has also been proposed[20]); our finding that photoreaction 2 can be efficiently quenched by addition of diphenylisobenzofuran (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":

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

Since $\alpha$ and $\beta$ 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 $1/[\mathbf{2}]$ is linear with a slope of 1050 and an intercept of 300 (cc = 0.99). The low limiting quantum efficiency of ca. $3.3 \times 10^{-3}$ suggests that either the fraction of singlet oxygen quenching by **2** ($\gamma$) 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 $k_5 = 1.4 \times 10^5$ M$^{-1}$ 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 V[26]) should be moderately endothermic (by 7 kcal for **2**); the estimated value for $k_5$ could reasonably be interpreted as having both electron transfer ($\gamma$) and other ($1 - \gamma$) quenching components.[25,27] Since superoxide is indicated to be quite basic[28] 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, $\beta$-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 occuring or induced photodynamic action, in that this reaction is possible for a number of natural amino alcohols. For example, we find *N*-methylephedrine (**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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(22) An alternative mechanism[3,26] (Rodgers, M. A. J.; Peters, J. *Biochem. Biophys. Res. Commun.* **1980**, *96*, 770) whereby the same ion-radicals reacting in eq 8 and 9 are generated by single electron transfer quenching is probably ruled out by the DPBF quenching.

$$\mathrm{RB^{*} + O_2 \rightarrow RB^{+} + O_2^{\bullet-}}$$

$$\mathrm{RB^{+} + A \rightarrow RB + A^{\bullet+}}$$

$$\mathrm{O_2^{\bullet-} + A^{\bullet+} \rightarrow products}$$

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(24) Peters, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 6759.

(25) Direct quenching of the IR luminescence of singlet oxygen by **2** in deuteromethanol has been observed; $k_q = 6.5 \times 10^6$ M$^{-1}$ s$^{-1}$, a value reasonably somewhat higher than determined by the product analysis in benzene (Oliveros, E.; Maurette, M. T.; Braun, A., private communication).

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# Why Is the $\pi$ Bond in Tetrafluoroethylene Weaker Than That in Ethylene? An ab Initio Investigation

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Addition reactions to the $\pi$ 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 $\pi$ bond dissociation energy in tetrafluoroethylene,[2] which is about 12 kcal/mol less than the 64[3]–65[6] kcal/mol $\pi$ bond energy of ethylene.[7] Thus, most, if not all, of the greater exothermicity of addition reactions to tetrafluoroethylene is attributable to the weaker $\pi$ bond in this alkene. However, the mechanism by which the four fluorine substituents weaken the $\pi$ bond has remained unclear.[1]

In this communication we report the results of ab initio calculations of the $\pi$ bond energy in tetrafluoroethylene. Our results indicate that the origin of $\pi$ 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 $\pi$ bond strength in tetrafluoroethylene utilizes the definition of $\pi$ bond strength proposed by Benson.[4] This requires the energy change for the reaction

$$\mathrm{F_2C{=}CF_2 + XF_2C{-}CF_2X \rightarrow 2XF_2C{-}CF_2^{\bullet}} \tag{1}$$

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 $\pi$ bond strength of ethylene gives a value of 67.8

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(1) Reviews: Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Part 2, pp 603–655. Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: FL, 1986; Vol. 3, pp 158–170.

(2) Wu, E. C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112.

(3) Obtained by using the definition proposed by Benson[4] and the upwardly revised value of 28.3 kcal/mol for the heat of formation of the ethyl radical.[5]

(4) Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 503. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63–65.

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(6) From the rate of cis–trans isomerization of 1,2-dideuterioethylene. Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(7) 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 $CH_2$, $CF_2$ has a singlet ground state and a large energy is required to promote an electron from the highest occupied $\sigma$ orbital into the lowest empty $\pi$ 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 ($D_{2h}$) | −474.3367 |
| | twisted, pyramidal ($C_2$) | −474.2576[a] |
| | twisted, one C planar ($C_s$) | −474.2453[a] |
| | twisted, both Cs planar ($D_{2d}$) | −474.2369[a] |
| $HCF_2\text{-}CF_2^{\bullet}$ | equilibrium ($C_s$) | −474.9150 |
| | carbon planar ($C_s$) | −474.9004 |
| $HCF_2\text{-}CHF_2$ | equilibrium ($C_{2h}$) | −475.5749 |

[a] Triplet 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 optimizied 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 $\pi$ 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 $\pi$ bond energy is the energy required to break a $\pi$ bond by rotation to the diradical transition state for cis–trans isomerization. Dobbs and Hehre have found very close agreement between the $\pi$ 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 $\pi$ 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 $CF_2$ 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 $\pi$ 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 calculations indicate that the energetic cost of planarizing both carbons in tetrafluoroethylene is the major factor responsible for making the $\pi$ bond strength in this molecule significantly less than that in ethylene.

Another estimate of the reduction in the $\pi$ 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 $HF_2C\text{-}CF_2^{\bullet}$. Because of the differences in stereoelectronics between this monoradical and the twisted diradical, twice the energy necessary to planarize the $CF_2$ group in the monoradical is not the same as that required to planarize both $CF_2$ groups in the diradical. However, the energetic cost of 7.7 kcal/mol for planarizing just one carbon in the twisted diradical ($C_2 \rightarrow C_s$) 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 $\pi$ bond energy of tetrafluoroethylene, compared to ethylene, is largely attributable to the cost of planarizing the two $CF_2$ groups.[24] In this sense Bernett's assertion[21] 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.

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**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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(16) Dobbs and Hehre[10] performed singlet UHF calculations to locate the transition states. Singlet UHF wave functions are actually mixtures of singlet and triplet spin states, but the geometries and energies of the singlet transition states and the triplet minima are quite similar for twisted $\pi$ bonds.[17]

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(18) In addition to locating the triplet UHF minimum, we also found the transition state for a pure single state,[16] by using a two-configuration (TC) SCF wave function.[13] At the latter geometry the triplet UHF energy of −473.3759 hartrees is 0.3 kcal/mol higher than at the triplet UHF minimum. The TCSCF barrier height is 50.3 kcal/mol, which again is significantly lower than the TCSCF barrier of 65.6 kcal/mol for cis–trans isomerization in ethylene.

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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 $W_4(\mu_4\text{-}C)$ clusters supported by alkoxide ligands.

When CO (1 equiv) is allowed to react in hydrocarbon solvents with $W_2(OR)_6$ (2 equiv), there is evidence for the formation of $W_4(\mu_4\text{-}C)$ containing compounds when R = *i*-Pr and $CH_2$-*t*-Bu.[1] When CO is allowed to react with $W_4(OR)_{12}$ compounds (R = $CH_2$-c-Bu, $CH_2$-c-Pen, $CH_2$-c-Hex, and $CH_2$-*i*-Pr),[2] there is

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(1) Note the use of dry and oxygen-free atmospheres ($N_2$) and solvents. The synthetic strategy implied in this sequence involves the preparation of a $W_2(\mu\text{-}CO)$ compound that then reacts further with the $W{\equiv}W$ bond of $W_2(OR)_6$ 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.

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