

has also been proposed²⁰); our finding that photoreaction 2 can be efficiently quenched by addition of diphenylisbenzofuran (DPBF), a well-established singlet oxygen scavenger,²¹ concurrent with its photobleaching supports a mechanism whereby the reaction is initiated by reaction between singlet oxygen and amine as outlined in eq 3-10.²² From Scheme I the quantum yield of benzaldehyde from **1** or **2** can be derived (eq 11), where the "donor" amino alcohol is "Q":

$$\Phi_{\text{benzaldehyde}} = 2\alpha\beta \left(\frac{\gamma k_5[\text{Q}]}{k_5[\text{Q}] + k_6} \right) \left(\frac{k_7}{k_7 + k_8} \right) \quad (11)$$

Since α and β are expected to be fairly large,²³ the overall low efficiency is attributable to low values for either or both of the last two terms in eq 11. A plot of $1/\Phi_{\text{benzaldehyde}}$ vs $1/[\text{2}]$ is linear with a slope of 1050 and an intercept of 300 (cc = 0.99). The low limiting quantum efficiency of ca. 3.3×10^{-3} suggests that either the fraction of singlet oxygen quenching by **2** (γ) leading to electron transfer (eq 5) or the fraction of ion radical pairs fragmenting or both are low. The intercept/slope = $k_6/k_5 = 0.29$; since $k_6 = 4 \times 10^4$ in benzene,²⁴ an estimate can be made that $k_5 = 1.4 \times 10^5 \text{ m}^{-1} \text{ s}^{-1}$.²⁵ From the oxidation potentials for **1** (1.105 V) and **2** (0.98 V) it is reasonable that quenching of singlet oxygen (reduction potential = 0.67 V²⁶) should be moderately endothermic (by 7 kcal for **2**); the estimated value for k_5 could reasonably be interpreted as having both electron transfer (γ) and other $(1 - \gamma)$ quenching components.^{25,27} Since superoxide is indicated to be quite basic²⁸ and the radical ion pair decay (eq 8) by back electron transfer is spin-restricted, it is reasonable to expect the last component of eq 11 to be large. Back electron transfer (eq 8) from the geminate triplet ion-radical pair (eq 8) could be slow compared to diffusive separation; reencounters would not be likely due to the low light intensities involved, and radical ions of amines **1-3** escaping the caged pair can undergo unassisted fragmentation, albeit slowly.²⁹ Thus, in contrast to the fragmentation process observed with excited acceptors such as TI, β -lapachone, or cyanoaromatics with **1** and **2**,⁹⁻¹² in the singlet oxygen mediated reaction the limiting factor appears to be the rate and extent of electron-transfer quenching.

The roles of singlet oxygen as an electron acceptor and subsequent source of superoxide are certainly consistent with the reactivity of the activated oxygen species in other reactions. Nonetheless, this appears to be a new and previously unrecognized reaction path for net photosensitized oxidation by molecular oxygen. Interestingly, this reaction path is one which may play a role of some prominence in naturally occurring or induced photodynamic action, in that this reaction is possible for a number of natural amino alcohols. For example, we find *N*-methylphenedrine (**3**) (0.1 M) cleaves according to eq 1 and 2; with RB

an efficiency ($\Phi_{\text{benzaldehyde}} = 2 \times 10^{-5}$) comparable to that measured for **1** and **2** is observed. Since reactions analogous to eq 1 for 1,2-diamines and other structurally related donors with lower oxidation potentials than **1-3** have been observed,³⁰ it is reasonable to anticipate that many more examples of this type of oxidative fragmentation may be encountered in further investigations.

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Why Is the π Bond in Tetrafluoroethylene Weaker Than That in Ethylene? An ab Initio Investigation

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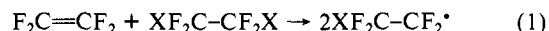
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Addition reactions to the π bond in tetrafluoroethylene are 10-16 kcal/mol more exothermic than the corresponding reactions of ethylene.¹ Wu and Rodgers have measured a value of 52 ± 2 kcal/mol for the π bond dissociation energy in tetrafluoroethylene,² which is about 12 kcal/mol less than the 64³-65⁶ kcal/mol π bond energy of ethylene.⁷ Thus, most, if not all, of the greater exothermicity of addition reactions to tetrafluoroethylene is attributable to the weaker π bond in this alkene. However, the mechanism by which the four fluorine substituents weaken the π bond has remained unclear.¹

In this communication we report the results of ab initio calculations of the π bond energy in tetrafluoroethylene. Our results indicate that the origin of π bond weakening in tetrafluoroethylene is the preference of fluorine-substituted radical centers for pyramidal geometries, which exacts an energetic price from the planar alkene.

