Nitration of Aromatic Compounds by Tetranitratotitanium(IV) in Carbon Tetrachloride Solution

By **Robert G. Coombes** * and **Leslie W. Russell**, Chemistry Department, The City University, St. John Street, London EC1V 4PB

Tetranitratotitanium(IV) reacts with some simple aromatic compounds of a wide range of expected reactivity in carbon tetrachloride solution at room temperature to give good yields of nitro-compounds. Results of direct rate measurements, competition studies, and determinations of isomeric product proportions are reported. The anomaly of the low intermolecular and high intramolecular selectivity of the substitution is discussed, and the existence of at least three stages of reaction is established. A special mechanism of nitration by this reagent is proposed to account for these observations.

THE nitronium ion is recognized as the species almost universally effective [1] in widely used nitration systems for aromatic molecules of moderate reactivity. There would therefore be considerable interest in a viable nitrating system in which a different species was involved. In this connection tetranitratotitanium(IV), in which the four nitrato-groups are bonded to the eight-co-ordinate titanium atom in a bidentate manner,[2] appeared to be of interest. It is usually [3] prepared as a white crystalline solid which must be handled in the absence of moisture. It is reported to nitrate and oxidize aliphatic hydrocarbons with ease (*e.g.* n-dodecane [3]) and to react rapidly with benzene [4] and toluene [5] when added directly to them. It also reacts violently with some oxygen-containing aliphatic compounds.[4] These reactions all occur at room temperature. This unusual combination of reactivity suggested that a special mechanism of nitration might be involved.

If this were the case various synthetic possibilities might arise. It might be possible to prepare nitro-compounds in different isomeric proportions from those usual in direct nitrations, and also to nitrate compounds at present considered unreactive. In view of the non-acidic conditions of the reaction, it might be possible to nitrate some basic compounds in the unprotonated form without the complications (*e.g.* *N*-nitration) which often attend nitronium ion reactions. Such considerations might be of particular importance for *N*-heteroaromatic compounds.

The apparent speed of the reaction [4] in the absence of solvent suggested that reactions should be studied in dilute solution and this was also a requirement for any meaningful mechanistic study. As carbon tetrachloride was known not to react with tetranitratotitanium(IV), and as several nitrating agents have been studied in this medium, it was chosen as solvent for this work.

This paper reports the results of a study of the nitration of a range of simple aromatic molecules, which have been extensively studied under other nitration conditions, by tetranitratotitanium(IV) in carbon tetrachloride solution. As this work was nearing completion a communication by D. W. Amos *et al.*[6] appeared describing some observations on the nitration of benzene, nitrobenzene, chlorobenzene, and toluene by tetranitratotitanium(IV) in the absence of solvent and with an excess of substrate. Product isomer ratios were reported and, with the exception of those from toluene, were similar to those found in conventional systems.

EXPERIMENTAL

Materials.—Carbon tetrachloride (AnalaR) was dried over type 4A molecular sieves (1/16 in pellets) and stored in

---

[1] *E.g.* J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, 1971, and references therein.

[2] C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1966, 1496.

[3] B. O. Field and C. J. Hardy, *J. Chem. Soc.*, 1963, 5278.

[4] B. O. Field, personal communication.

[5] C. C. Addison and N. Logan, *Adv. Inorg. Chem. Radiochem.*, Academic Press, 1964, vol. 6, p. 128.

