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Photochemistry of Quaternary Salts of 1,2-Bispyridylethylenes. Heavy Atom Induced Singlet–Triplet Intersystem Crossing as a Path for Decay in Charge-Transfer Exciplexes[1,2]

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Abstract: An investigation of the effect of heavy-atom-containing quenchers on the photochemistry of quaternary salts of 1,2-bispyridylethylenes is reported. Haloaromatics as well as non-halogen-containing aromatics quench the fluorescence of the electron-deficient olefins; the former induce trans → cis isomerization presumably via the olefin triplet. The quenching mechanism can be demonstrated to be formation of a charge-transfer exciplex with all of the quenchers studied; with non-halogen-containing quenchers the exciplex evidently decays rapidly without the occurrence of isomerization. For most of the halogen-containing quenchers, the "heavy-atom effect" involves quenching of the localized singlet to the exciplex followed by quantitative decay to the localized olefin triplet; this mechanism occurs provided the quencher oxidation potential is greater than 1.38 V, such that the exciplex lies energetically between the olefin excited singlet and triplet states. When the exciplex lies lower in energy than the triplet no isomerization is observed.

An area of interest to both photochemists and spectroscopists has been the induction of singlet–triplet intersystem crossing by external and internal heavy atoms.[3-11] Both the internal and external effects are believed to involve enhanced spin–orbit coupling, which occurs when electrons involved in the transition are subjected to the enhanced electric field in the vicinity of the heavy atom.[3] A major question concerning the external heavy-atom effect has been the nature of binding interactions between the heavy-atom-containing molecule and the excited substrate. McGlynn and co-workers have suggested that a charge-transfer interaction in the excited state is a prerequisite to the operation of the external heavy-atom effect.[4,5] Giachino and Kearns found, however, that the magnitude of the heavy-atom effect did not increase when heavy-atom perturbers were used with increased capabilities of forming charge-transfer complexes.[6] Until recently most examples where charge-transfer interactions were believed involved in external heavy-atom effects involved systems where the heavy-atom quencher, usually an alkyl halide, was the electron acceptor and the excited substrate was an aromatic hydrocarbon. In recent work, however, Herman and Schulte-Frohlinde found that intersystem crossing in 9-cyanoanthracene and 9,10-dicyanoanthracene could be induced by a series of heavy-atom quenchers having varying electron-donating abilities.[7] For these systems the quencher giving the highest fraction of triplet formation was *p*-bromoanisole, the best electron donor in the series studied. Although McGlynn and co-workers have suggested that donor–acceptor charge-transfer interactions contribute to the field of the heavy atom and give rise to enhanced spin–orbit coupling in the substrate,[8] the latter results suggest that donor–acceptor interactions may play their major role simply in bringing and holding the heavy atom into the vicinity of the excited substrate.

In the present paper we report results of an investigation of the effect of heavy-atom-containing quenchers on the photochemistry of quaternary salts of some 1,2-bispyridylethylenes. These electron-deficient olefins are attractive candidates for investigation of external heavy-atom effects, since in several instances both inefficient triplet formation and rather efficient, intense fluorescence is observed;[12,13] in addition, sensitization studies have indicated that triplets, once formed, undergo efficient isomerization such that triplet counting is easily accomplished.[14] In previous investigations we have found that these electron-deficient molecules react readily from their excited singlet states in processes involving nucleophilic attack as well as formation of charge-transfer exciplexes.[12,13,15] In

Table I. Quantum Yields for Bispyridylethylene Salts in Acetonitrile Solutions

Process	*trans*-**1**	*trans*-**2**
Fluorescence	0.8	0.05
Isomerization, degassed	0.12	>0.0001 ~(0.66 ± 0.1)
Isomerization, undegassed	>0.12	0.5 ± 0.1
Isomerization, sensitized by benzophenone	0.40 ± 0.05	0.16

a preliminary communication,[1] we reported prominent external heavy-atom induction of intersystem crossing when excited singlets of these compounds were quenched by aromatic chlorides and bromides. In the present report, we present results of a more extensive study which indicates not only the range of the external heavy-atom effect for the substrates, but also the mechanism for the phenomenon. An interesting aspect of this study is the finding that singlet quenching and triplet formation processes are evidently distinct and separable processes; thus the substrate singlet is quenched to form a donor-acceptor exciplex, subsequent reactions of which are controlled by heavy atoms in the electron-donating quencher.[16]

