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OXIDATIVE CLEAVAGE OF TRANS-STILBENE IN ACETONITRILE/WATER SOLUTIONS

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Abstract: trans-stilbene (St) reacts with OH radicals in presence of oxygen and via the stilbene radical cation (St^{+}) and oxygen in CH_3CN/H_2O solutions to give high yields of benzaldehyde.

Aromatic hydroxylations can be accomplished by two distinct routes: 1) Addition of OH radicals, followed by oxidation of the intermediate hydroxycyclohexadienyl radical (1) and 2) formation of a radical cation and subsequent nucleophilic addition of water to give a hydroxycyclohexadienyl radical (2). Previous studies (2) have shown that in the hydroxylation of substituted benzenes the two routes lead to different isomer distributions and that at low pH the isomer distribution obtained in the OH radical hydroxylations changes to the isomer distribution obtained via radical cations (1).

In the present study we have used the Fenton reaction (3) as OH radical source: $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH$

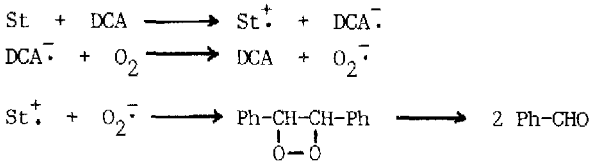
The formation of $St^{+\cdot}$ was accomplished with SO_4^{-}, which is produced via the following reactions (4):

$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-}$ or $S_2O_8^{2-} \longrightarrow 2\ SO_4^{\cdot-}$

In the reactions of stilbene with $Fe^{2+} - H_2O_2 - O_2$ or $Fe^{2+} - S_2O_8^{2-} - O_2$ we obtained benzaldehyde as the main product (Table I). In the $Fe^{2+} - H_2O_2 - O_2$ experiments we observed a considerable increase in both the absolute and % yields of benzaldehyde at low pH, whereas in the $Fe^{2+} - S_2O_8^{2-} - O_2$ experiments no such effect of pH was observed. The results of the thermal decomposition of $S_2O_8^{2-}$ in presence of O_2 are shown in Table II.

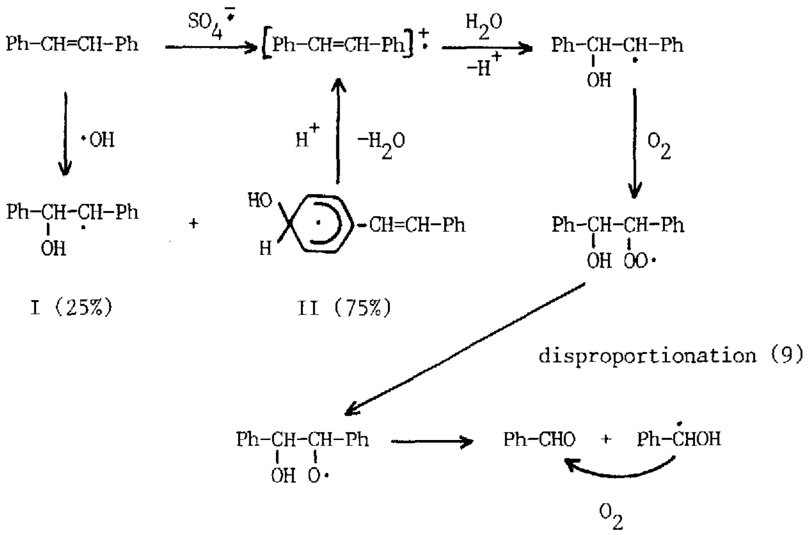
The photochemical oxidative cleavage of stilbene has been studied in great detail. Investigations by Foote and co-workers (7) on the DCA-sensitized photo-oxygenation of trans-stilbene have led to the following mechanism for benzaldehyde formation (Scheme I).

Scheme I.



$$St + DCA \longrightarrow St^{\overset{+}{\cdot}} + DCA^{\overset{-}{\cdot}}$$
$$DCA^{\overset{-}{\cdot}} + O_2 \longrightarrow DCA + O_2^{\overset{-}{\cdot}}$$
$$St^{\overset{+}{\cdot}} + O_2^{\overset{-}{\cdot}} \longrightarrow \underset{O-O}{Ph\text{-}CH\text{-}CH\text{-}Ph} \longrightarrow 2\ Ph\text{-}CHO$$

However in a recent paper Lewis et al. (6) have expressed reservations about the Foote mechanism. The possibility of radical cation reacting with $^3O_2$ was clearly recognized by Foote (5c). Reactions of radical cations of dienes with $^3O_2$ have been shown to give endoperoxides via a chain mechanism (7). This chain reaction was also observed in the reaction of the radical cation of adamantylidene-adamantane with $^3O_2$ in CH_2Cl_2 (8). In our thermal decomposition of $S_2O_8^{2-}$at 65°C for 1 hr. we do not observe any chain mechanism leading to benzaldehyde. In these experiments we have no reducing agent present which could conceivably reduce O_2 to $O_2^{-}\cdot$. We therefore conclude that $O_2^{-}\cdot$ is not involved in the formation of benzaldehyde. We suggest the mechanism outlined in Scheme II:



Addition of OH radicals to St occurs at the ring and at the double bond (10). According to pulse radiolysis data (11) aromatic radical cations react with H_2O very rapidly (<0.1 μs) to give a OH radical adduct.