[6] D. W. Amos, D. A. Baines, and G. W. Flewett, *Tetrahedron Letters*, 1973, 3191.

a dry-box. Water content (usually *ca.* 2 × 10^{-4} mol l^{-1}) was monitored by measuring the absorption at 5300 cm^{-1}.[7]

Anhydrous tetranitratotitanium(IV) was prepared by a method similar to that of Field and Hardy.[3] The hydrated hydroxide, obtained by hydrolysis of titanium tetrachloride, was treated with dinitrogen pentoxide for 12 h. The excess of dinitrogen pentoxide was removed *in vacuo* to leave a white residue from which the pure product was obtained by vacuum sublimation at 70—80° and 1 × 10^{-3} mmHg. Resublimation gave a white, transparent, crystalline, extremely hygroscopic solid [Found: Ti, 15·9; NO_3, 83·3. Calc. for $Ti(NO_3)_4$: Ti, 16·2; NO_3, 83·8%]. All solutions of this compound were prepared and handled under anhydrous conditions in a dry-box.

Substrates and nitro-compounds were suitably purified commercial reagents. Substrates were dried over type 4A molecular sieves.

Kinetic and Product Measurements.—A solution of tetranitratotitanium(IV) in carbon tetrachloride (25 ml) was thermostatted inside a dry-box, and the substrate was added by pipette or microsyringe. In the competition experiments, equimolar mixtures of substrates were added to the reagent solution. All reactions were carried out at 20 ± 1 °C. The reaction solution was briefly shaken and the reaction was followed by removal of samples (0·5 ml) at suitable times. These samples were treated with water to prevent further reaction, and the organic layer was analysed quantitatively by g.l.c. on a Pye 104 series gas chromatograph fitted with a flame ionization detector. For the majority of cases analysis was possible with 1/4 in × 5 ft columns of Silicone SE30, OV17, or OV225 at 130—180° with a nitrogen flow rate of 60 ml min^{-1}. For nitro-products from chloro-, bromo-, and *p*-dichloro-benzenes, however, a polyethylene glycol column at 150° was used.

The relative responses of the detector to the internal standard and authentic samples of the various nitro-compounds were determined. Thus the concentrations and proportions of nitro-products could be determined.

Analysis of Precipitate.—In each reaction a precipitate was formed. In some cases the solid was filtered off in the dry-box, washed with carbon tetrachloride (100 ml), and dried *in vacuo* for several hours. Analysis of the residue consisted of estimation of titanium content by atomic absorption measurement on a Perkin-Elmer 290B spectrophotometer, and determination of nitrate content by the nitron method.[8]

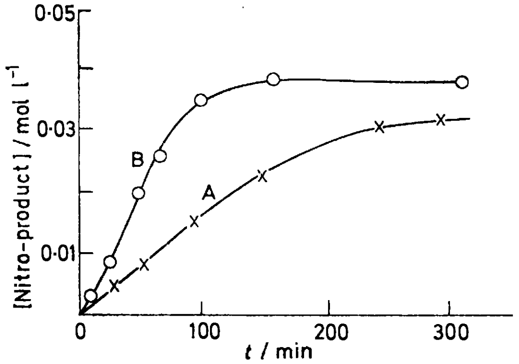
RESULTS

Tetranitratotitanium(IV) is soluble in anhydrous carbon tetrachloride to the extent of about 0·1 mol l^{-1} at 20°; i.r. spectra of such solutions remain constant for several weeks.

(i) *Benzene.* Addition of benzene to such solutions led to the formation of a small amount of precipitate and slow conversion of the benzene into nitrobenzene accompanied by further precipitation. Apart from changes due to addition of benzene and its conversion into nitrobenzene, there were no detectable changes in the i.r. spectra of solutions on mixing and during reaction. The yields of nitrobenzene after more than five half-lives, based on the assumption of a reaction between one mole of benzene and one mole of tetranitratotitanium(IV), were 86—98%.

Characterization of the precipitate was made difficult because it contained, after filtration under anhydrous conditions, 10—25% by weight of nitro-compounds, depending on initial concentrations. Addition of water removed the organic compounds but it would be expected to alter the nature of the solid. Solids from reactions carried out with a range of initial concentrations were separated by filtration under anhydrous conditions after a few half-lives and the NO_3 : Ti ratio was determined as 2·7 (±0·4) : 1. Exposure to the reaction solution for much longer periods led to changes in the composition of the solid although negligible further nitration occurred.

