Thermal and Photochemical Decomposition Pathways of Trinitromethylarenes. Part I. The Conversion of ArC(NO₂)₃ to ArNO₂ – a Rationalization of Apparent Solvent Effects

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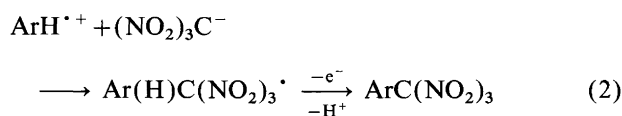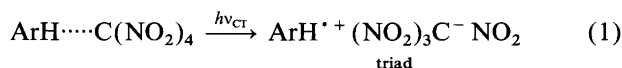
The thermal and photochemical decomposition of trinitromethylarenes in an inert solvent (dichloromethane or acetonitrile) has been investigated, using 1-methoxy-4-trinitromethylnaphthalene (2) and 2-trinitromethyl-4-chloroanisole (6) as representatives of reactive and unreactive ArC(NO₂)₃, respectively. Compound 2 underwent slow thermal decomposition in both solvents to give 4-methoxy-1-naphthoic acid (3) and 1-methoxy-4-nitronaphthalene (5). The reaction was speeded up by additives, such as 1-methoxynaphthalene or nitrous acid. The decomposition of 2 was strongly accelerated by irradiation with light of $\lambda > 430$ nm. Both the thermal and photochemical processes were faster in acetonitrile than in dichloromethane. Spin trapping experiments resulted in the trapping of ArCOO˙ radicals, in both the thermal and photochemical reactions, indicating that the decomposition reaction is at least partially of radical nature. The acid 3 was shown to undergo fast thermal nitrodecarboxylation by treatment with NO₂ in dichloromethane.

Compound 6 exhibited similar behaviour, except that the rates were much slower, less than 100 times slower than those of 2.
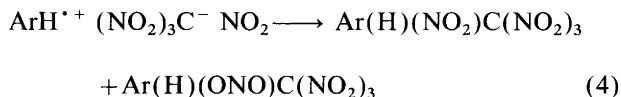
The mechanism suggested involves an initial nitro→nitrito rearrangement of ArC(NO₂)₃, followed by homolytic decomposition of the nitritodinitromethyl-arene formed. The finding that trinitromethylarenes have differing stabilities, depending on the nature of the ring substituent(s) and/or the solvents used, offers a reasonable explanation for the chemoselectivity of tetranitromethane-ArH photolyses.

The photochemical excitation of the charge transfer (CT) complex between tetranitromethane and an aromatic compound (ArH) within 3 ps gives a triad, consisting of the aromatic radical cation, the trinitromethanide ion and NO₂ [eqn. (1)].[1] It was originally believed[2] that the pathways leading from the triad to final products, nitro- and trinitromethyl-substituted ArH, were controlled by the competition between eqns. (2) and (3). However, later it was shown that the followup chemistry of the triad components is considerably more complicated and in fact completely different from the simple scheme of eqns. (2) and (3). In a number of cases, such as naphthalene,[3] dibenzofuran,[4] fluoranthene,[5] benzene,[6] methyl-[7] and dimethylnaphthalenes[8] and polymethyl-benzenes,[9] the primary products were shown to be adducts of trinitromethyl and NO₂ (ONO) across the aromatic ring in 1,2- and/or 1,4-fashion, as indicated in eqn. (4). The initial step was shown to be the radical cation-trinitromethanide reaction, the ArH˙⁺-NO₂ step being relatively slow.[10]

$$\text{ArH}\cdots\text{C(NO}_2\text{)}_4 \xrightarrow{h\nu_{CT}} \text{ArH}^{˙+}(\text{NO}_2\text{)}_3\text{C}^-\text{NO}_2 \qquad (1)$$
$$\text{triad}$$

$$\text{ArH}^{˙+} + (\text{NO}_2)_3\text{C}^-$$

$$\longrightarrow \text{Ar(H)C(NO}_2\text{)}_3^{˙} \xrightarrow[-\text{H}^+]{-\text{e}^-} \text{ArC(NO}_2\text{)}_3 \qquad (2)$$

$$\text{ArH}^{˙+} + \text{NO}_2 \longrightarrow \text{Ar(H)NO}_2^+ \xrightarrow{-\text{H}^+} \text{ArNO}_2 \qquad (3)$$

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$$ArH^{\cdot +}\ (NO_2)_3C^-\ NO_2 \longrightarrow Ar(H)(NO_2)C(NO_2)_3$$

$$+ Ar(H)(ONO)C(NO_2)_3 \qquad (4)$$

Nitro-trinitromethyl adducts are in many cases sufficiently stable to be isolated as solids and be subjected to single-crystal X-ray analysis. Their stability in solution is limited due to slow elimination of trinitromethane and/or nitrous acid with formation of $ArNO_2$ and/or trinitromethylarenes. The stability of the adducts toward elimination is lower in acetonitrile than in dichloromethane.

Nitrito-trinitromethyl adducts have not been isolated as such, since they are readily hydrolyzed to the corresponding hydroxy-trinitromethyl derivatives during the prevailing reaction conditions and/or workup. One such hydroxy-trinitromethyl adduct (from dibenzofuran) has been isolated and characterized by X-ray crystallography.[4b] From other hydroxy-trinitromethyl adducts stable products of intramolecular dipolar addition of one nitro group of the $C(NO_2)_3$ group across a suitably disposed double bond have been isolated and characterized by X-ray crystallography.[7,8b,8d,8e,8g] It is likely that trinitromethyl substitution products to some extent are derived from hydroxy(nitrito)-trinitromethyl adducts by elimination of HNO_2.

The pattern of formation of trinitromethylarenes, $ArC(NO_2)_3$, is a curious one. For anisole and a series of anisoles (2-, 3- and 4-CH_3, 4-F, 4-Cl and 4-Br) it was reported by Kochi and coworkers[2a] that trinitromethylation was favoured in dichloromethane, whereas nitration took place in acetonitrile. On the other hand, dialkoxybenzenes underwent exclusive nitration in both solvents.[2b] This solvent effect was rationalized on the basis of differences in ion pairing behaviour of the triad in the two solvents.

For naphthalene itself[3] adduct formation dominated strongly over nitration in both solvents, and trinitromethylation occurred only to an extent of 1–5%. In the case of 1-methoxynaphthalene (1) in dichloromethane long irradiation times gave predominantly nitration products, but the formation of 4-trinitromethyl-1-methoxynaphthalene (2) was inferred from the isolation of a


1

4   5   6

product of formal hydrolysis, 4-methoxy-1-naphthoic acid (3), in low yield (5–10%). In the presence of alcohols, the corresponding esters of 3 were obtained in yields up to about 50% [eqn. (5)].[11] Later[12] it was found that 2 was the major product in *both* dichloromethane and acetonitrile at short irradiation times, but decayed at longer times, concomitant with some increase in the yield of 2- (4), but predominantly 4-nitro-1-methoxynaphthalene (5). Low yields of unstable adducts were also found in both solvents, in dichloromethane about 18% and in acetonitrile about 5%.

A quantitative analysis of the 1-methoxynaphthalene results (see Discussion) suggested that the solvent effect might be of entirely different origin. Apart from the fact that adducts play an important role in the overall chemistry of the system, it was evident that the trinitromethylarene 2 was unstable under the conditions of the photolytic experiment, being converted by some route into nitro derivatives 4 and 5. In what follows, we give an account of the intricate chemistry of the trinitromethylarene, 2, selected as a suitable model for thermally and photochemically reactive trinitromethylarenes. For a comparison of its chemical behaviour with that of a fairly unreactive $ArC(NO_2)_3$, 2-trinitromethyl-4-chloroanisole (6) was chosen as a second model compound.[13] In this case, 6 was the major product (40–50% yield) from photochemical runs with 4-chloroanisole-tetranitromethane in dichloromethane, even at long reaction times, whereas in acetonitrile the yield of 6 ranged from 5 to 10%.

The results to be described below show that the solvent effect referred to above must be caused predominantly by the different stability of adducts and trinitromethylarenes under the conditions of the photochemical runs.

