of these related chromophores are in progress and will be reported in due course.

Registry No. 1a, 45358-43-8; (1*R*,2*R*)-**1b**, 123620-68-8; (1*R*,2*R*)-**1c**, 123620-69-9; (2′*S*)-**1d**, 138385-63-4; (2′*S*)-**1e**, 138385-64-5; (2′*S*)-**2a**, 138385-65-6; (α*S*)-**2b**, 138385-67-8; (2′*S*)-**3a**, 138385-68-9; (5*S*)-**3b**, 138385-69-0; (*S*)-**4**, 138385-70-3; (2*S*)-**5**, 123557-05-1; TABH, 126503-75-1; SBD, 138385-66-7; H_2NOSO_3H, 2950-43-8; (*S*)-(+)-2-methylbutyryl chloride, 27763-54-8; aziridine, 151-56-4; 2,2-dimethylaziridine, 2658-24-4; 3,3-dimethyldiaziridine, 4901-76-2; acetone, 67-64-1; dimethylamine, 124-40-3; (3*S*)-(−)-3-methylcyclohexanone, 24965-87-5.

Conformationally Dependent Heavy Atom Effect of Chlorine on Alkene Triplet Lifetimes. Experimental and ab Initio Calculations

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Contribution from the Chemistry Program, BE 26, The University of Texas at Dallas, Richardson, Texas 75083-0688, and Calspan Advanced Technology Center, Buffalo, New York 14225. Received June 27, 1991

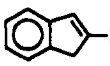
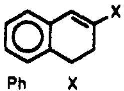
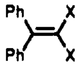
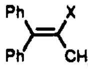
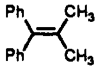
Abstract: The heavy atom effect of vinyl Cl in enhancing ISC rates of arylalkene triplets is shown to be much greater for substrates which can access nonplanar conformations. The experimental results are consistent with ab initio calculations of spin–orbit coupling.

Atoms of relatively high atomic number, when present in a molecule or in a solvent, cause enhanced rates of singlet–triplet or triplet–singlet intersystem crossing (ISC). This "heavy atom effect" is well understood to arise from an increase in spin–orbit coupling (SOC).[4] We now report that effects from the presence of chlorine on olefinic bonds in molecules which are not constrained to planarity are far larger than those for classic spectroscopic examples. SOC calculations on vinyl chloride provide a satisfactory rationale for this unexpected observation.

Table I presents triplet state lifetimes, obtained by kinetic absorption spectroscopy in the presence of benzophenone, *p*-methoxyacetophenone, or thioxanthone as photosensitizers, by techniques we have previously used.[5,6] We have determined the lifetime of at least one nonchlorinated model for each chlorine-containing arylalkene, and we presume that geometric constraints when present are unaffected by the presence or absence of the chlorine. All chlorine-containing compounds could be recovered satisfactorily from prolonged preparative scale irradiation in the presence of the same photosensitizers, showing that C–Cl bond cleavage is not significant. Indene and 1,2-dihydronaphthalene underwent photodimerization, and in these two cases a modest extrapolation of measured lifetimes to low concentration was required.

The lifetimes of triplets containing the styrene chromophore without heavy atoms are long (microseconds) when the chromophore is held planar by ring constraints and short (20–100 ns) when the chromophore can approach the energetically preferred perpendicular structure,[6,7] consistent with the expected effects of the diminished T_1–S_0 gap and much-increased spin–orbit coupling in nonplanar configurations of the ethylenic moiety.[8] In the present work the chlorine is always in the β position of an arylethylene chromophore, and the variation in the restriction to planarity among the compounds in Table I allows an examination of the geometric dependence of enhancement of ISC due to heavy atom induced SOC.

Table I. Lifetimes of Arylalkene Triplets with and without Chlorine Substituents

triplet	lifetime,[a] ns	
	X = H	X = Cl
	1400	1300
	6800	14
	38 (38[b])	(<1.5[b])
	(51[b])	(<1.5[b])
	113	

[a] In heptane, room temperature, except as noted. Precision ±5%. [b] In benzene.