The Figure shows the course of a typical reaction. The rate shows an initial increase which is general for these reactions. However, simple kinetic behaviour cannot be expected from the reaction, which involves a heterogeneous system. The requirements of a solvent which is unreactive to tetranitratotitanium(IV) but in which no precipitate might be formed appear irreconcilable. It was found however that rates were generally reproducible and two parameters were chosen to describe the results approximately: (i) the initial rate of production of nitro-compounds measured over 5—7% reaction, and (ii) the half-life for the reaction.



Nitrations of (A) benzene and (B) toluene by tetranitratotitanium(IV) in carbon tetrachloride (all reagents 0·039 mol l^{-1})

Some of the data are assembled in Table 1. The reproducibility of results is illustrated and it is shown that the presence of dissolved water in the solvent does not have a detectable effect on the rate. There was also no change in the rate if the solution was rapidly stirred during reaction. The result from nitration of hexadeuteriobenzene shows that there is no primary kinetic isotope effect on the rate-determining stage. The presence of urea or tetraethylammonium nitrate at the maximum possible concentration had no effect on rates of nitration.

As a precise kinetic study of the reaction was not possible, attention was then confined to broad trends in the change of the rate of reaction with change in reactant concentrations. In addition, as above, the effects of additives and other changes were studied from runs carried out at the same time under otherwise identical conditions. Such runs are bracketted together in Table 1. The results show that the initial rate increased with the initial tetranitratotitanium(IV) concentration. By contrast, the initial concentration of benzene had little effect on the initial rate of nitration. Up to *ca.* 5% of *m*-dinitrobenzene could be detected from the reactions. Its presence became apparent

---

[7] B. D. Pearson and J. E. Ollerenshaw, *Chem. and Ind.*, 1966, 370; R. L. Meeker, F. Critchfield, and E. T. Bishop, *Analyt. Chem.*, 1962, **34**, 1510.

[8] A. I. Vogel, ' A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1962, p. 583.

when the precipitated solid was analysed as already described or when reactions under equimolar conditions were left over ten half-lives.

(ii) *Toluene*. The characteristics of the reaction with toluene are similar to those of the benzene reaction (see Figure). Toluene reacted at a rate related to that of benzene under similar conditions by a factor of between one and three, and the concentration dependence of initial rates was similar.

TABLE 1

Reaction with benzene

[Benzene]/ 10^{-2} mol l^{-1}	[$Ti(NO_3)_4$]/ 10^{-2} mol l^{-1}	Initial rate ($k/10^{-6}$ mol l^{-1} s^{-1})	Half life ($t/10^3$ s)	Yield (%)
7·9 [a]	7·9	5·6	2·8	72
7·9	7·9	6·0	2·4	93
7·9 [b]	7·9	3·9	3·2	95
7·9 [c]	7·9	5·8	3·3	98
3·6	3·6	0·73	19	87
3·6 [d]	3·6	0·97	12	53
2·2 [e]	2·3	0·72	17	77
2·2	2·3	0·53	17	97
7·9	7·9	6·0	2·9	86
7·9	3·9	1·2	7·6	95
7·9	0·79	0·14	28	98
20	3·9	1·2	16	98
3·9	3·9	2·1	6·4	88
2·5	3·9	3·1	2·9	90
3·4	3·4	3·5	5·8	88
3·4 [f]	3·4	3·5	6·0	99

[a] In the presence of urea (*ca*. 6 × 10^{-3} mol l^{-1}). [b] [H_2O] = 3 × 10^{-3} mol l^{-1}. [c] [H_2O] = 2 × 10^{-4} mol l^{-1}. [d] In the presence of $Et_4N^+NO_3^-$ (*ca* 4 × 10^{-3} mol l^{-1}). [e] Hexadeuteriobenzene. [f] Rapidly stirred during entire reaction.

