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Singlet Oxygen Involvement in the Photochemical Reaction of C_{60} and Amines. Synthesis of an Alkyne-Containing Fullerene

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Photochemical addition of 3-diethylamino-1-propyne (DEAP) to C_{60} leads to a novel fullerene adduct (**1**). The addition of DEAP to C_{60} did not occur in the expected [2+2] fashion. Instead, addition took place at the methylene carbons alpha to the nitrogen, resulting in the replacement of two C−H bonds with C_{60}−C bonds. This reaction provides a facile route to a fullerene adduct containing an alkyne moiety. Study of the mechanism of addition disclosed the unexpected involvement of singlet oxygen. Other previously reported additions of amines to fullerenes also appear to involve singlet oxygen.

Introduction

Singlet molecular oxygen reacts with numerous biological compounds such as nucleic acids, amino acids, lipids, sulfur-containing compounds, a variety of olefins, and other oxidizable species.[1,2] Singlet oxygen can be produced by several methods; the simplest and most common is irradiation of photosensitizers in the presence of oxygen.[2−4] Originally studied for their novelty, fullerenes have been found to be excellent sensitizers for the formation of singlet oxygen.[5] Since they are also unreactive toward singlet oxygen, they are more useful than sensitizers which photobleach readily.

Amines quench singlet oxygen through both chemical and physical pathways.[6−9] Rate constants for quenching correlate with the amine ionization potentials.[10−12] Several authors have proposed a charge-transfer interaction between amines and singlet oxygen,[8,10,13,14] and calculations have supported this conclusion.[15] Dialkylamines have also been shown to add in an unusual [3+2] reaction to fullerenes in photochemical reactions.[16−18] We now show that this reaction proceeds via singlet oxygen.

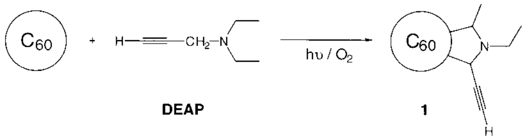
Results and Discussion

We previously reported the thermal addition of 1-diethylamino-1-propyne to fullerenes.[19] In studying the mechanism of this reaction, we investigated the reactivity of a precursor, 3-diethylamino-1-propyne (DEAP), with C_{60}. The only difference between the two compounds is the location of the triple bond; in the former it is attached to the amine, and in the latter it is isolated from the amine by a methylene group. Irradiation of C_{60} with DEAP in the presence of oxygen produced a novel acetylene-functionalized fullerene (**1**, Scheme 1).

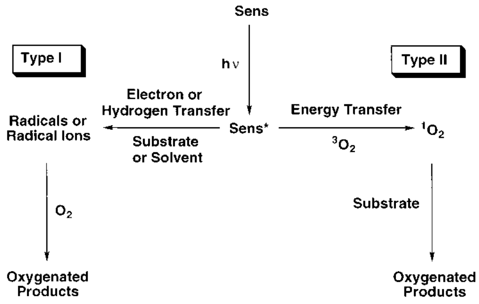
The expected photochemical [2+2] addition of the acetylene to the fullerene did not occur. Instead, two C−H bonds were replaced with two carbon−fullerene bonds. This paper describes this unexpected reaction and the involvement of singlet oxygen.

Reaction under argon led to a dramatic reduction in yield of product compared to reaction under air and no additional products, while a pure oxygen atmosphere increased the amount of product formed. No thermal reaction occurred upon refluxing the components in toluene in the dark. Since the reaction involves both oxygen and light, two competing reaction pathways are possible (Scheme 2).

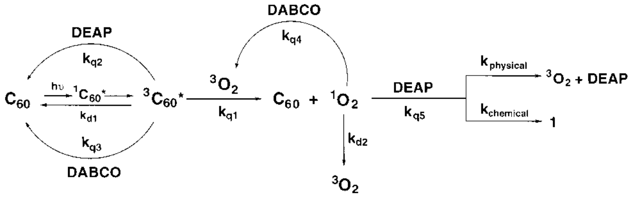
SCHEME 1



SCHEME 2



SCHEME 3



The excited sensitizer can react via a radical pathway (Type I) to give the oxidized product through electron transfer or hydrogen atom transfer. Alternatively, the sensitizer can produce singlet oxygen via energy transfer to ground state oxygen (Type II). Singlet oxygen is likely to be involved in the reaction pathway because both light and oxygen are necessary, and C_{60} is known to be an excellent photosensitizer for the formation of singlet oxygen.[5] In order to establish the mechanism, the rate constants for the overall scheme had to be determined (Scheme 3).

