Table I. Comparison of Observed and Predicted Hyperfine Splitting Constants

Position	Observed hfsc	Calcd hfsc[a]	Calcd hfsc[b]	Calcd hfsc[c]
Hexamethylbenzene				
CH_3	6.45	6.45	6.45	6.45
Pentamethylbenzene				
1,2,4,5-CH_3	10.05	9.7	9.87	9.34, 9.42
3-CH_3	<0.3	0	0.34	0.71
6-H	<0.3	0	0.24	0.32
Durene				
1,2,4,5-CH_3	10.70	9.7	9.87	10.85
3,6-H	0.80	0	0.24	1.61
1,2,3,4-Tetramethylbenzene				
1,4-CH_3	15.13	12.9	12.85	12.12
2,3-CH_3	2.78	3.2	2.95	3.79
5,6-H	2.21	2.2	2.45	2.35
1,2,3,5-Tetramethylbenzene				
2-CH_3	16.82	12.9	13.70	13.27
5-CH_3	14.36	12.9	12.09	11.76
1,3-CH_3	2.96	3.2	3.46	3.32
4,6-H	1.76	2.2	2.04	2.39
1,3,5-Tri-*t*-butylbenzene				
2,4,6-H	5.18	4.4	4.4	5.17
t-Bu-CH_3	0.63			
1,4-Di-*t*-butylbenzene				
2,3,5,6-H	2.1	2.2	2.28	1.41
t-Bu-CH_3	0.95			

[a] Simple unmodified HMO calculation using $Q_{\mathrm{H}} = 26.4$ and $Q_{\mathrm{CH}_3} = 38.7$ G, which are derived from the benzene and hexamethylbenzene radical cations. [b] Inductive MO model with $h = -0.13$ and McLachlan $\lambda = -1.2$, using the above Q values. [c] Valence-bond model[11] with the above Q values.

mum slope) was 0.3 G. Under the conditions used, no other radical derived from hexamethylbenzene was observed.[7]

The pentamethylbenzene radical cation spectrum contained at least nine evenly spaced lines with a line width of 0.8 G, separated by 10.05 G. Despite the relatively poor resolution, these results confirm the suggestion that the esr signal obtained by Hulme and Symons[8] from hexamethylbenzene in oleum was indeed not the pentamethylbenzene radical cation.

The esr spectrum of the durene (1,2,4,5-tetramethylbenzene) radical cation consisted of at least seven equally spaced triplets separated by 10.70 G. The small hyperfine splitting constant was 0.80 G and is no doubt due to the two hydrogen atoms in the 3 and 6 positions. This splitting had not previously been observed in concentrated oleum.[4]

The 1,2,3,4-tetramethylbenzene radical cation gave an esr spectrum from which the following hyperfine splitting constants (G) were extracted: $a_{2\mathrm{CH}_3} = 15.13$, $a_{2\mathrm{CH}_3} = 2.78$, and $a_{2\mathrm{H}} = 2.21$. The 1,2,3,5-tetramethylbenzene radical cation gave a more complex spectrum, which could be computer simulated using the following hyperfine splitting constants (G): $a_{1\mathrm{CH}_3} = 16.82$, $a_{1\mathrm{CH}_3} = 14.36$, $a_{2\mathrm{CH}_3} = 2.96$, and $a_{2\mathrm{H}} = 1.76$. The line width in both systems was 0.33 G.

The esr spectra of the radical cations derived from 1,3,5-tri-*t*-butylbenzene and *p*-di-*t*-butylbenzene are shown in Figure 1. The hyperfine splitting constants (G) obtained from these spectra were $a_{3\mathrm{CH}_3} = 0.63$ and $a_{3\mathrm{H}} = 5.18$ (line width = 0.25 G), and $a_{2\mathrm{CH}_3} = 0.95$ and $a_{4\mathrm{H}} = 2.1$ (line width 0.35 G), respectively.

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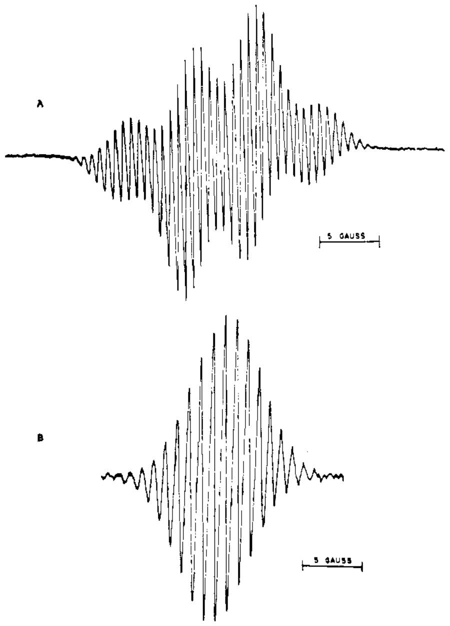

Figure 1. Esr spectra of the radical cations of 1,3,5-tri-*t*-butylbenzene (A) and 1,4-di-*t*-butylbenzene (B).