TABLE 2

Products of reaction with toluene; variation with initial concentrations

[Toluene]/ 10^{-2} mol l^{-1}	[$Ti(NO_3)_4$]/ 10^{-2} mol l^{-1}	Nitrotoluenes [a–c]	
		% *o*-	% *p*-
70	7·0	35	65
40	4·5	47	53
40 [d]	4·5	44	56
9	9	37	63
9·4	3·4	44	56
7·9	7·9	36	64
7·9 [e]	7·9	44	56
7·9	3·9	44	56
7·9	0·79	46	54
6·9	6·9	36	64
4·7	3·4	39	61
4·7 [f]	3·4	42	58
3·9	3·9	45	55
1·9	3·9	41	59
18 [g,h]	4·3	46	54

[a] ±2%. [b] All yields of nitrotoluenes 87—98%. [c] % *m*-0·5 ± 0·4% in all cases. [d] In the absence of light. [e] In the presence of urea (*ca*. 6 × 10^{-3} mol l^{-1}). [f] In the presence of $Et_4N^+NO_3^-$ (*ca*. 4 × 10^{-3} mol l^{-1}). [g] Analysis of complete product including any associated with precipitated solid. [h] % *m*-Nitrotoluene 0·8 ± 0·1 in this case.

The proportions of nitrotoluenes formed did not vary during the course of one reaction, indicating that only one nitrating species was involved. Dinitration was not important and in fact <2% dinitration was observed in all the reactions quoted. The proportion of *m*-nitrotoluene was always low (0·5 ± 0·4%). Table 2 shows the variation of isomer proportions at complete reaction over a wide range of conditions. The *ortho* : *para* ratio was 0·72 (±0·18) : 1 but there were apparently random variations over this range which were well outside experimental uncertainties.

In one case (see Table 2) a reaction was allowed to go to completion before the entire product was treated with water and analysed, so that any organic compound in the solid was also estimated. No change in the *o* : *p* ratio was apparent and the % of *m*-nitrotoluene was 0·8 (±0·1).

(iii) *Other aromatic compounds*. The rates of nitration of mesitylene, ethylbenzene, t-butylbenzene, chlorobenzene, and *p*-dichlorobenzene were determined under conditions where they could be compared with one another and also with benzene and toluene. A factor of about three in rate covered all these results under comparable conditions except those for chlorobenzene and *p*-dichlorobenzene. These compounds both showed an initial rate *ca*. 10 times less than that of benzene, and the plots analogous to those of the Figure for these compounds showed larger initial curvature. The ratios of isomers produced from these compounds are shown in Table 3.

TABLE 3

Products of reactions with aromatic compounds

Substrate	[Substrate]/ 10^{-2} mol l^{-1}	[$Ti(NO_3)_4$]/ 10^{-2} mol l^{-1}	Nitro-products 2-	3-	4-	Yield (%)
m-Xylene	90	9	12		88	
Ethylbenzene	35, 45	3·5, 4·5	36	2	62	90
t-Butylbenzene	35, 90	3·5, 9	8	4	88	98
Chlorobenzene	3—100	3—10	21	<0·5	79	94
Bromobenzene	36	3·6	24	0·5 ±0·4	76	

(iv) *Competition experiments*. These were conducted between pairs of aromatic compounds selected from those already mentioned to establish a scale of reactivity relative to benzene. An equimolar mixture of two aromatic compounds in an at least ten-fold excess was added to a solution of tetranitratotitanium(IV) in carbon tetrachloride and the composition of the mixture of nitro-compounds produced was determined. The detailed results are shown in Table 4. No primary kinetic isotope effect was observed.

