# INTERCEPTION OF O_2^- BY BENZOQUINONE IN CYANOAROMATIC-SENSITIZED PHOTOOXYGENATIONS

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Abstract: Benzoquinone decreases the rate of dicyanoanthracene-sensitized photooxidation of trans-stilbene, apparently by intercepting the reactant O_2^-.

We have reported the electron transfer initiated oxidation of trans-stilbene (TS) sensitized by the singlet excited state of dicyanoanthracene (DCA).[1,2] We proposed that oxidation products were formed by reaction of TS^+ with O_2^- (Scheme 1). The characteristic absorption spectrum of TS^+ was observed in these reactions by laser flash photolysis.[2] The presence of O_2^-, formed by oxidation of DCA^- by $^3O_2$, was not directly established, but was inferred from the exothermicity of the electron transfer from DCA^- to O_2 (0.7 kcal/mole)[1] and the rapid disappearance of DCA^- absorbance in the flash system in the presence of O_2.[2]

Scheme 1:
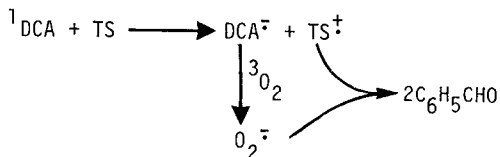
The intermediacy of O_2^- in these reactions remains questionable. Several other oxygenation reactions of olefins (Ol) are known to proceed via an olefin radical cation[3,4]; in most of these reactions, O_2^- is not present, so that $^3O_2$ must be the oxygen source; a chain process is often the major reaction path:

$$Ol \xrightarrow[\text{[OX]}]{} Ol^+ \xrightarrow{O_2} Ol \cdot O_2^+ \xrightarrow{Ol} Ol \cdot O_2 + Ol^+$$
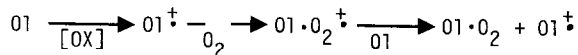
For example, adamantylideneadamantane radical cation (Ad=Ad[+]) reacts with $^3O_2$ in a chain process leading predominantly to dioxetane.[3,4] This reaction seems to be an example of the Barton-Haynes mechanism, originally proposed for diene systems.[5-7] An analogous reaction is the TiO_2 sensitized photooxidation of olefins.[8,9] The radical cation is also intermediate in this reaction, but O_2^- was discounted because of the lack of inhibition by phenylglyoxylic acid, a superoxide trap. We now report that the DCA-sensitized photooxidation of TS is inhibited by benzoquinone (BQ), an excellent trap for superoxide[10], which provides strong additional support for intermediacy of O_2^-.

Addition of 2.5 X 10^{-3} M BQ to the DCA (2 x 10^{-4} M) sensitized photooxidation of 0.1 M TS in CH_3CN reduced the rate of formation of C_6H_5CHO by a factor of 15 to >40 under O_2 or air, respectively[11] (Table 1). The added BQ had similar effects on the minor products, trans-stilbene epoxide and benzil, reducing them below the limits of detection, but had little effect on the amount of cis-stilbene formed during photolysis. Addition of more BQ had little further effect on the reaction, suggesting that the affected species are already trapped at the concentration used.
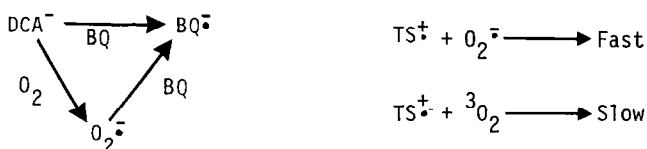
Table 1. Effects of Benzoquinone and Stilbene Concentration on Rates of Trans-Stilbene (0.1 M) Oxidation.[a]

[BQ], M	Atmosphere	C_6H_5CHO	Relative Product Amounts		
			cis Stilbene	Stilbene Epoxide	Benzil
0	O_2	116 ± 2	1.90 ± .03	26.9 ± 1.0	16.3 ± 1.1
0	Air	206 ± 9	1.00 ± 0.10	45.8 ± 4.0	29.4 ± 1.8
2.5 X 10^{-3}	O_2	7.8 ± 0.3	3.07 ± 0.07	< .05	< .05
2.5 X 10^{-3}	Air	4.7 ± 0.1	2.00 ± 0.13	< .05	< .05

a. Average of at least two independent runs. Errors are range of values.