For the rigidly planar indene/2-chloroindene pair the effect of chlorine is clearly negligible. The somewhat more flexible but still near-planar pair 1,2-dihydronaphthalene/3-chloro-1,2-dihydronaphthalene can twist modestly toward the perpendicular minimum expected for the styrene chromophore. In this pair an enormous enhancement of ISC by chlorine results. For 2-chloro-1,1-diphenylpropene and 2,2-dichloro-1,1-diphenylethylene, the perpendicular minimum can be attained since there are no

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0002-7863/92/1514-1623$03.00/0

Table II. T_1–S_0 Spin–Orbit Coupling (cm^{-1}) Calculated for Ethylene, Propene, and Vinyl Chloride

geometry	ethylene	propene	vinyl chloride
planar	8.25×10^{-7}	2.93×10^{-3}	6.28×10^{-4}
planar but X 15° out of plane	0.28		3.87
planar but H cis to X 15° out of plane	0.28		0.987
15° twist	0.27	0.26	5.10
30° twist	0.49	0.47	8.79
45° twist	0.61	0.59	10.58
60° twist	0.59	0.58	10.00
75° twist	0.39	0.39	6.55
90° twist	1.48×10^{-6}	1.20×10^{-3}	0.20
planar but CHX pyramidalized 15°	0.53	0.61	4.52
planar but CH_2 pyramidalized 15°	0.53	0.53	1.31
90° twist, CHX pyramidalized 15°	.034	.043	.909
90° twist, CH_2 pyramidalized 15° away from X	.034	.033	.103
90° twist, CH_2 pyramidalized 15° toward X	.034	.037	.279

ring constraints. For each, the lifetime was too short to be observed. No signal other than the decay of sensitizer triplet at the rate expected from the separately determined bimolecular quenching rate constants was observed even at 320–340 nm, where the maximum T–T absorption for the 1,1-diphenylalkene chromophore occurs. Since perpendicular triplets exhibit a dependence of lifetime on the degree of substitution at the double bond,[6,7] all three hydrocarbon analogues 1,1-diphenylethylene and its 2-methyl and 2,2-dimethyl derivatives are reported for comparison. Regardless of the comparison compound chosen, the immeasurably short lifetimes of the chlorodiphenylethylene triplets require substantial *minimum* ISC rate enhancements.

The best-known quantitative studies of heavy atom effects are on halogen-substituted aromatic hydrocarbons, for which S_1–T_1 and T_1–S_0 radiationless rates are enhanced by halogens.[4] For naphthalene (0.39 s^{-1}), 1-chloronaphthalene (2.35 s^{-1}), 1-bromonaphthalene (36.5 s^{-1}), and 1-iodonaphthalene (310 s^{-1}) the rate of the radiationless T_1–S_0 process increases regularly in order of atomic number.[9] Chandra et al. reported distance and overlap dependent perturbation of phosphorescence lifetimes of benzo- and naphthonorbornenes when remotely brominated.[10] The largest effects were about two orders of magnitude for a single bromine, and chlorine would be expected to show a far smaller effect based on atomic ζ values.[11] Heavy atom effects on short-lived transients in organic photochemistry[12] generally are small, cf. observations on Norrish II biradicals with *p*-bromo- or *p*-chlorophenyl vs phenyl substituents.[13] The large effects we report here are unprecedented.

We accordingly undertook a study of SOC, the presumed dominant factor in ISC of alkene triplets,[5] in vinyl chloride as a model compound, using the CAS-MCSCF technique[14,15] as previously applied to ethylene.[8] Ab initio calculations of a heavy atom effect on SOC are rare and those of direct relevance to the present problem nonexistent. Calculated SOC constants for NH and PH ($X^3\Sigma^- - b^1\Sigma^+$) are ca. 115–120 and 283–285 cm^{-1}, respectively.[14,16] Bond lengths were the following: C–C(vinyl), 1.48 Å;[8] C–H, 1.08 Å; C–methyl, 1.50 Å; C–Cl, 1.73 Å. All bond angles were taken as 120°. With 2-in-2 CAS and with the 3-21G basis set, the SOC results of Table II were obtained. Results for ethylene and propene are included for comparison. Propene was studied to determine whether the replacement of H by a non heavy atom substituent affected SOC significantly. As the table shows, replacement of H by the CH_3 group causes no significant change in SOC. The effect of Cl, however, is universally large.

