AUTOXIDATION OF ADAMANTYLIDENEADAMANTANE IN A PROTIC SOLVENT.
FACILE PROTON-INDUCED ELECTRON TRANSFER FROM THE OLEFIN TO OXYGEN

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Summary: Addition of trifluoroacetic acid to adamantylideneadamantane in
dichloromethane solution under oxygen in the dark results in a rapid
oxygenation of the olefin. The reaction is proposed to proceed through a
mechanism involving proton-induced electron transfer from the olefin to
oxygen giving its radical cation and a hydroperoxy radical followed by their
subsequent reactions.

During the course of investigation on photochemical and thermal reactions
of contact charge transfer pairs of electron-rich substrates and oxygen[1,2]
we have found, as reported below, that adamantylideneadamantane 1 is facilely
oxygenated in the presence of trifluoroacetic acid in dichloromethane in the
dark; the reasonable mechanism would be a proton-induced electron transfer
from 1 to oxygen giving the radical cation $1^{+\cdot}$ and a hydroperoxy radical
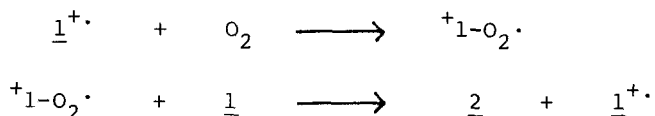followed by their subsequent reactions.

Table 1 summarizes the results obtained under various conditions.
In a typical run, trifluoroacetic acid (2 ml) was added to an oxygen-bubbled
solution of 1 (134 mg, 0.50 mmol) in dichloromethane (8 ml), and the mixture
was left standing with continuous bubbling of oxygen. After one hour, the
mixture was worked up to give the following products after TLC separation
(entry 1): dioxetane 2[3a] (74% based on 1 used), epoxide 3[3b] (1%), spiroketone
4[3b] (11%), and adamantanone 5 (2%) together with a small amount of recovered
1 (2%)(Scheme 1).

The reaction carried out in the dark (entry 3) led to nearly the same
results as obtained under room light in the same reaction time (entry 2).
This shows that oxygenation proceeds without any assistance of room light.
However, use of acetic acid (pK_a = 3.7)[4] in place of trifluoroacetic acid
(pK_a = 0.3)[5] did not cause any oxygenation of 1 in 1 hour under room light.

Examination of the products at the earlier stage (10 min, entry 4) as well
as following the reaction by TLC indicates that both of 3 and 4 as well as 2
are produced at the early stage of the reaction. A control run to leave 2
under oxygenation conditions (entry 8) gave neither 2 nor 4 but gave only 5
(4%). Is is known that 4 is produced by acid-catalyzed rearrangement of 3[3b].

Accordingly, in the above oxygenation, both of 2 and 3 are the primary products, whereas 4 and 5 are the secondary products arising from 3 and 2, respectively.

For the present reaction, we propose the mechanism, as depicted in Scheme 1, involving a proton-induced electron transfer from 1 to oxygen probably within a contact charge transfer pair of 1 with oxygen to give the radical cation $1^{+\cdot}$ and a hydroperoxy radical followed by their reactions. The resulting $1^{+\cdot}$ reacts rapidly with oxygen to give 2 through the following chain processes as reported recently by Nelsen[6] and Clennan[7].

$$1^{+\cdot} \quad + \quad O_2 \quad \longrightarrow \quad ^+1\text{-}O_2\cdot$$

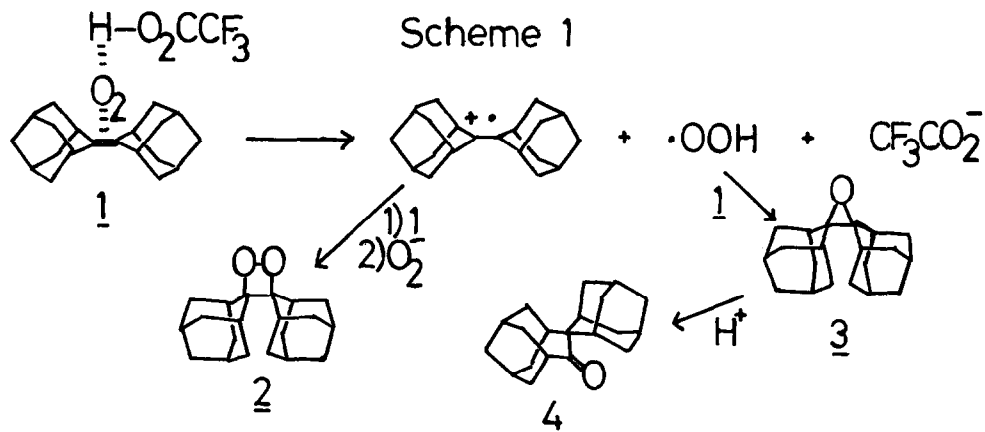$$^+1\text{-}O_2\cdot \quad + \quad 1 \quad \longrightarrow \quad 2 \quad + \quad 1^{+\cdot}$$

On the other hand, the hydroperoxy radical adds to 1 to give an adduct radical 6, in which the radical center undergoes the intramolecular substitution on the peroxide linkage to give epoxide 3. The result that AIBN-initiated autoxidation of 1 afforded 3 exclusively with a low efficiency (entry 7) suggests that 3 may arise from addition of peroxy radicals to 1 with a short radical chain length[8]. The mechanism for epoxide formation shown below is further supported by a recent report by Hendry and Schuetzle[9] that hydroperoxy radicals generated in situ react with tetramethylethylene to give its epoxide.

