One-Electron Oxidation of Alkylbenzenes in Acetonitrile by Photochemically Produced NO₃[•]: Evidence for an Inner-Sphere Mechanism

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The reaction between NO₃[•] and polyalkylbenzenes was studied using 308-nm laser flash photolysis of cerium-(IV) ammonium nitrate in the presence of the alkylbenzenes in acetonitrile solution. For all benzenes, with the exception of monoalkylbenzenes and o- and m-xylene, the reaction with NO₃[•] was found to yield the corresponding radical cations and to proceed in an apparently straightforward bimolecular manner. For monoalkylbenzenes and o- and m-xylene, radicals were seen which are derived from the parents by formal loss of H[•] from the side chain of the aromatic. This reaction proceeds via a complex between the aromatic and NO₃[•] with the decomposition of the complex being rate determining at higher concentrations of aromatic (rate constants for decomposition between 6×10^5 and 4×10^7 s⁻¹). In the complex, electron transfer from the aromatic to NO₃[•] is suggested to be concerted with deprotonation of the incipient radical cation. Formation of a complex between NO₃[•] and aromatic is likely even in those cases where radical cations are observed, with the assumption that in these cases the complex decomposition rate is $\geq 6 \times 10^7$ s⁻¹.

Introduction

The reaction of NO_3° radicals with organic substrates in solution⁴⁻¹⁵ and in the gas phase¹⁶ has received considerable attention. The NO_3° radical can be generated in acetonitrile solutions by photolysis of cerium(IV) ammonium nitrate or in aqueous phase by radiolysis^{5,15} or photolysis of potassium or ammonium nitrate in concentrated nitric acid solutions. In the photochemical process, the NO_3° radical has been suggested^{4,13,17} to be formed by an intramolecular electron-transfer process in the excited Ce^{IV} complex (eq 1). The formation of NO_3° has

$$(\mathrm{NH}_{4})_{2}\mathrm{Ce}^{\mathrm{IV}}(\mathrm{NO}_{3})_{6} \xrightarrow{h_{\nu}}{\overset{h_{\nu}}{\longrightarrow}} (\mathrm{NH}_{4})_{2}\mathrm{Ce}^{\mathrm{IV}}(\mathrm{NO}_{3})_{6}^{*} \xrightarrow{} (\mathrm{NH}_{4})_{2}\mathrm{Ce}^{\mathrm{III}}(\mathrm{NO}_{3})_{5}^{*} + \mathrm{NO}_{3}^{*} (1)$$

been directly seen by use of the laser flash photolysis technique.^{7,10,11,13,14} The involvement of (photochemically produced) NO_3 in the oxidation of alkylbenzenes has also been investigated using product analysis methods. This reaction leads to the formation of benzyl nitrates.^{6,7}

On the basis of these product and time-resolved studies, a mechanism has been postulated for the reaction of NO_3° with alkylarenes with an oxidation potential lower than that of toluene which involves a radical cation intermediate generated by electron transfer from the π system of the aromatic to NO_3° , whereas for toluene, abstraction of a hydrogen atom from the methyl group has been proposed.^{7,18} In contrast, Ito et al. have recently suggested an electron-transfer mechanism only for 4-methoxy-toluene, since in this case only, the intermediate radical cation was detected. For other (nonmethoxylated) alkylbenzenes a hydrogen atom transfer was proposed.¹⁰

To remove these inconsistencies and to get a better understanding of the general mechanism of oxidation of alkylaromatics by NO_3^{\bullet} , we have now carried out a detailed laser photolysis investigation of the reaction between NO_3^{\bullet} and the complete family of methylated benzenes with the aim of detecting the oneelectron-oxidized species directly.

Results and Discussion

(1) Nature of the Transients Generated by Photolysis of Cerium(IV) Ammonium Nitrate (CAN) in CH₃CN in the Absence and Presence of Methylbenzenes. (a) Photolysis of CAN in the

Absence of Substrates. The absorption spectrum of the transient species obtained on photolysis by a 20-ns pulse of 308-nm light of 0.2 mM cerium(IV) ammonium nitrate in deoxygenated acetonitrile is shown in Figure 1. The spectrum has been corrected for depletion of CAN (for details see Experimental Section). The three absorption peaks in the visible region at 595, 630, and 670 nm, with the largest absorbance at 630 nm, agree with published spectra^{4,5,13-15} of NO₃[•] in aqueous solution.¹⁹ The band between \approx 450 and 700 nm can thus be attributed to the nitrate radical. The lifetime of the transient absorbing at 630 nm was found to be ca. 85 μ s and not to be influenced by oxygen.²⁰ The latter observation is in agreement with the assignment in terms of NO₃[•].

