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Light-Initiated and Thermal Nitration Reactions during Photolysis of Naphthalene/Tetranitromethane or 1-Methoxynaphthalene/Tetranitromethane in Dichloromethane[1]

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Abstract: The photolysis of naphthalene or 1-methoxynaphthalene together with tetranitromethane in dichloromethane, using light with a cutoff at $\lambda < 435$ nm, has been investigated. It is shown that naphthalene, a representative of less reactive aromatics, predominantly (85–90%) reacts to give nitro compounds with a low α/β ratio (ca. 1.5) via a photochemical addition/elimination mechanism, the remaining part being formed via thermal, NO_2-promoted nitration (α/β ratio ca. 20). The adducts are formed by photochemical excitation of the CT complex between naphthalene and tetranitromethane, resulting in formation of the triad $[ArH^{\bullet+}\, NO_2\, (NO_2)_3C^-]$ from which the observed chemistry develops by attack of trinitromethanide upon the radical cation. For 1-methoxynaphthalene, a representative of more highly reactive aromatics, the reaction is again photochemically initiated and again adducts seem to be responsible for the further development of thermal nitration reactions, apart from the NO_2-induced reaction. Elimination of HNO_2 from one of the 1,4-adducts induces a novel HNO_2/tetranitromethane-dependent nitration process, shown separately to operate in the dark on reactive substrates. The aryltrinitromethane formed in this step is "hydrolyzed" to the corresponding carboxylic acid, 4-methoxy-1-naphthoic acid, under the anhydrous conditions prevailing during photolysis. Nitrous acid is a likely candidate as the proton source for this reaction. With an alcohol present, moderate yields (up to ≈50%) of alkyl 4-methoxy-1-naphthoates are obtained. From other adducts, nitro compounds are formed by elimination of nitroform. Trinitromethanide ion was shown to possess greatly differing reactivity (ratio $>10^3$) toward a model radical cation, tris(4-bromophenyl)aminium ion, in dichloromethane and acetonitrile, respectively.

Introduction

Aromatic nitration continues to be fertile ground for synthetic and mechanistic exploration.[2] In recent years, a thought-provoking suggestion by Perrin[3] about the possible intervention of an initial electron transfer step (eq 1), followed by coupling between the radical cation and NO_2 (eq 2), in the reaction between

$$ArH + NO_2^+ \rightleftharpoons \underset{\substack{\text{electronic}\\ \text{interaction in}\\ \text{TS} < 1\ \text{kcal mol}^{-1}}}{[ArH^{\bullet+}\ NO_2]^{\ddagger}} \rightleftharpoons ArH^{\bullet+} + NO_2 \quad (1)$$

$$ArH^{\bullet+} + NO_2 \rightarrow {}^{+}Ar(H)NO_2 \xrightarrow{-H^+} ArNO_2 \quad (2)$$

an aromatic compound (ArH) and a nitronium ion, has caused much experimentation and discussion. As stated elsewhere,[4,5] we consider the classical Ingold mechanism appropriate for most "normal" substrates and deem an outer-sphere ET step of the type shown in eq 1 unlikely in such cases, mainly because of the very high reorganization energy of the NO_2^+/NO_2 couple, ca. 140 kcal mol^{-1},[6] but we cannot exclude an inner-sphere variety (for example formulated as in eq 3) where a sizable electronic interaction in

$$ArH + NO_2^+ \rightleftharpoons \underset{\substack{\text{electronic}\\ \text{interaction in}\\ \text{TS} > 5\ \text{kcal mol}^{-1}}}{[ArH^{\bullet+}\cdots NO_2]^{\ddagger}} \rightleftharpoons ArH^{\bullet+} + NO_2 \quad (3)$$

$$ArH + NO_2^+ \rightleftharpoons [ArH^{\bullet+}\cdots NO_2]^{\ddagger} \rightleftharpoons [{}^{+}Ar(H)NO_2] \rightleftharpoons ArH^{\bullet+} + NO_2 \quad (4)$$

the TS compensates for the angle deformation in going from the linear nitronium ion to the bent structure. In this mechanism, the Wheland intermediate in itself *might* lie along the pathway of ET (eq 4), since this species should be able to undergo homolytic cleavage along the C–N bond under favorable thermodynamic conditions (easily oxidizable ArH, like perylene[11]). We consider the inner-sphere pathway the likely route to the radical cation phenomena observed in many aromatic nitrations,[12] in view of its thermodynamic preference for radical cation formation.

