

THERMAL DECOMPOSITION OF PEROXYDISULFATE IN AQUEOUS SOLUTIONS OF TOLUENE.

OXIDATION OF BENZYL RADICALS BY NITROBENZENE.

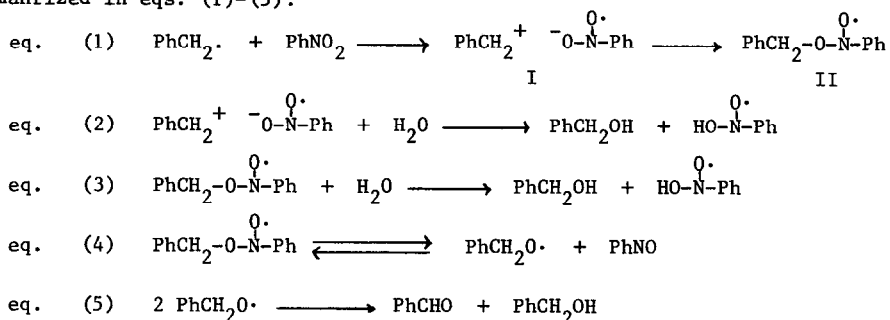
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The oxidation of benzyl radicals by nitrobenzene is described. A mechanism involving formation of an adduct followed by homolytic cleavage to $\text{PhCH}_2\text{O}\cdot$ radical is proposed.

The oxidation of radicals with nitro compounds in aqueous as well as non-aqueous solutions has received considerable attention. It has been recognized that many of these oxidations proceed via the intermediate formation of an adduct (1-8). Schulte-Frohlinde and coworkers(1) have shown by pulse radiolysis that the adduct formed in the reaction of monoalkoxyalkyl radicals with tetranitromethane disappears unimolecularly via heterolytic rupture of the C-O bond ($\text{S}_{\text{N}}1$ reaction).

We wish to present some experimental results which suggest that in the oxidation of benzyl radicals with nitrobenzene the adduct decomposes via a homolytic β -cleavage to give benzyloxy radicals, which in turn disproportionate to benzaldehyde and benzyl alcohol.

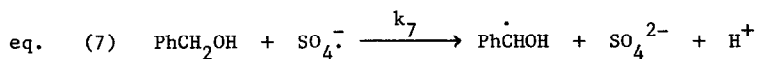
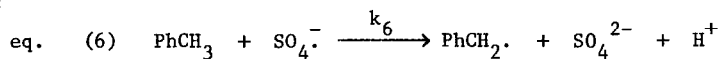
These results are shown in Table I. The possible reaction steps in this oxidation are summarized in eqs. (1)-(5):



The reaction of toluene with $\text{SO}_4^{\cdot-}$ to give $\text{PhCH}_2\cdot$ radicals has been discussed in detail (9-10). Based on the rate constants(11) under our conditions the $\text{SO}_4^{\cdot-}$ reacts practically quantitative with PhCH_3 and not with PhNO_2 . Whether the zwitter ion structure I or the adduct II (eq. (1) are intermediates we only expect primary formation of benzyl alcohol and no benzaldehyde. According to the two mechanisms (eq. (2) and (3) benzaldehyde must be formed via a secondary oxidation of benzyl alcohol. This appears unlikely due to the large excess of toluene and small percentage of $\text{S}_2\text{O}_8^{2-}$ decomposition.

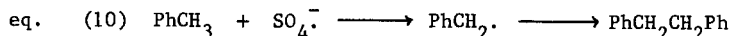
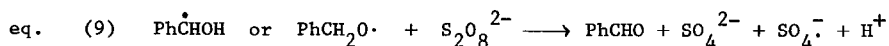
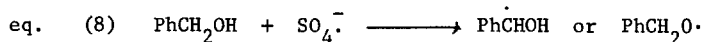
Our results, however, show considerable benzaldehyde formation with a $\text{PhCHO}/\text{PhCH}_2\text{OH}$ ratio of greater than 1 even at very low peroxydisulfate decomposition (Table I). We therefore suggest the formation of adduct II, followed by homolytic cleavage (eq. 4) to give benzyloxy radical, which then disproportionates to benzaldehyde and benzyl alcohol.

In Table II we show results of competition kinetic experiments between toluene and benzyl alcohol:



From these results we can see that the two rate constants k_6 and k_7 are of the same order of magnitude. This is as expected based on the results by Neta et al. (11). These workers determined the rate constants of a number of substituted benzenes with $\text{SO}_4^{\cdot -}$ by pulse radiolysis. The large amount of benzaldehyde formed cannot be due to secondary oxidation of benzyl alcohol. Only a small amount of secondary oxidation takes place and this is possibly one of the reasons for the $\text{PhCHO}/\text{PhCH}_2\text{OH}$ ratio of greater than 1. Another possibility is oxidation of $\text{PhCH}_2\text{O}\cdot$ by $\text{S}_2\text{O}_8^{2-}$ (eq. 9 below).