The rate constant for the quenching of the excited triplet state of the fullerene ($^3C_{60}$*) was determined by transient absorption techniques while the 1268 nm luminescence of singlet oxygen was used to determine the rate constant for quenching singlet

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TABLE 1: Rate Constants for the Quenching of $^3C_{60}$* and $^1O_2$ for DEAP and DABCO (in M^{-1} s^{-1})

DEAP		DABCO	
k_{q2}	2.8×10^5	k_{q3}	4.2×10^9
k_{q5}	3.4×10^7	k_{q4}	2.6×10^8 [a]

[a] From the literature.[20]

TABLE 2: Calculated and Observed Ratio for Fraction of $^1O_2$ Quenched by DEAP in Deuterium and Competition Quenching Tests

test	ratio obsd	ratio calcd
benzene-d_6/benzene (R_D)	1.8	2.0
without/with DABCO[a] ($R_O \cdot R_T$)	5.8	5.3

[a] Performed under an oxygen atmosphere.

oxygen (Table 1). The rate constant for decay of singlet oxygen, k_{d2} in C_6H_6 = 3.3×10^4 M^{-1} s^{-1} and in C_6D_6 = 1.5×10^3 M^{-1} s^{-1}, for quenching of $^3C_{60}$* by $^3O_2$, $k_{q1} = 1.9 \times 10^9$ M^{-1} s^{-1}, and the decay rate for $^3C_{60}$*, $k_{d1} = 2.5 \times 10^4$ M^{-1} s^{-1}, are available from the literature.[5,20]

Mechanistic tests were performed to determine whether this reaction is a Type I (radical) or Type II (singlet oxygen) mechanism.[21] The lifetime of singlet oxygen is dramatically affected by the solvent, being significantly longer in deuterated solvents than in their proteated counterparts.[21] Under conditions where the lifetime of singlet oxygen is dictated by the solvent, an increase in product yield on changing to a deuterated from a proteated solvent indicates the involvement of singlet oxygen. The ratio of products expected under these conditions is given by eq 1.

$$R_D = \frac{k_{q5}[\text{DEAP}] + k_{d2}(C_6H_6)}{k_{q5}[\text{DEAP}] + k_{d2}(C_6D_6)} \qquad (1)$$

In this equation, R_D is equal to the fraction of $^1O_2$ quenched by DEAP in C_6D_6 divided by the fraction of $^1O_2$ quenched in C_6H_6. The reaction of C_{60} and DEAP was enhanced in C_6D_6 as compared to C_6H_6 and the observed ratio of product **1** as determined by HPLC analysis correlated well with the ratio calculated from eq 1 (Table 2).

Another test for singlet oxygen is to monitor product formation upon addition of a molecule known to competitively quench singlet oxygen. A decrease in product indicates singlet oxygen involvement. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was chosen as the quencher because of its high rate constant for quenching and its low chemical reactivity with singlet oxygen.[9] The ratio of product formed in the absence of quencher to that in its presence, R_0, is shown in eq 2:

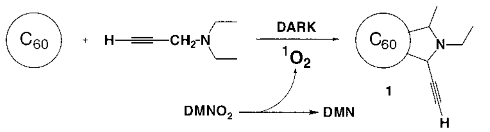
$$R_0 = 1 + \frac{k_{q4}[\text{DABCO}]}{k_{q5}[\text{DEAP}] + k_{d2}} \qquad (2)$$

The expected product ratio in the presence of versus in the absence of DABCO reaction has to be corrected for the quenching of $^3C_{60}$* by DABCO. The ratio after simplification leads to eq 3:

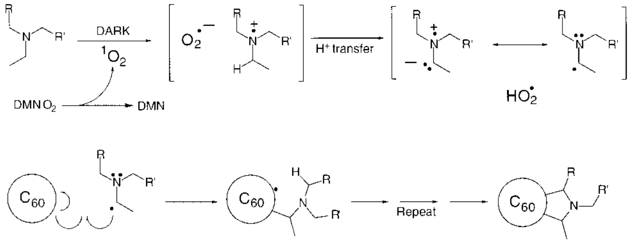
$$R_T = 1 + \frac{k_{q3}[\text{DABCO}]}{k_{q1}[^3O_2] + k_{q2}[\text{DEAP}] + k_{d1}} \qquad (3)$$

R_T is equal to the fraction of $^3C_{60}$* quenched by $^3O_2$ in the absence of DABCO over that in the presence of DABCO. In order to correct for the quenching of $^3C_{60}$*, the values obtained from eq 2 ($R_O = 4.4$) and eq 3 ($R_T = 1.2$) were multiplied to give the expected ratio, $R_O \cdot R_T = 5.3$. The observed ratio of product formation in the presence versus absence of DABCO correlated well with the expected value after correction for the quenching of $^3C_{60}$* (Table 2).