Recent work has provided new calibration marks for the borderline between the classical Ingold mechanism and the ET process. Thus it appears from consideration of CIDNP effects[13] that nitration of naphthalene [$E°(ArH^{\bullet+}/ArH) = 2.08$ V vs NHE[14]] by NO_2^+ to some extent (ca. 2%) proceeds via ET (most likely via eq 3), thus indicating that the borderline between the two mechanisms lies in a range around 2 V. For the *outer-sphere* mechanism, we had earlier[5] estimated a much lower limit, ca. 0.2 V, on the basis of an old value of $E°(NO_2^+/NO_2) = 1.56$ V in

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[5] Eberson, L.; Radner, F. *Acta Chem. Scand., Ser. B* **1984**, *38*, 861.

[6] The high value of $\lambda(0)$ of the NO_2^+/NO_2 couple[5] is composed of an inner-sphere reorganization energy of 105 kcal mol^{-1} and a solvent component of 35 kcal mol^{-1}, both calculated by Marcus' classical equations.[7-10] An ab initio calculation of the former quantity, using the CPF method, gave $\lambda_i(0)$ = 99 kcal mol^{-1}, close to the above value (Merchan, M.; Roos, B.; Eberson, L. To be published). Thus the classically estimated value for the outer-sphere case is a realistic one, and any *experimentally* determined $\lambda(NO_2^+/NO_2)$ might be lower due to significant electronic interaction in the transition states of the reactions studied (cf. the analogous problem of determining the reorganization energy of the $O_2/O_2^{\bullet-}$ couple; see for example: McDowell, M. C.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 2232).

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[14] Unless otherwise indicated, potentials are given with the normal hydrogen electrode (NHE) as reference electrode.

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acetonitrile.[15] This value now has been more accurately measured by Boughriet et al. and placed at 1.95 V in sulfolane[16] and 2.2 V in nitromethane,[17] increasing the *outer-sphere* limit to 0.6–0.8 V.

We have earlier[18,19] supported our reasoning by carrying out reactions between presynthesized radical cation salts and solutions of NO_2/N_2O_4[20] (eq 2) and determining isomer distributions of the nitro compounds formed. For radical cations of naphthalene and several methylnaphthalenes this reaction was more selective than nitration of ArH by NO_2/N_2O_4,[18,19] or NO_2^+, as exemplified by α/β nitro product ratios from naphthalene of >50, 25, and 11, respectively.[4,21] An argument against the validity of this comparison is the fact that radical cations exist in equilibrium with their CT complexes with their parent compounds (eq 5, equilibration constant of the order of 10^2 for anthracene[22]), thus questioning the identity of the step(s) that is (are) actually responsible for nitro product formation.[12] At least for naphthalene itself, this criticism was shown early on to be unfounded,[18] since preparations of both $(ArH)_2^{\bullet+}PF_6^-$ and $(ArH)^{\bullet+}PF_6^-$ give identical, high α/β ratios of the magnitude that we consider characteristic of the coupling between $ArH^{\bullet+}$ and NO_2, but it still might apply to the methylnaphthalene cases.[19] One might also argue that N_2O_4 is the predominant species of the NO_2/N_2O_4 equilibrium and might supply an NO_2 radical to $ArH^{\bullet+}$. This would however require cleavage of the N–N bond in the TS, amounting to ca. 14 kcal/mol.

$$ArH^{\bullet+} + ArH \rightleftharpoons (ArH)_2^{\bullet+} \qquad (5)$$

Another approach for generating the components of eq 1 is the photoexcitation of a charge transfer (CT) complex of tetranitromethane (TNM) and ArH (eq 6), as first outlined by Kholmogorov and Gorydskii[23] and recently elaborated by Kochi et al.[24-30] The radical anion of TNM decomposes within a few picoseconds to NO_2 and $^-C(NO_2)_3$, thus providing a means of instantaneous generation of the triad $[ArH^{\bullet+}NO_2{}^-C(NO_2)_3]$. The products of the reaction were nitro- and trinitromethyl-substituted ArH, assumed to be formed via the competing steps of eq 2 and eqs 7 + 8, respectively. Nitration was favored in acetonitrile and trinitromethylation in dichloromethane, interpreted as involving the participation of ion pairs in the latter solvent. Both first-order (within the triad) and second-order processes (from species that had leaked from the triad) were responsible for product formation, depending on the reactivity of the radical cation. Similar findings were reported by Maslak and Chapman,[31] who found predominantly products of trinitromethylation during photolysis of a series of 4-methoxy-4′-X-bicumenes with TNM in dichloromethane.