Results

Choice of substrates. The trinitromethyl compounds 2 and 6 were chosen to represent trinitromethylarenes of different photochemical and chemical reactivity under the conditions employed in the photochemical experiments (light of $\lambda > 430$ nm, ambient temperature). Preliminary studies indicated that these two compounds represented a suitably wide span of reactivity. Moreover, it was important to select systems where the development of individual products with time had been monitored[12,13] throughout the whole run in order to identify interrelated decays/appearances. Previous product analyses pertaining to the solvent effect were carried out after long irradiation times with focused light of high intensity, typically 5–25 h with light sources of 500–1000 W.[2]

2   3
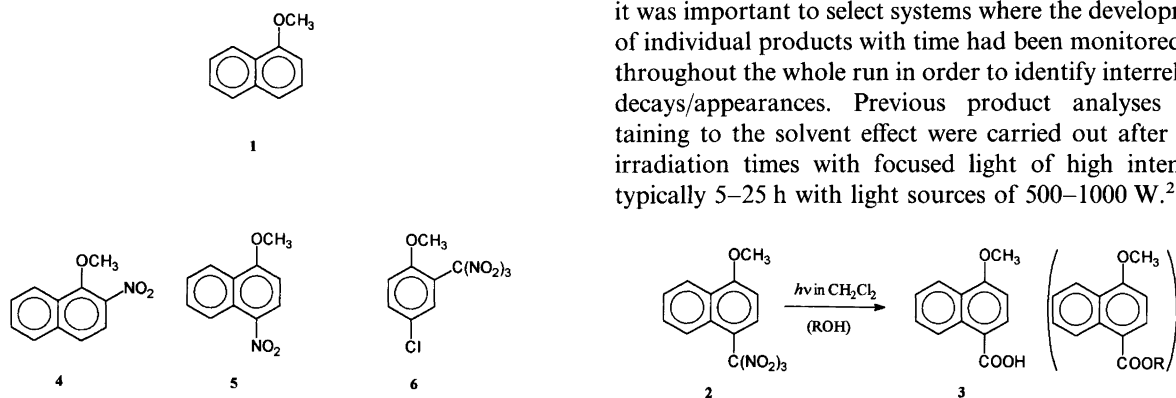
UV–VIS spectroscopy of 2 and 6. The UV/VIS spectrum of **2** in dichloromethane ([**2**] ≈ 0.5 mmol dm^{-3}) showed that only a weak tailing of the maxima/shoulders at lower wavelengths (Fig. 5, lower set of spectra) penetrated into the region of $\lambda > 430$ nm, the extinction coefficient at 460 nm, ε, being ca. 30. Addition of 1-methoxynaphthalene in a concentration up to 80 mmol dm^{-3} increased the absorbance at 460 nm somewhat beyond the value corresponding to the sum of the solutions of **2** and 1-methoxynaphthalene, recorded separately. For **6**, no such changes were noticeable from a similar set of spectra.

Stability of trinitromethylarenes in the solid state. Trinitromethylarene **2** underwent only minor changes upon storage at $-20\,°C$, being converted into 2-nitro-1-methoxynaphthalene (**4**) to an extent of 17–18% in about 10 months. The sample also had a brief period at ambient temperatures during 5–6 days of transport. Compound **6** was more stable in this respect and showed no sign of decomposition during storage at $-20\,°C$ for more than one year.

Thermal reactivity of 2 in dichloromethane and acetonitrile. A solution of **2** (20 mmol dm^{-3}) in [^{2}H$_2$]dichloromethane was kept in the dark at room temperature and analyzed at suitable intervals by ^{1}H NMR spectroscopy. The concentration of **2** slowly decreased [$k = 3.0(2) \times 10^{-4}$ min^{-1}] and the products, 4-methoxy-1-naphthoic acid (**3**) and 4-nitro product **5**, built up [$k = 1.0(1) \times 10^{-3}$ and $1.4(1) \times 10^{-4}$ min^{-1}, respectively; Fig. 1]. The final state was reached in ca. 150 h, the product composition being **3** (29%) and **5** (68%). In a second experiment the reaction was stimulated by the addition of a solution of NO$_2$ (a known component of
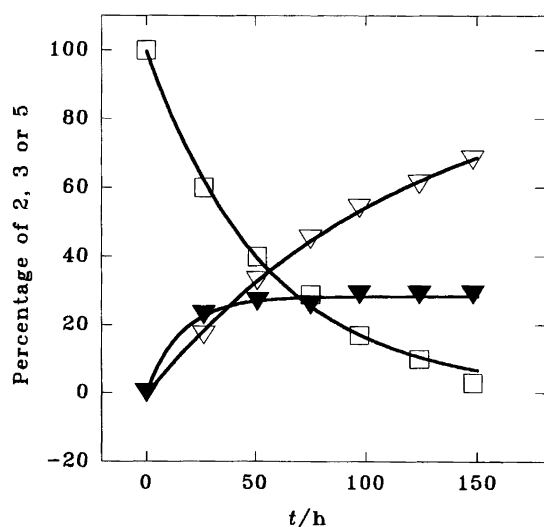
the photolysis mixture)[12] after 1.5 h; this had little or no effect at a concentration level of 2 mmol dm^{-3} (Fig. 2).

After 5 h, 'HNO$_2$', another known component of the photolysis mixture,[2a] was added in a concentration of ca. 80 mmol dm^{-3} as an equimolar mixture of trifluoroacetic acid and tetrabutylammonium nitrite. This increased the rate of the reaction, **2** disappearing with $k \approx 5 \times 10^{-3}$ min^{-1} and the final product composition being reached after about 25 h, comprising **3** (56%), **4** (32%) and **5** (12%); note that 17% of **4** was present in the sample from the beginning.

Qualitatively, the changes in solutions of **2** (ca. 0.5 mmol dm^{-3}) in dichloromethane upon addition of additives could be monitored by UV spectroscopy at 360 or 380 nm. At these wavelengths, **4** and **5** absorb strongly, whereas the acid **3** has a maximum at 310 nm. With no additive, little change was observed over a period of 24 h. Since the acidity of the photolysis mixtures builds up during the run due to formation of the strong acid trinitromethane,[3,8a] the first additive being tried was trifluoroacetic acid (TFA). Figure 3 shows the short-time effect of the addition of trifluoroacetic acid in increasing concentrations (0.26, 0.46 and 0.63 mol dm^{-3}); a sigmoid increase in absorbance takes place, more rapidly the higher the concentration of TFA is. This is then followed by a steady increase in absorbance over ca. 20 h. At the lowest concentration of TFA (0.26 mol dm^{-3}), addition of 'NO$_2$' in increasing concentration (0.39, 0.65 and 1.3 mmol dm^{-3}) caused the domain of sigmoid change to be reached earlier at the higher concentrations (Fig. 4); analogous short- and long-term changes were induced by the addition of tetrabutylammonium nitrite in the same range of concentrations. The
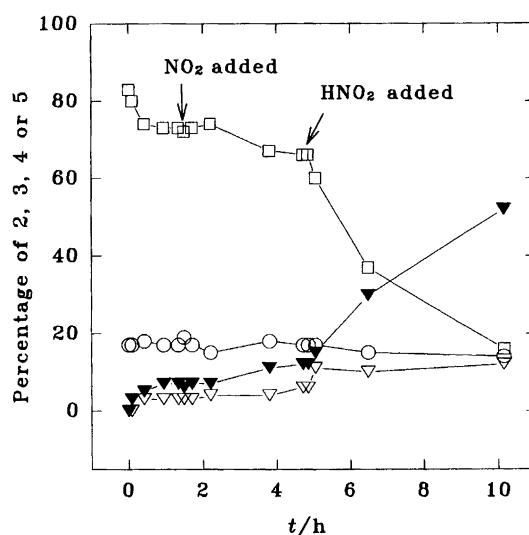

Fig. 1. Decay of **2** (20 mmol dm^{-3}) in [^{2}H$_2$]dichloromethane at 22 °C. Empty squares, **2**; filled triangles, **3**; empty triangles, **5**. The curves are the exponentials best fitting to the data (see text).

Fig. 2. Decay of **2** (20 mmol dm^{-3}) in [^{2}H$_2$]dichloromethane at 22 °C in the presence of various additives. 'NO$_2$' was added in a concentration of 2 mmol dm^{-3} (after 1.5 h) and 'HNO$_2$' in a concentration of ca. 80 mmol dm^{-3} (after 5 h). Empty squares, **2**; filled triangles, **3**; empty circles, **4**; empty triangles, **5**. The sample contained 17% of **4** from the beginning of the reaction.
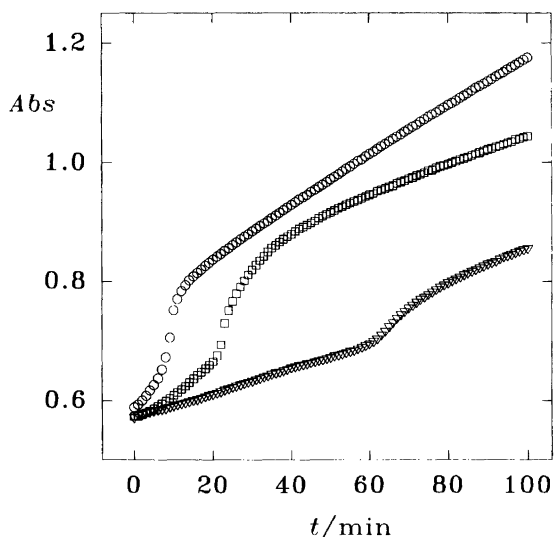
Fig. 3. Change of the absorbance at 380 nm with time of a solution of 2 (ca. 0.5 mmol dm^{-3}) in dichloromethane to which trifluoroacetic acid was added in a concentration of 0.26 (triangles), 0.46 (squares) and 0.63 (circles) mol dm^{-3}. Temperature 22 °C.
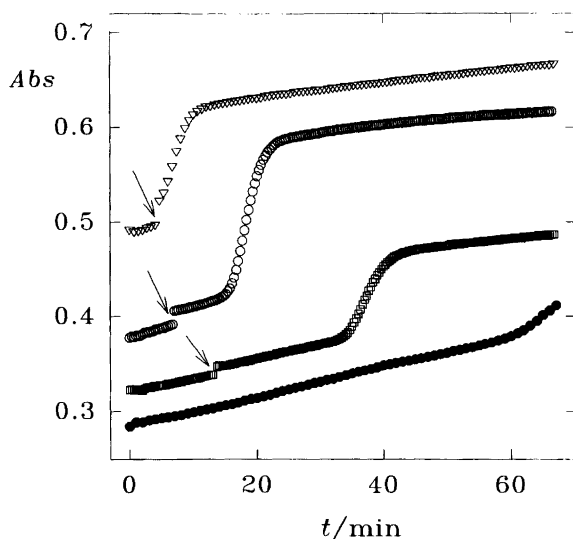

