The Addition–Elimination Mechanism in the Photonitration of Naphthalene by Tetranitromethane

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By the isolation and kinetic studies of an adduct (*cis*-1,4-dihydro-1-nitro-4-trinitromethylnaphthalene) from the photolysis of naphthalene–tetranitromethane in dichloromethane or acetonitrile, it is shown that the route to nitro substitution products proceeds *via* addition–elimination, the latter step being either thermal or base-catalysed.

It was recently shown[1] that the photonitration of naphthalene by tetranitromethane (TNM) in dichloromethane takes place *via* two pathways, both initiated by photoexcitation of the charge-transfer (CT) complex between the reactants [eqn. (1)]. Extensive product studies suggested that the predominant (*ca.* 85%) pathway begins with attack of trinitromethanide ion upon $ArH^{\cdot +}$, followed by reaction of the naphthalenyl radical with NO_2 to give adducts, as exemplified in Scheme 1. This scheme further assumed that the addition products are stable in dichloromethane but undergo elimination of nitroform $[CH(NO_2)_3]$ to give nitro products with low α/β ratios (1.2–5) in the presence of a hindered base or upon thermal treatment (GLC). The second, minor pathway proceeded *via* slow nitration by NO_2–N_2O_4, which had escaped from the triad of eqn. (1), and gave the characteristically high α/β ratio (≈20) of this process. We now present direct experimental evidence for the major mechanism by isolation of a pure adduct from naphthalene and studies of its reactivity.

$$\underset{\text{CT complex}}{ArH\,C(NO_2)_4} \xrightarrow{h\nu_{CT}} \underset{\text{triad}}{[ArH^{\cdot +}\ {}^{-}C(NO_2)_3\,NO_2]} \qquad (1)$$

After irradiation of a dichloromethane solution (16 ml) of naphthalene (0.5 mol dm^{-3}) and TNM (1 mol dm^{-3}) at ≈ 20 °C for 113 h with filtered light (cut-off <435 nm) the reaction mixture was worked up by the pentane extraction method described earlier.[1] The pentane-soluble material consisted mainly of α- and β-nitronaphthalene in a ratio of 9 : 1 (GLC, 32% yield). The pentane-insoluble material was recrystallized from dichloromethane–pentane and gave a 20% yield of *cis*-1,4-dihydro-1-nitro-4-trinitromethylnaphthalene **1**. The structure was inferred from NMR spectral data and confirmed by an X-ray crystallographic study (Fig. 1).‡

An identical experiment in acetonitrile gave a complex mixture including the nitronaphthalenes (total *ca.* 40%); the same adduct was present in this mixture (*ca.* 6%) and could be isolated in 4% yield.

The adduct was stable for weeks in dichloromethane. Addition of a hindered base, 2,6-di-*tert*-butylpyridine (DtBPY), promoted rapid elimination of nitroform with an average rate constant of 0.15 dm^3 mol^{-1} s^{-1} at 20.0 °C with [DtBPY] in the range 1.7–35 mol dm^{-3}.§ In acetonitrile the rate constant of the base-promoted elimination was 0.16 dm^3 mol^{-1} s^{-1}. Thus photochemical experiments[1] with [DtBPY] in the range 0.16–0.68 mol dm^{-3} will presumably reflect the initial composition of the adduct mixture, since adduct half-lives will be < 30 s. It is likely that other possible adducts will have similar half-lives for elimination of nitroform, since it is the acidity of an ionizable proton on a carbon substituted by a nitro group that determines the rate.

In neat acetonitrile **1** underwent spontaneous elimination with a pseudo-first-order rate constant of (3–9) × 10^{-4} min^{-1}, corresponding to half-lives between 40 and 13 h.¶ These are of the same order as irradiation times and therefore adduct yields are lower from runs in acetonitrile at ambient temperature. A similar behaviour of *cis*- and *trans*-1,4-dihydro-1,4-dimethyl-1-nitro-4-trinitromethylnaphthalene has been noted; upon standing at room temperature in acetonitrile, the mixture of adducts slowly eliminated nitroform to give 1-methyl-4-nitromethylnaphthalene.[2]

During GLC analysis, **1** behaved exactly as inferred from product studies.[1] It was earlier (*a*) trivially assumed that a nitro–trinitromethyl naphthalene adduct would eliminate nitroform to give nitro products, (*b*) less trivially assumed that an adduct of suitable steric disposition would eliminate trinitromethyl nitrite to give naphthalene and (*c*) assumed that adducts might eliminate nitrous acid to some extent and give trinitromethyl substitution product(s). Upon thermal treatment, the latter might be the source of nitriles, found as

