

CERIUM (IV) AMMONIUM NITRATE CATALYZED PHOTOCHEMICAL AUTOXIDATION OF ALKYL BENZENES

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Summary: The autoxidation of alkylbenzenes can be promoted photochemically in the presence of catalytic amounts of cerium (IV) ammonium nitrate (CAN) under very mild conditions, the efficiency of the process being significantly increased by added acids. It is suggested that the reaction is promoted by NO_3 radicals formed in the light induced decomposition of CAN and that Ce(III) may be reoxidized to Ce(IV) by benzylperoxy radicals.

The metal catalyzed autoxidation of alkylbenzenes is generally carried out at relatively high temperature and dioxygen pressure.¹ The search for reactions which can occur under milder conditions is therefore warranted.

Following our recent discovery² that cerium (IV) ammonium nitrate (CAN), when irradiated in acetonitrile, can promote the side-chain nitroxylation of alkylbenzenes at room temperature, we now present results indicating that, under very mild conditions, CAN is also able to catalyze the photochemical autoxidation of alkylbenzenes. The efficiency of the process is significantly enhanced in the presence of added acids (HClO_4 or HNO_3).

Reactions have been carried out by bubbling dioxygen through the reaction mixture (4 mmol of alkylbenzene, 0.01-0.8 mmol of CAN, 0-1.6 mmol of acid in 100 ml of CH_3CN) irradiated by a high pressure mercury lamp (125 W, filtered by pyrex), at room temperature. The reaction mixture poured into water, was extracted with ethyl ether. After removing of the solvent, the crude product was analyzed by NMR (comparison with authentic specimen) using *p*-dimethoxybenzene as an internal standard (see Table).

For methylbenzenes the main oxidation product is the corresponding benzaldehyde. Benzyl nitrates, benzoic acids and small amounts of benzyl alcohols are also observed. Interestingly, oxidation of the methyl group predominates over that of the isopropyl group in the reaction of *p*-cymene. With cumene as substrate cumyl alcohol and cumyl hydroperoxide are the major products. The oxidation rate is enhanced by electron donating substituents as shown by some of the data in the Table (compare for example entries 2 and 13).

Data in the Table also clearly show that the addition of acids significantly enhances the catalytic efficiency of CAN; thus in the presence of 0.08 mmol of CAN the overall yield of

TABLE. Products Yields^a in the CAN-Catalyzed Photochemical Autoxidation of Some Alkylbenzenes in CH₃CN at Room Temperature.

Entry	Substrate ^b	Catalyst, mmol	Reaction time, h	ArCHO ^c	ArCH ₂ ONO ₂ ^c	ArCH ₂ OH ^c	ArCH ₂ O ₂ H ^c	ArCO ₂ H ^c
1.	<u>p</u> -Xylene	CAN, 0.8	1	19			21	
2.		0.8	6	43	11	3		7
3.		0.8	15	44	13			9
4.		CAN, 0.08	5	6	3			
5.		CAN, 0.8; HNO ₃ , 0.8	5	53	10	10		20
6.		CAN, 0.02; HNO ₃ , 1.6	5	26 ^d		3	4	3
7.		CAN, 0.02; HClO ₄ , 1.6	5	22				5
8.		CAN, 0.08; HNO ₃ , 0.8	5	27	2	4	10	4
9.		CAN, 0.01; HNO ₃ , 1.6	5	19			3	3
10.		HNO ₃ , 1.6	5	2				
11.		HNO ₃ , 1.6 (dark)	15			no reaction		
12.		AIBN, 0.8	5	7				
13.	Toluene	CAN, 0.8	15	24	12	4	4	6
14.	<u>p</u> -Cymene ^e	CAN, 0.8	5	31	9	9	6	
15.	Cumene	CAN, 0.8	5	9(PhC ^O _{Me})		14(PhC ^{Me} _{OH})	8(PhC ^{Me} _{CO₂H})	

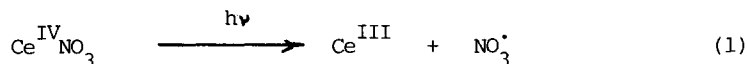
^aWith respect to the starting material (determined by NMR analysis). The material balance, including the unreacted substrate, was between 90 and 100%. ^b4 mmol in 100 ml of CH₃CN.

^cAr is p-CH₃C₆H₄ for p-xylene, C₆H₅ for toluene, and p-CH(CH₃)₂C₆H₄ for p-cymene. ^d22% yields of isolated compound. ^eBesides products reported in the Table ca. 5% of a mixture of p-CH₃C₆H₄C(CH₃)₂OH, p-CH₃C₆H₄C(CH₃)₂O₂H and p-CH₃C₆H₄COCH₃ has been obtained.

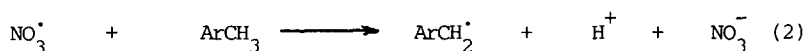
oxidation products increases from 9 to 47% when 0.8 mmol of HNO₃ are added (entries 4 and 8); HClO₄ has a similar effect (compare entries 6 and 7). It also appears that HNO₃ alone can promote photochemical (but no thermal) autoxidation of p-xylene (entries 10 and 11), however

to a much less extent than when in combination with even very small amounts of CAN (compare, for example, entries 6 and 9 with entry 10).

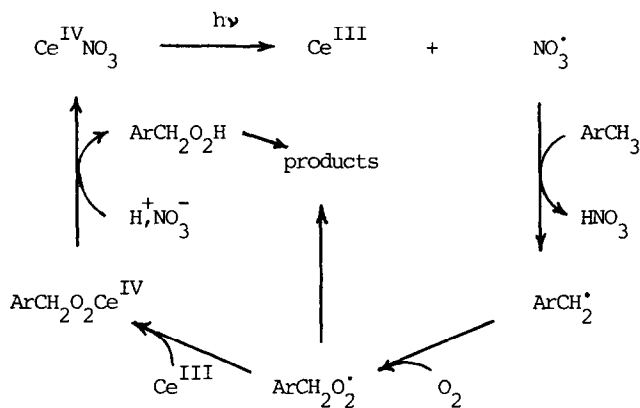
On the basis of previous mechanistic observations³ there should be little doubt that this reaction is promoted by NO_3^\bullet radicals, generated in the photochemical decomposition of CAN (eq. 1); these radicals react with the substrate, presumably by an electron transfer mechanism,



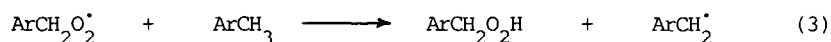
to give a benzyl radical as shown in eq. 2.



The subsequent reaction of the benzyl radical with dioxygen leads to a benzylperoxy radical which may be able to regenerate Ce^{IV} from Ce^{III} in a presumably photochemical process. The formed Ce^{IV} species still possesses nitrate ligands and may therefore be again involved in the formation of NO_3^\bullet radicals; it is, however, also possible that nitrate ligands are reintroduced in the Ce^{IV} coordination sphere by an acid catalyzed reaction of the Ce^{IV} species with NO_3^- which would also explain the favorable role of the acid.⁴ The catalytic cycle reported in the scheme may be suggested.



The possibility that alkylperoxide radicals can promote the $\text{Ce}^{\text{III}} \rightarrow \text{Ce}^{\text{IV}}$ oxidation has already been suggested by Sheldon and Kochi to rationalize the Ce^{IV} -catalyzed photochemical decarboxylation of pivalic acid in the presence of dioxygen.⁵ On the other hand an important contribution of a direct hydrogen atom abstraction by peroxide radicals, eq. 3, to the oxidation chain has been made unlikely by the following observations: (i) the photochemical autoxidation of *p*-xylene in the presence of azoisobutyronitrile (AIBN)



produces only 7% of *p*-toluic aldehyde (entry 12), whereas, under the same conditions but in the presence of CAN this aldehyde is formed in 43% yield together with 21% of other oxidation products (entry 2); (ii) some competitive experiments have shown that the substrate selectivity of CAN-catalyzed autoxydation (*p*-xylene/toluene = 5.2, toluene/cumene = 2.8) is very similar to that observed in the stoichiometric photochemical side-chain nitroxylation of the same substrates,³ thus suggesting that reactions (1) and (2) may take part in the propagation process; (iii) toluene is more reactive than cumene and the methyl group is more reactive than the isopropyl group in *p*-cymene whereas the reverse is expected in both cases if reaction (3) would play a significant role.⁶

The present results in some respect resemble those obtained in the photochemical autoxidation of alkylbenzenes catalyzed by 9,10-dicyanoanthracene.⁷ However, in the latter reaction, the observation that oxidation of *p*-cymene occurs preferentially at the isopropyl group, led to suggest that initial electron transfer is followed by a chain where reaction (3) plays an important role.⁸

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