Fig. 4. Change of absorbance at 380 nm with time of a solution of 2 (ca. 0.5 mmol dm^{-3}) and trifluoroacetic acid (0.26 mol dm^{-3}) in dichloromethane with no additive (filled circles) and with NO$_2$ added in a concentration of 0.39 (squares), 0.65 (empty circles) and 1.3 (triangles) mmol dm^{-3}. The arrows mark the time of addition of the NO$_2$ solution. The curves have been moved vertically in order to improve the readability. Temperature 22 °C.

repetitive scans recorded during the two phases show the spectral changes following the addition of NO$_2$ (Fig. 5) at [TFA]=0.26 mol dm^{-3}. During the first phase, an isosbestic point at 340 nm indicates that the reaction approaches a well defined intermediate product or set of products, and three isosbestic points ca. 295, 320 and 415 nm during the second phase similarly show that the intermediate product(s) are converted into a single set of products.

Similar changes took place in acetonitrile, but reactions were faster. NMR spectral monitoring of a solution of 2 (20 mmol dm^{-3}) in [^{2}H$_3$]acetonitrile with no additives showed that the spontaneous decay of 2 is about four times faster in this solvent than in [^{2}H$_2$]dichloromethane, k_{decay} being 1.1(1) × 10^{-3} min^{-1}. The final product composition was different, 3 [46%, building up with $k=$ 1.4(1) × 10^{-3} min^{-1}], 4 (37%, again starting from a 17% level in the sample of 2) and 5 (7%).

An attempt to identify possible intermediates was made by monitoring a solution of 2 in [^{2}H$_3$]acetonitrile by ^{14}N NMR spectroscopy. The ^{14}N signal of 2 appeared at -25.6 ppm (on the screening-constant scale referred to CH$_3$NO$_2$) and had a half-height width of 16 Hz, whereas the nitro products 4 and 5 had signals at -8.8 and -6.4 ppm, respectively, both with a half-height width of 86 Hz. Other species of interest were NO$_2$ (ca. 15 ppm) and R–O–NO (ca. -200 ppm).[14a] It was estimated that signals lower than 14% of the original 2 signal would not be detectable, assuming the half-height width to be the same. During the run, the only detectable nitrogen-containing species were 2, disappearing with $k=2.0(2) \times 10^{-3}$ min^{-1} and an unknown species X (at $\delta = -40.8$ ppm, located in the nitro group range) appearing at approximately the same rate. No ^{14}N signals were detectable in the nitrite region. However, signals smaller than 14% of the original, rather narrow signal of 2 would not be detectable. For broader signals, the limit of detection would be correspondingly higher.

The UV spectral monitoring at 360 nm of a ca. 0.5 mmol dm^{-3} solution of 2 in acetonitrile with no additive demonstrated that the spontaneous reaction took place in two phases, the first one with an increase in absorbance (ca. 1.5 h), and the second one with a decrease (ca. 15 h), k_{up} and k_{down} being 1.3 × 10^{-2} and 1.0 × 10^{-2} min^{-1} (Fig. 6) assuming the reactions to be first-order and coupled via a common intermediate. The development of isosbestic points at ca. 285, 320 and 380 nm (first phase) and 300 and 340 nm (second phase) support this assumption.

This seems to indicate that an unstable intermediate is formed during phase 1 since the rate constants for decay of 2 into products and their buildup were about 10 times smaller (see above). In dichloromethane similar UV spectral changes occurred, but at a higher rate, the initial phase showing $k_{up}=0.034(2)$ min^{-1} for *Abs* at 360 nm. The second phase, with a decrease in absorbance, was shorter, (ca. 2 h), and was followed by an increase in absorbance for a period of at least 30 h.

Clearly, a relatively fast process involving an unstable intermediate (or several) with absorbance around 360 nm occurs in the initial stages of the reaction in both dichloromethane and acetonitrile. However, the ^{1}H or ^{14}N NMR spectra showed no significant evidence for the appearance of an intermediate during the first phase, possibly indicating that it is formed in such a low concentration that it cannot be detected. We therefore resorted to monitoring the reaction by the FTIR tech-
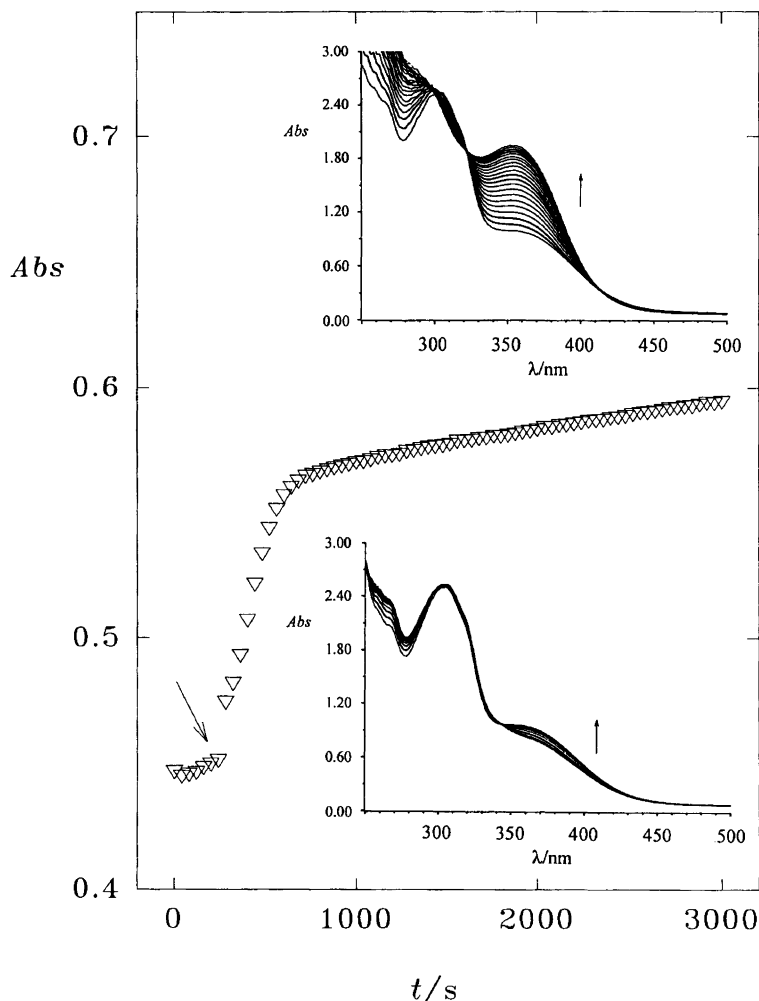
Fig. 5. Change of absorbance with time at 380 nm of a solution of **2** (ca. 0.5 mmol dm^{-3}) and trifluoroacetic acid (0.26 mol dm^{-3}) in dichloromethane with NO_2 added in a concentration of 1.3 mmol dm^{-3}. The arrow marks the time of addition of the NO_2 solution. The spectra were recorded with 100 s intervals in the sigmoid portion of the curve (lower set of spectra) and with 1 h intervals (upper set of spectra) in the linear part of the curve (only first 35 min shown). Temperature 22 °C.

nique, in principle capable of better resolution of the spectra of the species involved.

A solution of **2** (43 mmol dm^{-3}) in acetonitrile was monitored by FTIR spectroscopy at ambient temperature. The characteristic IR maxima[12] of **2** at 1589 and 1618 cm^{-1} disappeared within the first 3–4 h, k_{decay} being 0.011(1) min^{-1} in both cases; a maximum at 798 cm^{-1} also disappeared completely in this time interval, $k_{decay} =$ 0.015(1) min^{-1}. Several peaks appeared and decayed during the run, but none gave data of such quality that a kinetic evaluation could be performed.