SCHEME 4



SCHEME 5



Another test to assess for the involvement of $^1O_2$ is to use singlet oxygen produced by nonphotochemical methods, such as from 1,4-dimethylnaphthalene endoperoxide ($DMNO_2$), which decomposes in solution at room temperature to give singlet oxygen and 1,4-dimethylnaphthalene (DMN).[22−24] This reaction provides a clean $^1O_2$ source that avoids any competing pathways that could result from irradiation. The reaction of C_{60} and DEAP in the presence of $DMNO_2$ in the dark led to formation of product **1**, as confirmed by HPLC analysis and ^1H NMR (Scheme 4).

The three tests described above, solvent deuterium isotope effect, competitive quenching, and formation of product by thermally generated singlet oxygen, all provide evidence in favor of singlet oxygen involvement. We conclude that singlet oxygen is a key participant in the reaction of DEAP with C_{60}, and that any mechanistic scheme must include it. A likely but not definitive mechanism involves singlet oxygen, formed via the fullerene triplet, reacting with the amine to give a radical anion/cation pair through electron transfer, as suggested by other authors for other amines and singlet oxygen reactions.[7] Deprotonation of the methylene carbon alpha to the amine cation leads to the neutral amine radical, which can react with the fullerene. Repeating this process a second time leads to the observed product (Scheme 5).

Other Amines. We explored the scope of singlet oxygen involvement with other amines known to react with C_{60}. Zhou et al. observed that glycine esters add to C_{60} upon irradiation.[25] Later, the authors found that both oxygen and light were necessary, and speculated that singlet oxygen was involved.[26] The test for singlet oxygen employed by these authors was simply exclusion of oxygen. However, this, test does not distinguish between a Type I (radical) or a Type II (singlet oxygen) pathway. The mechanism proposed was solely radical chemistry and did not involve singlet oxygen or even oxygen. The same group later proposed a mechanism in which oxygen regenerates C_{60} from the protonated C_{60} radical, but again oxygen was not involved in the formation of the product.[27]

To confirm that the reaction of the glycine ethyl ester with C_{60} was singlet oxygen based, we performed the reaction thermally under the reported conditions,[26] but in the absence of light, with $DMNO_2$ as the singlet oxygen source. These conditions resulted in the formation of a product with the identical ^{1}H NMR and ^{13}C NMR spectra to that of a control reaction irradiated with a xenon lamp. These spectra, as well as high-resolution mass spectra matched those published.[26] We conclude that singlet oxygen is involved in the reaction mechanism.

Inoue et al. discussed the photochemical reaction of morpholine and other amines with C_{60}.[30] Since these reactions resulted in products with excess oxygen as determined by elemental analysis, they performed a control reaction in the absence of oxygen. They concluded that oxygen is necessary for these reactions and proposed that the mechanism involves $C_{60}O_n$. $C_{60}O$ is reported to be formed in only 7% yield after irradiating C_{60} for 18 h,[31] whereas Inoue and co-workers report that these reactions immediately produce a brown precipitate. We propose an alternative mechanism, in which singlet oxygen is the active oxygen species. To test this theory, morpholine and C_{60} were dissolved in the presence of $DMNO_2$ in the dark. HPLC analysis showed a new peak that is absent in the control reaction in the dark without $DMNO_2$. The peak, presumably the adduct analogous to those from other amines, has the same retention time as an identical irradiated reaction.

Liou and Cheng reported the photochemical addition of dimethyl aniline (DMA) to C_{60}.[17] The mechanism put forth by these authors involves electron transfer from the amine to C_{60}. To test for singlet oxygen involvement, we again performed the reaction in the dark in the presence of $DMNO_2$. An HPLC peak with the same retention time as a product obtained from an identical solution subjected to irradiation was formed. A control kept in the dark showed no such peak.

A number of papers have reported the photochemical and thermal reaction of triethylamine (TEA) with fullerenes.[16,18,32,33] The mechanism offered for the photochemical pathway is electron transfer to the triplet fullerene.[16,18] When the reaction of TEA and C_{60} was carried out in the presence of $DMNO_2$, a brown precipitate was obtained with a new peak in the HPLC analysis. The control reaction kept in the dark without $DMNO_2$ showed only a small product peak in the HPLC analysis and no precipitate. Irradiation of an identical solution produced a peak at the same retention time and formation of a brown precipitate as reported by Ma et al.[18]

Conclusion

We report the facile synthesis of a novel fullerene derivative that has an alkyne moiety. This alkyne has the potential for further fullerene functionalizations, and perhaps even polymerization. This reaction and that of several other amines previously reported involves primary interaction of singlet oxygen with the amine followed by addition of the resulting radical to the fullerene to give a good yield of the pyrrolidine adduct.

