the order of 2 ps.

As an experimental approximation to this limit, we irradiated 1,1,2,2-tetramethylcyclopropane which gave **7** and **8**[30] (plus dimer). Escape from the cage as indicated by disulfide formation was somewhat less (6%) than in the other hydrocarbons, but again indicated the incursion of a radical process. No sulfide or thiol product of ring opening of the cyclopropylcarbinyl radical[31] was detected. The rate of opening of the carbinyl radical, in the radical pair, is $>1.3 \times 10^8\ \text{s}^{-1}$.[31] Assuming 5% opening would have been detected, the lifetime of the radical in the radical pair must be less than 400 ps. The lifetime predicted in the preceding paragraph is far less, and hence the absence of ring-opened products is rational.

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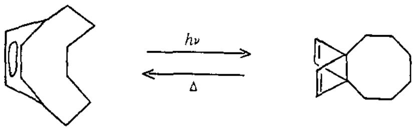
Interconversion of [6]Paracyclophane and 1,4-Hexamethylene(Dewar benzene)[1]

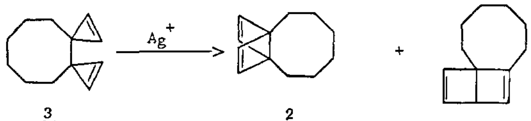
Sir:

Although many valence isomerizations of substituted benzenes are known,[2] photochemical isomerizations to a single Dewar form are rare, and there seems to be no example of a quantitative isomerization to a Dewar form followed by an equally clean thermal rearomatization. Hexafluorobenzene is photochemically isomerized in modest yield to a Dewar form which is reconverted to the aromatic form on heating.[3] Similarly, photolysis of *peri*-di-*tert*-butylnaphthalenes produces a photostationary state in which the Dewar form greatly predominates. Here too, thermal rearomatization has been achieved.[4] We present here our results on the light-induced closure of [6]paracyclophane (**1**) to 1,4-hexamethylene(Dewar benzene) (**2**) and the subsequent thermal rearomatization.



1 **2**

Irradiation of a solution of [6]paracyclophane[5] in cyclohexane-d_{12} with an unfiltered 450-W Hanovia medium-pressure mercury arc led to slow and apparently quantitative conversion to a single new product (33% in 90 min) which was identified as 1,4-hexamethylene(Dewar benzene) by a comparison of spectra with those of a sample prepared by the silver-catalyzed[6] rearrangement of the bicyclopropenyl **3**.[7] Treatment of **3** [NMR ($CDCl_3$): δ 7.10 (s, 4 H), 1.60 (m, 12 H)] with silver perchlorate in acetonitrile at 0 °C gives **2** and its 1,2 isomer **4** in the ratio 1:9. Separation by gas chromatography on a 3% S.E. 30 column at 55 °C gave **2** [NMR ($CDCl_3$): δ 6,53 (s, 4 H), 1.80 (m, 4 H), 1.50 (m, 8 H)] contaminated only by a few percent benzocyclooctene.[7]



3 **2** **4**

Heating **2** between 50 and 90 °C results in a rapid and clean reversion to **1**. The activation parameters for the formation of **1** from **2** were determined both by integration of the signals for the aromatic protons in the NMR spectrum of **1** (E_a = 20.9 ± 1.5 kcal/mol; log A = 9.8 ± 0.9) and by monitoring the band at 253 nm in the ultraviolet spectrum (E_a = 19.9 ± 0.9 kcal/mol; log A = 9.3 ± 0.6). Thus only 1-chloro- and 1-fluoro-(Dewar benzene) exceed **1** in their measured rates of rearomatization.[8]

This work establishes the "breakpoint" in the series of [m]paracyclophanes and their Dewar isomers. In the hexamethylene case (**1**) and doubtless all higher homologues, it is the aromatic partner that is the more stable. For the pentamethylene case it has already been shown that the Dewar form is favored thermodynamically.[6] Here the Dewar form does not rearrange to the open compound on heating in solution, but instead undergoes a remarkable rearrangement to benzocycloheptene. At higher temperatures [5]paracyclophane may be formed as an intermediate on the way to other compounds.[6] It is not yet known if [5]paracyclophane is protected by a sufficiently high kinetic barrier to be isolable at lower temperatures.

Under conditions sufficient to completely rearrange **1** to **2**, the higher congener, [7]paracyclophane, undergoes only a slow photochemical polymerization. We are now testing to see if a Dewar benzene is formed, only to revert rapidly at room temperature to the aromatic compound.

References and Notes

(1) The work at Princeton was generously supported by the National Science Foundation through Grant MPS-74-05690. Grant 1071 from the NATO Research Grants Programme greatly aided this collaborative effort and is warmly acknowledged.
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