As seen in Figure 1, there is in addition a strong absorption between ≤ 230 and ≈ 400 nm,²¹ which is present immediately after the laser pulse. This absorption was found not to change with time over ≤ 1 ms. Therefore, the absorption must be due to a species different from NO₃[•]. On the basis of its undelayed formation, the species is assigned to (NH₄)₂Ce^{III}(NO₃)₅[•], the other fragment produced in the primary photochemical process (eq 1). That this absorption is not that of NO₃[•] is also evident from its different chemical reactivity (see later).

If it is assumed that the ϵ of NO₃[•] and that of (NH₄)₂-Ce^{III}(NO₃)₅[•] at 370 nm (where there is a minimum in the spectrum, see Figure 1) are zero, the extinction coefficient of NO₃[•] can be determined by comparing the positive Δ OD at, e.g., 630 nm with the negative Δ OD (due to depletion of CAN) at 370 nm, where the ϵ of CAN is 4485 M⁻¹ cm⁻¹. On this basis, the ϵ of NO₃[•] at 630 nm results as 1350 M⁻¹ cm⁻¹.²² This value compares well with the number (1300 M⁻¹ cm⁻¹) recently determined¹⁵ for NO₃[•] in water using the pulse radiolysis technique.

(b) Photolysis of CAN in the Presence of Alkylbenzenes. On addition of an alkylaromatic (usually in concentrations ≥ 0.5 mM), the lifetime of NO₃ • as measured at 630 nm decreased drastically, indicating a reaction of this radical with the aromatic.

Toluene: Photolysis of 0.2 mM CAN in Ar-saturated acetonitrile in the presence of 10 mM toluene, the least reactive substrate in the methylbenzene family, produced a transient whose absorption spectrum, recorded 1.4 μ s after the pulse, is shown in Figure 2 (circles). The spectrum has been corrected for depletion



Figure 1. Absorption spectrum measured at 20 ns after the pulse on 308-nm photolysis of 0.2 mM CAN in Ar-saturated acetonitrile. The spectrum is corrected for depletion of CAN. Inset: The absorption spectrum of CAN in acetonitrile.



Figure 2. Corrected absorption spectrum (in the inset: *un*corrected absorption spectrum) recorded $1.4 \,\mu s$ after the pulse on 308-nm photolysis of 0.2 mM CAN in the presence of 10 mM toluene in deoxygenated acetonitrile (circles). For comparison the absorption spectrum of the benzyl radical produced by 248-nm photolysis of a 5 mM solution of 1,3-diphenylacetone is shown (triangles).

of toluene and of CAN, and for formation of $(NH_4)_2Ce^{III}(NO_3)_5^{\circ}$ which did not show any reactivity with toluene (for details of the correction procedure, see Experimental Section). The spectrum shows peaks in the region 250–320 nm ($\lambda_{max} = 260, 305, and 315$ nm), which are assigned to the benzyl radical. In support of this is the fact that the same peaks were observed when the benzyl radical was independently generated by 248-nm photolysis of 1,3-diphenylacetone in acetonitrile (Figure 2, triangles).^{23,24} When the experiment was performed in the presence of O₂, the benzyl radical decayed rapidly and its spectrum was replaced by a new one (not shown) with a broad band at ca. 250 nm which is attributed to the benzyl peroxyl radical.

o- and m-Xylene: With these substrates the only transients detected were the corresponding benzyl radicals, o-methyl and m-methylbenzyl, respectively. These radicals could be independently produced by reaction in aqueous solution of the aromatics with the O⁻⁻ radical, which is known to react predominantly by H abstraction.²⁷

p-Xylene: In Figure 3 are shown the absorption spectra following the reaction of NO_3 with 10 mM *p*-xylene. The NO_3 decay was considerably faster than in the presence of the same concentration of toluene. At 95 ns after the flash *two* transients are apparent, one of which is identified as 1,4-dimethylbenzene



