The Reduction of 1,2-Dioxetanes to cis-1,2-Diols by Superoxide. The Mechanism of the Process found in the Rose Bengal-Sensitized Photooxygenation

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The Reduction of 1,2-Dioxetanes to cis-1,2-Diols by Superoxide. The Mechanism of the Process found in the Rose Bengal-Sensitized Photooxygenation

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Superoxide radical anion reduced 1,2-dioxetanes to cis-1,2-diols by: a) visible-light irradiations under Methylene Blue-sensitized photooxygenation conditions with added sodium acetate, and b) chemical reductions with potassium superoxide and dibenzo-18-crown-6 ether in dichloromethane solutions.

For the mechanism of formation of cis-1,2-diols from the dioxetane-forming olefins during Rose Bengal (RB)-sensitized photooxygenation reactions, we have already shown the intermediacy of dioxetanes by $^{18}$O-labelling experiments as well as low-temperature detection with the NMR spectroscopy. Herein, we wish to show the reducing agent to be superoxide (SO), a radical anion.

First of all, it has been noticed that only RB-sensitized photooxygenation can produce the 1,2-diols. Therefore, we intended to isolate the diol-free samples of the dioxetanes (1 and 2) from thujopsene (3) and the Diels-Alder dimer (4) of spiro[2.4]hepta-4,6-diene by a careful Methylene Blue (MB)-sensitized photooxygenation by low-temperature irradiations. However, all attempts to remove the sensitizer resulted in a quantitative cleavage of dioxetanes, and we carried out the reaction by means of polymer-bound MB in view of a convenient workup. Surprisingly, when 3 and 4 were respectively photooxygenated with this heterogeneous sensitizer in various solvents at -20 to -50°C, the 1,2-diols (5 and 6) were indeed formed in a trace amount (~1%). Thus, even MB-sensitized reaction could form 1,2-diols, and this clear-cut difference between the homogeneous and heterogeneous MB-sensitized reactions suggested that the reduction must be not sensitizer-dependent, but pH-dependent. Indeed, the MB-sensitized photooxygenation of 3 and 4 in methanol solution with sodium acetate, under homogeneous conditions, produced 5 (5%) and 6 (16%), respectively. Moreover, and addition of water to this methanol solution has caused a complete inhibition of the diol formation. From these findings, an involvement of an acid- and water-sensitive species in the reduction was suggested.

In this regard, SO is well known to be acid-and water-sensitive, and SO, therefore, likely to be the active species, and this was indeed the case. Thus, the diol-free dioxetanes were at first prepared by polymer-bound MB-sensitized photooxygenation at -45°C in dichloromethane solution which usually contains a trace amount of hydrochloric acid to prevent an accumulation.

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Scheme 1

Scheme 2

Then, the sensitizer was filtered off, and to the filtrate, potassium superoxide (KO₂) and dibenzo-18-crown-6 (CE) were added and stirred at -40 to 0°C for 12 h. Preparative thin-layer (silica gel) chromatography of the mixture afforded 5 in 4% yield. Furthermore, when a mixture of photooxygenation products derived from 3 by means of MB in homogeneous dichloromethane solution at -45°C was treated similarly with SO and CE for 12 h, 5 was obtained in 6% yield.

Thus, with or without MB, SO yielded the 1,2-diol. But, without SO and CE, the photoproduct mixture afforded no 5 at all after standing for 12 h at -40 to 0°C.

In conclusion, SO is solely responsible for the photochemical reduction of 1,2-dioxetanes to cis-1,2-diols, and in view of the one-electron reducing nature of SO, the reduction should be proceeded in the two-step manner, via dioxy radical anions to diols. It is already known that the reduction of hydroxy radical to hydroxide is very rapid.

References


7) According to potentiometry, with Hirayama RAT-11S apparatus, following pH were obtained: 0.005M aqueous MB solution, 3.8; 0.005M MB in 0.1M aqueous NaOAc, 7.5; 0.005M aqueous RB solution, 7.5.
8) SO is very unstable in acidic media as recorded in literature as D.T. Sawyer and M.J. Gibian (*Tetrahedron*, 35, 1471 1979)) has determined the rate constants:
   \[ \text{SO} + \text{SO} + \text{H}^+ \rightarrow \text{O}_2 + \text{HOO}^- \quad k_1 = 1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \]
   \[ \text{SO} + \text{HOO}^- \rightarrow \text{O}_2 + \text{HOO}^- \quad k_2 = 8.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \]
   \[ \text{SO} + \text{HO}^- \rightarrow \text{O}_2 + \text{OH}^- \quad k_3 = 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \]
9) Second step of the reduction must be very rapid: \[ \text{SO} + \text{HO}^- \rightarrow \text{O}_2 + \text{OH}^- \quad k_3 = 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \].