Reactions of Cerium(IV) Ammonium Nitrate with Aromatic Compounds in Acetonitrile. Part 2.[1] Nitration; Comparison with Reactions of Nitric Acid

By **Suphi Dinçtürk** and **John H. Ridd**,* Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ

The nitration of benzene and a number of alkylbenzenes by cerium(IV) ammonium nitrate in acetonitrile shows the same intra- and inter-molecular selectivity as nitration with nitric acid under the same conditions but the extent of the other products formed in the two sets of reactions is very different. Nitration by cerium(IV) ammonium nitrate (but not side-chain substitution) is suppressed by the addition of water. The results suggest that these nitration reactions by cerium(IV) ammonium nitrate occur through the intermediate formation of a nitronium ion from the cerium(IV) complex but the order with respect to the aromatic compound shows that this nitronium ion must then be formed in the presence of the aromatic substrate as a ' spectator '. The relative reactivities with respect to benzene in the nitration of anisole and naphthalene are much greater than those observed in nitration by nitric acid and, with both, the isomer proportions are also anomalous.

THE work in Part 1[1] shows that the reaction of a number of aromatic compounds with cerium(IV) ammonium nitrate in acetonitrile leads to both side-chain substitution and aromatic nitration. The side-chain substitution appears to occur through the intermediate formation of the aromatic radical cation but the mechanism of the concurrent nitration is unknown. Earlier observations of nitration by cerium(IV) ammonium nitrate in acetonitrile have been interpreted as a reaction of the radical cation[2] (presumably with $NO_2^{\bullet}$ or NO_2^-) or as a molecular rearrangement in some co-ordination complex of the aromatic compound and the cerium ion.[3] The latter suggestion was made for the nitration of *NN*-dialkylanilines, where it was noted that the loss of one alkyl group appeared to precede nitration.[3] Suggestions of complex formation have been made previously to explain nitration by other metallic nitrates, notably $Ti(NO_3)_4$,[4,5] $Zr(NO_3)_4$,[6] and $Fe(NO_3)_4{\cdot}NO$.[6]

In the present study of the nitration reaction it was unfortunately necessary to abandon a conventional analysis of the kinetic form for the reasons outlined for the substitution reaction in Part 1. The kinetic form of the nitration reaction is probably more complex than that of the substitution reaction since, as outlined previously,[1] there is reason to believe that the nitric acid set free in the course of side-chain substitution contributes to the extent of ring nitration. Our evidence on the mechanism of nitration comes mainly from studies of the product composition and from studies of relative rates determined by competition.

The product composition obtained from nitration by cerium(IV) ammonium nitrate is compared with that for nitration by nitric acid under the same conditions in Table 1. Both sets of results were obtained by extraction of the reaction mixtures followed by analysis by g.l.c. Almost all the results are based on a number of determinations and the standard deviations are also given. The results for nitration by nitric acid are generally similar to those reported previously for reaction in other solvents at room temperature; the only significant difference concerns the greater amount of *meta*-substitution in the present work but this is a natural consequence of the higher temperature used. If the result for *meta*-substitution in toluene is recalculated for 25 °C on the assumption that the *ortho*-, *meta*-, and *para*-substitutions have the same *A* factor, the percentage of *meta*-substitution is reduced to 3.4%. For the alkylbenzenes, the results for nitration by cerium(IV) ammonium nitrate are very similar to those for nitration by nitric acid. We believe however that the discrepancy between the two sets of results for naphthalene is significant (see Experimental section) and note that that for anisole is much more marked.

TABLE 1

Comparison of the product compositions[a] from the nitration of aromatic compounds with cerium(IV) ammonium nitrate in acetonitrile at 84 °C with those from nitration by nitric acid under the same conditions (in parentheses)

	Isomer proportions (%)		
Substrate	2-	3-	4-
Toluene	55.5 ± 1.5	5.0	39.5 ± 1.5
	(57.7 ± 1.2	5.5 ± 0.6	39.6 ± 0.8)
Ethylbenzene	46.1 ± 0.3	5.8 ± 0.4	48.1 ± 0.5
	(47.5 ± 1.2	6.7 ± 0.4	45.8 ± 1.4)
Isopropylbenzene	26.1 ± 0.9	8.8 ± 1.3	65.1 ± 2.0
	(27.8 ± 1.6	9.2 ± 0.9	63.0 ± 2.0)
t-Butylbenzene	15.3 ± 0.8	14.0 ± 0.3	70.8 ± 0.6
	(15.8 ± 0.5	15.5 ± 0.6	68.7 ± 1.1)
m-Xylene	19.3		80.7
	(18.8		81.2)
Anisole	36.5 ± 0.5		63.7 ± 0.5
	(65.9 ± 0.6		34.1 ± 0.6)
Naphthalene	α 93.8	β 6.2	
	(α 91.4	β 8.6)	

[a] Excluding products from side-chain substitution.

Only one of these compounds (toluene) has been nitrated previously by cerium(IV) ammonium nitrate and the product composition was then considered to be anomalous in that 78% *ortho*-substitution was obtained after analysis by g.l.c.[2] The previous workers made no mention of side-chain substitution, the main component of which (benzyl nitrate) cannot be separated from *o*-nitrotoluene on some g.l.c. columns. If this material were accidentally included with *o*-nitrotoluene in the analysis, the percentage of *o*-nitrotoluene would appear to be *ca.* 70% (*cf.* Part 1, Table 1).

Relative reactivities have been calculated from g.l.c. analysis of the products of nitration of mixtures of two aromatic compounds by cerium(IV) ammonium nitrate. Several analyses were done on samples taken from the early stages of reaction to check the consistency of the results. These relative reactivities, with the standard deviations, are listed in Table 2 taking the reactivity of benzene as unity and the results are compared with those for nitration by nitric acid under the same conditions. In general, the differences between the two sets of results are no greater than might be expected from the combined experimental errors but the two values for the relative reactivity of ethylbenzene differ by more than this and the discrepancy in the results for anisole is much more marked. Naphthalene is also much more reactive than would be expected from the studies of nitration by nitric acid (under other conditions, see Table 2). The results for ethylbenzene may be affected by the difficulty of separating the products of side-chain substitution from those of ring substitution but this explanation cannot apply to the results for anisole and naphthalene.

TABLE 2

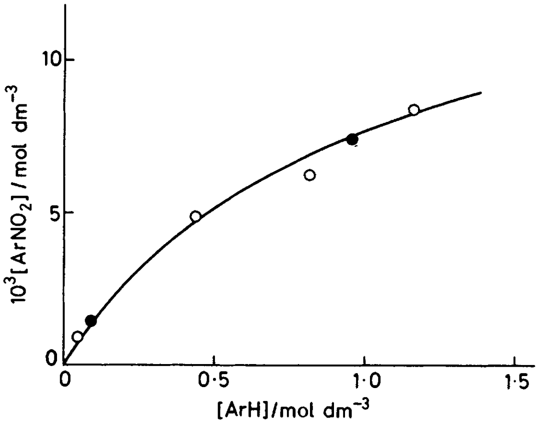
Reactivities relative to benzene for nitration by cerium(IV) ammonium nitrate (CAN) and by nitric acid

	Relative reactivities		
Substrate	CAN (CH_3CN, 84 °C)	HNO_3 (CH_3CN, 84 °C)	HNO_3 [a] ($C_4H_8SO_2$, 25 °C)
Toluene	22.8 ± 0.2	19.2 ± 0.9	20
Ethylbenzene	22.4 ± 1	14.6 ± 0.4	
Isopropylbenzene	15.6	13.3 ± 0.7	
t-Butylbenzene	10.0 ± 0.5	9.6 ± 0.3	
m-Xylene	151 ± 25	122 ± 14	100
Mesitylene	686 ± 94	618 ± 12	350
Anisole	4 899	296	175
Naphthalene	7 340		33

[a] J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1969, 1.

Studies of the first two percent of reaction in the nitration of mesitylene by cerium(IV) ammonium nitrate have been carried out as described for side-chain substitution in Part 1: the results for the amount of nitration after 3.5 min are shown as a function of the initial concentration of mesitylene in the Figure. If these yields are taken as a guide to the initial reaction rates, the overall order with respect to mesitylene comes to 0.7 but the curvature in the Figure shows that this order decreases as the concentration of mesitylene is increased. These results are very different from the zeroth-order kinetics observed for the nitration of mesitylene by nitric acid in acetonitrile.[7] The corresponding order for changes in the concentration of the cerium salt over the range [Ce^{IV}] 0.09—0.4 mol dm^{-3} is 1.5. The initial reaction rates are the same in the presence and absence of normal laboratory lighting.

