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Oxygen Atom Transfer from Peroxide Intermediates to Fullerenes

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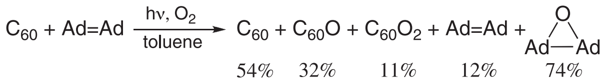
Photoreaction of C_{60} and C_{70} with adamantylideneadamantane or sulfide under oxygen flow gives fullerene epoxide together with adamantylideneadamantane epoxide or sulfoxide via peroxide intermediates.

The oxidation of C_{60} has attracted much attention since the early days of fullerene chemistry. Since that time, [6,6]-closed fullerene epoxide has been synthesized by UV irradiation in the presence of oxygen,[1] dioxirane,[2,3] *m*-chloroperoxybenzoic acid,[4] O_3,[5] a transition-metal complex of an acetylacetonates,[6] methyltrioxorhenium–H_2O_2 system,[7] and cytochrome P450 chemical models.[8] Preparation of [5,6]-open $C_{60}O$ synthesized through photolysis of fullerene ozonide, $C_{60}O_3$, has also been reported.[9] Fullerene oxide ($C_{60}O$) is regarded as a promising reagent for subsequent functionalization of fullerene.[10] The chemistry of fullerenes with active oxygen species is an important subject not only in the bioapplication of fullerene and its derivatives but also in synthetic organic chemistry. The ability of C_{60}, C_{70}, and these derivatives to convert molecular oxygen to singlet oxygen is known already.[11] These are synthetically useful photosensitizers, on a preparative scale, for photooxygenation with singlet oxygen.[12] Meanwhile, it has been known that photooxygenation of olefin and sulfide with singlet oxygen generates the corresponding peroxide intermediates, perepoxide[13] and persulfoxide,[14] respectively. These peroxide intermediates behave as nucleophilic oxidizing agents. In this context, this report describes novel oxidation of C_{60} and C_{70} with peroxide intermediates, which are produced from adamantylideneadamantane or sulfide with singlet oxygen.

In a typical experiment, a toluene solution of C_{60} (7.2 mg, 1 mM) and adamantylideneadamantane (2.7 mg, 1 mM) was photoirradiated under oxygen bubbling with a 500 W halogen lamp (Scheme 1 and Table 1). The resulting mixture was submitted to analytical GLC and MS.[20] In the ^{13}C NMR spectrum of $C_{60}O$, we observed 17 signals from nonequivalent carbon atoms in the fullerene skeleton. This result was consistent with that of reported [6,6]-$C_{60}O$. Both $C_{60}O$ and $C_{60}O_2$[4,8] were apparently produced in 32% and 11% yields, respectively, together with adamantylideneadamantane oxide (74%). The yield of $C_{60}O$ using adamantylideneadamantane is comparable to that using *m*-chloroperoxybenzoic acid and methyltrioxorhenium–H_2O_2 system.[4,7] Very similar results were also obtained with C_{70}.[15]



Scheme 1.

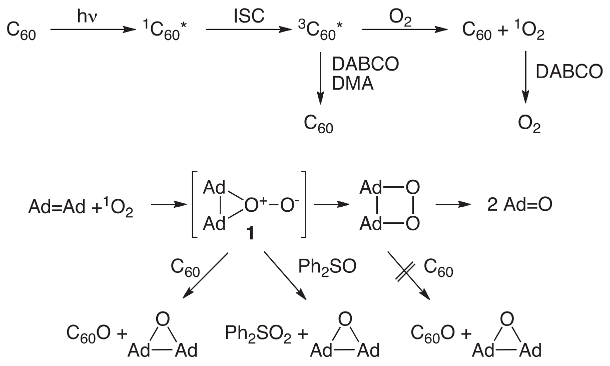
Table 1. Photoreaction of fullerene with Ad=Ad under oxygen bubbling

Run	Fullerene	Additives	Recovered fullerene /%	Fullerene oxide Mono- /%	Di- /%	Olefin /%	Epoxide /%
1	C_{60}		54	32	11	12	74
2	C_{60}	Ph_2SO (50 equiv)	87	13	0	9	66
3	C_{60}	DABCO (1 equiv)	90	9	1	88	12
4	C_{60}	DMA (1 equiv)	65	27	8	44	40
5	C_{60}	DMA (5 equiv)	97	3	0	93	5
6	C_{70}		57	31	10	11	88
7	C_{70}	Ph_2SO (50 equiv)	88	12	trace	9	85
8	C_{70}	DABCO (1 equiv)	88	12	trace	85	15
9	C_{70}	DMA (1 equiv)	71	22	7	45	55
10	C_{70}	DMA (5 equiv)	92	7	trace	77	9

