Rate and Mechanism for the Reaction of the Nitrate Radical with Aromatic and Alkylaromatic Compounds in Acetonitrile

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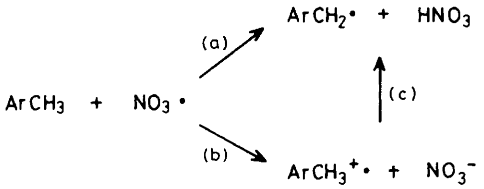
The results of a laser photolysis study indicate that an electron transfer process occurs in the reaction of the nitrate radical with aromatic and alkylaromatic compounds.

It has recently been observed that the photolysis of cerium(IV) ammonium nitrate (CAN) in MeCN in the presence of alkylaromatic compounds leads to side-chain nitro-oxylated products.[1] The effective reagent is the nitrate radical, formed in the photolysis of CAN, which reacts with the alkylaromatic compounds to give a benzyl radical eventually undergoing a ligand transfer process with another molecule of CAN.[2]

Side-chain reactions of alkylaromatic compounds with one electron oxidants can involve an H atom transfer or an electron transfer process. A distinction between these processes is particularly difficult for the reaction of $NO_3^{\cdot}$ (Scheme 1), since this radical should be a good H-atom abstractor[3] as well as a strong oxidizing species.[4]

Our previous observations that the reaction of $NO_3^{\cdot}$ with



Scheme 1

Table 1. Kinetic data for the reactions of $NO_3^{\bullet}$ with aromatic and alkylaromatic compounds in MeCN.

Substrate	k_2/dm^3 mol^{-1} s^{-1} [a]
1 Chlorobenzene	1.3×10^5
2 Bromobenzene	2.1×10^5
3 t-Butylbenzene	6.0×10^6
4 Isopropylbenzene	3.0×10^7
5 Toluene	1.3×10^8
6 Ethylbenzene	1.8×10^8
7 *m*-Xylene	1.7×10^9
8 *o*-Xylene	3.4×10^9
9 *p*-Xylene	5.5×10^9
10 Mesitylene	5.9×10^9
11 Anisole	1.0×10^{10}
12 *m*-Methylanisole	1.2×10^{10}
13 *p*-Methylanisole	1.3×10^{10}
14 1,4-Dimethoxybenzene	1.3×10^{10}

[a] The average error is ±10%.

alkylaromatic compounds exhibits a very high intramolecular selectivity and that $NO_3^{\bullet}$ reacts with 2,3-dimethyl-2,3-diphenylbutane, a substrate without benzylic hydrogens, to give C–C bond cleavage products, suggested an electron transfer mechanism.[2] We felt, however, that a further test of this suggestion was highly desirable.

To this end and also in view of the present strong interest in the reactivity of the nitrate radical with organic compounds,[4,5] we have carried out a kinetic study of the reaction of $NO_3^{\bullet}$ with a series of aromatic and alkylaromatic compounds. The result of this study is presented here.

CAN was photolysed (J. K. System 2000 ruby laser, $\lambda_{exc.}$ 347 nm)[6] at 23 °C and the rate of disappearance of the $NO_3^{\bullet}$ formed was measured at 630 nm in the presence of an excess of the aromatic compound. Good first order plots were obtained from which the second order rate constants (k_2) displayed in Table 1 were calculated.

The kinetic data span a reactivity range of 10^5. The reactions are very fast and electron donor substituents increase the reaction rate up to the diffusion controlled limit (methoxy substituted compounds). Where tested, no significant variation in the k_2 value was observed in the presence of 0.1 M $Et_4N(PF_6)$.

For the substrates without an alkyl group and for *p*- and *m*-methoxytoluene, the formation of an intermediate with the spectroscopic characteristics of an aromatic radical cation was observed.† Thus, there is no doubt that the reaction of $NO_3^{\bullet}$ with these compounds is an electron transfer process. The significant lifetime of *p*- and *m*-methoxytoluene cation radicals is in line with the expected slowing down of the deprotonation rate (path c in Scheme 1) of alkylaromatic radical cations by electron donating substituents.[9]

