a gas phase, or in a hydrophobic environment, the two reaction mechanisms would be equally possible and that in the stepwise reaction, although the first step would be slower, both steps affect the overall rate.

The results of the parallel MNDO calculations given in Table VI show that excellent agreement in both ΔS and thermal energies with those calculated by the ab initio method. These results also favor a stepwise reaction, with the second step rate determining. However, all the activation energies calculated with MNDO are much higher than with the ab initio method. Overestimation of the activation energy by MNDO is due mainly to the lack of direct incorporation of correlation effects. The consequence of this lack is reflected in the fact that the relative enthalpy of the intermediate suggests that it is more stable than the reactant, a result also obtained from the Hartree–Fock calculations with a small basis set.

Conclusions

Several conclusions can be drawn from this study.

(1) Stepwise and concerted reaction mechanisms of amide bond formation have been characterized which involve simultaneous nucleophilic attack of the amine on the carboxyl carbon atom and transfer of a hydrogen atom to an oxygen atom. In both the gas phase and hydrophobic environments, both the stepwise and concerted reaction mechanisms for amide bond formation would be equally competitive, with the former predicted to be slightly favored by both MNDO and a higher level of ab initio calculations. For the stepwise mechanism the first step, reactant to intermediate, is slower than the second step, intermediate to product, due mainly to the entropy contribution to the free energy of activation. However, the activation energy of the second step relative to the reactant is predicted to be slightly higher than that of the first step by both MNDO and a higher level of ab initio calculations, indicating that the overall rate-determining step for this mechanism is affected by both steps. The intermediate is found to be less stable than the reactant.

(2) Entropy contributions to free energy are much greater than thermal energy contributions. MNDO and ab initio calculations of entropy and of thermal energy are in excellent agreement with each other, but MNDO yields much higher activation energies. Neglect of correlation effect in MNDO seems to be primarily responsible for the calculated high activation energies.

(3) Correlation effects and p polarization functions lower the activation energies which are raised by d polarization functions. The total effect of correlation and polarization is to lower the activation energies by 4.0–5.4 kcal/mol; nearly equal values are calculated for each of the three transition states of interest. Therefore, the relative order of free energies of activation predicted at the highest level of theory used here is the same as that predicted by the HF/3-21G or HF/6-31G level of calculations, i.e., $\Delta G_2^* < \Delta G_1^* < \Delta G_3^*$.

(4) STO-3G optimized structures used for single-point calculations of activation energies at higher levels of theory yield results qualitatively identical with those from the four highest level calculations.

In subsequent studies we plan to further characterize peptide bond formation between amino acids and to investigate the role of acid–base catalysis and divalent metal ions in this process, using STO-3G optimized structures and single-point energy calculations at higher levels of theory.

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Registry No. Ammonia, 7664-41-7; formic acid, 64-18-6; formamide, 75-12-7.

Structural Effects on Twisted Olefin Triplet Lifetimes. Styrene Derivatives

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Abstract: The triplet lifetimes in methanol of a series of anisylalkenes and anisylcycloalkenes, including several phenyl analogues, have been determined by nanosecond flash kinetic absorption spectrophotometry with nitrogen laser excitation. Electron-transfer scavenging by paraquat dication, PQ^{2+}, (methyl viologen) afforded the readily detectable reduced species $PQ^{+}\cdot$. Both triplet lifetimes and rate constants for electron transfer from triplet to PQ^{2+} were determined. The results indicate that acyclic styrene triplets prefer the twisted, "1,2-biradical" structure. Lifetimes are increased by vinyl deuteration, by increasing alkylation, and by constraint within a small ring; in the absence of geometric constraints, the dominant influence on the triplet lifetimes is the extent of substitution at the double bond. Mechanisms for intersystem crossing are discussed, and the tentative conclusion is reached that nuclear motions are important.

Despite their central importance in a variety of photochemical reactions and their interest in both experimental and theoretical photophysical studies,[1] olefin triplets in fluid solution have until the relatively recent advent of nanosecond laser flash photolysis techniques been difficult to detect. Interception of stilbene triplets by azulene,[2] di-*tert*-butyl nitroxide,[3] and oxygen[4] in steady-state experiments was reported some years ago, but determination of lifetimes from such studies was subject to assumption of the relevant rate constant in each case. These studies were further complicated by the planar-twisted ($^3t \rightleftarrows {}^3p$) equilibrium for

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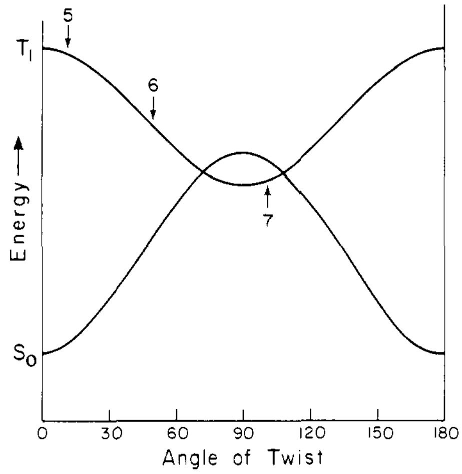

Figure 1. Schematic potential energy surface for S_0 and T_1 states of simple olefins as a function of twist angle. Arrows indicate maximum twist (estimated from Dreiding models) accessible to cycloalkenes of the stated ring size (see text).

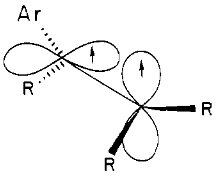

Figure 2. Structure of the perpendicular triplet.

stilbene[2,5] and substituted stilbene[6,7] triplets.

Unconjugated olefin triplets are expected, on good theoretical grounds,[8] to be twisted at equilibrium to the "perpendicular" conformation. Bonneau[9] has noted that styrene triplets also are expected to be twisted at their relaxed geometries. As Figure 1 shows, the energy of the ground (S_1) state is expected to approach that of the first triplet (T_1) state and probably exceed it at the perpendicular geometry. Figure 2 sketches the perpendicular geometry.

When two states approach one another in energy in an excited species, the possibility of rapid interconversion exists. Current theory, most cogently elaborated by Michl,[10] describes most photochemical processes as including a surface-hopping internal conversion step at just such a point. The products of the reaction are likely determined by the geometries at which such "funnels" occur, by the shapes of the surfaces near such geometries, and by dynamics of the molecule on the surfaces. These geometries are termed "biradicaloid", including as a subset the (1,*n*)-biradicals familiar in organic photochemistry.

