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1,2-DIOXETANES AS CHEMILUMINESCENT INTERMEDIATES IN THE TRIPLET OXYGEN OXYGENATION OF OLEFINS.

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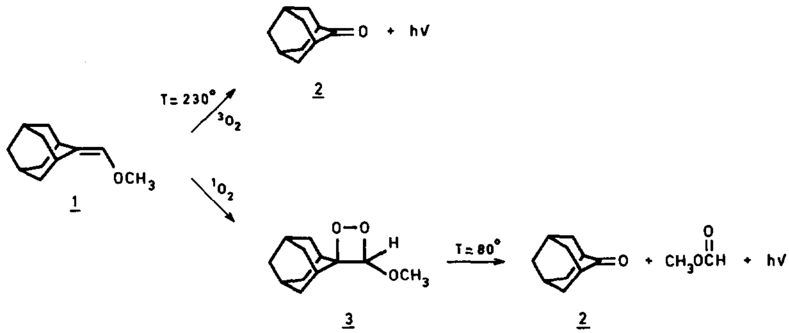
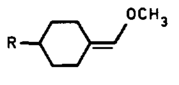
Abstract: *Several enol ethers react in the dark at elevated temperatures with triplet oxygen, producing ketones and chemiluminescence. Other electron-rich olefins were investigated.*

The current interest in the reaction of $^1O_2$ (singlet oxygen) with olefins to produce 1,2-dioxetanes[1] prompts us to report our experience using $^3O_2$ (triplet oxygen) at elevated temperatures.

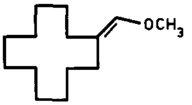
Methoxymethyleneadamantane 1 reacts in the dark at a temperature of ∿ 230°C with atmospheric oxygen to produce adamantanone 2 in a good yield while a bright blue chemiluminescence (fluorescence of 2) is clearly visible. We have observed the same chemiluminescence (λ_{max} = 420 nm) in the thermal decomposition of the 1,2-dioxetane 3, synthesized by photooxygenation of 1.[2] Although the chemiluminescence produced by the reaction of 1 and $^3O_2$ is (spectrally) identical with that produced by the thermal decomposition of 1,2-dioxetane 3, the latter occurs with a greater intensity. The resemblance of the two chemiluminescent reactions as well as the identity of the reaction product 2 makes it credible that the thermal oxygenation with triplet oxygen occurs via the 1,2-dioxetane 3. Attendant evidence for the similarity of the



$^1O_2$ and $^3O_2$ reaction is found in the oxidation of three other enol ethers. Recently Asveld and Kellogg have investigated the $^1O_2$ oxidation of the enol ethers 4, 5 and 6 in several solvents.[3] Under all circumstances used, hydroperoxides (ene mode of reaction) as well as 1,2-dioxetanes were formed. When we heated the three enol ethers 4, 5 and 6 at 230°C in an oxygen atmosphere in the dark, the corresponding ketones could be isolated in two cases, while chemiluminescence was observed in all three cases.[4]



4 R=H
5 R=$(CH_3)_3C$



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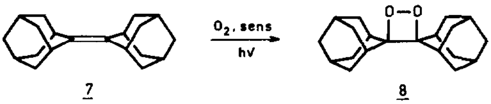
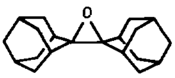
The experiments described above resemble the reaction of acetylenes and $^3O_2$ reported by Turro.[5] A few examples of compounds, which give chemiluminescent reactions when brought in reaction solely with $^3O_2$ have been reported.[5-8] In the reaction of $^3O_2$ with strained acetylenes[5] and tetraaminoethylenes[6] respectively intermediate 1,2-dioxetene and 1,2-dioxetane formation has been proposed. In the autoxidation of cyclobutadienes[7] and ketenes[8] 1,2-dioxetanes have been detected.

Adamantylideneadamantane 7, when it reacts with singlet oxygen (CH_2Cl_2; methylene blue as sensitizer) is converted quantitatively into adamantylideneadamantane-1,2-dioxetane 8.[9] However depending on the reaction conditions (solvent and sensitizer) the amount of the epoxide 9 varies.[10]





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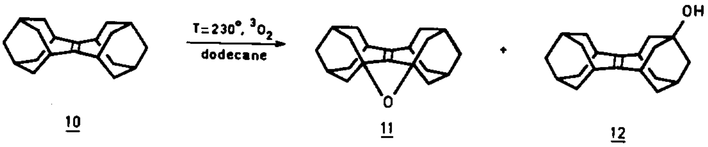
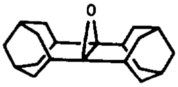
When a solution of 7 in dodecane is saturated with oxygen and heated in the dark at 230°C for two hours the products are adamantanone 2 (minor) and epoxide 9 (major). The yield of 9 can be raised to 60%.[11] Although in this reaction no chemiluminescence is observed, it is reasonable to suggest that 2 is formed from the intermediate 8. Remarkable is the phenomenon that samples of originally pure 7 contain small amounts of 8, after a normal storage for several months at room temperature.