Experimental Section

Preparation of *N*-Methyl Fluoroborate Salts. Dimethyl iodide salts of the 1,2-bispyridylethylenes were prepared as previously described from the free bases.[13] The iodide anion was replaced by dissolving 1-3 g of the iodide salt in 50-75 ml of water, followed by the addition of a very slight excess over the stoichiometric quantity of silver tetrafluoroborate, which had been dissolved in 5 ml of water. The mixture was stirred while adding silver salt and for at least 15 min afterwards. The AgI was filtered and the filtrate was evaporated to a small volume. Cooling afforded white crystals, which were recrystallized from water and then from a 90% methanol solution.

***trans*-1,2-Bis(*N*-methyl-3-pyridyl)ethylene Fluoroborate.** Anal. Calcd for $C_{14}H_{16}N_2B_2F_8$ (mol wt 385.91): C, 43.57; H, 4.18. Found: C, 43.31; H, 3.94. NMR (D_2O) δ 4.46 (s, 6, *N*-methyl), 7.60 (s, 2, vinyl), 8.6 (m, 8, aromatic); internal standard sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). Uv agreed with literature values.[18]

***cis*-1,2-Bis(*N*-methyl-3-pyridyl)ethylene Fluoroborate.** NMR (D_2O) δ 4.36 (s, 6, *N*-methyl), 7.14 (s, 2, vinyl), 7.3 (m, 8, aromatic); internal standard DSS. Uv (acetonitrile) λ_{max} 287 (ϵ 15 200), shoulder 317 nm (ϵ 10 200).

***trans*-1,2-Bis(*N*-methyl-4-pyridyl)ethylene Fluoroborate.** Anal. Calcd for $C_{14}H_{16}N_2B_2F_8$ (mol wt 385.91): C, 43.57; H, 4.18. Found: C, 43.38; H, 4.25.

Materials. Matheson, Coleman, and Bell spectroquality acetonitrile was purified by distillation from P_2O_5. Although the purified solvent was used for most experiments, it gave the same results as the undistilled spectroquality solvent. Liquid haloaromatics were distilled at reduced pressure and passed through alumina columns. Solid bromoaromatics were generally recrystallized from ethanol.

Quantum Yield Determinations. All quantum yields were measured in acetonitrile, purified as indicated above. Samples were degassed, using 4-5 cycles of freeze-pump-thaw and sealed under a vacuum of approximately 10^{-5} Torr. The samples were degassed in 12-13-mm o.d. quartz tubes having quartz to Pyrex graded seals and Pyrex ground-glass joints. The samples were irradiated in a merry-go-round apparatus by a Hanovia 450-W medium-pressure mercury lamp. The mercury lines were isolated by using combination Corning glass filters and/or solution filters as previously described.[13] Light intensities were measured using ferrioxalate actinometry. Quantum yield determinations were made spectrophotometrically by comparing the ultraviolet absorption spectrum of the sample before and after irradiation. Absorption spectra were recorded on the following spectrometers: Cary 17, Shimadzu-Bausch & Lomb UV-210, or a Unicam SP800. Emission spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer.

Treatment of Data. In the quantitative studies of fluorescence quenching and induced isomerization it was first established that light was absorbed only by the 1,2-bispyridylethylene; all of the substrate-quencher combinations were also checked to insure that there were no spectral changes in the long-wavelength regions that could be attributable to ground-state complexation. Slopes of Stern-Volmer plots for quenching and induced isomerization were obtained by a computer least-squares treatment; correlation coefficients were generally 0.995 or higher for the fluorescence quenching but somewhat lower (0.98 ± 0.01) for the induced isomerization reciprocal quantum yield plots. Graphed plots showed good linearity both for the fast quenchers ([Q] up to ~0.02 M) and the less effective quenchers ([Q] up to ~1-2 M). The fluorescence quantum yields were obtained using *trans*-stilbene as a standard and are uncorrected.