Triplet species pose no exception to the general concepts above. It was suggested early on[2] that $T_1 \rightarrow S_0$ interconversion was greatly accelerated by the molecular facility to approach such geometries; what has been difficult to assess is by how much. Lifetime measurements for triplet species at or near biradicaloid geometries have been hampered by the facts that, at such geometries, the strong optical absorption (the kinetic probe *par excellence* for short-lived transients) is often at inconveniently short wavelength. Recent progress has been made in detecting perpendicular olefin triplet transients, notably by Bonneau,[9,11] Görner and Schulte-Frohlinde,[12] and Gorman and co-workers.[13]

Olefin triplets are effectively "1,2-biradicals". They serve as the prototypical system for a large number of potential photochemical triplet processes. The general absence of knowledge of the structural factors influencing the rates of $T_1 \rightarrow S_0$ interconversion at triplet biradicaloid geometries prompted us to search for experimental techniques which would facilitate measurement of these rates for olefin triplets, since the information so gained will afford general insight into intersystem crossing in triplet biradicaloid species. Following Scaiano's[14] use of methyl viologen (paraquat dication, PQ^{2+}) as an electron-transfer scavenger for Norrish II biradicals, we initially examined the anethole (*p*-methoxy-*β*-methylstyrene) triplet in methanol by the same technique.[15a] This paper presents the extension of that study to include structural variants of the basic styrene chromophore.[15b] Our key conclusions are: that styrene triplets are essentially perpendicular; that vinyl deuterium, alkyl substitution, and constraint within a small ring all increase the lifetime; and that vinyl hydrogen apparently is important in enhancing the rate of the $T_1 \rightarrow S_0$ process.

Experimental Section

Preparation of Materials. Solvents were MCB Omnisolv and were used as received. **Paraquat dichloride**, obtained from Aldrich Chemical Co., was either used as received or was recrystallized several times from methanol, with no detectable difference in results. **Alkenes** were synthesized by appropriate Grignard reactions and dehydration of the secondary or tertiary alcohols so obtained. All products showed the expected IR and NMR spectra and were demonstrated by gas chromatography to be 97–99.5$^+$% pure. A typical preparation is described below.

Preparation of 1-Anisylcyclohexene. To 1.44 g (0.06 g-atom) of Mg under nitrogen in a flamed 3-L flask was added 30 mL of dry ether. A total of 0.06 mol of 4-bromoanisole (Aldrich) was used, a few percent added directly at the start and the remainder added dropwise in 70 mL of ether to maintain ebullition. The solution was stirred for 30 min after the cessation of ebullition, and 0.05 mol of distilled cyclohexanone was added dropwise in 50 mL of ether. After 30 min of stirring, 25 mL of saturated aqueous NH_4Cl was added slowly, and stirring was continued for 15 min. The ether layer was decanted, the solid residue washed with more ether, and the solvent evaporated.

The crude alcohol (7 g) was refluxed for 1 h with 0.35 g of TsOH in purified benzene (110 mL) using a Dean-Stark trap. The reaction mixture was filtered by suction through $NaHCO_3$ and dried over anhydrous $MgSO_4$, the solvent evaporated, and the product distilled, bp 170 °C (17 torr), purity 97% by GC, yield 63%.

Other alkenes were prepared similarly, except as noted below, affording the following boiling points, overall yields, and purities by GC: *p*-methoxystyrene, $NaBH_4$ reduction of *p*-$CH_3OC_6H_4COCH_3$ followed by dehydration with TsCl in pyridine, 95–105 °C (20 torr), 48%, >99%; *p*-methoxy-*α*-methylstyrene (2-anisylpropene), 78–80 °C (2 torr), 12%, 97%; 3-(*p*-methoxyphenyl)-2-pentene, 86 °C (4 torr), 35% as equal mixture of *E* and *Z* isomers, >99%; *p*-methoxy-*β*,*β*-dimethylstyrene, 118 °C (17 torr), 38%, 97%; *p*-methoxy-*α*,*β*,*β*-trimethylstyrene, 124 °C (18 torr), 73%, 99%; 1-anisylcycloheptene, 116–117 °C (2 torr), 60%, 97%; 1-anisylcyclopentene, mp 83–84 °C (from hexane), 30%, >99%; *β*,*β*-dimethylstyrene, 38–40 °C (3 torr), 51%, 99%; 1-phenylcyclohexene, 59–60 °C (3 torr), 61%, 99%; 1-phenylcyclopentene, 69–71 °C (3 torr), 74%, 99.5%. For acyclic arylalkenes, the benzaldehyde or acetophenone was used with the appropriate aliphatic Grignard reagent. For arylcycloalkenes, the cyclic ketone and the arylmagnesium bromide were used. For anisylcyclopentene, phenylcyclohexene, phenylcyclopentene, and *p*-methoxy-*α*,*β*,*β*-trimethylstyrene, the crude dehydration product was passed through silica gel and/or basic alumina before distillation or crystallization. In some cases, crude alcohol gave poor results, and the alcohol was then distilled before dehydration. Anethole and *β*-methylstyrene were obtained commercially (Aldrich) and distilled under vacuum before use.

***trans*-Anethole-*α*,*β*-d_2** was prepared from *p*-methoxypropiophenone (Aldrich). Three sequential exchanges with Et_3N and D_2O (2–3 days reflux, partitioning between hexane and 10% HCl, washing, drying, and vacuum distilling) provided material in which the *α* hydrogen of the ketone was undetectable (≤5%) by NMR. The ketone (5 g) was added

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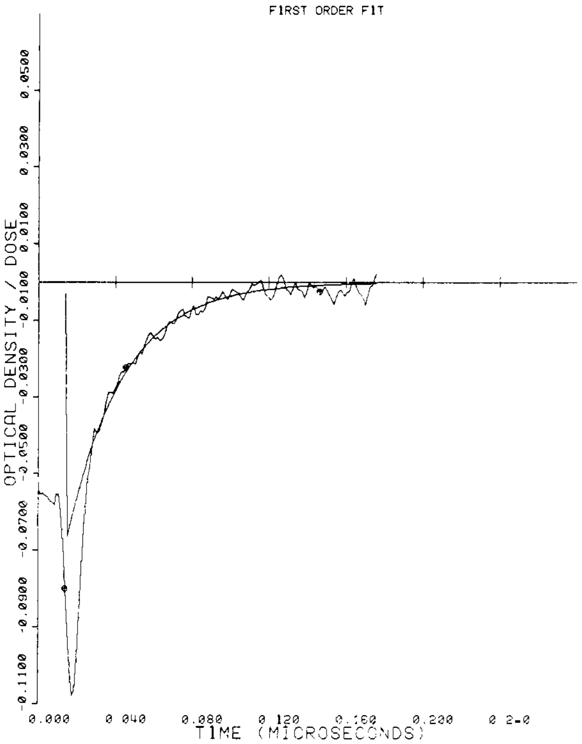