Figure 3. Absorption spectra (corrected) obtained on 308-nm photolysis of a deoxygenated 0.2 mM solution of CAN in acetonitrile in the presence of 10 mM *p*-xylene. Full triangles: Recorded at 95 ns after the pulse. Open triangles: The 400-500-nm band magnified by a factor of 10. Circles: spectrum (recorded at 400 ns after the pulse) of the 4-meth-ylbenzyl radical. The insets (uncorrected) show the decay of the radical cation at 450 nm (inset c) and the resulting formation of 4-methylbenzyl radical at 270 and 322 nm (insets a and b).



Figure 4. Absorption spectrum (corrected) of the durene radical cation produced on 308-nm photolysis of 0.2 mM CAN in the presence of 10 mM durene, observed 150 ns after the pulse (circles). Spectrum (corrected) of the 2,4,5-trimethylbenzyl radical, produced in the same solution after addition of 20 mM tetrabutylammonium nitrate, recorded at 700 ns after the pulse (triangles). Insets b and d show the decay of the radical cation, and in a and c the formation of 2,4,5-trimethylbenzyl radical is displayed, all in the presence of 20 mM NO₃⁻.

radical cation $(\lambda_{max} = 305 \text{ and } 450 \text{ nm})$,^{28,29} the other as 4-methylbenzyl radical $(\lambda_{max} = 265, 310, \text{ and } 320 \text{ nm})$.^{25,30} The absorption spectrum of the latter is well developed 400 ns after the laser pulse, a time at which the radical cation has completely disappeared (see insets). From the insets it is evident that at 322 nm (inset b) the absorption due to CAN (apparent as a *negative* signal, due to depletion of CAN) is in part replaced by the absorption due to the 4-methylbenzyl radical (also seen at 270 nm, see inset a), with a rate identical to that of the disappearance of the radical cation at 450 nm (inset c).

Durene: The (corrected) absorption spectrum recorded on reaction of NO₃[•] with 10 mM durene is shown in Figure 4. At short times (150 ns after the laser pulse), the radical cation is clearly visible. The spectrum has bands at $\lambda_{max} = 235$, 297, and 475 nm. It is very similar to that produced in acidic aqueous solution from the OH adduct of durene by H⁺-induced water elimination.²⁸ The peak at 235 nm (see Figure 4) was not seen in the pulse radiolysis work.²⁸ The decay of durene radical cation is slower than that of *p*-xylene.

It was found that the decay of the radical cation of durene could be considerably accelerated by adding NO_3^- (as the tetra*n*-butylammonium salt) to the solution. In the presence of NO_3^- ,



Figure 5. Dependence of k_{obsd} for decay of NO₃[•] measured at 630 nm on [aromatic] for p-, o-, and m-xylene.

the radical cation generated a transient (with 20 mM NO₃present, fully developed at 700 ns after the flash, see Figure 4) with $\lambda_{max} = 270$, 304, 318, and 330 nm. This spectrum is in perfect agreement with that reported²⁵ for 2,4,5-trimethylbenzyl radical produced by the reaction of O⁻⁻ with durene in aqueous solution. From the insets it is seen that the decay of the radical cation at $\lambda = 290$ and 455 nm (insets b and d) is synchronous with the buildup of the neutral radical at 265 and 330 nm (insets a and c).³¹ The effect of NO₃⁻ can be understood in terms of this anion acting as a Brönsted base with respect to the radical cation.

Hexamethylbenzene, pentamethylbenzene, prehnitene, isodurene, pseudocumene, hemimellitene, and mesitylene: All these substrates when reacted with NO₃• gave rise to radical cations, as shown by the absorptions at 490 (hexamethylbenzene), 470 (pentamethylbenzene), 450 (prehnitene), 470 (isodurene), 460 (pseudocumene), 470 (hemimellitene), and 480 nm (mesitylene), in agreement with the spectroscopic data reported by Schested.²⁸ With the substrates with ≥ 4 methyl groups, the decay of the radical cations did not follow (clean) first-order kinetics.