In the reaction with OH radicals we obtain both adduct I and II but we propose that in the reaction with SO_4^- we obtain only adduct I. The formation of different adducts via the two pathways has been observed previously in the hydroxylation of substituted benzenes (1,2). The exclusive formation of adduct I from St^+ is supported by analogous results of Walling et al. (12) on the reaction of styrene radical cation with water and by Yasuda and Shima (13) on the amination of stilbene radical cation. Assuming that only adduct I gives 2 PhCHO we can expect a higher % yield in the reaction with SO_4^-. In presence of H^+ however adduct II can undergo reversible acid - catalyzed dehydration to give adduct I. In this way the yield of benzaldehyde is considerably increased. Based on these assumptions and the 4-fold increase in benzaldehyde (Table I, exp. No. 2,4), we can conclude that initially 75% of OH radicals add to the ring and 25% to the double bond.

Table I

Conditions [1]		products (moles x 10^6)		
$HClO_4$	O_2/Ar	PhCHO	-St	% yield[2]
--	Ar	35	158	11
--	O_2	57	74	39
(+)	Ar	31	375	4
(+)	O_2	250	225	55
--	Ar	129	312	21
--	O_2	575	389	74
(+)	Ar	55	217	13
(+)	O_2	526	355	74

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1. All reactions were carried out with 0.5 x 10^{-3} moles of trans-stilbene in 80ml acetonitrile and 50 ml water. All reactions contained 2.5 x 10^{-3} moles Fe^{2+} and expts. 1-4 1.76 x 10^{-3} moles H_2O_2. Expts. 5-8 contained 10^{-3} moles $S_2O_8^{2-}$. In the experiments with $HClO_4$ 500 microliters of conc. $HClO_4$ was added. All reactions were analyzed after shaking the solutions for 1 hour in a mechanical shaker. Analysis was carried out by HPLC, 1 foot μ-Bondapak (Millipore) C-18 reverse phase, using methanol/water and solvent programming (30% methanol to 85% methanol in 20 min. at 1 ml/min.).
2. Yields were calculated on the assumption of 2PhCHO formed/1St consumed.

Table II

Thermal decomposition of peroxydisulfate in aqueous solutions of trans-stilbene in presence of $^3O_2$.

conditions[1]					
$S_2O_8^{2-}$ (moles)	time	°C	PhCHO (moles)	-St (moles)	$-S_2O_8^{2-}$ (moles)
10^{-3}	1 hr	69	525 x 10^{-6}	500 x 10^{-6}	150 x 10^{-6}
10^{-3}	30 min	69	235 x 10^{-6}	203 x 10^{-6}	
2.5 x 10^{-4}	1 hr	69	157 x 10^{-6}	150 x 10^{-6}	38 x 10^{-6}
5 x 10^{-3}	24 hr	25	158 x 10^{-6}	121 x 10^{-6}	

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1. All reactions contained 0.5 x 10^{-3} moles St in 80ml CH_3CN/50 ml H_2O. Oxygen was continuously bubbled through the solution during heating. In the room temperature experiment the solution was saturated with oxygen for 30 min.

Our results on argon saturated solutions show a considerable higher stilbene consumption than in oxygen saturated solutions (Table I, exp. 1-4). Since under both conditions the amount of OH radicals produced is the same, we conclude that the OH adduct or the St^{+} react with another St to give dimer radical cation or hydroxy- substituted dimer radical or polymer.

The reaction of O_2 with OH radical adducts to aromatics is very fast (14). We therefore believe that O_2 competes efficiently with St for intermediate (I). The situation may however be different in non-aqueous solutions. Lewis et al. (6) have suggested that the formation of PhCHO proceeds via a reaction of dimer radical cation with $^3O_2$. It appears quite possible that in aqueous solutions $^3O_2$ reacts with the monomeric OH adduct and in non-aqueous solutions with the dimeric radical cation.

Conclusion: Our results show that the formation of benzaldehyde from stilbene radical cation - oxygen in aqueous solutions proceeds via $^3O_2$ and does not involve O_2^{-}. It is unlikely that a dioxetane is an intermediate in this oxidative cleavage.

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