$$ArH, C(NO_2)_4 \xrightarrow{h\nu_{CT}} \underset{\text{triad}}{[ArH^{\bullet+}\ NO_2\ {}^-C(NO_2)_3]} \qquad (6)$$

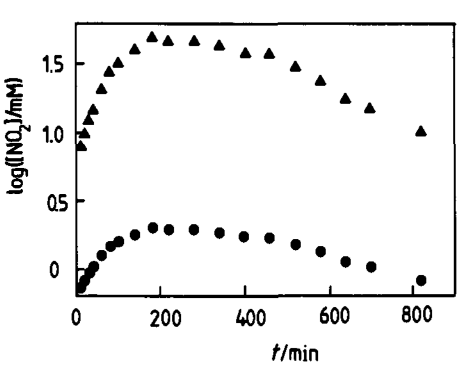

Figure 1. Time development of log ($[NO_2]$/mM) (●, actual concentration; ▲, computed[20] total $[NO_2]$) in a solution of naphthalene (0.43 M) and tetranitromethane (0.85 M) in dichloromethane at 25 °C upon irradiation with filtered light (cutoff <435 nm).

$$ArH^{\bullet+} + {}^-C(NO_2)_3 \rightarrow {}^{\bullet}Ar(H)C(NO_2)_3 \qquad (7)$$

$${}^{\bullet}Ar(H)C(NO_2)_3 + NO_2 \rightarrow ArC(NO_2)_3 + HNO_2 \qquad (8)$$

Isaacs and Abed[32] proposed a different mechanism for the photochemical nitration by TNM, namely photoinduced homolytic splitting of TNM followed by recombination to trinitromethyl nitrite (eq 9). This species would act as a nitronium ion transferring reagent. It could not be isolated but its presence was inferred from IR spectroscopy and its reactivity toward azulene in the dark. The isomerization of TNM took place rapidly in the UV region (366 nm) and occurred slowly in visible light (<500 nm) as well.

$$C(NO_2)_4 \xrightarrow{h\nu} {}^{\bullet}C(NO_2)_3\ NO_2 \rightarrow ONO{-}C(NO_2)_3 \qquad (9)$$

We decided to use this potentially unambiguous way of generating an $ArH^{\bullet+}/NO_2$ pair (eq 6) in the naphthalene systems to obtain isomer distributions for comparison with our earlier data. In the course of this study, we noticed additional phenomena originating from the participation of species, in particular NO_2 and HNO_2, that have either leaked from the triad or been formed in its further reactions. By themselves (NO_2) or in combination with TNM (HNO_2), these species induce *light-independent* nitration chemistry. We also have established that the ArH/TNM/$h\nu$ system[33] is exceedingly complex, with a number of possible systematic errors to control and/or compensate for. In what follows, we describe the reasoning and experiments that have led to this conclusion. We have emphasized two substrates, naphthalene and 1-methoxynaphthalene (1-MON), which represent compounds of low and high reactivity toward NO_2, respectively. Other substrates were occasionally used because of one desirable property or another.

Results and Discussion

Nitration Procedure. Photochemical nitrations were performed at 25 ± 1 °C on TNM/ArH solutions in dichloromethane, irradiated by light with a cutoff at λ < 435 nm.[34] In a few cases,

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(20) Solutions of N_2O_4 in organic solvents actually contain predominantly N_2O_4, since K_{diss} is in the range of 10^{-4}–10^{-5} M. In CH_2Cl_2, the solvent used in this study, K_{diss} is 1.78×10^{-4} M. Thus a dichloromethane solution, 10 mM in N_2O_4, contains 1.3 mM of NO_2 at equilibrium at ambient temperature. Since the rate constants pertaining to this equilibrium are high, NO_2 will always be available for participation in bimolecular processes with other species. For simplicity, concentrations of solutions of N_2O_4 in this paper will be given in terms of $[NO_2]_{total} = [NO_2] + 2[N_2O_4]$, unless specifically stated. For a discussion of the N_2O_4/NO_2 equilibrium in the context of nitration, see ref 18.