According to Fermi's Golden Rule, radiationless rates should exhibit a quadratic dependence on the matrix elements connecting final to initial states. SOC values we calculate for vinyl chloride relative to ethylene predict the effects of Cl, albeit only semiquantitatively. We consider first the planar arenes, which exhibit SOC dominated by out-of-plane (pyramidalization) modes.[17] SOC is minimal for all three alkenes when planar. Pyramidalization in our calculations affords $[H_{SO}(Cl)/H_{SO}(H)]^2 \sim 6$–$70$, where H_{SO}(Cl or H) stands for the value of $\langle\Psi(T_1)|H_{spin-orbit}|\Psi(S_0)\rangle$ for vinyl chloride or ethylene, respectively. Bending only the Cl (H) out of plane to the same angle affords 191, and bending the H cis to Cl out of plane affords 12. The 6-fold enhancement in ISC of 1-chloronaphthalene relative to naphthalene is smaller than these values, but should have been so since (a) the influence of the Cl on a larger chromophore should have been diluted [note that the Hückel coefficients of the HOMO and LUMO at the position bearing the Cl in naphthalene (0.425) are substantially smaller than those in ethylene (0.707); the impact of the heavy atom on the chromophore should be larger when the coefficients at the adjacent C are larger, since the odd-electron density at that position is controlled by these coefficients] and (b) the heavier Cl could in its out-of-plane vibration have its turning point at a smaller angle that that for H. The observed lifetimes for the also planar indenes may not be ISC controlled; note that the same chromophore, when held rigid in 1-phenylcyclopentene, is more than an order of magnitude longer-lived.[6,18]

For dihydronaphthalene, some twisting is possible, which will cause T_1 and S_0 to approach. Both the diminished energy gap and the increased SOC enhance ISC, and the lifetime for dihydronaphthalene itself is much shorter than that for naphthalene. Twisting 15 or 30° produces $[H_{SO}(Cl)/H_{SO}(H)]^2$ values of 360 or 325. The Hückel HOMO and LUMO coefficients again can measure odd-electron density simply.[19] For the β position of twisted styrene, they are somewhat dependent on twist angle, being 86% of the ethylene value for 15° twist 89% of the ethylene value for 30° twist, and approaching the value for ethylene as a limit as the twist angle approaches 90°. The value of $[H_{SO}(Cl)/H_{SO}(H)]^2$ in twisted ethylene should by this model be a close upper limit to that to be expected for a twisted styrene, even for small twist angles. The rate enhancement of 3-chloro-1,2-dihydronaphthalene is 480 relative to 1,2-dihydronaphthalene. We consider this good agreement although it is somewhat larger than predicted.

The ISC in perpendicular ethylene depends on excursions away from perfect perpendicularity.[8] The $[H_{SO}(Cl)/H_{SO}(H)]^2$ value for 75° twist is 282 and that for pyramidalization in the optimum mode is 67. These cannot be compared quantitatively with ex-

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(18) We have determined that the lifetime can approach 100 μs in glycerol and is still not ISC controlled.

(19) Although we have emphasized the role of interaction of the heavy atom through the carbon to which it is directly bonded, in nonplanar configurations we cannot rule out 1,3 interactions of the chlorine atom, through its lone pairs, with the other ethylenic carbon.

perimental values for the perpendicular haloalkene triplets since only minimum ISC rates could be obtained; however, the prediction as well is clearly for lifetimes shorter than our observation limit.

These results show that heavy atom effects of chlorine can be far larger than previously reported and highlight the role of nonplanar geometries in the enhancement of SOC even for heavy atoms. The range of possible analogous effects on biradicals and the magnitude of effects due to other third-row elements are under study.