The effect of additives on the balance between nitration and side-chain substitution in the reaction of mesitylene with cerium(IV) ammonium nitrate is shown in Table 3. Addition of 0.56 mol dm^{-3} of water reduces the extent of nitration without having much effect on the extent of side-chain substitution to form 3,5-dimethylbenzyl nitrate. The addition of a larger amount of water (20% v/v) almost completely suppresses the nitration and reduces the amount of the side-chain nitrate present.



The amount of nitro-compound formed after 3.5 min in the reaction of cerium(IV) ammonium nitrate (0.2 mol dm^{-3}) with various initial concentrations of mesitylene in acetonitrile at 84 °C. Open circles, normal laboratory lighting; filled circles, in the dark

Under these conditions, however, the product composition is extremely complex: after 15 min reaction it also includes 3,5-dimethylbenzaldehyde (11.4%), 3,5-dimethylbenzyl alcohol (7.5%), 2,6-dimethylquinone (3.1%), and 2,4,6-trimethylphenol (1.4%). From a study of the product composition as a function of time, it appears that 3,5-dimethylbenzyl nitrate reacts further to give some of the other products. The presence of the water does not therefore have a marked effect on the overall rate of side-chain substitution.

The last two experiments in Table 3 show that cerium ammonium nitrate and nitric acid when present together are more effective in nitration than would be expected from studies with the separate reagents.

TABLE 3

Reaction of mesitylene (0.5 mol dm^{-3}) with cerium(IV) ammonium nitrate (0.5 mol dm^{-3}) in acetonitrile at 84 °C. Effect of added species (X) on the balance between nitration and side-chain substitution.

			Product composition (%)		
t/min	X	[X] / mol dm^{-3}	ArH	$ArNO_2$	$ArCH_2ONO_2$
15			58.3	14	27.7
120			32.9	33.6	33.3
15	H_2O	0.56	58.4	8.4	33.1
15	H_2O	20% v/v	65.0	1.2	8.1 [a]
15	HNO_3 [b]	0.24	98	2	
15	HNO_3	0.24	44.5	24.8	30.8

[a] A complex mixture of products is formed: see text. [b] In the absence of cerium(IV) ammonium nitrate.

DISCUSSION

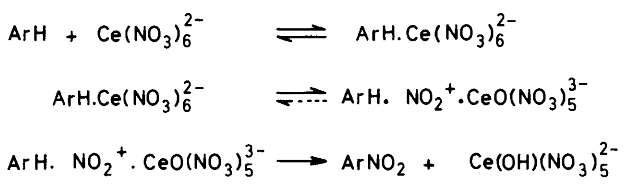
In considering the mechanism of nitration by cerium ammonium nitrate, it is helpful to consider first the reactions of benzene and the alkylbenzenes, and then to consider separately the unusual features shown by the nitration of anisole and naphthalene.

The comparison of the isomer proportions and relative reactivity in the nitration of toluene by cerium ammonium nitrate with the results for nitration by nitric acid under the same conditions shows that the nitrating agent from the cerium salt has the same intra- and inter-molecular selectivity as the nitronium ion (Tables 1 and 2). The decrease in the extent of *ortho*-nitration along the series toluene, ethylbenzene, isopropylbenzene, and t-butylbenzene is generally considered to arise from the increase in steric hindrance between the alkyl group and the nitronium ion. The similarity in the isomer proportions from nitration by cerium ammonium nitrate and nitration by nitric acid indicates therefore that the effective size of the nitrating agent from the cerium salt is also the same as that of the nitronium ion.

Mesitylene is generally recognised to react on encounter with the nitronium ion [8] for otherwise, from the additivity principle, its reactivity with respect to benzene should be $>20\,000$. The value found is always much less than this and depends markedly on the solvent.[8] The fact that the relative reactivity in nitration by nitric acid under our conditions is greater than that in nitration by nitric acid in sulpholan [9] (Table 2) is consistent with the lower viscosity of the solutions in acetonitrile,* and hence with a reaction on encounter. The similar relative reactivities for mesitylene (and also for *m*-xylene) in nitration by nitric acid and by cerium(IV) ammonium nitrate (Table 2) indicate therefore that the latter reaction also involves a reaction on encounter. The effective reagent in nitration by cerium(IV) ammonium nitrate appears therefore to be a highly reactive species, that is present in low concentration and resembles the nitronium ion in its selectivity, size, and diffusion-controlled processes.