(2) Kinetics of the Reaction of NO₃[•] with Alkylbenzenes. The bimolecular rate constants for reaction of NO₃[•] with the aromatics were determined by measuring the rate of optical density (OD) decrease at 630 nm as a function of the concentration of added alkylbenzene. In all cases except *m*-xylene and the monoalkylated benzenes, the k_{obsd} (decay at 630 nm) values increased linearly with [alkylbenzene] up to rates of $\approx 6 \times 10^7$ s⁻¹ which represents the limit of the time resolution of the apparatus (given by the 20-ns laser pulse). From the slopes of the linear plots (for an example see Figure 5) the bimolecular rate constants were obtained (error limits ±10%). The data are collected in Table I. The rate constants are of the order 10^9-10^{10} M⁻¹ s⁻¹. The reactivity of NO₃[•] approaches the diffusion-controlled limit (1.8 × 10¹⁰ M⁻¹ s⁻¹ in acetonitrile)³² as the number of methyl groups on the ring increases from two to six.

(a) Monoalkylbenzenes and m-Xylene. In the case of m-xylene and toluene, toluene- d_8 , ethylbenzene, isopropylbenzene (cumene), *tert*-butylbenzene, and bibenzyl, the k_{obsd} for decay of NO₃ values level off at higher concentrations of aromatic, i.e., plateau values of k_{obsd} are reached (see Figures 5 and 6).³³ The plateau means that in this range the rate of depletion of NO₃ is *in*dependent of the concentration of the aromatic.

This type of behavior can be explained in terms of a reaction which involves the formation followed by decomposition of an intermediate into reactants and products with the latter step being rate-determining at higher concentrations of aromatic. The intermediate is proposed to be an adduct between aromatic and NO_3° , possibly a π -complex.³⁴ π -complexes between aromatics and electron-deficient radicals such as Cl[•] have been previously proposed.³⁵ The formation of a complex in the reaction of NO_3° with aromatic substrates has also been suggested¹² to explain the primary:tertiary H-atom abstraction ratios observed in the reactions of NO_3° with isomeric cymenes. Reversible addition

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TABLE I: Rate Constants for Reaction of NO₃ with Methylbenzenes in Acetonitrile at Room Temperature and Approximate Lifetimes of Radical Cations

methylbenzene	structure	IP ^a /eV	k ^b /M⁻¹ s⁻¹	lifetime of radical cation ^c /µs
o-xylene	1,2-dimethylbenzene	8.56	3.7 × 10 ⁹	≤0.02
p-xylene	1,4-dimethylbenzene	8.44	6.2 × 10 ⁹	0.1
p -xylene- d_{10}	-	8.44 ^d	5.6×10^{9}	
mesitylene	1,3,5-trimethylbenzene	8.40	6.5 × 10 ⁹	0.2
hemimellitene	1,2,3-trimethylbenzene	8.42	9.2 × 10 ⁹	0.2
pseudocumene	1,2,4-trimethylbenzene	8.27	9.3×10^{9}	0.3
isodurene	1,2,3,5-tetramethyl- benzene	8.06	1.1 × 10 ¹⁰	0.4
prehnitene	1,2,3,4-tetramethyl- benzene	8.14	1.2 × 10 ¹⁰	0.45
durene	1,2,4,5-tetramethyl- benzene	8.03	1.3 × 10 ¹⁰	(1. 0) "
pentamethyl- benzene		7.92	9.6 × 10 ⁹	(4.2) ^e
hexamethyl- benzene		7.85	1.1 × 10 ¹⁰	(9 .1) ^e
cyclohexane		9.88⁄	2.2 × 10 ⁶ g.i	

^a From Schlesener, C. J.; Amatore, C.; Kochi, J. K. J. Phys. Chem. **1986**, 90, 3747. ^b Obtained from the slope of the straight lines in the k_{obsd} (decay of NO₃*) vs [aromatic] plots. Error limits ±10%. The range of concentration of aromatic was 0-20 mM. ^c Recorded at laser powers of $\approx 6 \text{ mJ/pulse}$. The values were obtained from first-order fits to the OD decay in the λ range 440-460 nm. ^d From: Brown, R. G.; Phillips, D. J. Chem. Soc., Faraday Trans. 2 **1974**, 70, 630. ^e The decay kinetics is not first order. See also ref 44. ^J From Turner, D. W. Adv. Phys. Org. Chem. **1966**, 4, 31. ^g The k_{obsd} vs [cyclohexane] dependence is not curved. ⁱ For H-abstraction reactions of NO₃* from alcohols and ethers, see: Shastri, L. V.; Huie, R. E. Int. J. Chem. Kinet. **1990**, 22, 505.