Preparative tetranitromethane–ArH photolyses are usually run under conditions during which the trinitromethylarene is formed in the presence of an excess of the substrate. A control experiment involving the thermal reaction of **2** (20 mmol dm^{-3}) in [$^2H_2$]dichloromethane with 1-methoxynaphthalene (40 mmol dm^{-3}) present was therefore performed. Monitoring this solution by NMR spectroscopy established the following important features: (i) the rate constant for the decay of **2** increased to

4(1) × 10^{-3} min^{-1}, a factor of 13 larger than for the non-promoted decay, (ii) only one nitro product, 4-nitro-1-methoxynaphthalene (**5**, 52% yield), was formed with a rate constant of 4(1) × 10^{-3} min^{-1}, and (iii) the yield of the carboxylic acid **3** was 19%, about one third of the yield of **5** (Fig. 7). Compound **3** was formed with a rate constant of 5(2) × 10^{-3} min^{-1}. Toward the end of the run (after 7 h), the solution was irradiated for 15 min with light of λ > 430 nm, which strongly increased the rate (half-life period after irradiation ca. 30 min) but left the product composition largely unchanged.

Finally, an experiment was performed with both 1-methoxynaphthalene and HNO_2 added, in the same concentrations as above, to a dichloromethane solution of **2**. The effect of the combination was additive; **2** decomposed with a rate constant of 8.2(6) × 10^{-3} min^{-1}, i.e., a rate increase of 27 as compared to the spontaneous decomposition.

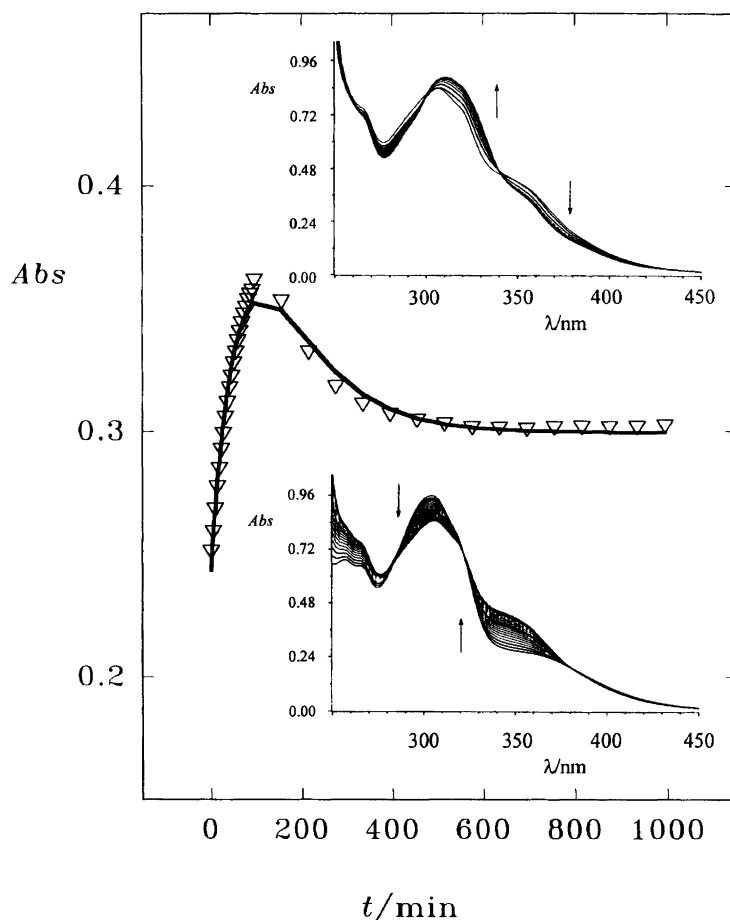An experiment analogous to that shown in Fig. 7 was also performed in [$^2H_3$]acetonitrile (Fig. 8). The results

Fig. 6. Change of absorbance with time at 360 nm of a solution of **2** (ca. 0.5 mmol dm^{-3}) in acetonitrile. The spectra were recorded with 270 s intervals in the ascending part of the curve (lower set of spectra) and with 1 h intervals in the descending part (upper set of spectra). Temperature 22 °C. The curve is the best fit of a double exponential function to the data (rate constants, see text).

were similar; **2** decayed with a rate constant of 1.8(1) × 10^{-3} min^{-1}, while **3** and **5** were formed with rate constants of 2.4(2) × 10^{-3} and 6.1(4) × 10^{-4} min^{-1}, respectively. The concentration of added 1-methoxy-naphthalene was also monitored; as seen in Fig. 8, only about 10% was left at the end of the reaction period and its decay rate was 4(1) × 10^{-4} min^{-1}.

Photochemical reactivity of 2 in dichloromethane and acetonitrile. The spontaneous reactions of **2** described above show that trinitromethylarenes are thermally unstable and that the thermal reaction is accelerated by the presence of a protic acid, the parent compound and/or HNO$_2$. However, the rates of these reactions are too low to allow for any decisive influence on the product composition. The photolysis of 1-methoxynaphthalene is typically carried out within 1–2 h,[12] and faster reactions are thus needed to explain the variation of product composition within that time range. Thus photochemically promoted decay mechanisms are likely to be important. A promising candidate is available in the photolysis of the trinitromethylarene in the presence of its parent compound (Fig. 7, second phase). The rate increase caused

by 15 min of irradiation was significant (ca. six-fold), while the product distribution was not changed. This finding was further substantiated by UV spectrally monitored runs at 360 nm where the cell content was irradiated from above with filtered light ($\lambda > 430$ nm) from a fiber-optical lamp with adjustable light intensity in arbitrary units between 0 and 10. With this setup it could be shown that the trinitromethylarene **2** was more rapidly decomposed in acetonitrile than in dichloromethane. Experiments, run over a typical irradiation period in a preparative run and performed at two concentrations of 1-methoxynaphthalene, are shown in Fig. 9. Calibration experiments without irradiation were also included.

To obtain a quantitative measure of the rate of decomposition, initial rates were calculated for the first 5–10 min of the irradiation period. These results are given in Table 1, where also results from experiments with varying light intensities are listed. In general, rates in acetonitrile are 2–3 times larger than in dichloromethane. As expected, initial rates increased with increasing light intensity.

Since the phenomena described above might have their origin in the homolytic cleavage of **2** to give first an
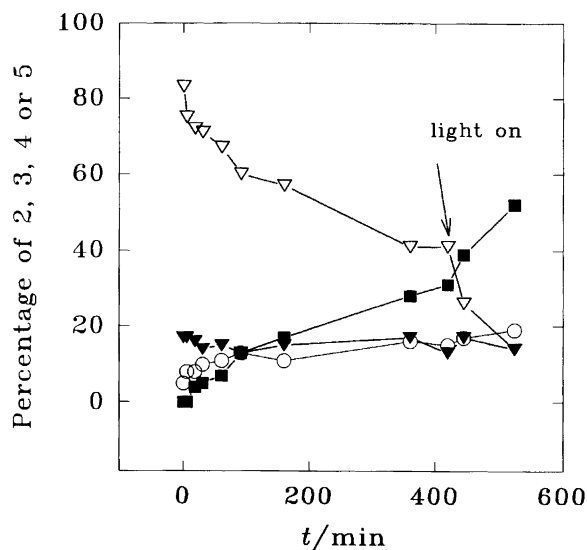
Fig. 7. NMR spectral monitoring of a solution of **2** (20 mmol dm^{-3}) and 1-methoxynaphthalene (40 mmol dm^{-3}) in dichloromethane showing the decay of **2** [empty triangles, $k = 5(1) \times 10^{-3}$ min^{-1}] and formation of **3** [circles, $k = 5(2) \times 10^{-3}$ min^{-1}] and **5** [squares, $k = 4(1) \times 10^{-3}$ min^{-1}]. The 2-nitro derivative (**4**), present in the sample from the beginning, remained at constant level during the whole reaction period (filled triangles). The solution was illuminated for 15 min after 7 h (arrow) with light of $\lambda > 430$ nm. Temperature 22 °C.
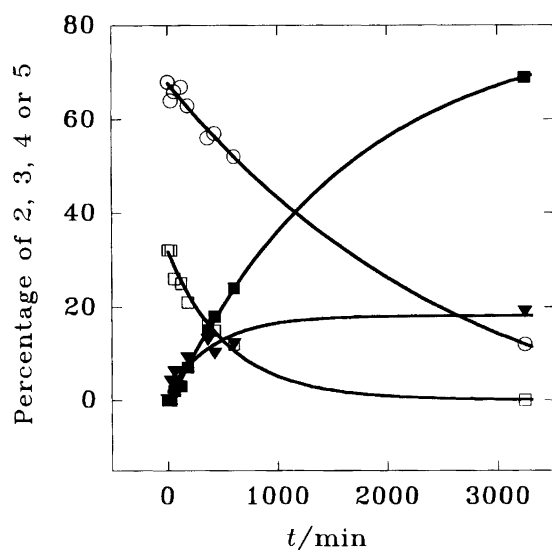

Fig. 8. Decay of **2** (9.3 mmol dm^{-3}) in [^{2}H$_3$]acetonitrile in the presence of **1** (18.6 mmol dm^{-3}) at 22 °C. Empty circles, **1**; empty squares, **2**; filled triangles, **3**; empty triangles, **5**. The curves are the exponentials best fitting to the data (see text).