TABLE 4

Competition of aromatic compounds for tetranitratotitanium(IV)

Substrates		[A] = [B] (mol l^{-1})	[$Ti(NO_3)_4$]/ 10^{-2} mol l^{-1}	Product ratio (A/B)
A	B			
Toluene	Benzene	0·15	3·3	4·1
		0·26	3·6	4·2
		0·26 [a]	3·6	5·7
		0·26 [b]	3·6	5·5
	c	0·15	3·3	4·9
	c	0·26	3·6	5·1
Mesitylene	Toluene	0·17	3·3	5·7
Mesitylene	Benzene	0·26	3·6	20
		0·37	3·7	19
t-Butylbenzene	Benzene	0·26	3·6	1·3
Chlorobenzene	Benzene	0·26	3·6	0·12
p-Dichlorobenzene	Benzene	0·26	3·6	0·018

[a] [H_2O] = 2 × 10^{-4} mol l^{-1}. [b] [H_2O] = 3 × 10^{-3} mol l^{-1}. [c] Hexadeuteriobenzene.

(v) *Nitrobenzene, anisole, and biphenyl*. These compounds gave results which did not agree with the pattern established for the compounds already described. In particular the yields of nitro-compounds at complete reaction were low and (where studied) variable.

Nitrobenzene reacted several times more slowly than benzene under similar conditions to give a 10—20% yield of *m*-dinitrobenzene (containing $<5\%$ of other isomers).

Anisole reacted much more rapidly than any of the other compounds to produce typically *o*- and *p*-nitroanisole in the ratio 0·7 (±0·2) : 1. Attempted competition experiments of biphenyl with benzene, toluene, and mesitylene gave inconsistent results in the presence or in the absence of urea.

(vi) *n-Pentane*. This compound (0·34 mol l^{-1}) reacted with tetranitratotitanium(IV) (0·07 mol l^{-1}) in carbon tetrachloride to produce $<1\%$ yield of any product after 24 h.

DISCUSSION

The results from the reaction of tetranitratotitanium(IV) with benzene indicate that one mole of benzene reacts with one mole of tetranitratotitanium(IV) to give one mole of nitrobenzene and a solid which has a Ti : NO_3^- ratio of 1 : 3. The simplest formulation of this process would be $C_6H_6 + Ti(NO_3)_4 \longrightarrow PhNO_2 + (OH)Ti(NO_3)_3$, although the precise nature of the inorganic product must remain uncertain. Any further reaction is very slow by comparison although the production of up to 5% of dinitro-products indicates that some minor complications occur.

The concentration dependence of the initial rate of reaction indicates to a first approximation that the rate-determining stage involves only the tetranitratotitanium(IV) molecule, the rate being independent of the concentration of benzene. The lack of a primary kinetic isotope effect is compatible with this hypothesis as is the absence of an effect on rate of change in water concentration. The similarity of the initial rates of reaction of benzene, toluene, mesitylene, ethylbenzene, and t-butylbenzene under similar conditions reinforces the idea that the substrate is not involved in the rate-limiting stage. The fact that both chlorobenzene and *p*-dichlorobenzene react much more slowly may perhaps be associated with the heterogeneity which is discussed later.

We conclude that the rate-limiting stage involves the production of a reactive nitrating intermediate from tetranitratotitanium(IV). The results of the competition experiments describe the selectivity of this species amongst the aromatic substrates. These data are so different from those from the rate measurements that it is clear that a different stage is being studied, even when reasonable consideration is given to the effect of heterogeneity.

