

and it was expected that a distinction could be made by measurement of the volume of activation of a typical example. The dissociation mechanism of Bruice would be expected to show a positive value of ΔV^\ddagger 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 studied¹⁰. Nitration of 1,1 diphenylethane (at the β -position) is similarly affected¹¹, a photolytic nitronium ion transfer being inferred here from trapping experiments.

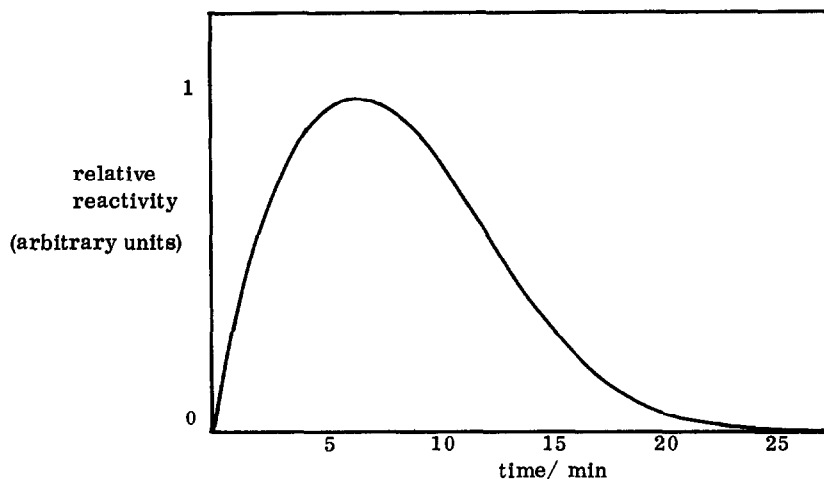
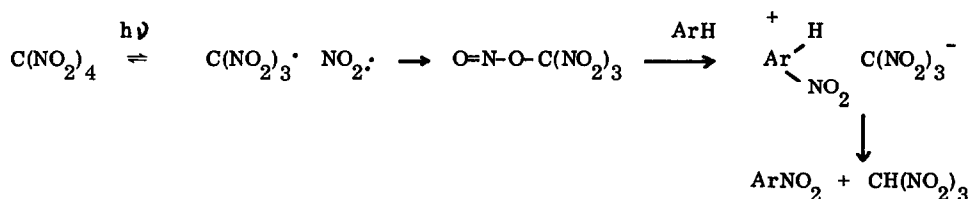


Fig. 1 Effect of duration of pre-irradiation on nitrating activity of a solution of TNM

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.



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 nitrite from the uv irradiation of 9-nitroanthracene ¹⁸ and the corresponding isomerisation of nitromethane has been reported ¹⁹. Irradiation of TNM solutions at 366 nm brought about changes in the infrared spectrum bands at 800, 1616 and 1645 cm^{-1} 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 -NO_2 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 spectrometer. The characteristic bands of both NO_2 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 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 ¹⁵.

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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