Figure 6. Dependence of k_{obsd} for decay of NO₃ on [aromatic] for toluene (open triangles), toluene- d_8 (open circles); ethylbenzene (open squares), cumene (filled triangles), *tert*-butylbenzene (filled circles; the k_{obsd} values have been multiplied by the factor 17), and bibenzyl (filled squares).

of NO_3 to the aromatic ring has also been proposed for phenolic compounds in the gas phase.³⁶

The processes described are symbolized by the following reaction scheme:

$$\operatorname{Ar} + \operatorname{NO}_{3} \stackrel{k_{f}}{\underset{k_{r}}{\rightleftharpoons}} \operatorname{Ar} \cdots \operatorname{NO}_{3} \stackrel{k_{d}}{\rightarrow} \operatorname{products}$$
 (2)

If it is assumed that the rate constant for the decomposition of the complex into the reactants, k_r , is much larger than that into products, k_d , an equilibrium constant can be defined as $K = k_f/k_r$ = $[Ar \cdots NO_3^*]/[Ar][NO_3^*]$. Since the concentration of Ar is always much larger than that of NO₃*, at any time $[Ar] = [Ar]_0$ and the forward reaction (rate constant k_f) is of pseudo-firstorder nature. At sufficiently high concentration of Ar, the rate of disappearance of NO₃* will be determined by k_d .

The experimentally observed dependence of k_{obsd} on [Ar] can be analyzed and further information on k_d and on the equilibrium constant K can be obtained on the basis of the following considerations: The total amount of NO₃[•] consists of uncomplexed NO₃[•] (observed at 630 nm) and of Ar--NO₃[•]. On the basis of



Figure 7. Double reciprocal plots of k_{obsd} vs concentration according to eq 6 for toluene (filled triangles), toluene- d_8 (filled squares), cumene (open triangles), *tert*-butylbenzene (open circles), and bibenzyl (filled circles).

TABLE II: Equilibrium and Rate Data Relating to NO_3 -Alkylbenzene Complexes in Acetonitrile at 20 ± 1 °C

alkylbenzene	IP ^a /eV	$k^{d}/M^{-1} s^{-1}$	<i>K</i> ^e /M ⁻¹	$k_{\rm d}^{f}/{\rm s}^{-1}$	$k_{\rm d}^{g}/{ m s}^{-1}$
m-xylene	8.56	2 × 10 ⁹	70	4.2×10^{7}	4.4×10^{7}
bibenzyl	9.1 ^b	2×10^{8}	40	6.6×10^{6}	6.0×10^{6}
toluene	8.82	1×10^{8}	17	8.7×10^{6}	7.3×10^{6}
toluene-d ₈	8.82 ^c	6×10^{7}	12	5.6×10^{6}	4.5×10^{6}
ethylbenzene	8.77	2×10^{8}	17	1.3×10^{7}	1.3×10^{7}
isopropylbenzene	8.71	4×10^{7}	14	4.7×10^{6}	4.4×10^{6}
tertbutylbenzene	8.71	1×10^{7}	19	6.7 × 10 ⁵	6.0 × 10 ⁵

^a From Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. J. Am. Chem. Soc. **1984**, 106, 3968. ^b From Pignataro, S.; Mancini, V.; Ridyard, J. N. A.; Lempka, H. J. Chem. Commun. **1971**, 142. ^c See footnote d in Table I. ^d The numbers in this column are from the tangents of (the curved) k_{obsd} vs [alkylbenzene] plots in the concentration range 1–20 mM. The values, which are lower limits due to the curvature of the plots, are a measure of the reactivity of the alkylbenzene. If there was no curvature, the numbers would be interpreted as the bimolecular rate constants for reaction of NO₃^{*} with the substrate. ^c Evaluated from the slope and the intercept of the straight lines as reported in Figure 7; see text. ^f Reciprocal of the intercept from the 1/ k_{obsd} vs [alkylbenzene] plots.