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light with a UV component was employed. The only difference between these light sources was that reactions performed with the "UV" source were faster; no qualitative difference was noticeable. In the dark, none of the substrates underwent any reaction; the most reactive compound, 1-methoxynaphthalene, was recovered unchanged after treatment with a 5-fold excess of TNM in the dark for 250 h.

Possible Sources of Error. Experimentation aimed at finding the variables affecting the $h\nu$/ArH/TNM system revealed several sources of systematic error which made interpretation difficult and/or ambiguous. We first suspected that NO_2 might be formed by leakage from the triad of eq 6 and possibly cause nitration according to a well-documented mechanism,[35] for which catalysis by H^+ and/or NO^+ is a characteristic feature. Indeed, NO_2 was formed during photolysis of naphthalene (0.43 M) and TNM (0.85 M) in dichloromethane, as seen in Figure 1. Here $[NO_2]$ is seen to increase rapidly during the first hour, reach a maximum of ca. 2 mM after 3 h, and then slowly decrease. Since the dissociation constant of N_2O_4 is small,[20] $[NO_2]$ at equilibrium corresponds to a much larger $[NO_2]_{total} = [NO_2] + 2[N_2O_4]$, also shown in Figure 1. At the maximum, $[NO_2]_{total} \approx 50$ mM. Naphthalene is known to react slowly with NO_2 and thus NO_2 persists for a long period.[36] Also 1-MON/TNM solutions produce NO_2 upon irradiation, but with a different $[NO_2]$/time dependence (see below).

To keep NO_2 nitration at a minimum, one can inhibit H^+ and/or NO^+ catalysis by addition of a base.[35c,37] Thus addition of a hindered base, like 2,6-di-*tert*-butylpyridine (DTBPy), should inhibit NO_2 nitration, and it indeed does so (see below). However, in applying this principle, any HNO_2 possibly formed (e.g., via eqs 7 and 8) will give nitrite ion, known[38] to react with TNM according to eq 10. Thus attempts to inhibit NO_2 nitration in

$$NO_2^- + C(NO_2)_4 \rightarrow 2NO_2 + (NO_2)_3C^- \qquad (10)$$

this way might lead to an increased rate of production of NO_2. For both naphthalene and 1-methoxynaphthalene the net effect still appears to be inhibition of NO_2 nitration, as seen below for experiments conducted in the presence of DTBPy, nitrite ion, and pentaisopropylguanidine. In dichloromethane at 20.0 °C, the rate constant for reaction between nitrite ion and TNM was determined to be 2.5 (5) × 10^{-3} M^{-1} s^{-1}, relatively fast compared to the reaction periods normally employed. Nitrate ion also reacted with TNM at a rate comparable to that of nitrite ion, although the kinetics were complex. Nitrate ion had however no influence on the nitration process, if added as tetrabutylammonium nitrate.

Table I. Rate Constants for the Reaction between Tris(4-bromophenyl)aminium Ion and Charged Nucleophiles in Acetonitrile at 20.0 °C

nucleophile	rate const, M^{-1} s^{-1}	rel rate const	ref
$(AcO)_2H^-$	5.8 × 10^4	1.5 × 10^5	41
Cl^-	4.5 × 10^2	1.2 × 10^3	41
CN^-	>4 × 10^5	>10^6	41
$(NO_2)_3C^-$	0.38	1	this work
$(NO_2)_3C^-$ (in CH_2Cl_2)		>10^3	this work; cf. Figure 2