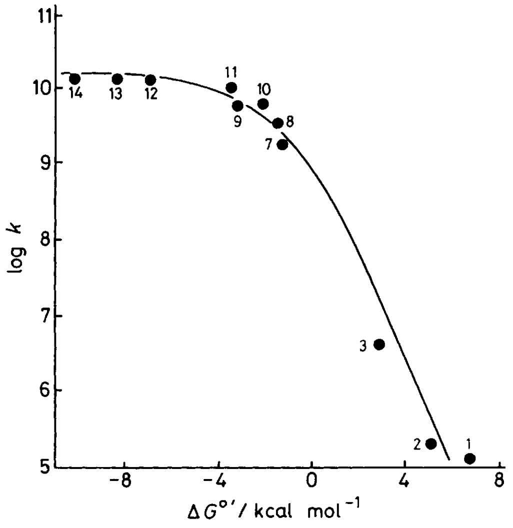


Figure 1. Plot of log k_2 *vs.* $\Delta G^{\circ\prime}$ (ΔG° corrected for the electrostatic work term) for the reaction of $NO_3^{\bullet}$ with aromatic and alkylaromatic compounds (for key to numbering of substrates see Table 1). The curve was calculated using the following values (see Scheme 2): $k_d = k_{-d} = 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $Z = 5 \times 10^{12}$ s^{-1}, and $k_p = 5 \times 10^9$ s^{-1}. For $\Delta G^{\circ\prime}$ value calculations E^0 ($NO_3^{\bullet}/NO_3^-$) was taken as 2.0 V (*vs.* S.C.E.) and the E^0 values (*vs.* S.C.E.) for alkylaromatic compounds were those determined in CF_3CO_2H,[13] corrected for the change of solvent.[14] For the halogenobenzenes and methoxybenzenes, the E^0 values in CF_3CO_2H were estimated from the existing correlation[13] between E_p (in MeCN)[15] and E^0 (in CF_3CO_2H). The electrostatic work term was calculated by putting r(Ar) = 3.5 and $r(NO_3)$ = 1.2 Å.

In the reactions of the other alkylbenzenes, no evidence for the formation of cation radicals was obtained, although the kinetic data reported in Table 1 suggest that these reactions also proceed predominantly *via* an electron transfer mechanism. Accordingly, *p*-xylene is *ca.* 40 times more reactive than toluene and such a high intermolecular selectivity, whilst compatible with an electron transfer mechanism, is inconsistent with a hydrogen atom transfer reaction.‡ Moreover, toluene is more reactive than cumene, whereas the reverse is expected in H atom transfer reactions.[11]

However, whereas *p*-xylene and perdeuterio-*p*-xylene exhibited the same reactivity within experimental errors, a small but significant deuterium kinetic isotope effect (k_H/k_D = 1.6) was calculated from the rate constants of toluene and perdeuterio-toluene.

It is unlikely that with toluene the deprotonation of the radical cation (step c in Scheme 1) becomes partially rate determining as no retarding effect of NO_3^- was observed. We therefore suggest that in the reaction of $NO_3^{\bullet}$ with toluene, there is some contribution of a hydrogen atom transfer process. This suggestion is reasonable since a k_2 value of 4×10^7 M^{-1} s^{-1} has recently been calculated (BEBO method) for the rate constant of the α-hydrogen atom abstraction from toluene by $NO_3^{\bullet}$.[3] It is therefore possible that with toluene, and of course also with ethylbenzene and cumene, both the electron transfer and the hydrogen atom transfer processes may contribute to the observed overall reaction rate.§ With dimethyl- and trimethyl-benzenes only the electron transfer

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† Absorption at λ 430 nm (anisole,[7] *p*- and *m*-methoxytoluene) and at λ 490—550 nm (bromobenzene, chlorobenzene).[8] The definition of the maximum in the latter case was uncertain owing to the absorbance of $NO_3^{\bullet}$ above 480 nm.

‡ In H-atom abstractions by bromine atoms the *p*-xylene–toluene reactivity ratio is only 3.[10]

§ An exclusive hydrogen atom transfer process for all three hydrocarbons would not account for the observation that toluene is more reactive than cumene (even after statistical correction).

$$A + D \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (A\ .\ .\ .\ D) \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} (A^{\cdot -}\ D^{\cdot +}) \xrightarrow{k_p} A^{\cdot -} + D^{\cdot +}$$

Scheme 2

mechanism holds since these substrates have a significantly lower oxidation potential than monoalkylbenzenes.

An electron transfer mechanism is also supported by the observation that the data of Table 1 fit in reasonably well (Figure 1) with the equation, derived from Marcus and Rehn–Weller theory, which correlates the rate constants for an outer sphere electron transfer reaction (Scheme 2) with the free energy change in the electron transfer equilibrium.[12] For the reasons discussed above the data for toluene, ethylbenzene, and cumene have been excluded from the plot.

The best fit is obtained by assuming an E^0 value of 2.0 V (*vs.* standard calomel electrode, S.C.E.) for the $NO_3^{\cdot}/NO_3^-$ couple (estimated value in water 2.1—2.4 V)[5] and a total reorganization energy (λ) of 20 kcal mol^{-1}, which corresponds to an intrinsic barrier $\Delta G^{\ddagger}$ (0) of *ca.* 5 kcal mol^{-1}. Such a low value is plausible since both $NO_3^{\cdot}$ and NO_3^- are planar and little bond reorganization energy should be required for their interconversion. On the other hand very low intrinsic barriers have been observed in the electron transfer quenching of singlet and triplet states of thioxanthone by inorganic anions.[17]

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