the stoichiometry of the reaction it follows that

$$d[P]/dt = -d([NO_3^{\circ}] + [Ar \cdots NO_3^{\circ}])/dt = k_d[Ar \cdots NO_3^{\circ}]$$
(3)

Replacing $[Ar \dots NO_3^{\circ}]$ by $K[NO_3^{\circ}][Ar]_0$ (from the equilibrium definition) yields

$$-(d[NO_{3}^{*}]/dt)(1 + K[Ar]_{0}) = k_{d}K[NO_{3}^{*}][Ar]_{0} \quad (4)$$

After taking into account the term $k_{obsd} \equiv (1/[NO_3^{\bullet}])(d[NO_3^{\bullet}]/dt)$, one obtains

$$k_{\rm obsd} = k_{\rm d} \mathbf{K} [\mathbf{A}\mathbf{r}]_0 / (1 + \mathbf{K} [\mathbf{A}\mathbf{r}]_0)$$
(5)

Taking the reciprocal affords

$$1/k_{\rm obsd} = 1/k_{\rm d} + 1/k_{\rm d}K[{\rm Ar}]_0$$
 (6)

from which it is evident that a plot of $1/k_{obsd}$ vs $1/[Ar]_0$ should give a straight line whose intercept (from which k_d can be obtained) if divided by its slope yields K. In Figure 7 are shown examples which demonstrate that the double reciprocal plots according to eq 6 do in fact yield satisfactorily straight lines for the monoalkylbenzenes. The equilibrium constants K and the k_d values derived from the analyses according to eq 6 are collected in columns 4 and 5 of Table II.

In column 6 the corresponding numbers directly obtained from the plateau values of the k_{obsd} vs [Ar] plots (see Figure 6) are listed for comparison. The numbers are quite similar which suggests that the kinetic scheme shown above is not a bad representation of the reactions going on. From the low K values it is clear that the interaction of NO₃ with the aromatic within the complex is relatively weak.

Once the complex is formed, its decomposition to a benzyl radical can take place either by a direct route, involving a hydrogen atom transfer process, or by deprotonation of an intermediate radical cation (lifetime ≤ 20 ns), formed by one electron transfer. The former possibility seems supported by the observation that, for the case of toluene/toluene- d_8 , the kinetic isotope effect k_d -(H)/ k_d (D) is 1.6, a value larger than that (1.1–1.3) expected³⁷ for a secondary isotope effect, which indicates a contribution of the breakage of the C_{α} -H bond in the transition state of the reaction.³⁸ On the same line is the finding that k_d is a factor of ca. 2 larger with ethylbenzene than with toluene, in agreement with the smaller C-H strength in the former compound. On this basis, however, a further increase in k_d would be expected in going from ethyl- to isopropylbenzene since the C_{α} -H bond strength is further reduced. In fact, the opposite is true since k_d for isopropylbenzene is three times *lower* than for ethylbenzene. The latter observation is therefore inconsistent with an H-atom transfer mechanism, whereas it is better in line with an electron transfer reaction concerted with deprotonation since it is known that the ease of deprotonation from C_{α} of an aromatic radical cation depends on the orientation of the C_{α} -H bond relative to the aromatic ring.³⁹ The most favorable situation is when the C_{α} -H bond is collinear with the p orbitals as in conformer 1. It is evident that replacement of H by CH₃ increases the relative weight of the unfavorable conformer 2, due to steric interactions with the ortho hydrogens in the ring, thereby leading to a decrease of the rate constant for deprotonation.