Results and Discussion

Photochemistry of 1,2-Bispyridylethylene Salts in Acetonitrile. Irradiation of 1,2-bispyridylethylene salts such as the dimethylfluoroborates of *trans*-1,2-bis(3-pyridyl)ethylene (**1**) and *trans*-1,2-bis(4-pyridyl)ethylene (**2**) in degassed acetonitrile solution leads to only two detectable processes, cis-trans isomerization and fluorescence. Table I summarizes the efficiencies for these processes. Admission of oxygen to the solutions containing **1** or **2** leads to photocyclization in addition to the two aforementioned processes. Oxygen also effects the efficiencies of fluorescence and isomerization; however, the effects are different for the two salts. For **1**, introduction of oxygen lowers the fluorescence efficiency while at the same time increasing the efficiency of trans-cis isomerization. In contrast, introduction of oxygen to solutions of *trans*-**2** results in virtually no effect on the fluorescence, but a very large enhancement of the trans-cis quantum efficiency. For **1**, it appears quite reasonable that the only effect of oxygen is to quench singlets with concurrent enhancement of triplet formation. For **2**, however, it appears evident that the situation is somewhat more complex. Previously[1] we suggested that the results observed with **2** could be accounted for by formation of a nonfluorescent exciplex between *trans*-**2** and acetonitrile, which could itself in turn be quenched by oxygen to yield triplet **2**. Further investigation suggests that interaction between *trans*-$\mathbf{2}^{1*}$ and solvent acetonitrile does occur; however, flash spectroscopic investigation indicates that the product of this interaction is the one electron reduced form of *trans*-**2** (BPE$\cdot^+$). A reasonable explanation for the low isomerization quantum efficiencies would then be that the BPE$\cdot^+$, in low steady-state concentrations, reacts rapidly with the *cis*-**2** formed in the direct irradiation to regenerate *trans*-**2** and giving apparent quantum efficiencies that are unusually low. That this reaction can occur has previously been demonstrated.[19]

To determine if photochemical trans-cis isomerization was occurring and was undetectable due to reaction of the cis with radical cations, a solution containing *trans*-**2** along with 0.085 M ethanol as a potential scavenger for the radical cation was degassed and irradiated. Quenching of the fluorescence of *trans*-**2** by this concentration of ethanol is less than 7%, and since the quantum yield for photoadduct formation in pure ethanol is only 0.05,[12,13] little or no photoaddition should occur. Irradiation produced trans-cis isomerization as the only detectable process; moreover, the quantum yield for isomerization was 0.66 ± 0.10. These data suggest, therefore, that in contrast to behavior of *trans*-**1**, isomerization on direct irradiation of *trans*-**2** is a highly efficient process. While it is not possible to assess whether the isomerization is a singlet or triplet process in either case, the pronounced difference in fluorescence and isomerization yield between trans isomers of **2** and **1**, compounds which differ only in the positions of nitrogen, is noteworthy.

For *trans*-**1**, which has a reduction potential 0.35 V less favorable than *trans*-**2**,[18] reaction with acetonitrile from the excited singlet state to yield radical cation is evidently unimportant, since no radical production is observable on flash

Table II. Fluorescence Quenching and Induced Trans-Cis Isomerization of **1** by Aromatic Compounds[a]

Quencher	$(k_q\tau)_{\rm fluor}$[b]	$(k_q\tau)_{\rm rxn}$[c]	Intercept	Slope
Acenaphthene	84 ± 2	nd[e]		
Anisole	71 ± 3	nd		
Biphenyl	84 ± 3	nd		
p-Bromoanisole	83 ± 1	0		
p-Methylanisole	83 ± 3	nd		
Iodobenzene	70 ± 3	104	3.1 ± 0.3	0.030 ± 0.005
Pyridine	57[d]	nd		
Toluene	41 ± 2	[f]		
Bromobenzene	39 ± 0.3	38	3.0 ± 0.5	0.078 ± 0.0009
m-Bromopyridine	28 ± 1	nd		
Chlorobenzene	23 ± 0.4	29	2.3 ± 0.2	0.082 ± 0.006
Benzene	19 ± 0.6	0		
o-Dichlorobenzene	12 ± 0.7	nd		
p-Bromobenzonitrile	12 ± 1	9	2.8 ± 0.5	0.31 ± 0.04
m-Bromobenzonitrile	12 ± 0.3	15	3.6 ± 0.5	0.24 ± 0.02
Benzonitrile	~0	nd		