To ascertain the character of the active oxidizing species, photoreaction of C_{60} under various conditions was conducted. Addition of *N*,*N*-dimethylaniline (DMA),[13b] $^3C_{60}{}^*$ quencher,[16] and also 1,4-diazabicyclo[2.2.2]octane (DABCO), which acts as a quencher of singlet oxygen[17] and $^3C_{60}{}^*$,[18] suppressed the photoreaction. Photooxidation of C_{60} in the presence of 50 equiv of diphenyl sulfoxide as a nucleophilic oxygen-atom acceptor gave adamantylideneadamantane oxide and diphenyl sulfone accompanying inhibition of the formation of $C_{60}O$.[13c] Foote et al. reported that C_{60} reacts with dimethyldioxirane to give $C_{60}O$.[2,3] When the reaction of C_{60} with the dioxetane, formed from adamantylideneadamantane with $^1O_2$, was conducted, no reaction occurred.[13] The results might be explained by a mechanism involving the perepoxide intermediate **1**, as shown in Scheme 2.[12c,13c] The reaction might be initiated by $^1O_2$ produced by energy transfer from $^3C_{60}{}^*$ to O_2. **1**, generated from $^1O_2$ and adamantylideneadamantane, oxidized C_{60} to $C_{60}O$.

Then, irradiation of a toluene solution of C_{60} (7.2 mg, 1 mM) and diethyl sulfide (45 mg, 50 mM) under oxygen bubbling using a 500 W halogen lamp was performed. The irradiation led to consumption of C_{60} and diethyl sulfide (Scheme 3 and Table 2). Apparently, $C_{60}O$ was produced in 12% yield, together with diethyl sulfoxide (41%) and diethyl sulfone (4%). Very similar results were also obtained using C_{70}.

When the photoreaction of fullerenes and diethyl sulfide under oxygen was done in the presence of DABCO[16–18] or



Scheme 2.

$$\underset{83\%}{C_{60}} \xleftarrow{} \!\!\!\! $$

$$C_{60} + Et_2S \xrightarrow[\text{toluene}]{h\nu,\ O_2} \underset{83\%}{C_{60}} + \underset{12\%}{C_{60}O} + \underset{1\%}{C_{60}O_2} + \underset{44\%}{Et_2S} + \underset{41\%}{Et_2SO} + \underset{4\%}{Et_2SO_2}$$

Scheme 3.

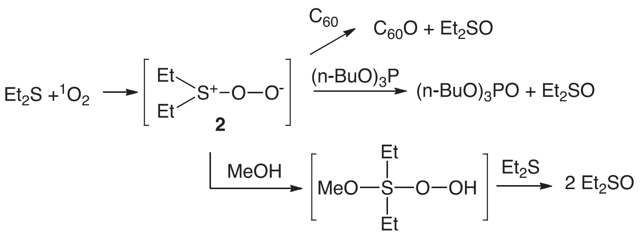
Table 2. Photoreaction of fullerene with EtSEt under oxygen bubbling

Run	Fullerene	Additives	Recovered fullerene /%	Fullerene oxide/%	Et_2S /%	Et_2SO /%	Et_2SO_2 /%
1	C_{60}		83	12	44	41	4
2	C_{60}	DMA (0.5 equiv)	94	3	71	4	0
3	C_{60}	DABCO (0.5 equiv)	96	0	90	0	0
4	C_{60}	$(BuO)_3P$ (1.8 equiv)	96	0	63	28	3
5	C_{60}	MeOH[a]	95	2	0	88	4
6	C_{70}		81	13	13	70	12
7	C_{70}	DMA (0.5 equiv)	88	6	64	14	1
8	C_{70}	DABCO (0.5 equiv)	94	0	81	0	0
9	C_{70}	MeOH[a]	92	2	0	86	2

[a] 1 mL of MeOH was added.

DMA,[13b,16] the photooxygenation was inhibited. Results of these control experiments confirm that $^1O_2$ is responsible for the production of fullerene oxides. The formation of $C_{60}O$, sulfoxide, and sulfone was suppressed by the addition of tributyl phosphite, a known persulfoxide quencher.[19] Furthermore, in the presence of methanol, the consumption of diethyl sulfide was observed accompanying the inhibition of $C_{60}O$ formation.[14b,14c] The results might be explained by a mechanism involving the persulfoxide intermediate **2**, as shown in Scheme 4.[12j,14d,14e] The reaction might be initiated by $^1O_2$ produced by energy transfer from $^3C_{60}$* to O_2. The reaction of $^1O_2$ with diethyl sulfide generates **2**, which acts as a nucleophilic oxidation reagent.

The results show novel photooxidation of fullerenes with oxygen in the presence of adamantylideneadamantane or sulfide. Control experiments revealed that peroxonium ion intermediates—perepoxide and persulfoxide—which act as nucleophilic oxygen atom transfer reagents, play an important role in the oxidation of fullerenes.



Scheme 4.

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