In general, our data (Table I) are qualitatively consistent with simple HMO predictions taking into account the inductive interactions of the alkyl substituents. As expected on the basis of symmetry considerations, the tetramethylbenzene cations showed the same spin density distributions as the xylene anions, while the pentamethylbenzene cation was similar to the toluene anion. Most significant is the finding that the degeneracy of the two highest filled π orbitals of the unsubstituted benzene cation is not lifted by 1,3,5 trisubstitution, as evidenced by the 1,3,5-tri-*t*-butylbenzene radical cation. The large methyl splittings in 1,2,3,4- and 1,2,3,5-tetramethylbenzene cations indicate the importance of hyperconjugation, and are in accord with the prediction that the effective $Q^{\mathrm{H}}{}_{\mathrm{CCH}_3}$ for the cation is larger than that for the anion.[9,10] The observed results also agree fairly well with valence-bond calculations,[11] which do not differ greatly from those obtained from a molecular orbital approach.

Extension of this work to other radical cations as well as temperature dependence studies and theoretical investigations are in progress.

Acknowledgment. The skillful technical assistance of Messrs. R. J. Cier and O. M. Epifanio, as well as helpful discussions with Dr. P. L. Corio, are acknowledged.

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Flash Photosensitizations by Cadmium and Zinc Atoms

Sir:

We wish to report a novel flash photolysis–kinetic spectroscopic technique for the study of metal atom reactions. To date the study of metal atom reactions has been limited largely to excited mercury, cadmium, and zinc. Our technique makes it possible to investigate the vapor phase reactions of metal atoms at room temperature in their ground or excited states irrespectively of their vapor pressure. The source of metal atoms is the *in situ* flash photolysis of a volatile alkyl metal compound, Me_2Cd, -Zn, -Te, Me_3As, -Sb, -Bi, -Al, -In, -Tl, Me_4Sn, etc. The technique involved and the scope of results obtained will be illustrated by the example of the dimethylcadmium (DMC) system.

DMC exhibits a broad absorption in the uv below 2700 Å which becomes more intense below 2300 Å. On flashing mixtures of DMC with Ar or CO_2 in a quartz vessel ($\lambda > 2000$), a rapid buildup in the Cd atom concentration can be observed. It is thus possible to produce several hundred micron Cd vapor at room temperature (exceeding the equilibrium value by approximately eight orders of magnitude) for a period of several milliseconds. This extremely high concentration coupled with the long lifetime of the atoms suggests the possibility of carrying out photosensitization by pressure-broadening the atomic absorption line. Hitherto, studies on cadmium sensitization have been done at temperatures in excess of 250°, whereas the present technique would provide a means of conducting such studies at room temperature and, in addition, of using kinetic spectroscopy for the investigation of atomic states and molecular intermediates involved in the reaction.

In flashed mixtures of DMC (0.1–2 Torr) with hydrogen and hydrocarbons (50–1000 Torr) all three components of the lowest excited P state of Cd were observed along with an intense spectrum of CdH (4100–4500 Å).[1] The relative concentrations of Cd $^3P_{2,1,0}$ were monitored by measurement of the intensities of the atomic absorption lines at 3611, 3466, and 3404 Å, respectively. When DMC was flashed in the presence of D_2, CD_4, and i-C_4D_{10} a shift of some 10 Å was observed in the hydride spectrum corresponding to the formation of CdD.[2] This is evidence for the photosensitization reactions of excited cadmium atoms.

In mixtures of DMC with either CO, CO_2, or N_2 excited atoms could not be detected. With Ar, at pressures >1 atm, faint absorption by both $^3P_1$ and $^3P_0$ atoms could be observed, with the $^3P_1$ line being the more intense. Intense lines corresponding to the $^3P_{1,0}$ states were observed in mixtures with methane, isobutane, and neopentane, in this case the $^3P_0$ being the more intense. Increasing pressures of methane (50–1000 Torr) resulted in increasing amounts of both $^3P_{1,0}$ cadium atoms; however, increasing pressures of isobutane and neopentane (50–1000 Torr) reduced the amount of $^3P_{1,0}$ cadmium atoms observed. When DMC was flashed with mixtures of methane and isobutane, increasing the ratio of butane to methane resulted in an increase in the ratio of $^3P_0$ to $^3P_1$, although the overall amount decreased.