[a] All data were processed by computer using the least-squares method. [b] $(k_q\tau)_{\rm fluor}$ = slope of $\phi_f{}^0\phi_f$ vs. quencher concentration. [c] $(k_q\tau)_{\rm rxn}$ = intercept/slope of $1/\phi_{t\to c}$ vs. 1/concentration. [d] J. Happ and M. McCall, unpublished results. [e] nd = not determined. [f] Toluene showed some reaction, but it was not isomerization.

photolysis and the effect of oxygen and ethanol is "normal". The high quantum efficiency for fluorescence and a relatively low quantum efficiency for isomerization, coupled with the observation of very efficient isomerization when **1** is sensitized make this system an attractive candidate for investigation of a structural dependence of the external heavy-atom effect.

Fluorescence Quenching by Substituted Aromatics. The strong fluorescence of *trans*-**1** is very readily quenched by a variety of aromatic hydrocarbons and nucleophiles.[12,15] In general it has been found that quenching of fluorescence by simple aromatic hydrocarbons is also accompanied by quenching of the trans-cis isomerization.[12] For example, fluorescence quenching by benzene at different concentrations resulted in a Stern-Volmer quenching constant ($k_q\tau$) equal to 19. No products were detected other than *cis*-**1**; a similar Stern-Volmer relationship was found to apply to the quenching of the trans → cis isomerization, giving a value for $k_q\tau = 16$. In contrast, when the aromatic quencher contains a bromine, chlorine, or iodine atom, enhancement of the trans-cis process is frequently observed. This pattern of behavior is consistent with a heavy-atom-induced singlet-triplet intersystem crossing in which the enhanced triplet formation results in an increase in the isomerization yield. A likely mechanism for quenching which results in enhanced isomerization is outlined in eq 1-7.

$$trans\text{-}\mathbf{1} \xrightarrow{h\nu} trans\text{-}\mathbf{1}^* \tag{1}$$

$$trans\text{-}\mathbf{1}^* \xrightarrow{k_f} trans\text{-}\mathbf{1} + h\nu \tag{2}$$

$$trans\text{-}\mathbf{1}^* \xrightarrow{k_i} \alpha\ cis\text{-}\mathbf{1} + (1-\alpha)\ trans\text{-}\mathbf{1} \tag{3}$$

$$trans\text{-}1^* + \mathrm{Q} \underset{k_{-q}}{\overset{k_q}{\rightleftarrows}} (trans\text{-}\mathbf{1} - \mathrm{Q})^* \tag{4}$$

$$(trans\text{-}\mathbf{1} - \mathrm{Q})^* \xrightarrow{k_t} \mathbf{1}^{3*} + \mathrm{Q} \tag{5}$$

$$(trans\text{-}\mathbf{1} - \mathrm{Q})^* \xrightarrow{k_d} trans\text{-}\mathbf{1} + \mathrm{Q} \tag{6}$$

$$\mathbf{1}^{3*} \to \beta\ cis\text{-}\mathbf{1} + (1-\beta)\ trans\text{-}\mathbf{1} \tag{7}$$

The induced quantum yield for isomerization ($\phi_c{}^{\rm in}$) can be obtained from the measured quantum yield and the quantum yield in the absence of quencher as shown in the equation

$$\phi_c{}^{\rm in} = \phi_c{}^{\rm measd} - \phi_c{}^0/(1 + k_q\tau) \tag{8}$$

From eq 9, it may be seen that a plot of $1/\phi_c{}^{\rm in}$ vs. $1/[\mathrm{Q}]$ should yield an intercept/slope value equal to the value $k_q\tau$ obtained by fluorescence quenching, where

$$\tau = 1/k_f + k_i$$

and

$$\gamma = k_t/k_d + k_t$$

$$\frac{1}{\phi_c{}^{\rm in}} = \frac{1}{\beta\gamma}\left[1 + \frac{1}{k_q\tau[\mathrm{Q}]}\right] \tag{9}$$