Various possible intermediates can be considered. The nitronium ion is known to show a much greater intermolecular selectivity in a wide range of solvents than that observed here (*e.g.* for the nitronium ion in carbon tetrachloride the rate ratio [9] benzene : toluene is 1 : 17, whereas the observed value here is 1 : 5). There are also significant differences between the intramolecular selectivity established for the nitronium ion [10] and that for the present system, particularly in the nitration of toluene. Nitration *via* nitrosation should show a primary kinetic isotope effect.[11] Dinitrogen pentoxide in carbon tetrachloride exhibits intra- and intermolecular selectivities very different from those observed here.[12] Dinitrogen tetroxide and nitric acid at suitable concentrations in carbon tetrachloride react with aromatic compounds much too slowly for either to be the effective intermediate.[10,12] We conclude that some other intermediate is involved in the present case. The relative reactivities of the aromatic molecules indicated for reaction with this intermediate by the competition experiments (Table 4) are in the sequence expected for reaction with an electrophile. The spread of rates however is less than that of any electrophilic substitution where proton loss is kinetically insignificant. It is difficult to see that any direct electrophilic nitration process could be so unselective, particularly in the absence of any evidence of a diffusion-controlled reaction.[1] We tentatively suggest then that this fast stage involves co-ordination from the π-electrons of the aromatic molecule to a titanium atom present in the intermediate, and that the complex thus formed then undergoes an intramolecular electrophilic substitution. Studies of reactivity in other systems might suggest that it is a nitrato-bonded ligand which is involved in the rearrangement process.[13]

This separation of the stages determining inter- and intra-molecular selectivity is necessary if we are to account for the apparently anomalous combination of these observed in this system. We observe the low intermolecular selectivity outlined before but the intramolecular selectivity is qualitatively similar to that of the nitronium ion. Indeed for toluene, which has been more widely studied here and elsewhere, the reagent is in fact more selective than the nitronium ion between *m*- and *p*-positions.

The operation of the mechanism depends on the aromatic character of the substrate, and it has been shown that n-pentane, which is easily nitrated in the absence of solvent,[4] does not react under similar conditions.

Several secondary features of the reactions are not covered by the foregoing mechanism; in particular the curved rate plots, the variation of product isomer proportions for toluene over a narrow range, and the lack of accurate reproducibility in the rate results. These features may well be due to the heterogeneous nature of the reaction medium caused by the solid precipitated. Equilibria, perhaps at each stage of reaction, may be set up between species in solution and in the precipitate. The importance of the species present would then depend on the nature of the substrate and the initial concentrations of reactants.

It remains to mention the anomalous behaviour of nitrobenzene, biphenyl, and anisole. The rate for

---

[9] R. G. Coombes, *J. Chem. Soc.* (*B*), 1969, 1256.

[10] Ref. 1, ch. 9.

[11] B. C. Challis, R. J. Higgins, and A. J. Lawson, *J.C.S. Perkin II*, 1972, 1831.

[12] R. G. Coombes and L. W. Russell, unpublished results.

[13] C. C. Addison, *Co-ord. Chem. Rev.*, 1966, **1**, 58.

nitration of nitrobenzene relative to benzene[10] by the nitronium ion is 6×10^{-8} It is an indication of the very different nature of the mechanism of nitration in the present system that any appreciable yield is obtained from nitrobenzene under conditions similar to those applicable to the nitration of benzene. We can attribute rate differences and low yields to the association of nitro-compounds with the precipitated solid. Anisole and biphenyl are known to be susceptible to nitration *via* nitrosation[14,15] and the low *o* : *p* ratios support this as a possible explanation of anomalies in the present case also.

In summary it has been shown that tetranitratotitanium(IV) exhibits a special mechanism of nitration of aromatic compounds, although this mechanism must be different from that by which it nitrates aliphatic compounds. However, the difficulties in its use and the relatively small differences in isomer proportions finally obtained suggest that there are only disadvantages in its use with these simple aromatic substrates. The mechanism proposed does not, however, rule out the idea that the reagent might have useful synthetic applications for the nitration of usually unreactive heterocyclic compounds, and we intend to investigate this possibility further.

We thank the S.R.C. for a studentship (to L. W. R.) and Mr. B. O. Field for discussions and for drawing our attention to the existence and properties of tetranitratotitanium(IV).

[3/2490 *Received, 6th December*, 1973]

---

[14] J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Comm.*, 1969, 605.

[15] R. Taylor, *Tetrahedron Letters*, 1972, 1755.