Figure 3. Temporal profile of the absorbance at 600 nm due to $PQ^{+\cdot}$ derived from reaction of PQ^{2+} with anisylcycloheptene triplet. $[Ph_2CO] = 0.068 M$, $[PQ^{2+}] = 3.1 \times 10^{-3}$ M, [anisylcycloheptene] = 0.07 M.

dropwise in 150 mL of dry ether to 50 mL of dry ether containing 1 g of $LiAlD_4$, and the reaction mixture was stirred for 30 min. About 150 mL of saturated aqueous NH_4Cl was added, the mixture filtered, and the residue washed with more ether; the combined ether layers were dried and distilled, affording the trideuterated carbinol (76%, bp 101–102 °C (2 torr). The trideuterated carbinol (1.5 g), 20 mL of dry pyridine, and 2 g of TsCl were refluxed overnight. After concentration, the reaction mixture was partitioned between 50 mL of saturated NaCl and 100 mL of ether, and the ether layer was washed further with water and distilled. The product (bp 81–82 °C (2 torr), 67%) showed negligible vinyl hydrogen in the NMR and was homogeneous to GC.

Kinetic studies were conducted at the Center for Fast Kinetics Research at the University of Texas at Austin using techniques previously described.[15,16] Deaeration of a solution (methanol unless otherwise noted) containing benzophenone (typically ca. 0.07 M) and the alkene (0.03–0.2 M) was effected by bubbling dry nitrogen through a syringe needle into the 10 × 5 mm quartz cuvette, which was fitted with a Teflon stopper containing a second aperture. A concentrated solution of paraquat (PQ^{2+}) dichloride in methanol was added via a microliter syringe through the second aperture, the constant nitrogen stream assuring outgassing and mixing of the sample. Pure methanol was added as needed to maintain the sample volume (±5%). Samples required only ca. 1 min of degassing to obtain lifetimes up to 1 μs.

Samples so purged were subjected to several (3–10) nitrogen laser pulses, the resultant temporal traces (Tektronix R7912 transient digitizer) at 395 or 600 nm (absorption maxima for reduced paraquat cation)[14] were averaged, and the averaged trace was analyzed by an iterative nonlinear least-squares curve-fitting procedure.[16b] In a number of cases a fast fluorescence interfered at earlier times, and only the last two-thirds (approximately) of the trace could be fit with a single exponential rise for reduced paraquat cation ($PQ^{+\cdot}$).

A series of such analyses following addition of aliquots of PQ^{2+} afforded the concentration dependence of k_{rise}, the first-order rate constant which fits the temporal profile.

Experiments with anisylcyclopentene and anisylcyclohexene used the 266-nm fourth harmonic of a Nd-YAG Q-switched laser, ca. 50–80 mJ/pulse, defocused and attenuated as necessary to minimize two-photon and higher order processes. Pulse-to-pulse reproducibility was ±5%. The software for data analysis has been described elsewhere.[16b]

Charge-transfer spectra for the complexes between paraquat and selected alkenes were measured in methanol in a 0.097-cm path length cuvette, improving substantially on an earlier measurement[15a] using a 1-cm cuvette. The path length was determined by comparison of the absorbance of a solution of anthracene in toluene with that of a 10-fold diluted sample in a 1-cm cuvette. Spectra were taken on a Cary 219 spectrophotometer at ambient temperature.

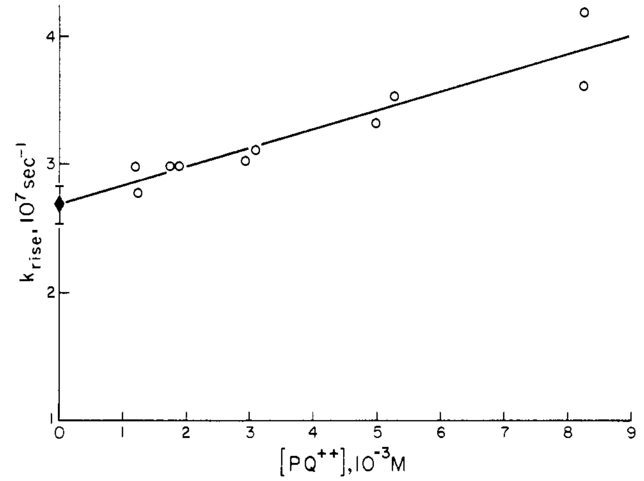

Figure 4. Plot of k_{rise} vs. $[PQ^{2+}]$ for anisylcycloheptene triplet. Error bar on intercept (♦) is twice its standard deviation.

Results

Figure 3 shows the temporal profile of the absorbance A of a sample from anisylcycloheptene and the best fit to a single exponential rise $A(t) = A_0 \exp(-k_{rise}t)$. Ignoring the fast fluorescence, the fit is good. The results are similar for the arylcyclohexenes and disubstituted styrenes. The acyclic di- and trimethylstyrenes showed a fast component at high $[PQ^{2+}]$ which increased relative to the exponential rise as $[PQ^{2+}]$ increased, sometimes approaching half the total signal. We presume that this rise resulted from direct photolysis of PQ^{2+} ($\epsilon \sim 10$ at 337 nm) or, more likely, of a PQ^{2+}–olefin charge-transfer complex (vide infra).

Figure 4 shows a plot of k_{rise} vs. $[PQ^{2+}]$ for anisylcycloheptene. Other plots are similar.