arenedinitromethyl radical and NO$_2$ [eqn. (6)] with recombination to a nitritodinitromethylarene,[11] a solution of **2** (15 mmol dm^{-3}) and the spin trap, *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN, 50 mmol dm^{-3}), in dichloromethane was monitored at ambient temperature by EPR spectroscopy in order to see if any spin adducts
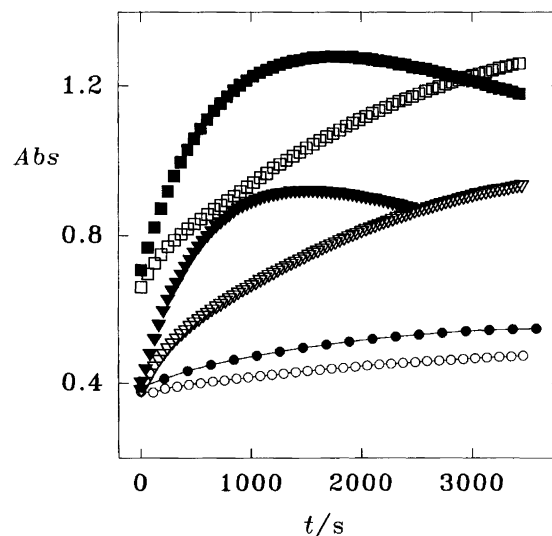

Fig. 9. UV spectral monitoring at 360 nm of a solution of **2** (ca. 0.5 mmol dm^{-3}) in the presence of **1**. Temperature 20 °C; lamp intensity 7.00. Circles, no irradiation, [**1**] = 2.0 mmol dm^{-3}; triangles, irradiation, [**1**] = 5.0 mmol dm^{-3}; squares, irradiation, [**1**] = 2.0 mmol dm^{-3}. Empty symbols, dichloromethane solution; filled symbols, acetonitrile solution.

Table 1. Photochemical rates of reaction in solutions containing **2** (ca. 0.5 mmol dm^{-3}) and 1-methoxynaphthalene (**1**) at 20 °C. The light was filtered, with cutoff at 430 nm.

[1]/mmol dm^{-3}	Light intensity	Initial rate/A min^{-1} in DCM[a]	in AN[b]	Ratio AN/DCM	Rel. rate DCM[a]	AN[b]
2.0	0	0.0023	0.0040	1.7	1	1
2.0	3.00	0.0073	0.015	2.1	3	4
2.0	5.00	0.0094	0.035	2.5	4	9
2.0	7.00	0.013	0.035	2.7	6	9
2.0	9.00	0.026	0.070	2.7	11	18
5.0	7.00	0.025	0.037	1.5	11	9

[a] DCM = dichloromethane. [b] AN = acetonitrile.

could be detected. Under *thermal* conditions, a 3×2 signal of typical spin adduct character ($a^N = 1.29$ mT, $a^H \approx 0.15$ mT) was detectable immediately after mixing. This signal disappeared within 10 min, while the familiar signal ($a^N = 0.80$ mT),[14b] originating from the acyl-nitroxyl [PhCON(O$^\bullet$)Bu^t, denoted PBNOx], started to appear [$k_{up} = 0.044(5)$ min^{-1}], reaching a maximum intensity after about 1 h and then decaying [$k_{down} = 0.006(1)$ min^{-1}]. A weaker, 3×4 lines signal ($a^N = 1.40$, $a^{N'} = 0.22$, $a^H = 0.22$ mT) showed approximately the same development with time.

$$ArC(NO_2)_3 \rightleftharpoons ArC(NO_2)_2^\bullet + NO_2 \rightleftharpoons ArC(NO_2)_2ONO \qquad (6)$$
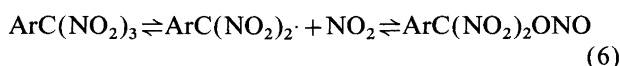
The latter signal was detected in solutions of NO$_2$ (at low concentration, 2 mmol dm^{-3}) and PBN (150 mmol dm^{-3}) in both dichloromethane and acetonitrile, together with the stronger PBNOx signal.

Upon irradiation of a solution of 2 (15 mmol dm^{-3}) and PBN (50 mmol dm^{-3}) with filtered light of $\lambda >$ 430 nm, the 3×2 lines signal became much stronger and rapidly attained a maximum concentration which then decreased during the irradiation period ($a^N = 1.29$ mT, $a^H = 0.139$ mT, average of three runs). The triplet from PBNOx also developed from the onset of irradiation. When the light was shut off the spin adduct signal continued to decay, whereas the signal of PBNOx increased strongly, reaching a maximum concentration as shown in Fig. 10 (empty symbols).

In acetonitrile, under dark conditions, a similar experiment showed the rapid appearance and slow decay of the 3×2 spin adduct ($a^N = 1.29$ mT, $a^H = 0.147$ mT), together with the appearance of the PBNOx signal. Upon irradiation, the intensity of the two signals increased.

The spin trap experiment in dichloromethane above was repeated with 1-methoxynaphthalene (50 mmol dm^{-3}) added. Again, the signal of the same spin adduct appeared upon irradiation but in ca. five times higher time-integrated intensity; the PBNOx signal behaved as in the experiment without substrate added (Fig. 10, filled symbols). A control experiment showed that the photolysis of PBN and 4-methoxynaphthoic acid (3) under identical conditions did not produce any EPR signal.

The spin trapping experiment was then performed at lower temperatures in order to examine whether any other radical species could be trapped under these conditions. The experiment was run in three phases with respect to temperature and irradiation (Fig. 11). During
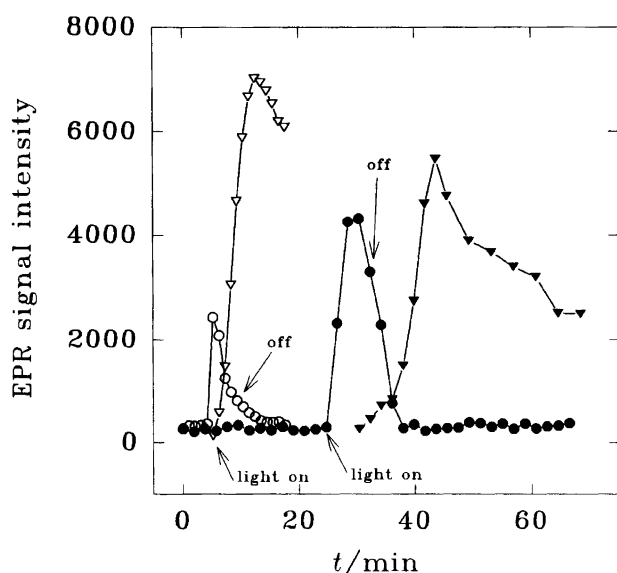

Fig. 10. EPR spectral monitoring of a solution of 2 (15 mmol dm^{-3}) and PBN (50 mmol dm^{-3}) in dichloromethane (3×2 signal, empty circles; PBNOx, empty triangles) and of a solution of 2 (15 mmol dm^{-3}), PBN (50 mmol dm^{-3}) and 1-methoxynaphthalene (50 mmol dm^{-3}) in dichloromethane (3×2 signal, filled circles; PBNOx, filled triangles). The arrows mark the beginning and end of the 5 min irradiation periods with light of $\lambda > 430$ nm. Temperature 22 °C.

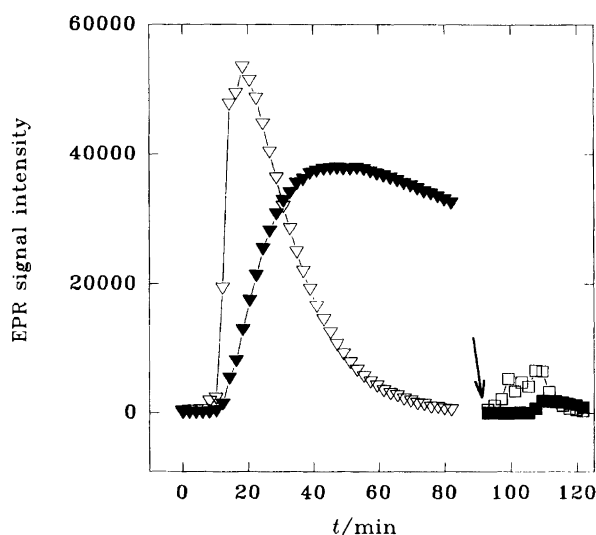*Fig. 11.* Formation of spin adduct from a solution of 6 (15 mmol dm^{-3}) and PBN (50 mmol dm^{-3}) in dichloromethane under various conditions of irradiation and temperature. Phase 1: 0–12 min, irradiation at −40 °C; phase 2: 13–18 min, no light, increase in temperature from −40 to −10 °C; phase 3: 19–82 min, no light, −10 °C. At 95 min, a fresh portion of the solution was irradiated for 12 min at −10 °C.

phase 1, irradiation for 12 min at −40 °C with light of $\lambda > 430$ nm gave no EPR signal. The light was then shut off and the solution allowed to warm up to −10 °C over a period of 5 min (phase 2) with continuous monitoring of the EPR activity. The 3×2 lines signal from the spin adduct appeared strongly during the dark period, beginning to appear in phase 2, and then went through a maximum and finally decayed (phase 3). The PBNOx signal also appeared and went through a similar development. When all EPR activity had subsided, irradiation for 12 min of a fresh portion of the same solution at −10 °C again produced the same signals, but with a ca. 10 times lower intensity (the two curves to the right in Fig. 11).