Table II compares Stern-Volmer quenching constants obtained from plots of the first two processes. As data in the table indicate, reasonable agreement was observed for several iodo-, chloro-, and bromoaromatics. A comparison of the intercept for the isomerization plots with $\beta = 0.6$, the fraction of cis isomer in the high-energy sensitized photostationary state,[14] indicates that triplets are formed with minimum efficiencies in the range 0.5-0.7.[20] If the reciprocal intercepts for the isomerization listed in Table II are compared with the limiting values for the high-energy sensitized trans-cis isomerization efficiency, values for the efficiency of triplet formation induced as a consequence of the quenching reaction can be estimated in the range 0.7-1.0. The observation that Stern-Volmer plots are linear for the isomerization up to the highest concentrations used in these studies indicates a lower than unity limiting triplet yield cannot be accounted for by a second intersystem crossing unless triplet to ground-state quenching occurs without affecting the cis-trans decay ratio. Modest scatter in the intercept values listed in Table II is probably best interpreted as indicating that all quenchers produce triplets with about the same efficiency/quench; it is probably also safe to conclude that with all of the heavy-atom quenchers which produce isomerization, triplet formation is the dominant if not the exclusive process. Notable among the heavy-atom quenchers used is the behavior of *p*-bromoanisole, which efficiently quenches fluorescence but does not induce trans → cis isomerization.

As mentioned previously, the electron-deficient nature of *trans*-**1** suggests that it should react with electron donors in both ground and excited states such that electron-transfer quenching by aromatic hydrocarbons should be a favored process. As data in Table III indicate, there is an apparent inverse correlation between available oxidation potentials for the quenchers and the quenching constant. This is better il-

Table III. Rate Constants and Their Logarithms for Fluorescence Quenching of **1** by Aromatic Molecules in Degassed Acetonitrile and, Where Available, the Oxidation Potential of the Quencher

Quencher	$k_q \times 10^{-9\,a}$	Log k_q	$E_{1/2}{}^{ox}$(SCE)^b
Acenaphthene	18.7	10.27	1.30
Anisole	15.8	10.20	1.76
Biphenyl	18.7	10.27	1.83
p-Bromoanisole	18.4	10.26	na^c
p-Methylanisole	18.4	10.26	na
Iodobenzene	15.6	10.19	2.12
Pyridine	12.7	10.10	2.17
Toluene	9.1	9.96	2.33
Bromobenzene	8.7	9.94	2.33
m-Bromopyridine	6.2	9.79	na
Chlorobenzene	5.1	9.71	2.42
Benzene	4.2	9.63	2.43
o-Dichlorobenzene- 012.7	9.43	na	
p-Bromobenzonitrile	2.7	9.43	na
m-Bromobenzonitrile	2.7	9.43	na
Benzonitrile	nq^d		na

^{a} $k_q = (k_q\tau)_{\text{fluor}}/4.5 \times 10^{-9}$ s, where 4.5×10^{-9} s $= \tau$ by single photon counting. ^{b} Converted from Ag/0.1 N Ag^+ reference to SCE by adding 0.35 V. Values from Weinberg, *Chem. Rev.*, **68,** 449 (1968). ^{c} na = not available. ^{d} nq = no quenching.

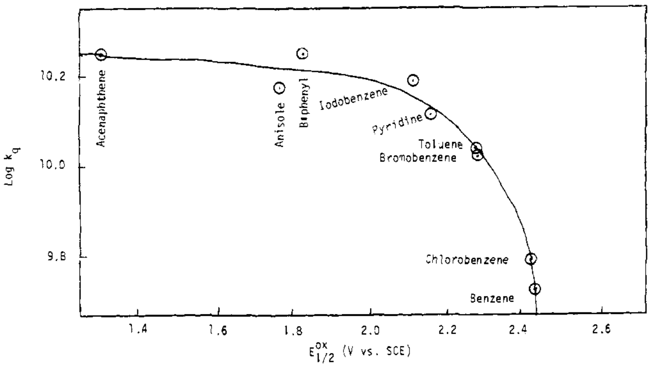

Figure 1. Quenching of *trans*-**1** fluorescence in acetonitrile vs. oxidation potential of aromatic quencher.