Analysis. We have previously[15a] shown that, for *trans*-anethole, the mechanism in eq 1–4 is the source of the transient $PQ^{+\cdot}$ when

$$Ph_2CO \xrightarrow{3371\ \text{Å}} {}^3Ph_2CO \tag{1}$$

$${}^3Ph_2CO + \text{olefin} \rightarrow Ph_2CO + {}^3(\text{olefin}) \tag{2}$$

$${}^3(\text{olefin}) + PQ^{2+} \xrightarrow{k_{PQ}} {}^2(\text{olefin})^{+\cdot} + {}^2PQ^{+\cdot} \tag{3}$$

$${}^3(\text{olefin}) \xrightarrow{\tau^{-1}} \text{olefin } (S_0) \tag{4}$$

Ph_2CO is the absorbing species. This mechanism leads trivially to eq 5. Justification for this mechanism followed from observations that (a) the trans–cis olefin isomerization quantum yield in methanol, sensitized by benzophenone, was expected for a triplet excitation transfer mechanism; (b) known ground-state redox parameters and a reasonable[17] estimate (2.6 ev) for the anethole triplet excitation energy predicted quite exothermic electron transfer, leading to a high expected rate constant k_{PQ} in eq 3; (c) the olefin concentration was maintained high enough to cause quantitative (>98%) quenching of $^3Ph_2CO$, thus eliminating $Ph_2\dot{C}OH$ (derived from H-atom transfer from the methanol solvent) as a source of reductant; and (d) the lifetime τ of the transient which reduced PQ^{2+} was much too long to permit assignment as $^3Ph_2CO$,[18] which is expected to show a $\lesssim$6-ns lifetime

$$k_{rise} = \tau^{-1} + k_{PQ}[PQ^{2+}] \tag{5}$$

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Table I. Lifetimes and k_{PQ} Values for Triplets

compound[a]	τ, ns[e]	k_{PQ}, 10^9 M^{-1} s^{-1} [e]
$AnCH{=}CH_2$	22 ± 1	1.1 ± 0.6
$AnCH{=}CHCH_3$[b]	30 ± 2	4.8 ± 0.7
$AnCD{=}CDCH_3$[b]	34 ± 1.5	4.1 ± 0.5
$AnC(CH_3){=}CH_2$	31 ± 3.5	1.64 ± 0.37
$AnCH{=}CHCH_2Ph$[b,c]	34 ± 3	3.1 ± 0.4
$AnC(C_2H_5){=}CHCH_3$[d]	38 ± 4	0.35 ± 0.05
$AnCH{=}C(CH_3)_2$	48 ± 5 (46.5[g])	1.2 ± 0.34 (1.4[g])
$AnC(CH_3){=}C(CH_3)_2$	91 ± 9 (89[g])	1.4 ± 0.34 (1.0[g])
1-anisylcycloheptene	37 ± 2	1.44 ± 0.36
1-anisylcyclohexene	68 ± 7	2.26 ± 0.31
1-anisylcyclopentene	29 000 ± 4000[f]	6 ± 1
$PhCH{=}CHCH_3$[b]	46 ± 2	0.65 ± 0.04
$PhCH{=}C(CH_3)_2$	78 ± 4	0.33 ± 0.4
$PhCH{=}CHCH_2Ph$[b,c]	33	1.3
1-phenylcyclohexene	56 ± 4	1.4 ± 0.2
1-phenylcyclopentene	15 000 ± 1000[f]	4.5 ± 1

[a] An = anisyl = *p*-methoxyphenyl. [b] Trans isomer. [c] Prepared by Dr. K. Mizuno by hydrogenation of *p*-methoxychalcone, reduction to the carbinol ($NaBH_4$), and dehydration with TsCl in pyridine. [d] Mixture of *E* and *Z* isomers. [e] Errors taken as twice the standard deviations of slopes and (reciprocal) intercepts of plots of eq 5 in text. [f] Obtained by direct observation of T–T absorption and of delayed fluorescence. See text. [g] Xanthone sensitization. Other values by benzophenone sensitization. Nd-YAG laser used in these two cases.

even at the lowest olefin concentrations.

In the other cases, we did not investiate the products of quenching of $^3Ph_2CO$ by olefin but assumed that eq 2 dominated. We did verify that $Ph_2COH\cdot$ (λ_{max} 550 nm) was undetectable (except as noted below) in the quenching of $^3Ph_2CO$ by the olefins. This is the expected product of either electron or H-atom transfer to $^3Ph_2CO$ from olefin. Since all olefins are styrene derivatives ($E_T \lesssim 60$ kcal/mol),[17] these processes are the only ones we can envision as even potentially fast enough to compete with eq 2. As the anisylalkenes and anisylcycloalkenes should have redox properties rather similar to *trans*-anethole, we feel that the electron transfer should be fast in these cases also; this is borne out by the values obtained for k_{PQ} in these cases (vide infra). All phenyl compounds afford values of k_{PQ} which are reasonable when compared to the corresponding anisyl compound, suggesting that the same kinetic scheme holds. We take as further confirmation the fact that our τ value for triplet phenylcyclohexene closely matches one in the literature.[9]

Lifetimes and Rate Constants. Values for τ^{-1} and k_{PQ} were determined as the linear regression parameters for fits to eq 5. When $k_{rise}(\max) \gtrsim 1.5k_{rise}(\min)$, good fits were obtained ($r > 0.95$, generally $\gtrsim 0.98$). In the alternative, low values of r presaged rather inaccurate values of k_{PQ}, but this does not affect τ significantly. We have determined the standard deviations of τ and k_{PQ} by the conventional procedure.[19] Values of τ and k_{PQ} with twice their standard errors are given in Table I.

Anisylcyclopentene and Phenylcyclopentene. The lifetimes of anisylcyclopentene and phenylcyclopentene are too long to determine readily by the paraquat technique. Rise profiles for PQ^{2+} absorption were not always simple first order, and first-order rate constants were not reproducible. At the laser intensities required, transient–transient interactions occur on the time scale of a very few microseconds, and such behavior obviates simple kinetic analysis. Phenomena which may be involved on this time scale include triplet–triplet annihilation, triplet quenching by $PQ^{+}\cdot$, and formation of $PQ^{+}\cdot$ by oxidation of secondary products (e.g., radicals) as well as the triplet.

Direct irradiation and subsequent intersystem crossing gave more satisfactory results. Excitation at 266 nm of 10^{-4}–10^{-3} M methanol solutions of phenylcyclopentene and 1.5–6×10^{-4} M solutions of anisylcyclopentene by a Q-switched Nd-YAG laser (10–30 mJ in <25 ns) afforded transients which both showed delayed fluorescence[20] and transient absorption. Agitation by N_2 bubbling and changing of the solution at least every 30 pulses assured that stable products did not accumulate in the excited volume. Both delayed fluorescence and transient absorption are totally eliminated in the presence of 0.05 M isoprene, showing that both are triplet derived. Radicals or strained isomers[21] should not afford delayed fluorescence. The prompt and delayed fluorescence spectra of phenylcyclopentene (λ_{max} 320 nm) and anisylcyclopentene (λ_{max} 340 nm) were in satisfactory agreement. This fact and the decay kinetics support the assignment of the absorbing transients as the triplet arylcyclopentenes, which are the precursors of P-type (T–T annihilation) delayed fluorescence.

