

NITRATION BY TITANIUM (IV) NITRATE

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Titanium (IV) nitrate¹ $[\text{Ti}(\text{NO}_3)_4]$ has been observed to react with a variety of aliphatic and aromatic hydrocarbons, both substituted and unsubstituted^{2,3}. Qualitative tests have shown that reaction is accompanied by nitration, and sometimes oxidation. We report a quantitative study of the reaction of titanium (IV) nitrate with benzene, nitrobenzene, toluene and chlorobenzene, and, in the light of this study, suggest a mechanism for the reactions.

An X-ray crystallographic study of $\text{Ti}(\text{NO}_3)_4$ ⁴ has shown that crystals of the compound consist of molecular units, with the four nitrate-groups bonded to the metal atom in bidentate fashion. The compound is volatile (subl. 30°C/10⁻⁴mm) and extremely hygroscopic, requiring all manipulations to be carried out in an inert atmosphere.

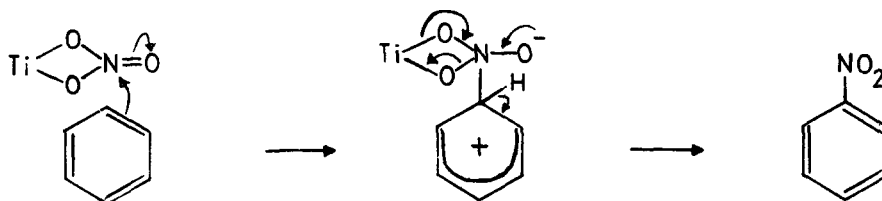
Reactions were carried out by shaking a few crystals of $\text{Ti}(\text{NO}_3)_4$ (~0.5g.) with an excess (~5 ml) of the organic compound under investigation. The reaction with benzene was fairly rapid, being complete after about ten seconds. The reaction with toluene was considerably faster, while that with nitrobenzene and chlorobenzene was somewhat slower. No reaction was observed with m-dinitrobenzene. The reactions were accompanied by formation of a precipitate containing titanium, the nitrated organic products remaining in solution. After removal of the precipitate, the liquid phase was examined by gas-liquid chromatography. The products were identified by comparing their retention times with those of known compounds, and the proportions of the various isomers present were calculated by measurement of the peak areas. The products and their relative abundances are listed in Table 1, together with the corresponding products obtained in the conventional nitration⁵ with the mixed nitric acid/sulphuric acid system.

TABLE 1

Starting material	Product	Isomer	% produced with $Ti(NO_3)_4$	% produced with HNO_3/H_2SO_4
Benzene	Nitrobenzene			
Nitrobenzene	Dinitrobenzene	ortho	8	6.4
		meta	92	93.2
		para	-	0.3
Toluene	Nitrotoluene	ortho	48	58.8
		meta	5	4.4
		para	47	36.8
Chlorobenzene	Nitrochlorobenzene	ortho	32	30.1
		meta	-	-
		para	68	69.9

A quantitative measurement of the yield has been carried out on the reaction of $Ti(NO_3)_4$ with benzene. This showed that each molecule of $Ti(NO_3)_4$ carries out two nitrations with 82% efficiency.

The similarity of the isomeric proportions for the two nitrating systems suggests that we have electrophilic attack on the aromatic ring by $Ti(NO_3)_4$. In these media of low dielectric constant, it would appear unlikely that $Ti(NO_3)_4$ would spontaneously release the NO_2^+ ion, which has been suggested as the nitrating agent in the mixed acid system. Further evidence for the absence of NO_2^+ in $Ti(NO_3)_4$ solutions is the lack of a strong band at 1400 cm^{-1} in the Raman spectrum of $Ti(NO_3)_4$ dissolved in CCl_4 ⁶ and $SiCl_4$ ⁷. An alternative suggestion is the release of the NO_3 radical from $Ti(NO_3)_4$ ³, accompanied by simultaneous reduction of the metal. However, one would not expect the NO_3 radical to be so specific as an electrophilic reagent. We therefore propose the mechanism shown below.

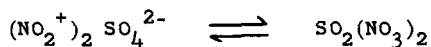


We shall now make tentative comment on the striking similarity between $\text{Ti}(\text{NO}_3)_4$ nitration and $\text{HNO}_3/\text{H}_2\text{SO}_4$ nitration. Compounds analogous to $\text{Ti}(\text{NO}_3)_4$ are $\text{VO}(\text{NO}_3)_3$ ^{1,6} and $\text{CrO}_2(\text{NO}_3)_2$ ¹, which have similarly bonded nitrate-groups and have been observed to take part in qualitatively similar reactions. Alternative formulations of these compounds are shown in Table 2.

TABLE 2

Nitrate formula	Nitronium formula
$\text{Ti}(\text{NO}_3)_4$	$(\text{NO}_2^+)_4 \text{TiO}_4^{4-}$
$\text{VO}(\text{NO}_3)_3$	$(\text{NO}_2^+)_3 \text{VO}_4^{3-}$
$\text{CrO}_2(\text{NO}_3)_2$	$(\text{NO}_2^+)_2 \text{CrO}_4^{2-}$

The many similarities between chromium and sulphur in their highest (VI) oxidation states leads us to propose that in the mixed acid system, where we have NO_2^+ and SO_4^{2-} ions, the reaction



is feasible. It is then possible that $\text{SO}_2(\text{NO}_3)_2$ may be responsible for nitration in the mixed acid system. We are now pursuing the preparation of pure $\text{SO}_2(\text{NO}_3)_2$ from SO_2Cl_2 and ClNO_3 to investigate the possibility further.

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