One method for calculating the π bond strength in tetrafluoroethylene utilizes the definition of π bond strength proposed by Benson.⁴ This requires the energy change for the reaction

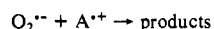
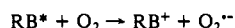


which we have computed for X = H. Dobbs and Hehre have shown that at the MP2/6-31G* level of theory this type of calculation of the π bond strength of ethylene gives a value of 67.8

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(8) Dissociation of tetrafluoroethylene to two molecules of difluoromethylene requires on the order of 100 kcal/mol less energy than dissociation of ethylene to two molecules of methylene.⁸ This very large difference in C=C dissociation energies is a consequence of the fact that, in contrast to CH₂, CF₂ has a singlet ground state and a large energy is required to promote an electron from the highest occupied σ orbital into the lowest empty π orbital.⁹

Table I. 6-31G* MP2 Energies (hartrees) Calculated at RHF and UHF Optimized Geometries

molecule	geometry	MP2 energy
CF ₂ =CF ₂	equilibrium (<i>D</i> _{2h})	-474.3367
	twisted, pyramidal (<i>C</i> ₂)	-474.2576 ^a
	twisted, one C planar (<i>C</i> _s)	-474.2453 ^a
	twisted, both C _s planar (<i>D</i> _{2d})	-474.2369 ^a
HCF ₂ -CF ₂ ·	equilibrium (<i>C</i> _s)	-474.9150
	carbon planar (<i>C</i> _s)	-474.9004
HCF ₂ -CHF ₂	equilibrium (<i>C</i> _{2h})	-475.5749

^aTriplet energy at UHF triplet geometry.

kcal/mol,¹⁰ which is in good agreement with the experimental estimates.^{3,6}

Our calculations were performed with GAUSSIAN 86,¹¹ with use of the 6-31G* basis set.¹² Geometries were optimized with SCF or UHF wave functions,¹³ and electron correlation was included in energy calculations at these geometries through the use of second-order Moller-Plesset (MP2) perturbation theory.¹⁴ The calculated energies are given in Table I and lead to a π bond energy of 51.2 kcal/mol for tetrafluoroethylene, which is in excellent agreement with the experimental value of Wu and Rodgers.¹⁵

Another definition of π bond energy is the energy required to break a π bond by rotation to the diradical transition state for cis-trans isomerization. Dobbs and Hehre have found very close agreement between the π bond energies computed in this way (e.g., 66.5 kcal/mol for ethylene) and those calculated by using Benson's definition.^{10,16} From the difference in the computed energies in Table I between planar (*D*_{2h}) tetrafluoroethylene and the twisted (*C*₂) triplet diradical,¹⁸ a value of 49.6 kcal/mol is obtained for the π bond energy.

Unlike the case in twisted ethylene, the presence of two electronegative fluorine substituents at each carbon causes the carbons to be highly pyramidalized in the twisted tetrafluoroethylene diradical.¹⁹ The pyramidalization angle between each CF₂ plane and the extension of the C-C bond is 43° in the *C*₂ diradical. As shown in Table I, going from the *C*₂ twisted diradical, where both carbons are pyramidalized, to the *D*_{2d} twisted diradical, where both carbons are planar, raises the energy by 13.0 kcal/mol. Consequently, recomputing the π bond energy of tetrafluoroethylene with the carbons in the diradical constrained to be planar gives a value of 62.6 kcal/mol, which is only slightly less than the 66.5 kcal/mol calculated for ethylene.^{10,23} Thus, our cal-

culations indicate that the energetic cost of planarizing both carbons in tetrafluoroethylene is the major factor responsible for making the π bond strength in this molecule significantly less than that in ethylene.

Another estimate of the reduction in the π bond energy of tetrafluoroethylene, due to the energetic cost of planarizing the two carbons, is provided by twice the energy of 9.2 kcal/mol that is computed to be required to planarize the radical center in HF₂C-CF₂·. Because of the differences in stereoelectronics between this monoradical and the twisted diradical, twice the energy necessary to planarize the CF₂ group in the monoradical is not the same as that required to planarize both CF₂ groups in the diradical. However, the energetic cost of 7.7 kcal/mol for planarizing just one carbon in the twisted diradical (*C*₂ → *C*_s) is much more nearly comparable to that required for the equivalent conformational change in the monoradical.

In summary, the results of our calculations indicate that the lower π bond energy of tetrafluoroethylene, compared to ethylene, is largely attributable to the cost of planarizing the two CF₂ groups.²⁴ In this sense Bennett's assertion²¹ that the difference between tetrafluoroethylene and ethylene is that the former is more strained in a planar geometry than the latter seems to have been correct.

Acknowledgment. We thank the National Science Foundation for support of this research and for partial funding of the purchase of the Convex C-2 computer on which some of these calculations were performed. We also thank the San Diego Supercomputer Center for a generous allocation of computer time.

Supplementary Material Available: SCF and UHF optimized geometries and energies for the molecules in Table I (10 pages). Ordering information is given on any current masthead page.

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Reductive Cleavage of Carbon Monoxide by Tetranuclear Tungsten Alkoxide Clusters

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We describe evidence for a general reaction leading to the cleavage of carbon monoxide and the formation of W₄(μ -C) clusters supported by alkoxide ligands.

When CO (1 equiv) is allowed to react in hydrocarbon solvents with W₂(OR)₆ (2 equiv), there is evidence for the formation of W₄(μ -C) containing compounds when R = *i*-Pr and CH₂-*t*-Bu.¹ When CO is allowed to react with W₄(OR)₁₂ compounds (R = CH₂-*c*-Bu, CH₂-*c*-Pen, CH₂-*c*-Hex, and CH₂-*i*-Pr),² there is

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(1) Note the use of dry and oxygen-free atmospheres (N₂) and solvents. The synthetic strategy implied in this sequence involves the preparation of a W₂(μ -CO) compound that then reacts further with the W≡W bond of W₂(OR)₆ as an inorganic analogue of a ketone. See: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Organometallics* **1985**, *4*, 986. Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.