The importance of deprotonation from the incipient radical cations is also evident from the very low k_d value for *tert*butylbenzene (whose IP is the same as that of isopropylbenzene): With this compound there is no C_{α} -H present. The conclusion is thus that in the reaction of NO₃[•] with the monoalkylbenzenes and with *m*-xylene electron transfer and deprotonation are to some extent concerted. There is precedence for this type of mechanism.³⁸

(b) p-Xylene and Tri-, Tetra-, Penta-, and Hexamethylbenzene(s). As pointed out in section 1b, in the case of p-xylenes and the benzenes with \geq 3 methyl groups, the corresponding radical cations were seen as the primary products from the reaction with NO3[•]. Thus an electron-transfer reaction certainly takes place, and the benzyl radicals seen at a later stage are formed by deprotonation of the intermediate radical cations. The fact that with *p*-xylene the measured kinetic isotope effect $(k_{\rm H}/k_{\rm D})$ is 1.1 (Table I) is in line with this picture. However, the problem is to decide whether one is dealing with an outer-sphere or an innersphere electron transfer. In view of the clear evidence for the formation of a weak complex between NO₃ and monoalkylbenzenes and m-xylene, we feel that the latter possibility is the most probable one. On this basis, the fact that for p-xylene and the other polymethylbenzenes the k_{obsd} vs [Ar] dependences are linear up to $\approx 6 \times 10^7 \, \text{s}^{-1}$ might simply indicate that the lifetimes of the corresponding complexes are ≤ 20 ns. If this is the case, the reaction between NO₃ and the aromatics which leads within ≤ 20 ns to the radical cations (provided the concentration of aromatic is sufficient to scavenge NO3* within that time) would thus only appear to proceed by outer-sphere electron transfer. The distinction between the two types of aromatics would then be artificial in these cases since it would be given by the time resolution of the apparatus.

It should be noted that in a recent work¹⁸ an outer-sphere electron-transfer mechanism was suggested for the reaction of NO₃• with alkyl aromatics with an oxidation potential lower than that of toluene, on the basis of a Marcus analysis of kinetic results.⁴⁰ However, it has been recently shown that Marcus behavior is also exhibited by inner-sphere electron-transfer mechanisms.⁴¹ In fact, an inner-sphere process could better rationalize the relatively low intrinsic barrier (20 kcal/mol) which has been measured¹⁸ for that reaction. The assumption of an inner-sphere process allows one to discuss the reactions of alkylaromatics with NO₃. on the basis of only one mechanism. Thus, with systems of relatively low oxidation potentials (less than that of p-xylene (8.44 eV)), electron transfer in the complex is very fast and the lifetime of the complex is so short (≤ 20 ns, since the $k_{obsd}/[Ar]_0$ plots are linear up to 6×10^7 s⁻¹) that it could not be detected. In this circumstance, experimentally observed are the radical cations. On the other hand, if the oxidation potential of the substrate is increased, the electron transfer becomes slower, whereas the lifetime of the radical cation with respect to deprotonation becomes shorter.⁴² On further increasing the oxidation potential, electron transfer and deprotonation occur on the same time scale, as outlined above, and benzylic type radicals are the experimentally detected "initial" products.43

(3) Summary and Conclusions. It has been shown that in acetonitrile the reaction between NO₃[•] and alkylaromatics proceeds, on the nano- to microsecond scale, to give radical cations and/or benzyl-type neutral radicals, depending on the oxidizability (oxidation potential) of the substrate. Radical cation formation is observed with *p*-xylene and benzenes with ≥ 3 methyl groups (IP $\leq 8.4 \text{ eV}$), whereas with monoalkylbenzenes and *m*-xylene (IP $\geq 8.6 \text{ eV}$) only benzyl radicals were seen at $\geq 20 \text{ ns}$. A kinetic study showed that with *m*-xylene and MO₃[•] first forms, which leads to the benzyl radical via a concerted electron transfer-deprotonation mechanism. It is conceivable that in the reactions of *p*-xylene and polymethylbenzenes a similar complex is formed whose lifetime must, however, be $\leq 20 \text{ ns}$, and which transforms into the corresponding radical cations and NO₃⁻.

Experimental Section

Cerium(IV) ammonium nitrate (CAN), tetra-n-butylammonium nitrate, and the alkyl aromatic compounds were commercial samples (from Aldrich, Baker, Fluka, or Merck). The alkyl aromatics were purified by distillation or chromatography over basic alumina. As solvent, spectrophotometric grade acetonitrile (Merck) was used.