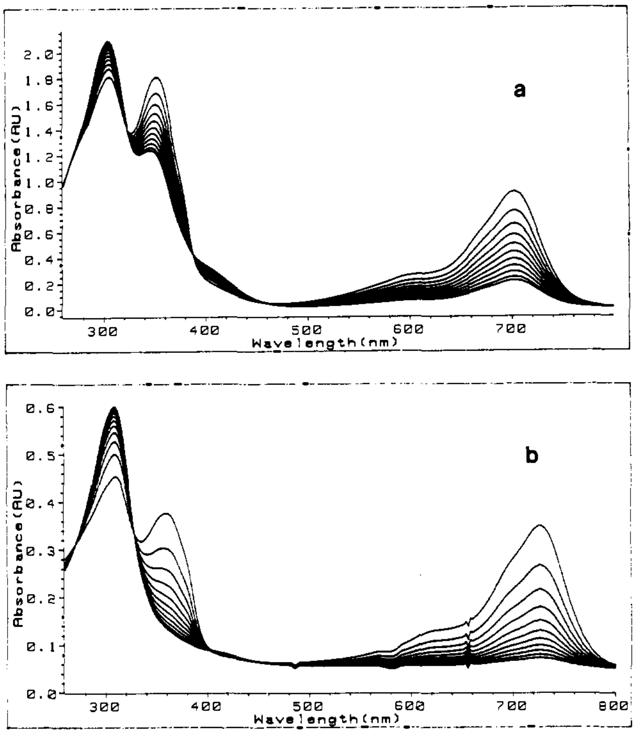

Figure 2. Reaction between tetrabutylammonium trinitromethanide (0.117 mM) and tris(4-bromophenyl)aminium hexachloroantimonate (0.083 M) in (a) acetonitrile and (b) dichloromethane at 20.0 °C, as monitored by UV spectroscopy. (a) The spectra were taken at 75-min intervals, the first spectrum being recorded after 75 min, and (b) at 4-s intervals, mixing being achieved by the stopped-flow technique.

In its reaction with nitrite ion, TNM acts as an electron transfer (ET) oxidant,[30,31,39] and it is thus of importance to know its $E°$ value. Even though the substrates studies are far too unreactive for such an ET reaction to be of concern as a nitration mechanism, TNM might be reactive enough to serve as an oxidant toward the (trinitromethyl)cyclohexadienyl radical formed in eq 7. Because of the extreme instability of its radical anion, electrochemical methods are of little value in this context (see the Experimental Section). To obtain an approximate $E°$ value, TNM was allowed to react in dichloromethane with an easily oxidizable substrate in the dark [tris(4-tolyl)amine with $E°(ArH^{\bullet+}/ArH) = 0.88$ V vs Ag/AgCl] and the rate constant determined (0.44 M^{-1} s^{-1} at 20.0 °C). From these values, one can deduce $E°[TNM/TNM^{\bullet-}] \approx 0.2$ V (Ag/AgCl) by the Marcus treatment[7-11,40] and reasonable estimates of the reorganization energies involved. We thus conclude that TNM might well serve as an electron sink in the conversion of the (trinitromethyl)cyclohexadienyl radical to the corresponding cation, thus creating another source of NO_2 in the reaction mixture (eq 11).

$$^{\bullet}Ar(H)C(NO_2)_3 + C(NO_2)_4 \rightarrow (NO_2)_3CH + NO_2 + ArC(NO_2)_3 \qquad (11)$$

Equation 7 requires trinitromethanide to be a relatively strong nucleophile, reacting with radical cations in fast processes,[28] sometimes with rate constants at or near diffusion-controlled values. We have previously measured the reactivity of several nucleophiles in acetonitrile toward the stable radical cation,

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(36) In acetonitrile, the yield of nitronaphthalenes was 26% after 20 h at 25 °C from a solution of 0.2 M NO_2 and 0.2 M naphthalene.[35c]

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(40) The Eyring equation, $\log k_{ET} = 11 - \Delta G^{*}/(2.303RT)$, in combination with the Marcus quadratic expression, $\Delta G^{*} = \lambda(1 + \Delta G^{\circ\prime}/\lambda)^2/4$, was used to estimate $E°(TNM/TNM^{\bullet-})$. The parameter λ is the reorganization energy, obtained as the average of the reorganization energies of the two self-exchange ET reactions involved, assumed to be 10 and 60 kcal mol^{-1}, respectively. The electrostatic correction was done with a value D of the dielectric constant of 11 and an r_{12} value, the distance between the two reactants in the transition state, of 10 Å.

tris(4-bromophenyl)aminium ion (TBPA$^{\bullet+}$), and found rate constants as listed in Table I.[41] The rate constant of the trinitromethanide/TBPA$^{\bullet+}$ reaction in acetonitrile was determined here to be $\approx$0.38 M^{-1} s^{-1}, and it is seen to be $>10^5$ times slower than that of acetate ion and TBPA$^{\bullet+}$. The slowness of the reaction is shown by the series of spectra shown in Figure 2a, recorded at 75-min intervals. The decay of the radical cation (702 nm) and the trinitromethanide ion (352 nm) was not yet over after ca. 12 h. Thus trinitromethanide appears to be a weak nucleophile in acetonitrile, as can also be inferred from its high redox potential, $E_{1/2}[(NO_2)_3C^\bullet/(NO_2)_3C^-]$ = 1.95 V (SCE) in acetonitrile/$LiClO_4$ (0.1 M).[42] A value of $E° \approx 1.9$ V in water and 1.5 V in acetonitrile was calculated with Pearson's method.[43]