The rate constant for first-order decay of P-type delayed fluorescence (DF) should be just twice the rate of triplet decay, since the fluorescence signal is proportional to $[\exp(-t/\tau)]^2 = \exp(-2t/\tau)$. The absorbing transients were recorded following subtraction of the fluorescence signal observed in the absence of the monitoring lamp. Their spectra showed λ_{max} 315–320 nm for phenylcyclopentene and 335–340 nm for anisylcyclopentene. Decay of either absorption was first order after a few microseconds, and in no case was significant deviation from first order behavior observed after 20 μs. While some of the early deviation might be due to the intervention of second-order behavior, some is probably due to pulse-to-pulse variations which affect the subtractions. Triplet lifetimes are consistent between the two techniques, which afford lifetimes (μs) for triplet phenylcyclopentene as 17 ± 7 (absoption) and 15 ± 1 (DF) and for triplet anisylcyclopentene as 33 ± 7 (absorption) and 25 ± 5 (DF), respectively. Best values are thus 15 ± 1 μs (phenylcyclopentene) and 29 ± 4 μs (anisylcyclopentene).

These are the longest lifetimes we have encountered. Whether they are intrinsic or whether they result from quenching by residual O_2 or by other impurities is not yet certain.

Charge-Transfer Complexes. With the anisylalkenes, the more concentrated solutions used in the kinetic studies were yellow, owing to the absorption of a complex between PQ^{2+} and the olefin. We studied the *trans*-anethole–PQ^{2+} complex (λ_{max} 420 nm) and the *p*-methoxytrimethylstyrene complex (no λ_{max}; only end absorption) to determine K_{eq} and ϵ, and to see whether absorption of light by the complexes is a serious interference.

Benesi–Hildebrand studies[22] required ca. 0.05 M PQ^{2+}, 0.2–2 M olefin, and a short (0.097 cm) pathlength cell due to the low K_{eq} values. For PQ^{2+}–*trans*-anethole, $K_{eq} = 0.36 \pm 0.10$ M^{-1}, $\epsilon^{337} = 520$ M^{-1} cm^{-1}, and $\epsilon^{420}(\lambda_{max}) = 330$ M^{-1} cm^{-1}. For PQ^{2+}–anisyltrimethylethylene, $K_{eq} = 0.34 \pm 0.12$ M^{-1} and $\epsilon^{337} = 410$ M^{-1} cm^{-1} (no λ_{max}).

From these parameters we calculate absorbances at 337 nm, 0.01 M PQ^{2+}, and 0.15 M olefin (typically the maximum concentrations employed) as only 0.27 and 0.21 cm^{-1}, respectively. Absorbances at 337 nm due to Ph_2CO were maintained about 10 cm^{-1}, and consequently the complexes absorb only about 2–3% of the light. While this is quite small, it can account for the fast rise observed with the di- and trimethylstyrenes. Irradiation of the PQ^{2+}–*trans*-anethole complex produced a modest, temporally flat absorption with a rise time of the order of the laser pulse width, which is not intense enough to be seen in competition with the anethole triplet derived $PQ^{+}\cdot$ signal.[15a] We have analyzed the cases in which a fast component appears on the basis that the fast rise is from the complex and is not related to the slow rise from the triplet. The consistency of k_{rise} at lower $[PQ^{2+}]$, where no fast component appears, with k_{rise} for the slow component at the higher $[PQ^{2+}]$ values is evident from the good fits of the type of Figure 4. This consistency supports our analysis.

Studies of *p*-Methoxytrimethylstyrene at 353 nm. In view of the importance of this compound to our conclusions, we repeated

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[20] Parker, C. A., *Adv. Photochem.* **1964**, *2*, 305. Parker, C. A.; Hatchard, C. G. *Proc. R. Soc. London*, **1962**, *Ser. A 269*, 574.

[21] Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329–4330.

[22] See Foster, R. "Organic Charge Transfer Complexes"; Academic Press: New York, 1969.

our first series of experiments with a recently acquired Q-switched Nd–YAG laser. Excitation in the third harmonic (353 nm) was at a wavelength at which PQ^{2+} is transparent and at which the extinction coefficient of the CT complex is approximately half the value that it has at 337 nm. The laser is much more stable (±1% estimated pulse-to-pulse energy reproducibility) and much more powerful; we attenuated to about 10 mJ/pulse. Under these conditions, the fast rise was no longer observed with *p*-methoxytrimethylstyrene, consistent with assignment of the fast rise to excitation of either PQ^{2+} or the CT complex in the 337-nm experiments.

The improved signal-to-noise revealed the presence of a small amount of $Ph_2\dot{C}OH$ formed by the quenching of $^3Ph_2CO$ with *p*-methoxytrimethylstyrene. The yield is about 11% of the yield of $Ph_2\dot{C}OH$ from the reaction of $^3Ph_2CO$ with CH_3OH, based on optical density at 550 nm. This behavior was not observed with the N_2 laser with any of the other olefins. We examined *p*-methoxy-β,β-dimethylstyrene with the Q-switched laser and observed no $Ph_2\dot{C}OH$ within the detection limit ($<10^{-3}$ OD, <3% yield).

The $PQ^{+}\cdot$ signal from *p*-methoxytrimethylstyrene at 600 nm affords the rise from the olefin triplet for the first 500 ns followed by an even slower one for several microseconds at $[PQ^{2+}] < 10^{-3}$ M. Above 10^{-3} M, the latter behavior becomes a decay. We attribute the very slow rise to the reaction of PQ^{2+} with $Ph_2\dot{C}OH$, for which we independently have measured the rate constant in methanol to be 1.8×10^9 M^{-1} s^{-1}. The longer term decay is similar to that noted previously in PQ^{2+} scavenging of biradicals[14] and presumably results from the reaction of secondary products with $PQ^{+}\cdot$.

The results for Ph_2CO-sensitized production of triplet *p*-methoxytrimethylstyrene in the table are derived from analysis of the first 300 ns of the temporal absorbance profile. The correctness of these results was confirmed by the use of xanthone as sensitizer (Table I), which afforded essentially the same values. Xanthone, as a π–π^* sensitizer, is not expected to afford significant hydrogen abstraction, and the very slow rise was never observed. We also confirmed the results for *p*-methoxy-β,β-dimethylstyrene by xanthone sensitization.