lustrated in Figure 1, which gives the plot of log k_q vs. quencher oxidation potential. The general pattern observed here is very similar to that observed for other systems, where it has been well established that electron transfer is the predominant quenching mechanism.[22-24] Significantly, it can be noted that for the three haloaromatics for which oxidation potentials are available, quenching data correlate well with the line generated primarily by non-halogen-containing aromatics. For example, the k_q values for bromobenzene and toluene, which have identical oxidation potentials, are 8.7×10^9 and 9.1×10^9 M^{-1} s^{-1}, respectively. Although quenching rates seem to depend upon quenching oxidation potentials for all of the compounds for which data are available, the occurrence of isomerization appears strictly dependent on the presence of a halogen atom in the quencher. The most reasonable interpretation of the results is that formation of the exciplex and its decay are kinetically separable processes. In terms of the mechanism outlined by eq 1-7, reaction 4 must be essentially irreversible for all the quenchers studied; for the halogen-containing quenchers used in this study $k_t \gg k_d$, while for the remaining quenchers $k_d \gg k_{-q}$ and k_t.[25]

A consideration of energetics suggests that for most of the quenchers used in this study the charge-transfer exciplex (D^+A^-) lies between the localized lowest singlet and triplet states of *trans*-**1**. The singlet of *trans*-**1** lies at 81 kcal/mol (uv onset), while a reasonable estimate of the triplet energy is 50 kcal/mol. Using the reduction potential of −0.85 V for *trans*-**1**,[18] it can be estimated that the exciplex state lies between the singlet and triplet of **1** for quenchers having oxidation potentials between 1.38 and 2.72 V. For the non-halogen-containing quenchers having oxidation potentials in this range, efficient deactivation of the exciplex must occur by paths bypassing the triplet of **1**, even though its formation should be energetically favorable. For the haloaromatics, intersystem crossing is evidently rendered rapid enough to compete with the normal deactivating paths. Thus the "round-about" route from localized singlet to D^+A^- exciplex to localized triplet results in enhanced triplet yields for these systems.[26]

It would be anticipated from the above discussion that for quenchers having oxidation potentials below 1.38 V the localized triplet of **1*** should lie above the exciplex and that intersystem crossing via the exciplex should not be a favored process. Examination of the data in Table II suggests that this may be the case with *p*-bromoanisole and other good electron donors as quenchers. For example, it can be noted that acenaphthene has an oxidation potential of 1.30 V, such that the charge-transfer state should lie approximately 1.8 kcal/mol below the triplet of **1**. Since *p*-bromoanisole and *p*-methylanisole have Stern–Volmer slopes nearly identical with that of acenaphthene, it does not seem unreasonable that for these quenchers, too, the exciplex state should lie below the isolated triplet of **1**. This could, then, be the explanation for the lack of induced isomerization in **1** when *p*-bromoanisole is used as a quencher.

In summary the results of this study indicate that the external heavy-atom effect for these systems operates via an exciplex in which two distinct processes are important. The actual quenching is governed largely by electron donor–acceptor interactions in which the heavy atom plays no role other than to influence the oxidation potential. However, once the exciplex is formed, the heavy atom can operate to induce triplet formation in a process that is evidently rapid enough to dominate all other normal paths for exciplex decay. The results are especially interesting for these systems in that what is probably the normal, though non-emissive, D^+A^- exciplex intervenes between localized excited singlet and triplet states of the substrate. It is not unreasonable to expect that this type of phenomenon should be a general one which could operate for a wide variety of other systems.

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(25) As pointed out earlier[1] steady-state kinetics lead to limiting values of k_q^{obsd} given by

$$k_q^{\text{obsd}} = \frac{k_q(k_c + k_d)}{k_{-q} + (k_c + k_d)} \tag{11}$$

$$\text{where } (k_c + k_d) \gg k_{-q} \qquad k_q^{\text{obsd}} = k_q \tag{12}$$

$$\text{where } (k_c + k_d) \ll k_{-q} \qquad k_q^{\text{obsd}} = K_q(k_c + k_d) \tag{13}$$

Since the k_q^{obsd} values are all within an order of magnitude of diffusion controlled and the differing rates of the exciplex appear to little affect the values of k_q^{obsd}, it appears reasonable that eq 12 applies and thus that the quenching is essentially irreversible.