However, the same low nucleophilic reactivity of trinitromethanide did not show up in dichloromethane; the reaction with TBPA$^{\bullet+}$ exhibited kinetics in the range of seconds. Since the kinetics were complex (see the Experimental Section), it was not possible to determine a proper second-order rate constant in dichloromethane. Instead, the reaction was run under conditions identical with those of the acetonitrile experiment of Figure 2a, whereby a similar set of spectra was recorded at 4-s intervals (Figure 2b). The ratio of reactivities of $(NO_2)_3C^-$ between dichloromethane and acetonitrile is thus of the order of 75 × 60/4, i.e., $>10^3$, and trinitromethanide is therefore a moderately strong nucleophile in dichloromethane. This is more in line with "normal behavior" of trinitromethanide, a nucleophile of moderate reactivity toward, e.g., activated olefins.[44] A similar reactivity trend was noted by Maslak and Chapman.[31]

The formation of HNO_2 via eqs 7 and 8 or any other set of reactions that cause oxidative trinitromethylation has been demonstrated earlier.[28] It amounted to 41% yield in a reaction (the substrate is 4-methylanisole) that gave 42% yield of a trinitromethylation product. As detailed below, HNO_2 and/or nitrogen oxide species derivable from it in combination with TNM can effect dark nitration of typical aromatic substrates; the dark reaction can be run either by preformed nitrous acid or by a short period of photolysis of an ArH/TNM mixture.

Finally, a possibly serious experimental source of error was discovered in the occurrence of nitration during GLC of product mixtures where TNM was still present ("injector nitration"). It is known[45] that injection of a naphthalene/TNM mixture onto a GLC column at an injector temperature of 300 °C causes a free radical nitration process to occur, characterized by a very low α/β ratio of ca. 1. We found this reaction to be a seriously disturbing one (for details, see the Experimental Section). It leads to unwanted nitration during GLC analysis and converts the substrate to nonvolatile products which remain on the GLC column. Evaporation of TNM/naphthalene or TNM/1-MON for several hours did not completely eliminate injector nitration, presumably due to the CT complexing properties of TNM. It also was dependent on the GLC instrument employed. For reactions run to high conversion, correction for injector nitration can be applied since yields from it are low.

Apart from nitration, other reactions took place during GLC analysis. Thus 1-MON gave a characteristic product with retention time and mass spectrum identical with that of 4-methoxy-1-naphthonitrile (4-MNN). This compound or a labile precursor thereof was present in most photonitration and some thermal nitration mixtures from 1-MON/TNM in yields of 0.5–10%. It is presumably formed from a trinitromethylation product in a thermal decomposition process occurring both in solution and in the injection block of a GLC instrument. The highest yields of 4-MNN were obtained with low concentrations of reactants during photolysis. Attempts at isolation gave pure samples of 4-MNN.

With the above factors in mind, the following sections to the best of our judgment describe the chemical behavior of the photolysis of ArH/TNM solutions in dichloromethane.

The Guiding Reaction Scheme. The experimental work to be described here will be discussed in terms of a scheme in which the photochemical part *initially* follows the triad hypothesis (eq 6), accompanied by nucleophilic attack by trinitromethanide ion upon the radical cation (eq 7), the regioselectivity being determined by the positive charge density of the latter.[28] We do not invoke coupling between ArH$^{\bullet+}$ and NO_2 as a prelude to the formation of $ArNO_2$ (eq 2) at any time, since we have earlier deemed this type of coupling to be relatively slow.[18] A similar conclusion was reached by Maslak and Chapman for both the radical cation/NO_2 and the neutral radical/NO_2 step.[31] Instead, we demonstrate that nitration products are formed by an addition/elimination mechanism, namely attack of NO_2 upon the (trinitromethyl)cyclohexadienyl radical of eqs 7 and 8, followed by elimination of nitroform. It is also shown that some elimination of HNO_2 takes place, leading to (trinitromethyl)naphthalene. This type of addition of TNM across a double bond system is the same chemistry as has been demonstrated for photolysis of anthracene/TNM.[24,25] The whole scheme is represented by eqs 12–15.