Discussion

Arylalkene triplet lifetimes, except for those for the near-planar arylcyclopentenes, are ca. 20–100 ns. Other work, notably that of Bonneau[9] and Schulte-Frohlinde and co-workers,[6,7,12] reports similar values for other alkene triplets. Salem and Rowland[23] have, in fact, predicted a lifetime in the range of 100 ns for short-chain biradicals based on reasonable estimates for spin–orbit coupling matrix elements.

These lifetimes are thus in good accord with prior expectation. The present work examines detailed questions of the geometry of the triplets, the influence of structure on lifetime, and the physical mechanisms for intersystem crossing which may influence these lifetimes.

Are Styrene Triplets Twisted in the Relaxed Geometry? To assess the structural factors which influence the lifetimes of olefin triplets in their twisted geometry, it is important to determine whether the triplets are twisted or whether a planar triplet-twisted triplet equilibrium exists as for the stilbenes.[1,12] The following analysis convinces us that there is essentially no contribution of a planar triplet species to the acyclic styrene triplets.

The "azulene effect", well documented for stilbene,[1,2] is diagnostic for the presence of planar alkene triplets. It arises from preferential quenching of the trans triplet, eq 6 and 7, and is

$$^3(\text{stilbene})_{\text{trans}} \rightleftarrows {}^3(\text{stilbene})_{\text{twisted}} \qquad (6)$$

$$^3(\text{stilbene})_{\text{trans}} + \text{azulene} \rightarrow \textit{trans}\text{-stilbene} + {}^3\text{azulene} \qquad (7)$$

manifested as an increase in the trans:cis photostationary ratio in the presence of azulene. We have previously shown that there is no azulene effect for the photosensitized isomerization of β-methylstyrene.[3] The striking similarity in photosensitized isomerization behavior between stilbene and β-methylstyrene[24] would suggest an azulene effect if the β-methylstyrene triplet lifetime were long enough to permit one and if there were any significant concentration of trans triplet.

Since the lifetime we now report for triplet β-methylstyrene (46 ns) is comparable to that for triplet stilbene,[12] we can now conclude that there is no significant concentration of trans species in this case. We estimate an upper limit of 5% considering the experimental errors.

The other acyclic styrenes we have studied are mostly even less likely to exhibit planar ⇄ twisted triplet equilibria. Since additional alkyl groups will increase steric hindrance in the planar form, we anticipate that the more substituted styrenes will unquestionably be twisted. For *p*-methoxystyrene, the consonance of its triplet lifetime with extrapolation of the series of more substituted analogues suggests that its triplet too has the same twisted structure; planarity would substantially increase the lifetime. The arylcycloalkene triplets, of course, have ring constraints and presumably can only twist to the degree consistent with these constraints.

Rate Constants k_{PQ} for Electron Transfer. The rate constants k_{PQ} of eq 3 are entirely consistent with the conclusions regarding arylalkene triplet structure. Arylalkene radical cations, the initial products of one-electron transfer via eq 3, are almost certain to be planar around the double bond. If electron transfer from a putative planar triplet occurred, structural effects on k_{PQ} would be expected to be largely electronic in nature. Alkyl groups on the double bond would be expected to increase k_{PQ} much as they would be expected to decrease the ionization potential of the arylalkene. Arylcyclopentenes would be expected to show rates similar to other arylalkenes of similar substitution.

The results differ markedly from these expectations. Anisylcyclopentene shows the highest rate constant k_{PQ} of any triplet we have studied. As the possibility for twisting of the alkene triplet becomes greater in the cycloalkene series, k_{PQ} decreases. The acyclic 3-anisyl-2-pentene triplet shows a much lower rate constant despite its identical substitution pattern, a fact difficult to explain without involving its increased capacity to twist.

Examination of the effects of alkyl substitution in the acyclic styrene triplets shows a maximum for k_{PQ} for β-monomethyl case anethole. One would expect a k_{PQ} value higher than for *p*-methoxystyrene, but not higher than for the dimethyl and trimethyl cases. Again, expectations based on planar triplets are not followed.

Assuming that the relaxed geometry is twisted, however, permits ready rationalization of the k_{PQ} values so long as it is assumed that the radical cation product of eq 3 is planar. The only triplets constrained to near planarity are the arylcyclopentene triplets. For both, k_{PQ} approaches diffusion controlled. Introduction of the capability to twist by increasing the ring size without other change in substitution causes a diminution in k_{PQ}. Note the sequence: anisylcyclopentene, 6×10^9 M^{-1} s^{-1}; anisylcyclohexene, 2.3×10^9 M^{-1} s^{-1}; anisylcycloheptene, 1.4×10^9 M^{-1} s^{-1}. The twisting permits a more stable triplet which prefers to return to planarity to transfer an electron. The more twist, the farther "downhill" the triplet has gone upon relaxation and the farther it must return "uphill" in energy to participate in eq 3; cf. Figure 1.

The rate maximum for anethole triplet in the acyclic anisylalkene series follows from a blend of the electron-donating ability of the methyl groups (which explains why *p*-methoxystyrene shows a lower k_{PQ}) and the expectations of steric hindrance to planarity. Anethole and β-methylstyrene triplets in the trans-planar form show no steric hindrance to planarity. The α-methyl, dialkyl, and trialkyl analogues all exhibit steric interactions between aryl and alkyl or alkyl and alkyl substituents when the styrene chromophore is planar, and such hindrance to planarity should diminish k_{PQ}. A twisted triplet model thus predicts the decrease in k_{PQ} from

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[23] Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

[24] Caldwell, R. A.; Sovocool, G. W.; Peresie, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 1496.

anethole triplet to any of the other acyclic styrenes.

Phenylalkenes invariably show lower values of k_{PQ} compared to the corresponding anisylalkene, as expected, whether cyclic or acyclic. The difference is within experimental error for the arylcyclopentenes, for which k_{PQ} is highest. At these near-diffusion-controlled rates, the electron-transfer rate is evidently not limited by thermodynamic considerations.

