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THE ROLE OF NITRATE FREE RADICALS IN THE PHOTOCHEMICAL SIDE-CHAIN NITROOXYLATION OF ALKYLBENZENES BY CERIUM(IV) AMMONIUM NITRATE IN ACETONITRILE

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Summary: It is suggested that the reactive species in the CAN-induced photochemical side-chain nitrooxylation of alkylbenzenes is the nitrate radical, which probably acts as one-electron oxidant.

Recently, it has been shown that methylbenzenes are side-chain nitrooxylated by cerium(IV) ammonium nitrate (CAN) when irradiated, in acetonitrile, by a high pressure lamp[1] (eq. 1). In this paper we wish now to report on the mechanism of this reaction.

$$ArCH_3 \xrightarrow[CH_3CN]{CAN,\ h\nu} ArCH_2ONO_2 \qquad (1)$$

When a CAN solution in acetonitrile has been subject to flash photolysis experiments (irradiation at 355 nm with a JK system 2000 neodymium-YAG DLPY 4 laser), the characteristic absorption spectrum of nitrate radicals[2] has been observed; it is therefore highly probable that the primary photochemical process is the transfer of an electron from one nitrate ligand to the central Ce(IV) atom (eq. 2), as it also occurs in the photolysis of CAN in aqueous nitric acid.[2,3]

$$Ce^{IV}NO_3^- \xrightarrow{h\nu} Ce^{III} + NO_3^{\bullet} \qquad (2)$$

When the flash photolysis experiment was carried out in the presence of p-xylene the decay rate of $NO_3^{\bullet}$ sharply increased, thus suggesting that this radical plays a key role in the side-chain substitution process (eq. 1). The most obvious hypothesis in this respect might be a α-hydrogen atom abstraction reaction leading to a benzyl radical (eq. 3). However, $NO_3^{\bullet}$ is a strong oxidant ($E° = 2.3V$[5]) and an electron transfer process with formation of a

$$ArCH_3 + NO_3^{\bullet} \longrightarrow ArCH_2^{\bullet} + HNO_3 \qquad (3)$$

radical cation,[6] which then undergoes proton loss to give the benzyl radical (eqs 4,5), is

$$\mathrm{ArCH_3} + \mathrm{NO_3^{\bullet}} \longrightarrow \mathrm{ArCH_3^{+\bullet}} + \mathrm{NO_3^{-}} \qquad (4)$$

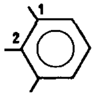
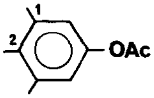
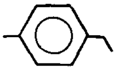
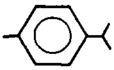
$$\mathrm{ArCH_3^{+\bullet}} \longrightarrow \mathrm{ArCH_2^{\bullet}} + \mathrm{H^{+}} \qquad (5)$$

also possible. In both cases the benzyl radical should be converted into the benzyl nitrate by a ligand transfer reaction promoted by another CAN species.[7]

Distinction between hydrogen atom transfer and electron transfer processes is generally difficult. However data in our hands are more consistent with the latter mechanism .

Thus, the intramolecular selectivity of the photochemical side-chain nitrooxylation (Table I) is quite similar to that (values in parentheses) found for the thermal side-chain oxidation of alkylaromatics by CAN in acetic acid,[8-11] a reaction which has been clearly shown to occur "via" a radical cation intermediate.[12] Particularly significant in this respect is the very drastic change in selectivity on going from hemimellitene to 5-acetoxyhemimellitene observed in both the thermal and photochemical processes.

TABLE I. Intramolecular selectivity in the side-chain photochemical nitrooxylation of some alkylbenzenes by CAN in CH_3CN at 30°C.[a]

Compound	k_{2CH_3}/k_{1CH_3}	$k_{C_2H_5}/k_{CH_3}$	$k_{CH(CH_3)_2}/k_{CH_3}$
	7.5(3.4)[b]		
	> 200(110)[c]		
		2.3(5.2)[d]	
			ca. 1(3.0)[e]

[a] VPC and/or NMR analysis of isomeric side-chain substituted products.[8-11] All data are statistically corrected for the different number of α-hydrogen atoms. Figures in parentheses refer to the corresponding thermal reactions by CAN in AcOH. [b] Ref. 8. [c] Ref. 9. [d] Ref.10. [e] Ref. 11.

The intermolecular selectivity of the photochemical process (Table II) is lower than that exhibited by the thermal oxidations promoted by CAN;[13,14] however, it is not significantly different from that found in the oxidations induced by $SO_4^{-\bullet}$, which certainly occur by an electron transfer mechanism.[15] Moreover, the greater reactivity of toluene with respect to cumene is certainly more in line with an electron transfer mechanism than with a hydrogen atom transfer mechanism.

TABLE II. Relative rates in the side-chain photochemical nitrooxylation of alkylbenzenes by CAN in CH_3CN at 30°C.

Substrate	Rel.rate[a]
p-xylene	3.9
m-xylene	3.1
ethylbenzene	1.3
toluene	1.0
p-chlorotoluene	0.8
cumene	0.3

[a] Obtained by competitive experiments (VPC analysis of unreacted substrates).

Another very significant observation is that photochemical oxidation can also take place with substrates which have no α-hydrogen atom available for the hydrogen abstraction process (eq. 3). Thus, irradiation of a solution of CAN and 2,3-dimethyl-2,3-diphenylbutane leads to products (t-cumyl alcohol, 2-phenyl-1,2-propanediol dinitrate and acetophenone)[16] which derive from the cleavage of the C(2)-C(3) bond. This reaction can be easily accounted for by assuming the formation of an intermediate radical cation in which the C(2)-C(3) bond is strongly weakened.[17]

Finally, the capability of $NO_3^\bullet$ to be involved in electron transfer processes has been clearly shown by the observation of the spectrum of the anisole radical cation (maximum at 430 nm[18]) when a solution of CAN and anisole has been subject to flash photolysis. Attempts to detect the p-xylene radical cation in corresponding experiments with p-xylene as the substrate have failed, but this may be probably due to the fact that the lifetime of the p-xylene radical cation is much shorter than that of the anisole radical cation.

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References and Notes

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2. R.W.Glass and T.W.Martin, J.Am.Chem.Soc., 92, 5084 (1970).
3. The observation that solutions of CAN in acetonitrile are stable under irradiation[1] can be probably explained by an electron back-exchange reaction ($Ce^{III} + NO_3^{\bullet} \longrightarrow Ce^{IV} NO_3^{-}$) which might be the predominant decay mode of $NO_3^{\bullet}$ in the absence of substrate.[4]
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6. The radical cation might also be formed by an addition-elimination sequence: $ArCH_3 + NO_3^{\bullet} \longrightarrow NO_3ArCH_3^{\bullet} \longrightarrow NO_3^{-} + ArCH_3^{+\bullet}$. At present we cannot distinguish between this possibility and an electron transfer process.
7. The overall process is very effcient since with p-xylene the quantum yield for the disappearance of the substrate is 0.9. In line with the stoichiometry of the reaction (2 moles of CAN for 1 mole of substrate)[1] the quantum yield for the disappearance of CAN is 1.8.
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