## THE MECHANISM OF AROMATIC NITRATION BY TETRANITROMETHANE

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Summary Aromatic nitrations by tetranitromethane are shown to be photochemically initiated and are believed to proceed via trinitromethyl nitrite.

Tetranitromethane (TNM) has become known as a mild and somewhat unpredictable nitrating agent of aromatic rings. It will give, for example, some 70% of 3-nitro-4-dimethylaminotoluene when treated with p-toluidine at room temperature <sup>1</sup>. Azulene is nitrated in the 1-position in good yield <sup>2</sup> and several nucleophilic heterocycles react likewise <sup>3, 4</sup>. Phenols, as phenoxide ions, are nitrated in variable yield at positions typical of an electrophilic attack although frequently accompanied by products of radical coupling. P-cresol, for instance, is reported to give 30% of 2-nitro-4-methylphenol together with 30% of Pummerer's ketone <sup>5</sup>. Nonetheless, this reaction has found favour for the nitration of tyrosyl residues in protein <sup>6, 7, 8</sup>. A mechanism was put forward by Bruice to account for these products and assumed a pre-homolysis of TNM

The dissociation energy of the C-N bond, estimated at 2 50 kJmol<sup>-1</sup>, is too great for this to be a feasible mechanism at room temperature <sup>9</sup> although it may account for nitrations of aromatic substances which take place in the injection block of a g. 1. c. 17.

An alternative which we considered would be a rate-determining nitronium ion transfer

$$C(NO_2)_4 + ArH \longrightarrow Ar'_{NO_2} C(NO_2)_3 \longrightarrow products$$

and it was expected that a distinction could be made by measurement of the volume of activation The dissociation mechanism of Bruice would be expected to show a posof a typical example. itive value of  $\Delta V^{\vec{\tau}}$  while the associative mechanism above, particularly having a dipolar transition state, should show a negative value. Accordingly, we repeated earlier measurements of the rate of nitration of azulene which appeared to be well behaved and could be easily followed by the colour change from blue to yellow. When conducted in dioxan or dichloromethane, the reaction followed second-order kinetics to at least 75% reaction. It was noticed, however, that the rate constants, while reproducible over a short period, became progressively larger with the storage time of the reagent solutions. Air appeared to have no effect nor did light affect the azulene solution. However, laboratory light and particularly ultraviolet radiation did bring about an increase in reactivity of the TNM solution and appeared to transform this compound into a long-lived species of greater activity as a nitrating agent. Fig.1 shows the results of a controlled irradiation at 366 nm on nitrating reactivity towards azulene. There have been previous reports of the effect of light on reactions of TNM. The nitration of carbazoles is effected by light though separate illumination of the components was not studied <sup>10</sup>. Nitration of 1, 1 diphenylethene (at the  $\beta$ -position) is similarly affected  $\frac{11}{1}$ , a photolytic nitronium ion transfer being inferred here from trapping experiments.



Fig. 1 Effect of duration of pre-irradiation on nitrating activity of a solution of TNM

Irradiation of TNM in the presence of carbonyl compounds has led to the formation of nitroxyl and other radicals directly observable by e.s.r.  $^{12, 13, 14}$ . The stability of the reactive nitrating agent, however, does not suggest a radical although these may be involved in the primary photo reaction. We suggest the following scheme to account for these observations  $^{16}$ .

$$C(NO_2)_4 \stackrel{h v}{=} C(NO_2)_3 \cdot NO_2 : \longrightarrow O=N-O-C(NO_2)_3 \xrightarrow{ArH} Ar \stackrel{+}{\underset{NO_2}{\longrightarrow}} C(NO_2)_3 \xrightarrow{ArNO_2} + CH(NO_2)_3$$

The reactive photoproduct is trinitromethyl nitrite which, plausibly, acts as a better nitronium transfer agent than does TNM. This compound has, so far, resisted isolation but the following evidence supports the structure assigned. Several other instances of photoisomerisation of nitro compounds to nitrites are known. Chapman and coworkers noted the formation of 9-anthryl nitriter from the uv irradiation of 9-nitroanthracene<sup>18</sup> and the corresponding isomerisation of nitromethane has been reported  $\frac{19}{2}$ . Irradiation of TNM solutions at 366 nm brought about changes in the infrared spectrum bands at 800, 1616 and 1645 cm<sup>-1</sup> were replaced by others at 1635 and 1725 at a rate which corresponded with the increase in reactivity as shown in Fig.1 . This is consistent with the replacement of symmetric and antisymmetric -NO2 bending modes by the -N=O stretching known to occur at a slightly higher wavenumber. Prolonged irradiation of TNM solutions led to the eventual destruction of the nitrating agent. Gaseous products were pumped off and their infrared spectra observed using a Fourier-transform spectrmeter. The characteristic bands of both NO, and NO were observed. The latter is expected to result from the photolysis of a nitrite but is unlikely to be a primary photoproduct from a nitro compound. The isomerisation of TNM takes place slowly in visible light of wavelength less than about 500 nm. The compound has an absorption maximum at 230 nm but with a long tail which stretches into the visible. There may be a weak absorption band centred around 360 nm. However, the extinction coefficient remains at around 10 up to 420 nm so that absorption of light from the uv into the blue region is occurring. It is likely that the C-N bond dissociation energy is not greater than that of nitromethane  $(255 \text{ kJmol}^{-1})$  since steric relief and delocalisation of the unpaired electron are possible. This corresponds to light of 460 nm hence there is sufficient energy in the light observed to bring about photolysis for the mechanism above to be plausible. Similar types of reaction of nitroso compounds occurring in daylight have recently been discussed by Ingold<sup>15</sup>.

Finally, nitrations of phenols by TNM catalysed by pyridine probably partake of a different route. Pyridine and tetranitromethane react together on standing to produce a yellow solid

which appears to be a mixture of N-nitropyridinium nitroformate and nitrate. This is a mild nitrating agent towards, for instance, phenols to which it presumably acts as a nitronium ion transfer agent. It should be noted that a mixture of TNM and pyridine has occasionally exploded several hours after mixing.

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