Nitrodecarboxylation of 3. In the course of the experiments described for 2 above and earlier,[11,12] it became clear that there must be a reaction sequence for conversion of the carboxylic acid 3 into the corresponding nitro derivative 5. Nitrodecarboxylation reactions are known from the nitration literature,[15] but usually take place under much harsher conditions allowing for the presence of NO_2^+. In the present case, it is necessary that NO_2, the available nitrating agent,[16] is capable of inducing this type of reaction, thermally and/or photochemically, with a rate behaviour compatible with photolysis periods of 1–3 h. This assumption turned out to be correct. When a solution of 3 (10 mmol dm^{-3}) and NO_2 (0.15 mol dm^{-3}) in dichloromethane was analyzed after standing for 3 h at 22 °C, an 80% yield of the nitro product 5 had been formed. Light did not appear to have any significant accelerating influence on the reaction.

Reactivity of 2-trinitromethyl-4-chloroanisole (6) in dichloromethane and acetonitrile. 2-Trinitromethyl-4-chloroanisole (**6**) underwent very slow transformation ($k \approx 3 \times 10^{-6}\,\mathrm{min^{-1}}$, ca. 100 times slower than the decomposition of **2**) into the corresponding carboxylic acid, 5-chloro-2-methoxybenzoic acid in [²H₂]dichloromethane at 22 °C. After 400 h the proportion of acid was ca. 8%. In [²H₃]acetonitrile, slow decay occurred ($k \approx 3 \times 10^{-5}\,\mathrm{min^{-1}}$; Fig. 12), about 10 times faster than the reaction in [²H₂]dichloromethane. The exclusive product was once more 5-chloro-2-methoxybenzoic acid. Irradiation by light of λ > 430 nm speeded up the reaction (Fig. 12).

In the presence of 4-chloroanisole (40 mmol dm⁻³) the rate constant of spontaneous decay of **6** (20 mmol dm⁻³) in [²H₃]acetonitrile was $8 \times 10^{-6}\,\mathrm{min^{-1}}$, slower than in the absence of 4-chloroanisole. The only product being detected was 5-chloro-2-methoxybenzoic acid. Photolysis experiments with mixtures of **6** and 4-chloroanisole, carried out in dichloromethane or acetonitrile under similar conditions as those referred to in Fig. 9, showed that the initial rates were very low and that the initial rate was 1.6 times larger in acetonitrile than in dichloromethane.

A spin-trapping experiment with PBN and **6** in dichloromethane at 22 °C showed that light of λ > 430 nm induced the formation of a weak signal of a spin adduct of similar nature as that recorded from **2** (3 × 2 line signal, $a^N = 1.30$ mT, $a^H = 0.163$ mT); UV light increased the intensity and also promoted the formation of PBNOx. In acetonitrile the 3 × 2 signal was very weak and only fleetingly seen. An experiment under similar conditions as those given in Fig. 11, showed similar features: no
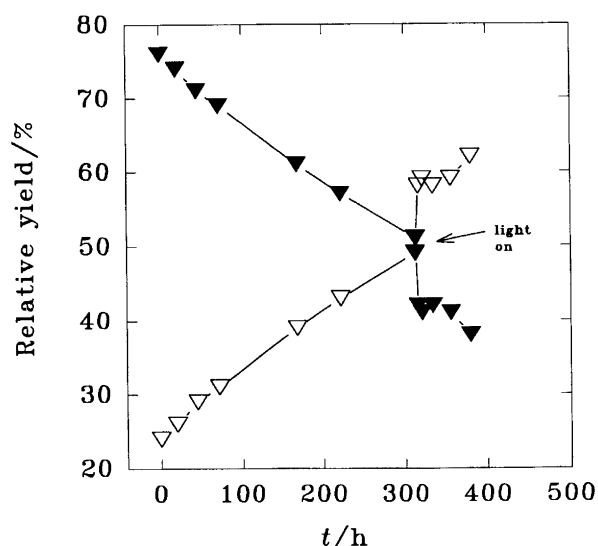
signal during irradiation at −40 °C and development of EPR activity as the solution was warmed up without irradition. The difference was only the appearance of the PBNOx signal at a temperature of 5–10 °C.

Nitrodecarboxylation of 5-chloro-2-methoxybenzoic acid. Irradiation with light of λ > 430 nm of a solution of 5-chloro-2-methoxybenzoic acid in dichloromethane with a five-fold excess of NO₂ gave after 4 h an 1.8% yield of the corresponding nitro compound and small amounts (4%) of other products.

Discussion

Mechanistic model. At the outset, this study was conceived to shed light on the nature of the solvent effect described above, i.e. that trinitromethylation was the major pathway in dichloromethane while nitration reactions were the predominant ones in acetonitrile for substrates of the anisole type.[2] The finding that the product distribution from ArH–tetranitromethane photolyses often changed significantly during the runs indicated that secondary processes due to possible interconversion of products might be of importance. An almost trivial case is by now the conversion of adducts into substitution products by elimination of HNO₂ or HC(NO₂)₃.[3] A less obvious case is the transformation of trinitromethylarenes into carboxylic acids and nitro products as dealt with in this study.

The case of 1-methoxynaphthalene (**1**) shows how important the secondary processes can be. Figure 13 shows the time development of products from the photolysis of a mixture of **1** and tetranitromethane in dichloromethane and acetonitrile. Both the adducts and **2** attain a maximum concentration during the run followed by a decline due to secondary processes, the latter being faster in acetonitrile. In both solvents the 4-nitro product **5** comes out as the major product at the end of the run. It should be noted that the 'solvent effect' claimed by Kochi *et al.*[2] does not operate for this substrate, the level of **2** being approximately the same in both solvents during the whole run.

Apparently, a reaction pathway for the conversion of a trinitromethylarene into the corresponding nitroarene [eqn. (7)] has to be available. It was earlier shown[2c,11] that the carboxylic acid corresponding to the trinitromethylarene sometimes appeared among the products; in the case of **1** it was also found that the corresponding esters could be obtained in yields up to about 50% with an alkohol ROH being present.[11] Since no water was present to effect the formal hydrolysis of the trinitromethylarene a mechanism involving a nitro–nitrito rearrangement of ArC(NO₂)₃, followed by loss of nitrogen dioxide from the isomeric species and by an eventual reaction of the hypothetical ArCONO₂ with HNO₂ to give ArCOOH or ROH to give ArCOOR [eqn. (8)], was

Fig. 12. NMR spectral monitoring of a solution of **6** (20 mmol dm⁻³) in [²H₃]acetonitrile, showing the decay of **6** [empty triangles, $k = 3(1) \times 10^{-5}\,\mathrm{min^{-1}}$] and formation of 5-chloro-2-methoxybenzoic acid (filled triangles) as the only product. The solution was illuminated for 15 min (arrow) with light of λ > 430 nm. Temperature 22 °C.
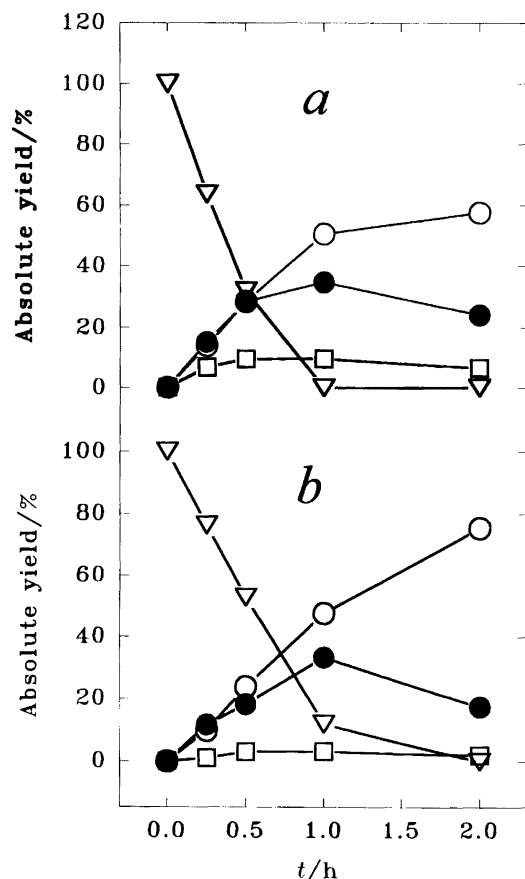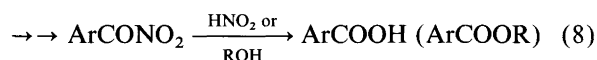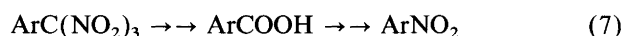
Fig. 13. Disappearance of **1** (triangles) and appearance of adducts (squares), **2** (filled circles) and **5** (empty circles) from the photolysis of **1** (0.4 mol dm^{-3}) and tetranitromethane (0.8 mol dm^{-3}) with light of $\lambda > 430$ nm at 20 °C in (a) dichloromethane and (b) acetonitrile. Data were taken from Ref. 12.

tentatively suggested.[11]

$$ArC(NO_2)_3 \rightarrow\rightarrow ArCOOH \rightarrow\rightarrow ArNO_2 \qquad (7)$$

$$ArC(NO_2)_3 \rightarrow ArC(NO_2)_2ONO$$

$$\rightarrow\rightarrow ArCONO_2 \xrightarrow{\text{HNO}_2 \text{ or}}_{\text{ROH}} ArCOOH \text{ (ArCOOR)} \qquad (8)$$

While the details of the reaction sequence sketched in eqns. (7) and (8) are still open to discussion, the kinetic results obtained for the decomposition of **2** under the conditions described are in agreement with its main features, as discussed below.