(26) For some of the quenchers, most notably biphenyl, benzonitrile, and acenaphthene (triplet energies, respectively, 69.8, 76.8, and 59.2 kcal/mol[27]), the quencher triplet lies below the excited singlet of **1**. For these exciplexes formation of A^{3*} should be possible; however, in each case rapid energy transfer to generate $\mathbf{1}^{3*}$ (which evidently does not occur) might be expected.

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Gas-Phase Reactivity of Alkenes Toward Methylmercury Cation

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Abstract: The gas-phase reactivity of the electrophilic methylmercury cation towards a series of alkenes has been determined by ion cyclotron resonance spectroscopy. The rate of mercurinium ion formation was established to increase with increasing methyl substitution on the double bond.

The nature of the intermediates involved in the reaction of alkenes with electrophilic species is of considerable interest to the physical organic chemist. The origin of the differences in the rate of formation and the stability of these complexes with increasing alkyl substitution on the carbon-carbon double bond continues to be a vexing problem. In general, a composite of electronic, steric, and strain effects has been invoked in explanation of the various reactivity trends. On the basis of frontier orbital concepts, an increase in the number of alkyl substituents will increase the energy of the highest occupied molecular orbital (HOMO), thereby increasing the reactivity of the nucleophilic π molecular orbital (MO) toward a specific electron acceptor. An opposing effect resulting from increased alkyl substitution is the increase in steric interactions with the electrophile. The relationship of alkene reactivity to molecular parameters such as ionization potential (energy of HOMO) and steric effects are further complicated by solvation phenomena. Solvation energies are often sufficiently large to render a study of subtle changes in these innate properties untenable. Thus, an unambiguous separation of these rate influencing factors is very difficult and still remains an unsettled question. Recently, gas-phase studies[1] on the acidity of molecules have amply demonstrated the discrepancies between gas-phase and solution behavior.

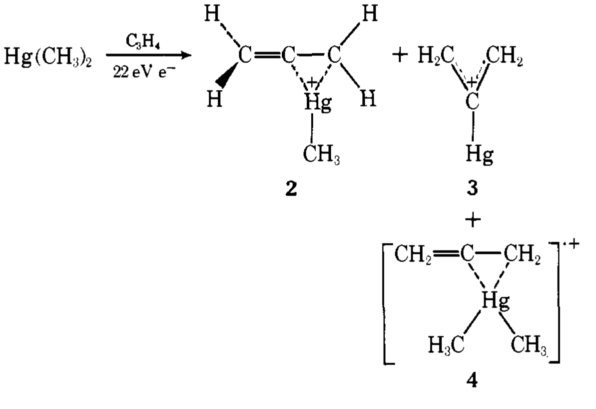
In continuing our mechanistic studies on the oxymercuration reaction, it became clear that data on this electrophilic addition reaction in the gas phase would provide information pertaining to our solution studies[2] and our theoretical investigations[3] of the nature of mercurinium ion intermediates. Although mercurinium ions have been postulated as intermediates in the oxymercuration of alkenes for many years,[4] unequivocal evidence for their existence under actual reaction conditions has not appeared. Olah and Clifford[5] recently reported the first observation of a long-lived mercurinium ion in magic acid solution. They established that these metal-alkene π complexes were stable at temperatures below 243 K.

The use of ion cyclotron resonance (ICR) spectroscopy for the study of ion-molecule reactions of heavy metals has not been employed extensively. Foster and Beauchamp[6] have reported gas-phase reactions of $Fe(CO)_5$ and Dunbar and coworkers[7] have described their experimental results on lead, nickel, and chromium derivatives. In a preliminary account we reported[8a] the first observation of the stable mercurinium ion **1** in the gas phase derived from the ion-molecule reaction of methylmercury cation with ethylene (eq 1). We have also

$$CH_3Hg^+ + CH_2{=}CH_2 \longrightarrow H_2C{=}CH_2\text{–}Hg^+\text{–}CH_3 \tag{1}$$

1

reported a similar observation of a mercurinium ion derived from the reaction of CH_3Hg^+ with allene[8b] (eq 2). The product



2 **3** **4**