$$ArH, C(NO_2)_4 \xrightarrow{h\nu_{CT}} [ArH^{\bullet+}\ NO_2\ (NO_2)_3C^-] \qquad (12)$$

$$ArH^{\bullet+} + (NO_2)_3C^- \rightarrow {}^\bullet Ar(H)C(NO_2)_3 \qquad (13)$$

$${}^\bullet Ar(H)C(NO_2)_3 + NO_2 \rightarrow O_2N\text{–}Ar(H)C(NO_2)_3 \qquad (14)$$

$$O_2N\text{–}Ar(H)C(NO_2)_3 \xrightarrow[-HNO_2]{-(NO_2)_3CH} ArC(NO_2)_3 + ArNO_2 \qquad (15)$$

Thus the photochemical initiation mechanism produces NO_2 and HNO_2, the former known to be a moderately active nitrating agent in dichloromethane[35] and the latter shown below to cause thermal nitration in combination with TNM. We have already defined several pathways by which NO_2 can be formed (by leakage from the triad, via eq 11, or via reaction between TNM and nitrite ion), and its formation in significant concentrations was shown in Figure 1 (cf. below). For substrates like 1-MON, with high reactivity toward electrophiles, we assume that thermal nitration reactions play an important role after the initial photochemical period. In addition, we cannot exclude that the photolysis reaction might produce trinitromethyl nitrite, a moderately active nitrating agent, as proposed by Isaacs and Abed[32] (eq 9), shown to extend into the wavelength region under consideration here (up to 500 nm). Thus we have found photolysis to be more efficient but not qualitatively different with respect to products with "UV" light than with filtered light. In addition, homolytic splitting of TNM might be possible also under conditions where only the CT band is irradiated;[46] the light employed corresponds to an energy of >60 kcal mol^{-1}, more than enough for effecting the step of eq 16. Then regeneration of ArH and NO_2 from the exergonic, very fast[47]

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(41) Eberson, L.; Larsson, B. *Acta Chem. Scand., Ser B* **1986**, *40*, 210; **1987**, *41*, 367.

(42) Kokorekina, V. A.; Feoktistov, L. G.; Shevelev, S. A.; Fainzil'berg, A. A. *Sov. Electrochem.* **1970**, *6*, 1770. See also Bedin et al. (Bedin, M. P.; Niyazymbetov, M. E.; Shcherbinin, M. B.; Bazanov, A. G.; Petrosyan, V. A.; Tselinski, I. V. *Bull. Acad. Sci. USSR* (*Engl. Transl.*) **1987**, 2493) who reported $E_{1/2}$ = 1.52 V vs Ag/Ag^+ (0.1 M) in acetonitrile/$LiClO_4$. We found E_p = 1.98 V vs Ag/AgCl in acetonitrile/Bu_4NPF_6 (0.1 M) by cyclic voltammetry at a sweep rate of 1600 mV s^{-1}.

(43) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109. The data used for estimating the proton affinity were the gas-phase dissociation energy of $H\text{–}C(NO_2)_3$ (100 kcal mol^{-1}: Orlov, Yu. D.; Lebedev, Yu. A.; Korsunskii, B. L. *Bull. Acad. Sci. USSR* (*Engl. Transl.*) **1984**, 1550), the gas-phase ionization potential of the hydrogen atom (314 kcal mol^{-1}: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement No. 1.), the gas-phase ionization potential of $(NO_2)_3C^-$ (70–80 kcal mol^{-1}: Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1989**, *111*, 4306) and the free energy of hydration of $HC(NO_2)_3$ = −4 kcal mol^{-1}, estimated to be the same as that of HNO_3. The pK_a of nitroform was taken to be ~0 in water and 7.3 in acetonitrile (Slovetskii, V. I.; Ivanov, A. I.; Shevelev, S. A.; Fainzil'berg, A. A.; Novikov, S. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1967**, 41.

(44) Kaplan, L. A. In *The Chemistry of the Nitro and Nitroso Groups. Part 2*; Feuer, H., Ed.; Interscience: New York, 1970. Noble, P., Jr.; Borgardt, F. G.; Reed, W. L. *Chem. Rev.* **1964**, *64*, 19.

(45) Olah, G. A.; Narang, S. C.; Olah, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3298.

(46) The possibility of different reactions taking place upon irradiation in different parts of a CT band has been demonstrated for arene/chloranil complexes: Jones, J., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922.