The simplest interpretation of these results is of course to assume that cerium(IV) ammonium nitrate gives rise to a small equilibrium concentration of nitronium ions in the solution and that the rate-determining step is the reaction of the nitronium ion with the aromatic substrate. The necessary concentration can be then calculated. From the temperature dependence of the viscosity (η) of acetonitrile,[10] the viscosity at 84 °C should be *ca.* 2.2×10^{-4} N m^{-2} s. The use of the conventional equation for bimolecular reactions occurring on encounter ($k_{en} = 8RT/3\eta$), gives the corresponding second-order rate coefficient as 3.6×10^{10} mol^{-1} s^{-1} dm^3. The substitution of this rate coefficient and the initial reaction rate for [ArH] 1.16 mol dm^{-3} (3.8×10^{-5} mol dm^{-3} s^{-1}) in the equation Rate $= k_{en}[\mathrm{ArH}][\mathrm{NO_2^+}]$ gives $[\mathrm{NO_2^+}]$ 9×10^{-16} mol dm^{-3} for a solution with [CAN] 0.2 mol dm^{-3}.

There is however one difficulty with this interpretation, for it is not easy to see how the necessary equilibrium concentration of the nitronium ion can be maintained in the solution. It is unreasonable to assume that the back reaction of the nitronium ion with the residual part of the cerium complex competes effectively with a reaction on encounter with a much greater concentration of mesitylene. Nevertheless, the fact that the reaction rate increases steadily with the concentration of mesitylene over the range [ArH] 0.045—1.16 mol dm^{-3} (Figure) shows that some back reaction competes with the attack on the aromatic compound. In contrast, the nitration of mesitylene by nitric acid in acetonitrile [7] gives zeroth-order kinetics with respect to the aromatic compound when its concentration is >0.01 mol dm^{-3}.



$$\mathrm{ArH + Ce(NO_3)_6^{2-} \rightleftharpoons ArH.Ce(NO_3)_6^{2-}}$$
$$\mathrm{ArH.Ce(NO_3)_6^{2-} \rightleftharpoons ArH.\ NO_2^+.CeO(NO_3)_5^{3-}}$$
$$\mathrm{ArH.\ NO_2^+.\ CeO(NO_3)_5^{3-} \longrightarrow ArNO_2 + Ce(OH)(NO_3)_5^{2-}}$$

SCHEME

This difficulty can be removed if the reaction is considered to involve a very short-lived ion pair consisting of the nitronium ion and the remaining part of the complex ion † (Scheme). It is then necessary to assume that this ion pair normally collapses to reform the complex without prior separation but that reaction may occur with an aromatic compound if that is present with the complex as an encounter pair when the nitronium ion is formed. For most of the aromatic substrates, the similarity of the relative rates and product compositions to those for nitration by nitric acid suggests that there is no significant interaction between the aromatic compounds and the complex at this time. The aromatic compound would then be present as a ' spectator ' [13] during the formation of the nitronium ion and the reaction would be of the pre-association type.[10] The suggested reaction path is illustrated in the Scheme. A reaction path involving pre-association can give a greater reaction rate than expected from diffusion control [10] but mesitylene may not be sufficiently reactive for this difference to be significant.

The formation of the nitronium ion in this way must require strong electron attraction by the cerium. The tendency to form the nitronium ion should therefore be reduced if some of the nitrate ligands are replaced by groups that donate electrons more readily. This would explain the retarding effect of water on the nitration reaction and why nitration by cerium(IV) ammonium nitrate is not observed in such solvents as acetic acid (where two nitrate ions are believed to be replaced by solvent molecules).[14]

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* If mesitylene reacts on encounter with the nitronium ion, the relative reactivity of mesitylene to benzene is equal to the average number of encounters required for the nitration of benzene. As the viscosity of the solvent is decreased, the number of collisions per encounter decreases and hence more encounters are required before reaction.

† The structure of crystalline cerium(IV) ammonium nitrate involves bidentate co-ordination of six nitrate groups about each cerium atom [11] but there is evidence that the $[\mathrm{Ce(NO_3)_6}]^{2-}$ ion forms dimers or polymers in some solutions [12] and these may be involved in the present reaction in view of the high order, with respect to the cerium(IV) salt.