Intersystem Crossing Rates at Twisted Geometries. Acyclic Styrenes. The lifetimes we report for the acyclic styrenes are thus measures of the rate of intersystem crossing at the twisted geometry, the structure of Figure 2 being applicable in the absence of ring constraints. The most striking structural effect in the acyclic cases is the effect of alkyl substitution on triplet lifetime. Note the series of triplets: *p*-methoxystyrene (22 ns), anethole (30 ns), *p*-methoxy-β,β-dimethylstyrene (48 ns), *p*-methoxy-α,β,β-trimethylstyrene (91 ns). Replacement of H on the double bond by methyl increases the lifetime monotonically and substantially. The similarity of *p*-methoxy-α-methylstyrene (31 ns) and anethole suggests that the position of substitution is less important than the number of alkyl groups. Several other compounds provide useful pairwise comparisons. Introduction of an α-ethyl group in anethole gives another trisubstituted styrene, 3-(*p*-methoxyphenyl)-2-pentene; its lifetime (38 ns) is intermediate between that of anethole and the other trisubstituted styrene above, but again shows that increasing substitution increases triplet lifetime. A remote aryl substituent makes little difference; compare 1-(*p*-methoxyphenyl)-3-phenylpropene (34 ns) to anethole.

Lifetimes of Other Twisted Triplets. A Striking Constancy. The lifetimes of twisted triplets appear sensitive to the number of substituents on the double bond and surprisingly insensitive to the nature of the substituents. Thus, for example, Bonneau's elegant study[11] of cyclohexenone triplet affords a lifetime of 30 ns; 2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene triplets have lifetimes of 32 and 45 ns, respectively;[25] and Görner's results for 1,1-diphenylethylene[26] (40 ns), perpendicular stilbene[12] (50 ns), triphenylethylene[26] (100 ns) and tetraphenylethylene[26] (175 ns) show the same trend we observe.

The latter results show about a twofold increase of the triplet lifetime per phenyl group. The presumable decrease in spin–orbit coupling with increase in average distance between the unpaired electrons[23] which would result from the increase in conjugation with each additional phenyl could have explained the effect of the phenyl groups. However, extension of this explanation to our series would require very nearly as much hyperconjugative delocalization per methyl as there is conjugative delocalization per phenyl. We find this unlikely, particularly since EPR studies of alkyl radicals (fair models for a terminus of the 1,2-biradical model for alkene triplets) suggest that the delocalization of spin density onto alkyl groups via hyperconjugation is only modest.[27]

The foregoing shows that whether alkyl, vinyl, phenyl, or carbonyl groups are adjacent to the termini, triplet lifetimes are similar. The *nature* of the substituent appears to be uncritical, but the *number* of substituents on the double bond is. This suggests that the intersystem crossing mechanism is dominated by some process (or processes) for which the presence of a substituent is more important that its nature. Since the commonality of all these substituents is that they replace hydrogen, we seek mechanisms for intersystem crossing which especially involve the vinyl hydrogens, causing a rate increase with an increase in the number of vinyl hydrogens.[28]

Deuterium Isotope Effect. Suggested Intersystem Crossing Mechanisms. The foregoing considerations led us to determine the effect of vinyl deuteration on anethole triplet lifetime, since if vinyl hydrogen were important in the decay then deuteration should alter the lifetime. Saltiel, Buu-Hoi, and co-workers[29] had previously determined that the isotope effect for bisvinyl deuteration of stilbene was $\tau(d_2)/\tau(h_2) = 1.35$. The results we have obtained are inherently less precise, but we observe an effect for anethole-α,β-d_2 of $\tau(d_2)/\tau(h_2) = 1.11 \pm 0.07$ (2σ) from the statistically derived[19a] values for $\tau^{-1}(h_2) = (3.30 \pm 0.095) \times 10^7$ s^{-1}, $\tau^{-1}(d_2) = (2.97 \pm 0.060) \times 10^7$ s^{-1} (1σ), and Student's *t* test[19] which afforded $Z = 2.90$ and $Q(Z) = 0.0019$. The isotope effect is thus significant at the 99% confidence level. Since Saltiel and Buu-Hoi have also shown that the same isotope effect results for stilbene-d_{12} as for stilbene-α,β-d_2, the vinyl hydrogens are clearly implicated in the decay in that case.[29] Our results suggest the same for anethole.

There are two possible explanations for the isotope effects. First, there may be contribution from Franck–Condon factors to the decay. This is well known in the radiationless decay rates of arene triplets,[30] with effects (per deuterium) of 1.15–1.25 being typical. The value for the anethole triplet is somewhat smaller and that for stilbene is in this range. Theory[30] for such Franck-Condon factors suggests that the effect should decrease with decreasing S_0–T_1 energy gap, which in the twisted triplets is vanishingly small compared to the 30–80 kcal/mol in the planar arenes. However, the theory applies only to small distortions or displacements of the relevant oscillators and assumes very similar excited- and ground-state geometries; twisted olefin triplets will therefore not be well described.

The second possibility is equally interesting, that the nuclear motions can be ascribed a more active role in the decay. Shaik and Epiotis[31] have discussed the ways in which nuclear motions can induce spin–orbit coupling in other triplet-state photoreactions. That substantial torsional excursions of the groups on the double bond are required to convert relaxed T_1 to relaxed S_0, and that such excursions will be greatest for the lightest atoms, immediately suggest that this possibility can explain *both the isotope effects and the effect of alkyl substituent.*

While a rigorous distinction of these two interpretations of the isotope effects is not now possible, we tentatively favor the latter.[32] The former implies the involvement of separable electronic and Franck-Condon contributions to the lifetime and does not suggest the apparent insensitivity to electronic factors. The latter suggests substantial dominance of nuclear motions over other factors in determining lifetimes and thus seems better in accord with the data. Further studies of substituent effects, particularly of potential dipolar effects,[23] are required.

Cyclic Arylalkene Triplets. The lifetimes of alkene triplets will be sensitive to constraints which affect the capability of the triplet to twist about the double bond. Inability to access the perpendicular conformation should prevent the near-degeneracy of S_0 and T_1 of Figure 1 and also should decrease spin–orbit coupling by maintaining the unpaired electrons in nonperpendicular orbitals. To determine the magnitude of such effects, we prepared a series of arylcycloalkenes and measured the triplet lifetimes.

The arylcycloalkenes in Table I all have on hydrogen, one aryl, and two alkyl groups on the double bond, so that the effects of substitution should be constant. We compared these compounds to an identically substituted acyclic styrene derivative, 3-anisyl-2-pentene. This compound, according to GC and NMR, was clearly a mixture of *E* and *Z* isomers, but, since either isomer would give the same twisted triplet, we neither required nor attempted a separation.

The triplet lifetime for 1-anisylcycloheptene (37 ns) is nearly identical with that for 3-anisyl-2-pentene. The seven-membered ring apparently introduces essentially no hindrance to twisting.