The deoxygenated solutions containing the aromatic and CAN (typically 0.2 mM) at room temperature were flowed through the quartz photolysis cell with rates of 3-5 mL/min. In the case of penta- and hexamethylbenzene, a dark reaction with CAN was observed. To minimize the effects of such a reaction, a solution containing only the aromatic was mixed with one containing only CAN immediately before reaching the photolysis cell, using a continuous-flow system (residence time in the cell \leq 3 s). The solutions were photolyzed with 20-ns pulses (6-40 mJ as measured at the position of the cell) of 308 nm (XeCl*) light from a Lambda Physik EMG150E laser (at this wavelength only CAN absorbs; at ${\approx}0.2~mM$ OD/cm ${\approx}$ 1–2). The optical absorption signals were digitized with Tektronix 7612 or 7912 transient recorders interfaced with a DEC LSI11/73⁺ computer, which was also used for process control of the apparatus and to on-line (pre)analyze the experimental data.

The extinction coefficient of NO_3° at 630 nm was determined by measuring the pulse-induced OD *in*crease at 630 nm and comparing it with the OD *de*crease at 370 nm of the same solution (ϵ (CAN) at 370 nm is 4485 M⁻¹ cm⁻¹), and assuming that ϵ ((NH₄)₂Ce^{III}(NO₃)₅) and ϵ (NO₃) at 370 nm are zero.

The absorption spectra induced by the laser pulse result from the positive contributions to ΔOD of the products formed (initially

NO₃[•] and (NH₄)₂Ce^{III}(NO₃)₅[•]) and the negative one due to depletion of CAN. The correction procedure for depletion of CAN and parent compound consisted in measuring the (positive) Δ OD at 630 nm immediately after the laser pulse and the negative Δ OD at 370 nm (due to depletion of CAN). At this time, [NO₃[•]] = [(NH₄)₂Ce^{III}(NO₃)₅[•]] = $-\Delta$ [CAN]. After complete reaction of NO₃[•] with the aromatic to yield product P, [P] = $-\Delta$ [aromatic] = [NO₃[•]]. It was found that the quality of the corrections (judged by the degree of agreement with model spectra such as benzyl or *p*-methylbenzyl) was not satisfactory at $\lambda \le 400$ nm unless it was assumed that NO₃[•] has *no* absorption there, i.e., that the absorptions observed at ≤ 400 nm (see Figure 1) are due to the unreactive (NH₄)₂Ce^{III}(NO₃)₅[•].

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- (19) The peaks recorded in acctonitrile are slightly blue-shifted (ca. 5 nm) with respect to the spectra obtained in aqueous solution.
- (20) The decay of NO₃[•] is by good first-order kinetics. The explanation could be in terms of H abstraction from the solvent.
- (21) An absorption band in the ultraviolet region has previously been seen⁴ on photolysis of potassium ceric nitrate in aqueous solution.
- (22) With this method, any absorption of a photochemical product at 370 nm *inc*reases the apparent ϵ of NO₃[•]. For this reason, the ϵ value of 1350 M⁻¹ cm⁻¹ is an upper limit. We chose $\lambda = 370$ nm because at the $\lambda(\max)$ of CAN (=330 nm) the radical (NH₄)₂Ce^{III}(NO₃)₃[•] absorbs.

(23) The formation of benzyl radicals occurs by β -fragmentation and decarbonylation.

(24) With an ϵ of 1,3-diphenyacetone at $\lambda_{max} = 260 \text{ nm of } 38 \text{ M}^{-1} \text{ cm}^{-1}$, the depletion of optical density due to the ketone is negligible compared to that of the benzyl radical ($\epsilon \approx 14000 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{max} \approx 258 \text{ nm}$, as produced in aqueous solution by reaction of O^{-} with toluene,²⁵ or by decarboxylation of phenylacetic acid.²⁶ The absorption spectrum reported in Figure 2 was therefore not corrected for depletion of parent compound.

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(30) As expected, the solvent effect is weaker for the neutral radical than for the radical cation.

(31) With inset c, the initial signal is negative, due to the depletion of CAN which at this wavelength has a high ϵ .

(32) This number is calculated from the viscosity of acetonitrile using the Smoluchovsky equation and is in agreement with experimentally determined values, see, e.g.: McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. J. Am. Chem. Soc. 1991, 113, 1009. Bartl, J.; Steenken, S.; Mayr, H. Ibid., 7710.

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