The alternative interpretation involving the intermediate formation of the radical cation ($ArH^{+\cdot}$) in nitration is less plausible. It is difficult to see how the reaction is completed since the obvious species to do this ($NO_2^{\cdot}$ or NO_2^-) are unlikely to be formed readily in the solution. Our own work shows that nitrogen dioxide is rapidly oxidised by cerium(IV) ammonium nitrate. The radical cation ($ArH^{+\cdot}$) could abstract $NO_2^{\cdot}$ from a side-chain nitrate but the fact that some nitration reactions occur without side-chain substitutions means that this cannot be a general explanation. It is doubtful whether the radical cation mechanism can explain the close similarity of the product composition to that for nitration by nitric acid since recent work indicates that the two reactions ($ArH + NO_2^+ \longrightarrow ArNO_2$) and ($ArH^{+\cdot} + NO_2^{\cdot} \longrightarrow ArNO_2$) can give markedly different isomer ratios despite the identical composition of the two transition states.[15] Finally, on the radical cation interpretation, it is not clear why the nitration reaction should be easily suppressed by added water or why the nitration of aromatic hydrocarbons should not occur when the solvent is acetic acid. It seems therefore more reasonable to assume that although side-chain substitution by cerium(IV) ammonium nitrate involves the radical cation,[1] substitution in the ring involves the nitronium ion.

The above arguments have ignored the possibility that the attack of the nitronium ion generates the aromatic radical cation by electron transfer.[16] This is unlikely as a general explanation of the similarity between nitration by nitric acid and nitration by cerium(IV) ammonium nitrate since the comparisons include monoalkylbenzenes and, for these, such an electron transfer would be unexpected.[16] For mesitylene, the absence of any side-chain substitution in nitration by nitric acid (see Experimental section) makes such a radical cation intermediate unlikely.[17] There is evidence from ^{15}N nuclear polarisation for intermediate aromatic radical cations in the nitrous acid-catalysed nitration of mesitylene but not when nitration occurs through the nitronium ion.[18] This accords with the above interpretation and is consistent with the recent work of Suzuki and his co-workers.[19]

The above discussion has been based on the reactions of benzene and the alkylbenzenes. The anomalous reactivities observed in the reaction of anisole and naphthalene could be understood as a consequence of the different limiting rates in reactions involving diffusion control and pre-association [10] but the accompanying differences in isomer proportions make this explanation inadequate. It is possible that the differences arise because these substrates interact more strongly with the cerium complex at the time of formation of the nitronium ion. Further work is needed to define these reaction paths.

EXPERIMENTAL

Materials.—Nitric acid (100%) was prepared by distillation under vacuum of 1 : 1 mixtures of AnalaR fuming nitric acid and concentrated sulphuric acid. Benzene and naphthalene were laboratory reagents and were shown to be pure by g.l.c. The other reagents were as described.[1]

Reactions.—A solution of nitric acid (0.5—2.0 mol dm^{-3}) in acetonitrile (45 cm^3) was heated under reflux and a solution of the aromatic compound or compounds in acetonitrile (5 cm^3) was added. After the required time (1—12 min for competitive nitrations: longer for individual nitrations), the reaction was quenched in water followed by extraction and analysis.[1] In the competitive nitrations several samples (10 cm^3) were extracted at different times over the first few percent of reaction and treated as above. The other details, and the experiments involving cerium(IV) ammonium nitrate, were as described.[1]

Product Composition.—The g.l.c. analysis of the nitration products of naphthalene was carried out as described for mesitylene [1] after correction of the integrated areas for the different response of the two isomers using synthetic mixtures of α- and β-nitronaphthalenes. The products from reaction with cerium(IV) ammonium nitrate included α-naphthoquinone (5%) and a compound precipitated from the reaction mixture and analysing as a nitronaphthoquinone. Heating a synthetic mixture of α- and β-nitronaphthalenes with cerium(IV) ammonium nitrate in acetonitrile under reflux for the time used for the nitration of naphthalene did not change the α : β ratio. Analysis by g.l.c.–m.s. of the product of nitration of toluene (0.5 mol dm^{-3}) with nitric acid (0.5 mol dm^{-3}) in acetonitrile (67 h, 84 °C) gave, excluding starting material and in addition to nitro-compounds, benzaldehyde, 3.4%; benzyl nitrate, 4.1%; phenylnitromethane, 2.1%. A corresponding reaction (3 h) of *p*-xylene (0.5 mol dm^{-3}) with nitric acid (2.0 mol dm^{-3}) gave, in addition to nitro-compounds, *p*-methylbenzyl nitrate, 16.5%; *p*-methylphenylnitromethane, 5.5%. The last compound decomposed during analysis by g.l.c. so the yield was determined by ^1H n.m.r. using comparison with an authentic sample. Corresponding experiments on the nitration of mesitylene gave nitromesitylene with no detectable by-product.

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