A third olefin, which in principle can react with $^1O_2$ without giving an ene mode of reaction is the eicosene 10.[12] Surprisingly 10 proved inert to $^1O_2$, generated chemically from triphenyl phosphite ozonide, and $^1O_2$, generated photochemically using methylene blue in CH_2Cl_2. The thermal oxidation of 10 in dodecane in the dark at 230°C affords as major products oxetane 11 (15%) and alcohol 12 (25%).[13]



No epoxide 13, which can be synthesized independently by *m*-chloroperbenzoic acid epoxidation, could be detected. It is plausible that the products 11 and 12 are formed *via* a radical mechanism.[14]



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In summary, the oxidation of enol ethers 1, 4, 5 and 6 and adamantylideneadamantane 7 with $^3O_2$ and $^1O_2$ is remarkably similar. In the reaction with $^1O_2$, 1,2-dioxetanes are isolated. In the thermal reaction with $^3O_2$, 1,2-dioxetanes are proposed, as intermediates for this chemiluminescent reaction. Whether the reaction occurs *via* a $^3O_2 \rightarrow {}^1O_2$ conversion,[5,8] or *via* an electron transfer, following by a radical cage coupling and cyclization[15] is not clear.[16] Electron rich olefins, which proved to be inert to $^1O_2$, react in the known radical fashion with $^3O_2$ at high temperature, as showed for eicosene 10.

References

(1) Wasserman, H.H.; Murray, R.W. "Singlet Oxygen"; Academic, New York, 1979.

(2) Meijer, E.W.; Wynberg, H. Tetrahedron Lett. **1979**, 3997.

(3) Asveld, E.W.H.; Kellogg, R.M. J. Am. Chem. Soc. **1980**, 102, 3644.

(4) The yield of isolated ketone is low, probably due to the production of allylic hydroperoxides (ene mode of reaction).

(5) Turro, N.J.; Ramamurthy, V.; Liu, K.-C.; Krebs, A.; Kemper, R. J. Am. Chem. Soc. **1976**, 98, 6758.

(6) a. Paris, J.P. Photochem. Photobiol. **1965**, 4, 1059.

b. Urry, W.H.; Sheeto, J. Photochem. Photobiol. **1965**, 4, 1067.

(7) Maier, G. Angew. Chem. Int. Ed. Engl. **1974**, 13, 425.

(8) Turro, N.J.; Chow, M-F.; Ito, Y. J. Am. Chem. Soc. **1978**, 100, 5580.

(9) Wieringa, J.H.; Strating, J.; Wynberg, H.; Adam, W. Tetrahedron Lett. **1972**, 169.

(10) Jefford, C.W.; Boschung, A.F. Tetrahedron Lett. **1976**, 4771.

(11) Epoxides have been isolated in small amounts in the autoxidation of olefins, for example: Pritzkow, W.; Radeglia, R.; Schmidt-Renner, W. J. Prakt. Chemie, **1979**, 321, 813.

(12) a. Boelema, E.; Wynberg, H.; Strating, J. Tetrahedron Lett. **1971**, 4029.

b. Gill, G.B.; Hands, D. Tetrahedron Lett. **1971**, 181.

(13) The yield is based on a G.L.C. analysis. The products are separated and isolated via H.P.L.C. All spectroscopic data support the assigned structures.

(14) Holman, R.T. "Progress in the Chemistry of Fats and other Lipids", Vol. 2., Holman, Lundberg and Malkin, eds., Pergamon, London, **1954**, p. 51.

(15) This mechanism is proposed by Adam for the autoxidation of tetraaminoethylenes, Adam, W., Adv. Heterocyclic Chem. **1977**, 21, 437.

(16) Quenching and trapping experiments designed to identify more explicitly the reacting species will not be useful, because the elevated temperatures of the reaction leads to rapid decomposition of the quenchers commonly used.

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