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A NOVEL PHOTOOXIDATION OF HYDROCARBONS SENSITIZED BY 2,7-DIAZAPYRENIUM DICATION IN THE PRESENCE OF IRON CATALYST

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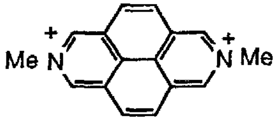
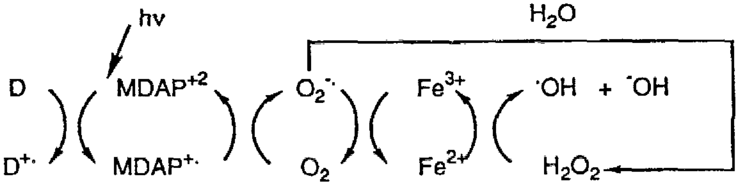
Summary: A novel photooxidation of hydrocarbons sensitized by N,N'-dimethyl-2,7-diazapyrenium dication in the presence of iron catalyst has been described. Formation of free hydroxyl radical from molecular oxygen has been demonstrated.

The oxidation of unactivated hydrocarbons with molecular oxygen under mild conditions is currently an important and intense area of research. Many systems, more or less biomimetic, based on the use of a transition metal catalyst have been developed for hydrocarbon oxidation.[1] However, very few are known for the oxidation of saturated hydrocarbons utilizing dioxygen as an oxygen-atom donor.[2] Our approach to the oxidation of hydrocarbons is based on the use of photochemical one-electron reduction of dioxygen in combination with Fenton type reaction in the presence of iron catalyst. We disclose herein a new type of photooxidation of hydrocarbons by the use of N,N'-dimethyl-2,7-diazapyrenium dication ($MDAP^{2+}$) as a photo-redox sensitizer. While several types of photochemical oxidations including singlet oxygenation and electron-transfer or free radical type photooxidations are known, the present system is a unique example for the direct photooxidation of unactivated saturated hydrocarbons utilizing molecular oxygen as an oxygen-atom donor.[3]

Upon visible-light irradiation in the presence of electron donors such as EDTA, $MDAP^{2+}$ is known to undergo photoreduction initially to the radical cation $MDAP^{+\cdot}$.[4] Under aerobic conditions $MDAP^{+\cdot}$ may react with triplet oxygen to revert to $MDAP^{2+}$ with concomitant formation of superoxide anion ($O_2^{-\cdot}$).[5]



$MDAP^{2+}$



Scheme 1

We envisioned the possibility that the presence of Fe^{3+} in such system might generate a powerful oxidizing species such as hydroxyl radical or its equivalent, since Fe^{3+} would be readily reduced by $O_2^{-\cdot}$ to Fe^{2+} which in turn reacts with hydrogen peroxide formed via disproportionation of $O_2^{-\cdot}$ in aqueous media to result in a formation of hydroxyl radical via Fenton reaction (Scheme 1). Actually, photoirradiation (> 320 nm) of a solution of adamantane in the presence of catalytic amounts of $MDAP^{2+}\cdot(BF_4^-)_2$[5a] and an iron salt in aqueous acetonitrile containing oxalate anion as an electron-donor under oxygen resulted in a smooth oxidation of adamantane to adamantan-1-ol (1), adamantan-2-ol (2) and adamantan-2-one (3). The results are listed in Table 1.

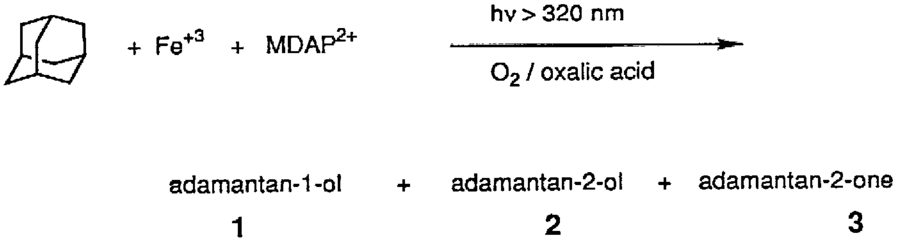


Table 1. Photooxidation of Adamantane[a]

	Catalyst	Product yield (%)[b]			C_2/C_3[c]	Turnover no[d]
		1	2	3		
1	$Fe(NO_3)_3$	7.6	3.1	3.5	0.86	109
2	$FeCl_3$	6.0	2.4	3.1	0.92	104
3	$Fe(ClO_4)_3$	5.0	2.0	2.7	0.94	138
4	$Fe_2(SO_4)_3$	7.7	2.9	3.3	0.80	139
5	$FeSO_4$	5.6	1.8	2.0	0.69	78

[a] Adamantane (7.4 x 10^{-2} mmol), oxalic acid (0.74 mmol), $MDAP^{2+}\cdot(BF_4^-)_2$ (1.5 x 10^{-3} mmol) and an iron salt (9.6 x 10^{-5} mmol) were dissolved in 10 ml of acetonitrile-water (9:1) in a Pyrex test tube. The solution was irradiated externally with a 400 W high-pressure mercury lamp through a filter solution (> 320 nm) under oxygen bubbling at ambient temperature for 7 h. [b] Yields based on adamantane initially used as determined by GC. [c] Total secondary products/tertiary products ratio. [d] mol of total oxidized products/mol of catalyst.