Connections between the various reactions of 2 or 6. The rate constants of the processes described above for **2** and **6** have been listed in Table 2. Bearing in mind the approximate nature of these values one can nevertheless establish a few starting points for the discussion. The half-life ($\tau_{1/2}$) of the spontaneous decomposition of **2** in dichloromethane is 38 h and the buildup of **3** and **5**

occurs on a similar timescale. The rate of decomposition is increased 13-fold by addition of HNO$_2$ or 11-fold by addition of a twofold excess of **1**. Thus, each of the additives brings $\tau_{1/2}$ of **2** into the vicinity of 3 h, 1 h longer than the total reaction period for preparative photolysis. Addition of **1** and HNO$_2$ together further decreased the thermal stability of **2**, $\tau_{1/2}$ now being 1.4 h.

Photolysis of **2** in the presence of **1** further decreased $\tau_{1/2}$ by a factor of 6, suggesting that $\tau_{1/2}$ of **2** is less than 1 h. This is clearly of a magnitude to strongly influence the development of the product distribution during a preparative run. It should be emphasized that this conclusion is based on experiments in which the compounds involved were directly monitored by ^{1}H NMR spectroscopy.

In acetonitrile, the ^{1}H NMR spectroscopically monitored runs indicated a $\tau_{1/2}$ for **2** in the thermal decomposition of ca. 10 h, almost four times shorter than in dichloromethane. The presence of **1** further decreased $\tau_{1/2}$ to 6.5 h, and the UV spectrally monitored photolysis of similar solutions (Fig. 8) showed that the photochemical reaction was about twice as fast in acetonitrile as in dichloromethane. Thus, in acetonitrile the photochemical decomposition of **2** in the presence of **1** may lead to a $\tau_{1/2}$ for **2** of less than 0.5 h.

The last process to be distinguished in Table 2 was deduced from UV, FTIR and EPR measurements in acetonitrile and is characterized by a $\tau_{1/2}$ of ca. 0.9 h, as compared with 10 h for the development of products. The reaction thus takes place during the initial phase of the decomposition of **2** and is connected with the disappearance of three characteristic IR bands of **2**; new bands appeared within the same time interval and disappeared later. Unfortunately, their kinetics could not be evaluated. In dichloromethane, the UV and EPR spectroscopic runs similarly defined an initial fast process with a $\tau_{1/2}$ of ca. 0.3 h. We associate the fast process in both solvents with an initial rearrangement of **2** to a second, fairly stable compound which then decomposes further and eventually gives the acid **3** according to the stoichiometry of eqn. (9). Since this intermediate must closely resemble **2** (the ^{1}H NMR spectrum did not change notably) we postulate that only a minimal change in connectivity occurs in the first step, namely that of a nitro–nitrito rearrangement taking place with formation of a nitritodinitromethylaromatic compound [eqn. (6)]. Unfortunately, no evidence for the presence of nitrito intermediates could be obtained from the ^{14}N NMR spectroscopic experiment, probably because the level of detection was unfavorable. We must therefore assume that the slow step of the $ArC(NO_2)_3 \rightarrow ArCOOH$ reaction will occur at some later stage in the reaction, as indicated by the appearance of intermediate X (^{14}N NMR) in an intermediate range of rates.

$$ArC(NO_2)_3 + HNO_2 \rightarrow ArCOOH + 2\ NO + 2\ NO_2$$
$$(9)$$

Table 2. Summary of rate processes observed in the thermal decomposition of **2** or **6** under various conditions. Temperature, 22(1) °C, unless otherwise stated.

| | Rate constant/min^{-1} | | | |
Conditions	Disappearance of **2** or **6**	Appearance of **3**	Appearance of **5**	Method
Decomposition of 2				
CH_3CN	1.3×10^{-2}	—	—	UV[c]
CH_3CN (1589 or 1618 cm^{-1})	1.1×10^{-2}	—	—	FTIR
CH_3CN (798 cm^{-1})	1.5×10^{-2}	—	—	FTIR
CD_3CN	1.1×10^{-3}	1.4×10^{-3}		^{1}H NMR
CD_3CN^a	2.0×10^{-3}			^{14}N NMR
CD_3CN, [1] = 18.6 mmol dm^{-3}	1.8×10^{-3}	2.4×10^{-3}	6.1×10^{-4}	^{1}H NMR[d]
CD_2Cl_2	3×10^{-4}	1.0×10^{-3}	1.4×10^{-4}	^{1}H NMR[e]
CD_2Cl_2, [HNO$_2$] ≈ 80 mmol dm^{-3}	5×10^{-3}	—	—	^{1}H NMR[f]
CD_2Cl_2, [1] = 40 mmol dm^{-3}	4×10^{-3}	5×10^{-3}	4×10^{-3}	^{1}H NMR[g]
CD_2Cl_2, [HNO$_2$] ≈ 80 mmol dm^{-3}, [1] = 40 mmol dm^{-3}	8.2×10^{-3}			^{1}H NMR
CH_2Cl_2	3.4×10^{-2}			UV
CH_2Cl_2	4×10^{-2b}			EPR
Decomposition of 6				
CD_2Cl_2	3×10^{-6}			NMR
CD_3CN	3×10^{-5}			NMR[h]
CD_3CN, [4-Cl-anisole] = 40 mmol dm^{-3}	8×10^{-6}			NMR

[a] At 27 °C. [b] Appearance of PBNOx and NO_2–PBN˙. [c] Fig. 6. [d] Fig. 8. [e] Fig. 1. [f] Fig. 2. [g] Fig. 7. [h] Fig. 12.

Nature of the followup steps. Eqn. (6) represents a homolytic nitrito–nitro rearrangement, of which several varieties are known.[8a,17] It is formulated as an equilibrium process, meaning that low concentrations of NO_2 and $ArC(NO_2)_2$˙ will coexist with the nitritodinitromethylarene. Further steps will then depend on the reactivity of these three components. In the absence of any additive NO_2 may only have access to slow reaction channels. However, if the parent compound ArH is added, there is a possibility that NO_2 will react with ArH to give nitration product(s) and thus force the equilibrium of eqn. (6) toward further development of stable products. As seen from Figs. 7 and 8, 1-methoxynaphthalene (1) is sufficiently reactive to be nitrated by NO_2, causing the thermal reaction to proceed with a more than tenfold rate, whereas 4-chloroanisole had no such effect upon the decomposition of **6**. Actually, the reaction became slightly slower in the presence of 4-chloroanisole and no nitro product was formed.

The further reactions of $ArC(NO_2)_2$˙ and $ArC(NO_2)_2ONO$ are less certain, but some restrictions are dictated by (i) the spin trapping results and (ii) the fact that ArCOOH is a product of the reaction. The spin adducts characterized in the thermal or photochemical reaction of $ArC(NO_2)_3$ in the presence of PBN are most probably acyloxyl adducts, as judged by the hfs coupling constants listed in Table 3 (data obtained from a third available trinitromethyl compound, 2-trinitromethyl-4-methyl-anisole, are also included). It is well known[18] that the hfs coupling constants of spin

Table 3. Spin adducts of acyloxyl radicals, RCOO–PBN˙, and the hfs constants of their EPR spectra in dichloromethane, unless otherwise stated.

R in RCOO–PBN˙	a^N/mT	a^H/mT	Ref.
4-Methoxynaphthyl	1.29	0.139	This work
4-Methoxynaphthyl (in CH_3CN)	1.29	0.147	This work
3-Chloro-6-methoxyphenyl	1.30	0.163	This work
3-Methyl-6-methoxyphenyl	1.31	0.151	This work
Phenyl	1.35	0.161	19a
Phenyl (in benzene)	1.32	0.141	25
Methyl	1.37	0.166	19a
tert-Butyl	1.36	0.15	19a

adducts of PBN may in many cases have low diagnostic power because of the similarity between different classes of trapped R˙. However, this is not valid for the particular case of acyloxyl adducts since their hfs coupling constants are both relatively small and outside the usual range of values. Thus, the spin adducts, found during decomposition of trinitromethylarenes can with confidence be identified as belonging to acyloxyl radicals. Moreover, RCOO-PBN˙ are relatively unstable species,[19] and this was also true for the spin adducts found here.