Table 1. Products from Oxygenation of Adamantylideneadamantane in
Dichloromethane-Trifluoroacetic Acid (4:1 by volume) under Oxygen

Entry	System	Solvent	Reaction Time /min	Isolated Yield/%[a]				
				1	2	3	4	5
1	$1/O_2/RL$[b]	CH_2Cl_2/CF_3CO_2H	60	2	74	1	11	2
2	$1/O_2/RL$[b]	CH_2Cl_2/CF_3CO_2H	30	5	66	3	10	2
3	$1/O_2/Dark$[c]	CH_2Cl_2/CF_3CO_2H	30	8	69	4	9	2
4	$1/O_2/RL$[b]	CH_2Cl_2/CF_3CO_2H	10	72	16	3	4	1
5	$1/O_2/7$[d]	CH_2Cl_2/CF_3CO_2H	10	99	unobs	unobs	unobs	unoba
6	$1/O_2/7$[e]	CH_2Cl_2/CF_3CO_2H	40	95	unobs	unobs	2	unobs
7	$1/AIBN/O_2$[f]	CCl_4	180	68	unobs	12	unobs	unobs
8	$2/O_2/RL$[b]	CH_2Cl_2/CF_3CO_2H	60	unobs	87	unobs	unobs	4

a) The entry "unobs" means that none of the compound was detected by TLC.
b) Under room light. c) In the dark. d) The phenol 7 in an equimolar amount to 1 was used. e) 7 in 16 mol% of 1 was used. f) 1 (70.8 mg, 0.26 mmol) and AIBN (10.2 mg, 0.026 mmol) were heated at 65°.

Scheme 1

H–O$_2$CCF$_3$

1 $\longrightarrow$ 1$^{+\cdot}$ + $\cdot$OOH + CF$_3$CO$_2^-$

1) 1
2) O$_2^-$

2   4 $\xleftarrow{\text{H}^+}$ 3

The lower yields of 3 and 4 than that of 2 must be due to a shorter radical chain length for the formation of 3 than that for 2[10].

HO$_2\cdot$ + (1) $\longrightarrow$ (6) $\longrightarrow$ 3 + $\cdot$OH

O$_2$H
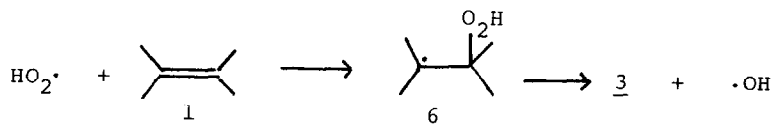
Addition of 2,6-di-t-butylphenol 7 in an equimolar amount to 1 completely inhibited the oxygenation (entry 5); however, addition of a small amount of 7 (16 mol% of 1) afforded only 4 (2%) without any detectable formation of 2 (entry 6). These results support the above mechanism (Scheme 1) in which 3 arises from a pathway different from that for 2. After the electron transfer from 1 to oxygen giving 1$^{+\cdot}$ and a hydroperoxy radical, 1$^{+\cdot}$ formed must be reduced with 7 to regenerate 1,[13] whereas the hydroperoxy radical would abstract phenolic hydrogen[14] from 7 in competition with addition to 1 leading to 3.

The initial process of the present mechanism, proton-induced electron transfer from the π-electron system to oxygen, may be further supported by the following reports. First, in strongly acidic media like trifluoroacetic acid and hydrogen fluoride, electron-rich aromatic hydrocarbons such as perylene and some anthracene derivatives can be oxidized by molecular oxygen to their radical cations as revealed by their electronic and ESR spectra[15]. Second, the reduction potential of oxygen in DMF with an equal concentration of perchloric acid is 0.72 V more anodic than that in neutral solution[16]. It is therefore reasonable to consider that the presence of a strong acid lowers the energy required for the electron transfer from 1 to oxygen.

The readiness of the present reaction must result from the effect of highly acidic media to accelerate the electron transfer from 1 to oxygen as well as from the unique properties of the resulting radical cation 1$^{+\cdot}$, the high reactivity toward triplet oxygen[6,7] and the strong reluctance to deprotonation and dimerization due to the steric protection[17].

Finally, it should be noted that the present proton-induced electron transfer to oxygen is remarkable in its possible application to many oxygenation systems, in its mechanistic features of the oxygenation reactions, and a potential source of hydroperoxy radicals which play an important role in environmental and biological systems[18].

References and Notes

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