Nitration *via* Nitrosation in Carbon Tetrachloride

By T. G. BONNER and R. A. HANCOCK*
(*Royal Holloway College, Englefield Green, Surrey*)

UNDER conditions where nitration of aromatic compounds proceeds *via* nitrosation, the two primary requirements are that the aromatic nucleus is strongly activated towards electrophilic attack and that both nitric acid and nitrous acid or a nitrosating species are present.[1] The formation of the nitro-compound is then represented by the two steps

$$\mathrm{ArH + NOX \rightarrow ArNO + HX} \qquad (1)$$

$$\mathrm{ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2} \qquad (2)$$

These conditions are found in the nitration of phenolic compounds and aromatic amines in aqueous nitric or acetic acid solutions containing nitrous acid. There is however no reported kinetic evidence showing that either the nitrosation step or the oxidation step is identifiable with the overall rate either of formation of the nitro-compound or of disappearance of the substrate. In fact, there has been very little direct demonstration of a nitroso-compound functioning as an intermediate.[2]

We have recently studied the nitration of 1,4-dimethoxybenzene by an excess of nitric acid in carbon tetrachloride and the data obtained indicates that the reaction does not proceed by direct nitration. This reaction is characterized by an induction period which is entirely eliminated by the addition of a very small quantity of isopentyl nitrite with the formation of the 2,5-dimethoxynitrobenzene then following a zeroth-order dependence on the aromatic substrate. U.v. absorption spectra show that isopentyl nitrite and nitric acid in this solvent rapidly form dinitrogen tetroxide (in equilibrium with nitrogen dioxide). Nitrosation of the substrate by dinitrogen tetroxide is also very rapid but maintenance of a stationary concentration of the latter would be possible by reaction (3), following the oxidation step (2),

$$\mathrm{HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O} \qquad (3)$$

Efforts to synthesize the suspected intermediate, 2,5-dimethoxynitrosobenzene, were unsuccessful and in order to examine step (2) with excess nitric acid in carbon tetrachloride, nitroso-*p*-xylene was used. There was a marked change in the u.v. absorption spectrum as reaction proceeded, but the product was only in part the expected nitro-*p*-xylene. An additional yellow product was present which could be extracted by aqueous alkali and had a much lower R_F value than either the nitroso- or nitro-derivatives of *p*-xylene when separation was effected by thin-layer chromatography.

The replacement of nitric acid by dinitrogen tetroxide as the oxidant in this system however resulted in the complete conversion of nitroso-*p*-xylene to nitro-*p*-xylene with the reaction proceeding much more rapidly.

TABLE

Anisole (10^4M)	*o*-NO-anisole (10^4M)	N_2O_4 10^2M)	HNO_3 (10^2M)	$t_{\frac{1}{2}}$ (very approx.) at 23° (min.)
3·27	0	1·11	0	55
3·27	0	0·74	0	75
3·27	0	0	2·5	(very slow)
0	3·20	0·74	0	10

Further evidence for the nitrosation mechanism and for oxidation of the nitroso-compound by dinitrogen tetroxide has been obtained in studies of the conversion of anisole to its mononitro-derivatives (Table). At the concentrations indicated, nitration of anisole occurs readily with dinitrogen tetroxide alone but hardly at all when nitric acid alone is used at more than double the dinitrogen tetroxide concentration.

Examination of the products from the reaction with dinitrogen tetroxide by thin-layer chromatography indicates the presence of both *o*- and *p*-nitroanisole but not the *m*-nitro-isomer.

The oxidation of *o*-nitrosoanisole by dinitrogen tetroxide, which the u.v. spectrum shows to be quantitative, is more rapid than the overall rate of nitration of anisole by the same reactant, and indicates that the initial nitrosation step is the slower step. The action of nitric acid alone on *o*-nitrisoanisole gave a similar result to that with nitroso-*p*-xylene *viz.*, the formation of products other than *o*-nitroanisole. Demethylation is a possible complication in this case.[1]

It would appear that with N_2O_4 replacing NOX in reaction (1), the nitration mechanism which operates is more adequately represented by the reaction sequence (1) → (4) → (5) rather than (1) → (2) → (3).

$$\mathrm{ArNO} + \mathrm{N_2O_4} \rightarrow \mathrm{ArNO_2} + \mathrm{N_2O_3} \qquad (4)$$

$$\mathrm{N_2O_3} + 2\mathrm{HNO_3} \rightarrow 2\mathrm{N_2O_4} + \mathrm{H_2O} \qquad (5)$$

Kinetic measurements are now being made on this system, particularly to clarify the nature of the oxidizing step.

(*Received, June 27th,* 1967; *Com.* 654.)

---

[1] C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff, and R. I. Reed, *J. Chem. Soc.*, 1950, 2628.

[2] R. M. Schramm and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1948, **70**, 1782.