Experimental Section

Materials. C_{60} was purchased from MER Corp.,[34] 99.5+%. All solvents were used as received from Fisher (Certified A.C.S.). HPLC analyses were carried out with a Waters 501 pump using toluene/acetonitrile (Fisher, Optima grade) 1:1 v/v, at a flow rate of 1 mL/min. A Hypersil, C_{18}, 5 micron, 250 mm, 4.6 mm i.d. column was used in conjunction with a UV detector at 340 nm. Column chromatography was performed using Silica Gel 60 (230−400 mesh) purchased from EM Science. DEAP was purchased from Fluka, methylene blue from Matheson, and 1,4-dimethylnaphthalene from Aldrich.

Methods. The transient absorption setup is similar to the one described previously.[35] The "pump" light source was a Quanta-Ray DCR-2 Nd:YAG laser, using the second harmonic (532 nm) with a pulse width of 6−7 ns. Perpendicular to this was the "probe" light source, a 75 W xenon arc lamp (Photon Technology International). After leaving the cuvette, the light was focused onto a monochromator (Jarrell-Ash, 6000 Å blaze). A photomultiplier tube (Hamamatsu R928) detector was connected to an oscilloscope (LeCroy 9410) which was in turn connected to a Macintosh IIci computer via Labview 2 software. The data were analyzed by Igor Pro 3.13 software and the observed rate constant extracted by curve fitting of the monoexponential decay. The Stern−Volmer equation gave k_t, the total (chemical and physical) quenching rate constant for the quencher.[36]

The singlet oxygen decay measurements were performed on a setup similar to that described previously.[35,37] The emission was observed perpendicular to the laser source, all wavelengths except the singlet oxygen luminescence, 1268 nm, were removed by filters, and the detector was a liquid nitrogen cooled germanium photodiode (Applied Detectors Corp. 403HS) which is sensitive in the near-infrared region.

Synthesis of Fullerene Adduct 1. In a round-bottomed flask, 97.5 mg of C_{60} was dissolved in ca. 200 mL of carbon disulfide.[38] Approximately 2 mL of 3-diethylamino-1-propyne (DEAP) was added and the solution irradiated with a 300 W xenon lamp under air-saturated conditions for approximately 1 h, upon which HPLC analysis showed the reaction had proceeded to ca. 50% completion.[39] The mixture was concentrated by rotatory evaporation and subjected to flash chromatography using carbon disulfide as the eluent. The first band to elute off the column was unreacted C_{60} followed by compound **1** as a brown band (25% yield).

^{1}H NMR 500 MHz ($CDCl_3$) d 1.55 (t, $J = 7.1$ Hz, 3H) 1.92 (d, $J = 6.3$ Hz, 3H), 2.90 (d, $J = 1.5$ Hz, 1H), 3.02 (m, 1H), 3.38 (m, 1H), 4.57 (q, $J = 6.3$ Hz, 1H), 5.71 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR 125 MHz ($CDCl_3/CS_2$) d 13.8, 17.0, 42.5, 63.8, 67.6, 72.5, 74.7, 78.9, 79.8, 136.8, 136.9, 137.1, 137.3, 139.7, 139.8, 140.0, 140.1, 141.69, 141.73, 141.8, 141.9, 142.0, 142.08, 142.10, 142.12, 142.14, 142.2, 142.3, 142.5, 142.64, 142.65, 142.7, 143.08, 143.1, 144.4, 144.5, 144.6, 144.7, 145.1, 145.2, 145.31, 145.34, 145.36, 145.4, 145.5, 145.5, 145.6, 145.7, 145.96, 145.99, 146.06, 146.1, 146.23, 146.28, 146.29, 146.31, 146.36, 146.6, 146.7, 147.3, 147.4, 153.1, 153.3, 153.7, 155.1. HRMS (FAB) calcd 830.09 (M+H) found, 830.10.

Synthesis of 1,4-Dimethylnaphthalene Endoperoxide ($DMNO_2$). The synthesis of $DMNO_2$ was accomplished by using a modified procedure described by Wasserman and Larsen.[22] Approximately 1−5 mg of methylene blue and 1 mL of DMN were dissolved in ca. 25 mL of CH_2Cl_2. The solution was immersed in an ice water bath and bubbled with O_2. Filters to absorb wavelengths below 547 nm and a water jacket were used while irradiating for approximately 5 h. The solution was then passed through a 2 cm column of silica gel (to remove methylene blue) and eluted with CH_2Cl_2. A yellowish solution was collected and concentrated by rotatory evaporation to a yellow solid. Cold hexanes were added to the solid and the suspension filtered and washed with more cold hexanes. The resulting white solid was dried by vacuum filtration (65% yield).

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR of adduct **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Benzene or toluene can be used just as effectively, avoiding the stench and flammability of carbon disulfide.

(39) The reaction is not usually carried out to completion because of diadduct formation.