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[25] Caldwell, R. A.; Singh, M. *J. Am. Chem. Soc.*, in press. Gorman et al.[13a] find 73 and ~50 ns by two different pulse radiolysis experiments for dimethylhexadiene.

[26] Görner, H. *J. Phys. Chem.* **1982**, *86*, 2028–2035. We thank D. Görner for a preprint.

[27] See Symons, M. "Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy"; Wiley: New York, 1968; p 41 ff.

[28] Interestingly and parenthetically, our data coupled with that of Görner[26] extrapolates to a lifetime of ca. 10 ns for ethylene triplet itself. To our knowledge, there are as yet no experimental determinations of this lifetime.

[29] Saltiel, J.; D'Agostino, J.; Herkstroeter, W. G.; Saint-Ruf, G.; Buu-Hoi, N. P. *J. Am. Chem. Soc.* **1973**, *95*, 2543.

[30] Siebrand, W. *J. Chem. Phys.* **1967**, *46*, 440. Siebrand, W. *Ibid.* **1967**, *47*, 2411.

[31] (a) Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18. (b) Shaik, S. *Ibid.* **1979**, *101*, 2736, 3184.

[32] We point out that Saltiel et al.'s suggestion[29] based only on the isotope effects was the same.

Dreiding models of the cycloheptene can access twist angles for the sp^2 carbons of the triplet in excess of 90°. The models thus confirm that the hindrance to twisting is minimal.

For 1-anisylcyclohexene (68 ns) and 1-phenylcyclohexene (56 ns) the somewhat longer lifetime suggests a moderate hindrance to twisting, confirmed by the observation of a maximum twist angle of 50–55° for the Dreiding model.

The much longer lifetimes for the arylcyclopentenes are similarly consistent qualitatively with the nearly negligible capacity to twist, as expected a priori. Dreiding models suggest a maximum twist of 10–15°.

We conclude that the effect of ring size is easily understood on the basis of constraint to twisting. In view of the general similarity for the seven-membered ring compound to the acyclic triplet lifetime model, we suggest that its lifetime is determined purely by intersystem crossing at the twisted geometry as for the acyclics. For the six- and five-membered ring compounds, the longer lifetimes may result from an energy barrier to reaching a more fully twisted geometry,[33] from a decrease in spin–orbit coupling at the relaxed geometry of the triplet, or a combination of the two.

Our value for phenylcyclohexene triplet lifetime is in perfect consonance with the value reported by Bonneau,[9] but the previous study[33] of phenylcycloalkene triplet lifetimes afforded much longer values than those we report. Since that work involved steady-state studies with unavoidable assumptions, and since the two independent flash kinetic studies agree for phenylcyclohexene, we believe that the flash kinetic lifetimes are the correct ones. Phenylcyclopentene is a possible exception since we cannot rule out the possibility of impurity control in our case.

Summary

We have determined the lifetimes of a series of arylalkene and aryycycloalkene triplets and have discussed possible origins for the effects of degree of substitution, deuterium substitution, and ring size on those lifetimes. To us, the most interesting extrapolation of the present results is the possible role of nuclear motions in govening intersystem crossing rates in triplet biradicaloid species. Further work is planned to examine this hypothesis, since its correctness would have rather general implications for triplet-state photochemistry.

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Registry No. $\mathrm{AnCH{=}CH_2}$, 637-69-4; (E)-$\mathrm{AnCH{=}CHCH_3}$, 4180-23-8; (E)-$\mathrm{AnCD{=}CDCH_3}$, 78180-80-0; $\mathrm{AnC(CH_3){=}CH_2}$, 1712-69-2; ($E$)-$\mathrm{AnCH{=}CHCH_2Ph}$, 35856-81-6; ($E$)-$\mathrm{AnC(C_2H_5){=}CHCH_3}$, 18421-23-3; ($Z$)-$\mathrm{AnC(C_2H_5){=}CHCH_3}$, 18322-83-3; $\mathrm{AnCH{=}C(CH_3)_2}$, 877-99-6; $\mathrm{AnC(CH_3){=}C(CH_3)_2}$, 13399-33-2; ($E$)-$\mathrm{PhCH{=}CHCH_3}$, 873-66-5; $\mathrm{PhCH{=}C(CH_3)_2}$, 768-49-0; ($E$)-$\mathrm{PhCH{=}CHCH_2Ph}$, 3412-44-0; $\mathrm{PQ^{2+}}$, 4685-14-7; $\mathrm{PQ^{2+}}$-*trans*-anethole, 83214-30-6; $\mathrm{PQ^{2+}}$-anisyltrimethylethylene, 83208-00-8; 1-anisylcycloheptene, 32960-45-5; 1-anisylcyclohexene, 20758-60-5; 1-anisylcyclopentene, 709-12-6; 1-phenylcyclohexene, 771-98-2; 1-phenylcyclopentene, 825-54-7; deuterium, 7782-39-0.

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Fourier Transform Infrared Matrix Spectra of Substituted Alkene–Hydrogen Fluoride Complexes

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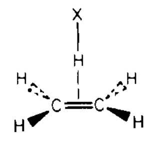
Abstract: FT IR matrix spectroscopy has been used to characterize hydrogen-bonded complexes prepared by condensing argon-diluted samples of substituted alkenes and hydrogen fluoride. The ν_s and ν_l modes for methyl-substituted alkenes indicate stronger hydrogen bonding than with ethylene, and the observation of only perturbed out-of-plane $\mathrm{C{-}H_2}$ modes shows that H–F is perpendicular to the molecular plane in these π complexes. The vinyl fluoride (VF) complex exhibits a weaker hydrogen bond, perturbed in-plane and out-of-plane bending modes, and a displaced C–F stretching mode, which suggest a σ complex with H–F attached to fluorine at an acute angle with the molecular plane.

Introduction

There has been a considerable amount of recent research activity on hydrogen-bonded π complexes of ethylenes or acetylene and hydrogen halides.[1-5] Infrared matrix-isolation[1,2] and microwave[5] spectra have been interpreted to indicate an out-of-plane alkene π complex (Chart I) with the acid perpendicular to the plane of the alkene. Earlier workers reported complexes of HI and substituted alkenes in matrix-isolation experiments.[6-8] The out-of-plane $\mathrm{CH_2}$ wagging modes of the alkene were particularly sensitive to perturbation by the HX ligand, which provided evidence for an out-of-plane π complex.[1,2,7] A complex involving three molecules of HCl and one propylene (PR) molecule has been

Chart I



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