Since quartz reaction vessels were used in the above experiments, it is possible that both $^1P_1$ and $^3P_1$ states may be involved in the sensitization reaction. The formation of $^3P_2$ Cd indicates that triplet cadmium atoms are formed, at least in part, by deactivation of the $^1P_1$ state. Filter experiments, to determine the roles played by these two states, indicate that ^3P Cd is formed principally by absorption of 2288-Å radiation with subsequent collisional deactivation of the ^1P state. That the ^3P cadmium atoms are formed *via* the $^1P_1$ state is not surprising since the extinction coefficient for absorption of the 2288-Å line is 2–3 orders of magnitude greater than that at 3261 Å, while the lamp outputs at the two wavelengths involved are essentially the same. Analogous quenching of the $^1P_1$ state of mercury to the $^3P_1$ level by N_2 and CO has been observed[3] and we consider it likely that the triplet state plays an important role in the $^1P_1$ mercury sensitization of hydrocarbons[4,5] as well.

Quantitative decay measurements in methane indicate a first-order decay, for both $^3P_0$ and $^3P_1$ atoms, which appears to be independent of the methane pressure. From the decay constant, the decay lifetimes for both states are the same and are equal to 1×10^4 sec^{-1}. Thus, methane does not appear to quench $^3P_{1,0}$ Cd atoms and we attribute the long triplet decay life to an enormously large imprisonment effect due to the high concentration of cadmium atoms. The approximately equal decay rates for the $^3P_0$ and $^3P_1$ states and the variation of their relative concentrations with the complexity of the quencher molecule seem to indicate that a degree of thermal equilibration is attained. From decay plots with added ethylene, a rate constant of 2×10^9 l. mol^{-1} sec^{-1} was obtained for the quenching of $^3P_{1,0}$ Cd by ethylene. This is about two orders of magnitude larger than the value derived from conventional fluorescence measurement with the neglect of imprisonment and appears to be more consistent with the nonvertical nature of the energy transfer reaction than the earlier value.[6]

Quantitatively similar results were obtained with dimethylzinc. Zinc $^3P_{2,1,0}$ atoms have been observed in flashed mixtures of dimethylzinc (2 Torr) and argon (600 Torr) in a quartz reaction vessel. Zinc hydride has been observed in mixtures flashed in both quartz and Vycor reaction vessels.

In principle it should also be possible to utilize the *in situ* generated metal atoms for light amplification. The photolysis of DMC in the presence of excess methane, for example, could give rise to stimulated emission for the Cd($5\,^3P_{1,0} \rightarrow 5\,^1S_0$) transitions in an appropriate laser cavity. Moreover flash photolysis in the vacuum uv may serve as a basis for the chemical laser

$$(\mathrm{Me})_x\mathrm{M} \longrightarrow x\mathrm{Me} + \mathrm{M}^*$$

for the resonance radiation of the metal atom. This aspect of the reaction is currently under investigation.

Illustrative examples of ground-state metal atom reactions are the combination reactions of Cd and Zn (M) with Br and I atoms (X) to form MX. Flashing $M(CH_3)_2$ with CF_3X intense spectra corresponding to the $^2\Pi \leftarrow {}^2\Sigma$ transitions of MX were obtained, which could be used to follow quantitatively radical concentrations. These spectra, previously not observed in absorption, all occur close to the metal resonance lines, 3261 Å for

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cadmium and 3076 Å for zinc, the iodides being slightly shifted toward the visible. A rapid buildup and decay was observed. In the cadmium plus bromine system under conditions producing an excess of bromine atoms, the decay of CdBr was found to be first order in CdBr, corresponding to

$$\mathrm{CdBr} + \mathrm{Br} \longrightarrow \mathrm{CdBr_2} \qquad (1)$$

Under conditions producing an excess of Cd atoms, the decay was found to be second order in CdBr, corresponding to

$$2\mathrm{CdBr} \longrightarrow \mathrm{Cd} + \mathrm{CdBr_2} \qquad (2)$$

Extensive studies of the flash photolysis of metal methyl compounds are currently being pursued in this laboratory. A preliminary report on the results obtained with the other compounds will be published shortly.