The second radical observed (Figs. 10 and 11) was PBNOx, the known[19,20] product from both the decomposition of RCOO–PBN˙ and from the the interaction of PBN with NO_2.
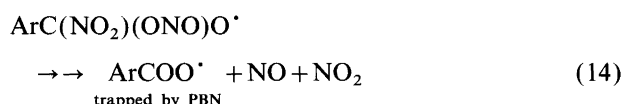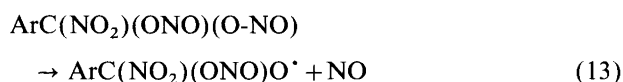
The nature of the third spin adduct observed, with the

3×4 lines EPR spectrum, is not altogether clear, but the fact that the same signal was detected from solutions of NO_2 in low concentration and PBN in dichloromethane or acetonitrile suggests that it should be assigned to the so far unknown N-connected adduct between NO_2 and PBN. The O-connected adduct is still the major product but is oxidized much faster by NO_2 to PBNOx [eqns. (10) and (11)].

$$PBN + NO_2 \longrightarrow O_2N-PBN^{\cdot} \xrightarrow[\text{slow}]{NO_2} PBNOx \qquad (10)$$

$$PBN + NO_2 \longrightarrow ONO-PBN^{\cdot} \xrightarrow[\text{fast}]{NO_2} PBNOx \qquad (11)$$

The experiment of Fig. 11 was performed in order to see if any other radical species could be trapped by photolysis of **2** and PBN at lower temperatures, for example of the $ArC(NO_2)_2^{\cdot}$ type [eqn. (6)]. However, no EPR activity was recorded at $-40\,°C$ showing that even during photolysis no significant production of stable or trappable radicals took place. Discontinuation of irradiation, followed by heating of the sample tube to $-10\,°C$, led to efficient production of the acyloxyl spin adduct and PBNOx, showing that some intermediate, formed in the photochemical process and being stable at $-40\,°C$, is thermally decomposed at higher temperatures and then gives the acyloxyl adduct. When the irradiation experiment was carried out at $-10\,°C$, spin adduct formation started immediately, but the resulting radical concentrations were much smaller (Fig. 11).

This behaviour is an indication that the reaction of eqn. (6) is speeded up by light and that $ArC(NO_2)_2ONO$ is photolytically transformed at $-40\,°C$ to a relatively stable, diamagnetic species which undergoes fast thermal reactions upon heating. A second nitronitrito rearrangement (possibly followed by a third one) is a logical candidate for this step [eqn. (12)]; it gives a diamagnetic species $ArC(NO_2)(ONO)_2$ which may decompose according to eqns. (13)–(15) with production of both $ArCOO^{\cdot}$ and some other species, in eqn. (15) suggested to be $ArCONO_2$ (or $ArCOONO$), which can react as an electrophile with HNO_2 or an added alcohol to give the acid or an ester.

$$ArC(NO_2)_2ONO \rightarrow ArC(NO_2)(ONO)_2 \qquad (12)$$

$$ArC(NO_2)(ONO)(O-NO)$$

$$\rightarrow ArC(NO_2)(ONO)O^{\cdot} + NO \qquad (13)$$

$$ArC(NO_2)(ONO)O^{\cdot}$$

$$\rightarrow\rightarrow \underset{\text{trapped by PBN}}{ArCOO^{\cdot}} + NO + NO_2 \qquad (14)$$

$$ArC(NO_2)(ONO)O^{\cdot}$$

$$\rightarrow \underset{\text{reacts with } HNO_2 \text{ or } ROH}{ArCONO_2 \ (ArCOONO)} + NO_2 \qquad (15)$$

Once the acid has been formed, it is either stable under the prevailing conditions or undergoes nitrodecarboxylation to the corresponding nitro compound.

Compound **3** seems to follow the latter reaction sequence, being converted into the nitro compound **5** within 3 h upon standing with NO_2 in dichloromethane, while 5-chloro-2-methoxybenzoic acid was practically unchanged under such conditions.

The suggested mechanism by which a trinitromethylarene is converted into the corresponding acid, or an ester with an alcohol present, neatly explains previous findings in the photolysis of tetranitromethane-**1** solutions in dichloromethane.[11] In this study it was noticed that the acid was formed in yields from 0.5 to 10%, together with high yields of nitro compound **5**, while esters were formed in much higher yields, 30–50%, together with correspondingly lower yields of **5**. The present results indicate that this difference must be due to the instability of the acid toward nitrodecarboxylation, leaving behind only a small part of the acid formed. In the particular case of **3**, this compound is not very soluble in dichloromethane, and may partly escape nitrodecarboxylation owing to precipitation.

Another remarkable feature of the tetranitromethane-**1** system was that photolysis for a short time (0.2–1 h) could initiate nitration during a subsequent dark period of 20–240 h.[11] During this period the yield of nitration product increased from 5% at the end of the irradiation period to 59% at the end of the dark period. The same phenomenon was observed for other reactive substrates, such as 1,2- and 1,4-dimethoxybenzene, whereas it was not seen for the much less reactive substrate, naphthalene. It is now clear that the initial irradiation period must lead to a mixture of NO_2 and nitro-trinitromethyl adducts of ArH which finally produce $ArC(NO_2)_3$; in the dark period slow decomposition of $ArC(NO_2)_3$ gives more NO_2 which cause nitration of the reactive substrates (**1**, 1,2- and 1,4-dimethoxybenzene).

Conclusions. The results described have shown that trinitromethylarenes are basically unstable compounds under the conditions required for their preparation, i.e. photolysis of ArH–tetranitromethane in a suitable solvent. They are photoactive through an at least partly radical mediated reaction which eventually transforms the trinitromethyl function into a carboxyl group. The same reaction may also take place thermally, but is much slower in the absence of additives; additives, such as the corresponding ArH or HNO_2, increase the reaction rate significantly for reactive systems.

The reactivity of any given trinitromethylarene in both the photochemical and thermal reaction is governed by the substituent(s) present at the ring positions. Electron-donating substituents increase the reactivity, whereas electron-withdrawing ones have the opposite effect, as exemplified by the two chosen substrates, **2** and **6**. It also appears that the decomposition reaction of $ArC(NO_2)_3$ is faster in the more polar solvent acetonitrile than in the weakly polar dichloromethane. This suggests that the 'solvent effect' as referred to in the introduction is partly due to a more efficient production of NO_2 in acetonitrile.

Thus, nitration by NO_2 will be favoured as compared to the other important nitration mechanism, elimination of nitroform from nitro-trinitromethyl adducts.

Concluding, we can categorize the outcome of tetranitromethane/ArH photolyses in both dichloromethane and acetonitrile in three groups: (1) formation of predominantly *adducts* from unreactive substrates (example: naphthalene[3]), (2) formation of predominantly *nitro compounds* from very reactive substrates [examples: 1,2-and 1,4-dimethoxybenzene,[2b,c] tris(4-bromophenyl)amine[21] and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene[22]] and (3) formation of *adducts, trinitromethylarene(s) and nitro compound(s)* from substrates of intermediate reactivity (example: 4-methylanisole[23] and 1-methoxynaphthalene[12]). Within the third group, variations are possible due to second-order effects caused by the variable reactivity of trinitromethylarenes with respect to decomposition. There is no need to invoke any influence of an ion-paring effect which, moreover, was only applicable to a limited range of substrates, as exemplified by anisole and some of its derivatives.[2a,c]

Experimental

Instruments and methods. NMR spectra were recorded at 27 °C by a Varian XL 200 spectrometer (^{1}H NMR spectra) or a Bruker ARX 500 spectrometer [^{14}N NMR spectra, recorded with an aquisition time of 100 ms, a relaxation delay of 0 s, a pulse width of ca. 30° (3 s) and with proton broadband decoupling]. FTIR spectra were recorded by the Nicolet 20 SXC instrument in a 0.05 mm NaCl cuvette. EPR spectra were recorded by the Upgrade Version ESP 3220–200SH of a Bruker ER-200D spectrometer. Photolyses in the photolysis cavity (ER 4104 OR) were performed using the 50 W high-pressure Hg lamp from Bruker (ER 202) and a filter with cut-off at 430 nm from Schott, Germany. The fiber optical lamp used for the experiments reported in Fig. 9 and Table 1 was from Euromex (fiber optic light source EK1).

Materials. 4-Trinitromethyl-1-methoxynaphthalene (**2**) and 2-trinitromethyl-4-chloroanisole (**6**) were prepared as described previously.[11–13] 2-Trinitromethyl-4-methylanisole was prepared as described in Ref. 23. 2- and 4-Nitro-1-methoxynaphthalene (**4** and **5**) and 4-methoxy-1-naphthoic acid (**3**) were available from an earlier study.[13] 5-Chloro-2-methoxybenzoic acid (Aldrich), 1-methoxynaphthalene (Fluka AG), 4-chloroanisole (EGA-Chemie) and *N*-benzylidene-*tert*-butylamine *N*-oxide (Aldrich) were purchased. Dichloromethane, acetonitrile and trifluoroacetic acid were of UVASOL® quality. Deuteriated solvents were obtained from Glaser AG. Tetrabutylammonium nitrite was purchased from Fluka AG and solutions of NO_2/N_2O_4 were made up as described previously.[24]

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