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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 $^1\text{O}_2$ (singlet oxygen) with olefins to produce 1,2-dioxetanes¹ prompts us to report our experience using $^3\text{O}_2$ (triplet oxygen) at elevated temperatures.

Methoxymethylenadamantane 1 reacts in the dark at a temperature of $\sim 230^\circ\text{C}$ 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 ($\lambda_{\text{max}} = 420 \text{ nm}$) 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 $^3\text{O}_2$ 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

$^1\text{O}_2$ and $^3\text{O}_2$ reaction is found in the oxidation of three other enol ethers. Recently Asveld and Kellogg have investigated the $^1\text{O}_2$ 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

The experiments described above resemble the reaction of acetylenes and $^3\text{O}_2$ reported by Turro.⁵ A few examples of compounds, which give chemiluminescent reactions when brought in reaction solely with $^3\text{O}_2$ have been reported.⁵⁻⁸ In the reaction of $^3\text{O}_2$ with strained acetylenes⁵ and tetraaminoethylenes⁶ respectively intermediate 1,2-dioxetene and 1,2-dioxetane formation has been proposed. In the autoxidation of cyclobutadienes⁷ and ketenes⁸ 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

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 $^1\text{O}_2$ without giving an ene mode of reaction is the eicosene 10.¹² Surprisingly 10 proved inert to $^1\text{O}_2$, generated chemically from triphenyl phosphite ozonide, and $^1\text{O}_2$, 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

In summary, the oxidation of enol ethers 1, 4, 5 and 6 and adamantylideneadamantane 7 with $^3\text{O}_2$ and $^1\text{O}_2$ is remarkably similar. In the reaction with $^1\text{O}_2$, 1,2-dioxetanes are isolated. In the thermal reaction with $^3\text{O}_2$, 1,2-dioxetanes are proposed, as intermediates for this chemiluminescent reaction. Whether the reaction occurs via a $^3\text{O}_2 \rightarrow ^1\text{O}_2$ conversion,^{5,8} or via an electron transfer, following by a radical cage coupling and cyclization¹⁵ is not clear.¹⁶ Electron rich olefins, which proved to be inert to $^1\text{O}_2$, react in the known radical fashion with $^3\text{O}_2$ at high temperature, as showed for eicosene 10.

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