The results in Table II show with increasing benzyl alcohol concentration an increase in benzaldehyde, but the yield of bibenzyl stays constant. This may seem at first sight surprising. Results on the oxidation of benzyl alcohol by peroxydisulfate show a quantitative oxidation of benzyl alcohol to benzaldehyde via a chain reaction (12, 13):



Due to this chain reaction the yield of bibenzyl is affected only insignificantly. Reactions of alcohol with $\text{SO}_4^{\cdot -}$ are known to give alkoxy radicals (14), but recent results by Arnoldi et al. (15) on alkenols may lead one to suggest the α -hydroxybenzyl radical as intermediate in the chain oxidation.

$\text{PhCH}_2\cdot$ radicals do not add to the ring of simple aromatic systems like benzene, but do react with some polycyclic aromatics (16) (anthracene, pyrene). This is contrary to the reactivity of alkyl radicals and is due to the greater stability of benzyl radicals. As expected on the basis of the frontier orbital theory $\text{PhCH}_2\cdot$ radicals attack nitrobenzene at the O atoms of the nitro group, which have the highest HOMO coefficients (17). Our results (Exp. No. 5, 8, 9, Table I) show that nitrobenzene is a very inefficient oxidizing agent. Dimerization of benzyl radicals competes with oxidation even at high nitrobenzene concentrations. A small rate constant was noted by us (18) previously in the oxidation of hydroxycyclohexadienyl radicals by nitrobenzene. Benkeser and coworkers (19) found that the stable triphenylmethyl radical does not react at all with nitrobenzene. If the oxidation would proceed via direct electron transfer the difference in reactivity between benzyl and triphenylmethyl radicals should be the opposite from the one observed. The formation of an adduct however is consistent with the results.

Support for reaction(4) may be deduced from spin trapping experiments. The reverse of reaction(4) is the well known spin trapping reaction between alkoxy radicals and nitrosobenzene, which is known to lead to unstable adducts(20).

In summary our results support formation of an adduct followed by homolytic cleavage to a $\text{PhCH}_2\text{O}\cdot$ radical, but leave open the possibility of both mechanisms (homolytic and heterolytic cleavage) occurring simultaneously.

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12. A 500 ml deoxygenated aqueous solution containing 2.5×10^{-3} moles $\text{S}_2\text{O}_8^{2-}$ and 2.88×10^{-3} moles PhCH_2OH heated at 80°C for 30 min (97% $\text{S}_2\text{O}_8^{2-}$ and 80% PhCH_2OH consumed) gave 2.23×10^{-3} moles PhCHO (97% yield).
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TABLE I

EXP. NO.	Reactants (in moles $\times 10^3$) and conditions ¹				Products (moles $\times 10^5$)			
	PhCH ₃	PhNO ₂	TIME (MIN)	-S ₂ O ₈ ²⁻ (%)	PhCHO	PhCH ₂ OH	(PhCH ₂) ₂	$\frac{\text{PhCHO}}{\text{PhCH}_2\text{OH}}$
1	4.7	0	30	10	Trace	Trace	13.5	
2	2.35	0	30	11	13.6	4.2	0	
3	2.35	0	30	13	Trace	Trace	12.8	
4	4.7	4.85	20	n.d.	4.2	3.2	Trace	1.31
5	4.7	4.85	30	12	10.0	7.2	2.0	1.39
6	4.7	4.85	40	14	13.1	8.9	2.5	1.47
7	4.7	4.85	60	27	22.5	13.9	3.8	1.62
8	4.7	2.42	30		8.4	6.3	4.0	1.33
9	4.7	1.21	30		6.4	5.2	6.7	1.23

1) All reactions were carried out in 500 ml solutions (5×10^{-3} M in K₂S₂O₈). All solutions except No. 2 were deoxygenated by bubbling argon through the solution (prior to the addition of the organic reactants) for 30 min. In Exp. No. 2 the solution was saturated with oxygen for 30 min. Only in Exp. No. 2 did we observe formation of cresols (2.8×10^{-5} moles ortho, 1.2×10^{-5} moles meta, and 3.0×10^{-5} moles para). In Exp. No. 4 no detectable peroxydisulfate decomposition was observed.

TABLE II

EXP. NO.	Reactants (in moles) ¹			-S ₂ O ₈ ²⁻ (%)	Unreacted PhCH ₂ OH	Products (in moles $\times 10^5$)	
	PhCH ₃	PhCH ₂ OH				PhCHO	(PhCH ₂) ₂
1	2.35×10^{-3}	0		13		Trace ²	12.8
2	2.35×10^{-3}	19.2×10^{-5}		11	13.4	2.7	13.8
3	2.35×10^{-3}	28.8×10^{-5}		14	19.4	3.9	14.3
4	2.35×10^{-3}	38.4×10^{-5}		13	25.7	5.0	13.2
5	2.35×10^{-3}	48.0×10^{-5}		14	29.1	6.0	13.8
6	2.35×10^{-3}	96.0×10^{-5}		14	69.3	14.5	14.0
7	4.7×10^{-3}	0		10		Trace ²	13.1
8	4.7×10^{-3}	19.2×10^{-5}		10	12.6	1.4	15.1

1) All reactions were carried out in 500 ml solutions (5×10^{-3} M in K₂S₂O₈) deoxygenated (argon bubbling for 30 min.) and heated at 80°C for 30 min. 2) In Exp. No. 1 and 7 trace amounts of PhCHO and PhCH₂OH are formed. This is due to traces of oxygen still present in the solutions.

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