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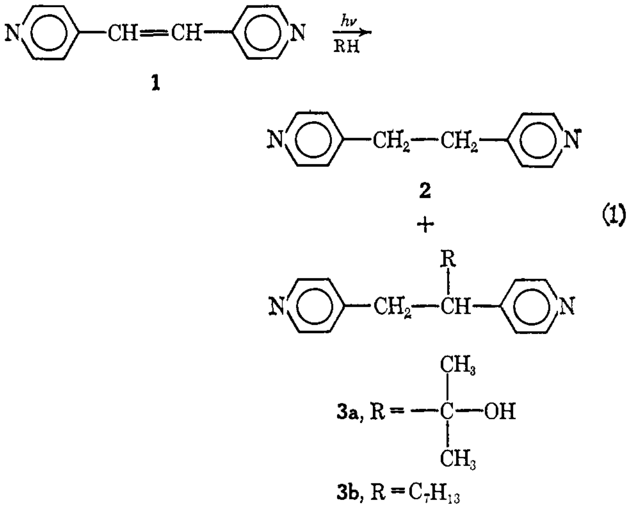
Reactions of Hidden n,π^* Excited States in N-Heteroaromatics. Photoreduction and Photoaddition[1]

Sir:

N-Heteroaromatic compounds frequently exhibit excited state behavior rather different from their hydrocarbon counterparts. For several nitrogen compounds rapid radiationless decay of initially formed excited singlets evidently competes favorably with fluorescence, intersystem crossing, and chemical reaction.[2-4] Acridine,[5,6] quinoline,[7] and purine[8] undergo photoaddition and photoreduction reactions which appear to involve radical intermediates under conditions where the corresponding hydrocarbons are unreactive. One possibility for explaining this behavior is the involvement of ^{1}n–π^* states having radical character and some excitation localization on nitrogen. For excited singlet states of quinoline, acridine, and other large N-heteroaromatics such an explanation seems unappealing; absorption and fluorescence spectra of these compounds show no sign of n $\rightarrow$ π^* transitions and are nearly identical with those of the corresponding hydrocarbons. In addition, studies of acridine indicate that the fluorescent state is a π,π^* singlet.[9,10] In the present communication we report novel photoaddition and photoreduction reactions of 1,2-bis(4-pyridyl)ethylene. The results suggest that for this compound, and probably for several other N-heteroaromatics, the presence and reaction of hidden n,π^* singlets having lower excitation energies than the initially formed, fluorescent π,π^* singlets accounts for many of the unusual photochemical phenomena.

Previously we reported that rapid radiationless decay of excited singlets of 1,2-bis(4-pyridyl)ethylene (**1**) and other nitrogen analogs of stilbene resulted in relatively low efficiencies for *cis–trans* isomerization and fluorescence.[4,11] In benzene the only primary product from direct irradiation of **1** is the *cis* isomer. The lifetime of the excited singlet of **1** in benzene is *ca.* 10^{-12} sec. In other solvent systems we found *cis*-**1** to be the chief product on short-term irradiation; however irradiation of **1** in methylcyclohexane and 2-propanol leads to the formation of additional products with low quantum efficiencies. These products, which build up gradually at the expense of **1**, proved to be substituted 1,2-bis(4-pyridyl)ethanes formed by addition of hydrogen or solvent across the acyclic double bond (eq 1).



(1)

In a typical experiment irradiation of **1** in 2-propanol led to a 21% yield of **2** and a 28% yield of **3a**. Long-term irradiation of **1** in methylcyclohexane yields **2** and **3b**. Although **2** is not produced initially by irradiation of **1** in benzene, long-term irradiation leads to slow formation of roughly equal quantities of 3,6-diazaphenanthrene and **2**. Quantum efficiencies for formation of **2** and *cis*-**1** are listed in Table I.

Table I. Initial Quantum Efficiencies for Photoreduction and Isomerization of 1,2-Bis(4-pyridyl)ethylene

	Solvent system[a]			
	Benzene	Methylcyclohexane	2-Propanol	Water–acetonitrile[b]
$\phi_{t\rightarrow c}$	0.003	0.005	0.04	0.3
$\phi_{t\rightarrow 2}$	0.0	0.0004	0.02	

[a] Degassed solutions, irradiated at 313 nm, olefin concentration 0.005 *M*. [b] 70% acetonitrile by volume.

The surprising observation of photoaddition and photoreduction reactions for an acyclic olefin such as **1** raises several questions regarding mechanism. It appears that products **2** and **3** arise from solvent hydrogen

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