There are four intermediates that BQ might affect: ^1DCA, TS[+], DCA[-] and O_2^-. At 2.5 X 10^{-3} M, BQ cannot compete with 0.1 M TS for ^1DCA since TS quenches it with k_q = 1.88 X 10^{10} M^{-1} sec^{-1}.[14] It is unlikely that BQ affects TS[+], because both species are electron deficient. However, BQ should oxidize both DCA[-] and O_2^- at nearly diffusion-controlled rates because

electron transfer to BQ is strongly exothermic in both cases ($E_{1/2}$: $BQ/BQ^- = -0.51$ V;[15] $DCA/DCA^- = -0.97$ V;[1] $O_2/O_2^- = -0.92$ V[1]). The most logical explanation for these effects is that removal of O_2^- from the reaction causes a decrease in efficiency since TS^+ can then react only with $^3O_2$, and that this reaction is much less efficient than that with O_2^-.

$$DCA^- \xrightarrow[BQ]{} BQ^{\cdot -}$$
$$O_2 \searrow \quad \nearrow BQ$$
$$O_2^{\cdot -}$$

$$TS^{\cdot +} + O_2^{\cdot -} \longrightarrow Fast$$

$$TS^{\cdot +} + {}^3O_2 \longrightarrow Slow$$

Our results suggest that in sensitized oxidations, the reaction of $O1^+$ with $^3O_2$ cannot compete with that with O_2^- or sensitizer$^-$. Back electron transfer from radical anions stops the chain reaction with $^3O_2$, effectively removing this pathway. The comparatively slow interaction of TS^+ with $^3O_2$ is consistent with previous findings of Schaap et al.[16] and Clennan et al.[4] which indicate that $^3O_2$ reacts slowly with stabilized radical cations. Clennan suggested that the slow reaction of 1,2-diphenylethylene radical cations reflects the extensive delocalization of the odd electron density of these systems.

Schaap also showed that addition of O_2^- to a solution of diphenyldioxene radical cation (DPD^+) led to more efficient oxidation than reaction with $^3O_2$, but could not exclude the possibility that back electron transfer from O_2^- to DPD^+ formed $^1O_2$, which can react with DPD to give the dioxetane.[16] We can exclude $^1O_2$ as a source of C_6H_5CHO in the present case since TS reacts very slowly with $^1O_2$.[17] We conclude that in agreement with our earlier proposal, O_2^- is an important intermediate in the DCA sensitized photooxidations.

The data in Table 1 indicate that oxygen concentration can also effect the relative rates of product formation. In the absence of BQ, going from air to oxygen saturation decreases the amount of all oxidation products while increasing cis-stilbene formation. In contrast, when BQ is present, higher $[O_2]$ increases C_6H_5CHO as well as cis-stilbene formation. These effects will require further study, but are too large to be accounted for solely by oxygen quenching of ^1DCA.

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(11) Photolyses were carried out in a merry-go-round apparatus designed for continuous gas saturation of the samples.[12] The appearance of products was monitored by G.L.C. (3% carbowax column, diphenylmethane added as internal standard). The solutions were photolysed using a 1200 W medium-pressure Hanovia lamp in a water cooled immersion well. Two 1-cm pathlength filter solutions, the first consisting of 4.4 g $CuSO_4.5H_2O$ with 200 ml conc. $NH_4OH/1000$ ml H_2O, the second consisting of 75 g $NaNO_2/1000$ ml H_2O, served to isolate the Hg lines at 405 and 436 nm.[13] All reactions were carried to <20% initial starting material disappearance. Under our conditions, DCA absorbed >95% of the light, BQ <5%.

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