Other saturated hydrocarbons such as cyclohexane and cyclododecane were also oxidized to the corresponding alcohols and ketones with the latter usually being the major products.[6] As clear from Table 1, soluble iron salts such as $Fe(NO_3)_3$, $Fe(ClO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$ are all effective as catalyst for adamantane photooxidation each with a reasonably high catalytic turnover number. Control experiments in the absence of iron catalyst or $MDAP^{2+}$ did not produce any significant oxidation product while the hydrocarbon being recovered unchanged. In the absence of oxalate anion as electron-donor,[7] the photooxidation proceeded only sluggishly being accompanied with a gradual photobleaching of $MDAP^{2+}$. The C_2/C_3 ratio for the selectivity of the oxidation at secondary *vs* tertiary positions implies that the present photooxidation is far distinct from Gif system ($C_2/C_3 \sim 8$)[2b] and close to the free radical oxidation initiated by benzoyl peroxide ($C_2/C_3 = 0.8$)[2b] or the cobalt-catalyzed radical oxidation ($C_2/C_3 = 0.13$).[8]

For determining the kinetic isotope effect we conducted competitive oxidation of an equimolar mixture of cyclohexane and perdeuterated cyclohexane. The k_H/k_D is 1.46 for the two cyclohexanones obtained in the present system. This value differs from those from Gif[9] and P-450 model[10] systems but is very close to that for the Fe^{2+}-hydrogen peroxide system ($k_H/k_D = 1.18$).[11] We therefore examined the inhibitory effect of hydroxyl radical scavengers on the present photooxidation. As shown in Table 2, addition of typical hydroxyl radical scavengers such as 2-propanol or dimethyl sulfoxide almost completely inhibited the oxidation. These results taken together strongly suggest that the active species in the present system is free hydroxyl radical which might be formed most likely via Fenton reaction as outlined in Scheme 1, although further work is required for the elucidation of the exact mechanism.

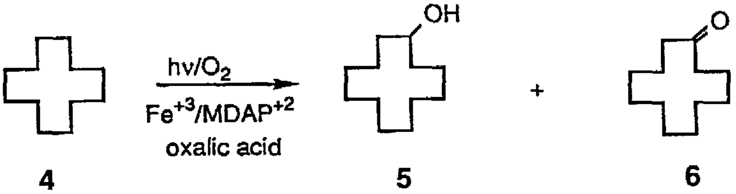


Table 2. Effect of Hydroxyl Radical Scavengers on the Photooxidation of Cyclododecane[a]

	Additive	Product yield (%)[b] 5	Product yield (%)[b] 6	Recovered 4[b] (%)
1	none	2.8	5.6	76
2	2-Propanol[c]	0.05	0.2	90
3	Dimethyl sulfoxide[c]	0.1	0.1	91

[a]Cyclododecane (6×10^{-2} mmol), oxalic acid (0.6 mmol), $MDAP^{2+\cdot}(BF_4^-)_2$ (1.2×10^{-3} mmol) and $Fe(NO_3)_3$ (9.6×10^{-5} mmol) in 10 ml of acetonitrile-water (9:1). Irradiation was conducted in a merry-go-round apparatus for 7 h. [b]Yields based on 4 initially used as determined by GC. [c]0.6 mmol.

Thus we have developed a new system for the photooxidation of hydrocarbons using 2,7-diazapyrenium dication as photo-redox sensitizer in the presence of iron catalyst, wherein hydroxyl radical is generated from molecular oxygen.[12]

References and Notes

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6. It is worth noting that MDAP^{2+}-sensitized photooxidation of olefins resulted in an ene reaction via singlet oxygen formation regardless of the presence of iron catalyst.
7. Fluorescence of $\mathrm{MDAP}^{2+}\cdot(\mathrm{BF_4}^-)_2$ was efficiently quenched by oxalate anion in acetonitrile-water (9:1) with $kq = 3.85 \times 10^9\ \mathrm{M^{-1}s^{-1}}$ as determined by Stern-Volmer plot (fluorescence lifetime of MDAP^{2+} = 10 ns). We thank Prof. Masahide Yamamoto, Kyoto University, for the measurement of fluorescence lifetime.
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