Acknowledgment. We thank the National Science Foundation for financial support (Grants 8516534 and 8820268). Flash kinetics were performed at The Center for Fast Kinetics Research at The University of Texas at Austin, supported by NIH Grant RR-00886.

Registry No. $(Ph)_2C{=}CH_2$, 530-48-3; $(Ph)_2C{=}C(Cl)_2$, 2779-69-3; $(Ph)_2C{=}CHCH_3$, 778-66-5; $(Ph)_2C{=}C(Cl)CH_3$, 781-34-0; $(Ph)_2C{=}C(CH_3)_2$, 781-33-9; $ClCH{=}CH_2$, 75-01-4; 1*H*-indene, 95-13-6; 2-chloro-1*H*-indene, 18427-72-0; 1,2-dihydronaphthalene, 447-53-0; 3-chloro-1,2-dihydronaphthalene, 138384-40-4.

The Photochemistry of Transition Metal Hydrides: A CASSCF/CCI Study of the Photodissociation of $HMn(CO)_5$

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Abstract: The photodissociation of $HMn(CO)_5$ has been studied through contracted configuration interaction calculations of the potential energy surfaces for the metal–hydrogen bond homolysis and the dissociation of the carbonyl ligand. The corresponding potential energy curves connect the ground and excited states of the reactant to the ground and excited states of the primary products. The calculations were carried out under C_{4v} constraint with a basis set that is at least of double-ζ quality. The multireference CCI calculations that correlate the 3d electrons and the two of the Mn–H bond were based on a unique CASSCF wave function with eight electrons in nine active orbitals ($3d_{xy}$, $3d_{\pi}$, σ_{Mn-H}, σ^*_{Mn-H}, $3d_{x^2-y^2}$, $4d_{xy}$, $4d_{\pi}$) optimized for the $^5A_2$ state, the principal cnfiguration being $(3d_{xy})^2(3d_{\pi})^2(\sigma)^2(\sigma^*)^1(3d_{x^2-y^2})^1$. It is proposed that excitation of $HMn(CO)_5$ at 193 nm will bring the molecule from the ground state a^1A_1 into the c^1E $d \rightarrow \pi^*$ excited state. From there, after intersystem crossing to the b^3A_1 at a Mn–H distance of about 1.7 Å and internal conversion into the a^3A_1 $\sigma \rightarrow \sigma^*$ state, the molecule will dissociate along the a^3A_1 potential energy curve to the products H and $Mn(CO)_5$ in their ground state. Irradiation of $HMn(CO)_5$ at 229 nm will bring the molecule into the b^1E state $d_{\pi} \rightarrow \sigma^*$. Then the system goes down along the b^1E potential energy curve corresponding to the Mn–CO elongation until it reaches a potential well. From there after internal conversion to the a^1E state the molecule will dissociate along the corresponding potential energy curve to the products CO and $HMn(CO)_4$ in the a^1E excited state with the fragment $HMn(CO)_4$ as a square pyramid with H apical. The main reasons responsible for the different behavior, upon irradiation, of the two hydrides $HCo(CO)_4$ and $HMn(CO)_5$ are outlined on the basis of these results.

Introduction

The photoreactivity of transition metal hydrides was mainly used to generate very active intermediates with a role in many catalytic processes and chemical reactions.[1] Monohydride complexes were shown to undergo a variety of photochemical reactions with experimental evidence obtained for both the homolysis of the metal–hydrogen bond[2–4] and the photoinduced ligand dissociation,[5–10] the latter being the dominant process. In spite of the intense experimental activity developed in this field during the last decade, mainly due to the improvement of new identification techniques, the mechanism of the primary photochemical reaction is partially understood and the nature of the photoactive excited states responsible for the photodissociation pathways is uncertained.

The first theoretical analysis of the photochemical reactions for organometallics[11] was based on molecular orbital diagrams. More recently, the use of state correlation diagrams,[12–16] potential energy surfaces (PES), or the more readily visualized potential energy curves (PEC)[17–23] has enabled us to get a better under-

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