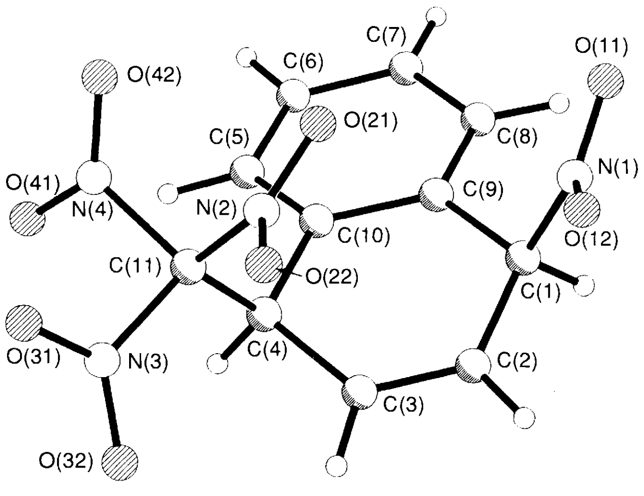

Fig. 1 Perspective view of the structure of **1**

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‡ *Crystal data* for **1**: $C_{11}H_8N_4O_8$, M = 324.20, orthorhombic, space group $P2_12_12_1$, a = 6.400(1), b = 12.085(2), c = 17.321(3) Å, V = 1339.68 Å^3, Z = 4, μ(Mo-Kα) 1.4 cm^{-1}, Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 293 K using a Siemens/Stoe hybrid 4-circle diffractometer for a colourless crystal of dimensions 0.84 × 0.12 × 0.09 mm. All 2329 reflections were used in all calculations with SHELXS92 for solution by direct methods and SHELXL92 for refinements using intensities (*WR*2 = 0.0797 for all data) and molecular geometry calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

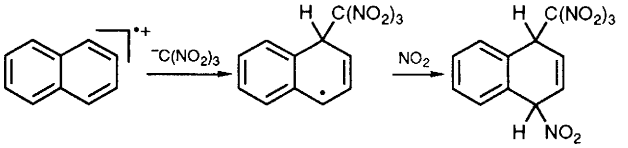
§ The reaction was actually of order 1.3(1) in [DtBPY] in the concentration interval studied.

¶ As expected, this rate constant was not very well reproducible owing to the difficulty of controlling the base concentration in highly purified acetonitrile (UVASOL quality from Merck, Darmstadt, Germany). In neat CD_3CN, a run monitored by NMR spectroscopy showed that **1** was converted into α-nitronaphthalene with a half-life of ≈ 50 h.

Table 1 Product composition in the GLC analysis of a solution of adduct in dichloromethane as a function of injection port temperature[a]

Injection port temperature/°C	Products (%)[b]			
	HNp	α-NO_2Np	β-NO_2Np	α-CNNp
100		100		
150		100		
200	<0.2	100		
250	3	96		1
300	13	80	<0.2	3
350	32	61	<0.5	4
400	56	38	0.5	2

[a] HP 5830 A instrument, column 2 m 5% neopentyl glycol succinate on Chromosorb W, 150–210 °C at 10 °C min^{-1}. [b] Np = naphthyl.



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Scheme 1

side-products from the photonitration of 1-methoxynaphthalene.[1]

The correctness of these assumptions is shown by the data of Table 1, in which product distributions from the GLC analysis of **1** are given as a function of the injector port temperature. At low temperatures (< 200 °C) only α-nitronaphthalene is formed, whereas elimination of trinitromethyl nitrite and nitrous acid is clearly evident at 300 °C. It also appears that the nitro group can migrate to a small extent during thermal treatment.

Thus our hypothesis [*cf.* Scheme 1] that nitro–trinitromethyl adduct formation, followed by elimination of nitroform, is the major pathway in the photonitration of naphthalene by TNM in dichloromethane or indeed in any solvent is further strengthened. It is the stability of the adduct towards elimination that determines the experimental outcome of the reaction; in dichloromethane the adduct is stable over long periods, whereas in acetonitrile it eliminates nitroform on a time-scale compatible with irradiation times, giving rise to primary product mixtures richer in nitro substitution product(s). Analysis by GLC, column work-up, *etc.* will give elimination products, thus masking the initial mechanistic complications.[1] The same situation may apply to other substrates, although further studies are needed to establish the generality of our findings. So far published product studies[2–8] do not contradict the idea that more or less stable adducts are the primary products from the photonitration of aromatics by tetranitromethane. In fact, adducts have been detected also from a monocyclic aromatic compound, 4-methylanisole.[6]

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References

1 L. Eberson and F. Radner, *J. Am. Chem. Soc.*, 1991, **113**, 5825.
2 S. Sankararaman and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1.
3 J. M. Masnovi, J. K. Kochi, E. F. Hilinski and P. M. Rentzepis, *J. Am. Chem. Soc.*, 1986, **108**, 1126.
4 S. Sankararaman and J. K. Kochi, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 278.
5 S. Sankararaman, W. A. Haney and J. K. Kochi, *J. Am. Chem. Soc.*, 1987, **109**, 5235.
6 S. Sankararaman, W. A. Haney and J. K. Kochi, *J. Am. Chem. Soc.*, 1987, **109**, 7824.
7 J. M. Masnovi, S. Sankararaman and J. K. Kochi, *J. Am. Chem. Soc.*, 1989, **111**, 2263.
8 P. Maslak and W. H. Chapman, Jr., *J. Org. Chem.*, 1990, **55**, 6334.