Table II. Attempts To Observe the Chain Reaction of Equations 16 and 17 in Solutions of Substrate (ArH), TNM, and NO_2 in Dichloromethane in the Dark at 25 °C

[ArH], M	[TNM], M	[NO_2], M	dark period, h	ArH recovered, %	$ArNO_2$ yield,[a] %	$ArNO_2$ yield,[b] %	α/β ratio
			Naphthalene				
0.25	0.25	0.013	144	70	10	290	20
0.20	0.50	0.020	20[c]	99	0.2	3	~2
			1-Methoxynaphthalene				
0.100	0.100	0.020	20	79	12	90	
0.066	0.132	0.100	20[d]	84	5.5	5.5	
			1,4-Dimethoxybenzene				
0.40	2.30	0.114	54	66	14	74	
0.10	0.23	0.020	54	60	15	113	

[a] Yield based on the amount of ArH. [b] Yield based on NO_2, assuming the stoichiometry of eq 8 in ref 11. [c] [DTBPy] = 0.10 M. [d] [DTBPy] = 0.26 M.

$ArH^{\bullet+}/NO_2^-$ process would readily explain the high yields of nitration products obtained from reactive ArH, like 1-MON (below) and 1,4-dimethoxybenzene[27] (formed via N_2O_4 nitration).

$$\mathrm{ArH} + \mathrm{C(NO_2)_4} \xrightarrow{h\nu_{CT}} [\mathrm{ArH^{\bullet+}\ NO_2\ {}^{-}C(NO_2)_3}] \rightarrow \mathrm{ArH} + \mathrm{NO_2} + {}^{\bullet}\mathrm{C(NO_2)_3} \qquad (16)$$

We have scrutinized several other possible routes to products and rejected them on the basis of experiments designed to test their feasibility. One would be the incursion of an NO_2-catalyzed radical chain reaction (eqs 17–19), demonstrated earlier for the addition of TNM across double-bond systems, e.g., 1,2-addition

$$\mathrm{ArH} + \mathrm{NO_2} \rightarrow {}^{\bullet}\mathrm{Ar(H)NO_2} \qquad (17)$$

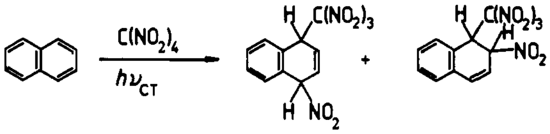
$${}^{\bullet}\mathrm{Ar(H)NO_2} + \mathrm{C(NO_2)_4} \rightarrow {}^{+}\mathrm{Ar(H)NO_2} + \mathrm{NO_2} + {}^{-}\mathrm{C(NO_2)_3} \qquad (18)$$

$${}^{\bullet}\mathrm{Ar(H)NO_2} + \mathrm{NO_2} \rightarrow \mathrm{ArNO_2} + \mathrm{HNO_2} \qquad (19)$$

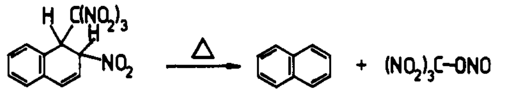
to *N*-vinylcarbazole and 1,6-addition to 9-vinylanthracene.[30] The facile addition of NO_2 in the radical mode to compounds like naphthalene,[37] fluoranthene,[37] anthracene,[48] and perylene[11] in a nonpolar solvent like carbon tetrachloride shows that the addition step of eq 17 *might* give access to a nitrocyclohexadienyl radical which then needs a moderately strong one-electron oxidant to be oxidized to the corresponding carbocation (eq 18) or perhaps a moderately reactive radical like NO_2 to abstract a hydrogen atom (eq 19). TNM may be such an oxidant (see above), capable of oxidizing a nitrocyclohexadienyl radical [$E°(R^+/R^\bullet)$ = 0.4–0.9 V for cyclohexadienyl radicals of the anthracene type[49]] in a reasonably fast process (cf. also ref 31).

However, much experimentation aimed at independent demonstration of a radical chain reaction according to eqs 17–19 in the case of naphthalene or 1-MON in dichloromethane was unsuccessful (Table II) and we therefore presently exclude this possibility.[50]

Photonitration of Naphthalene. Naphthalene represents substrates that are only slowly nitrated by nitrogen dioxide, especially if traces of acid and/or nitrosonium ion are neutralized by an added base and/or nucleophile. Also, it is very little affected by the nitrous acid/TNM combination that can nitrate more reactive substrates, like 1-MON (see below). Thus naphthalene should maximally exhibit the reactions that take place by photochemical excitation of its CT complex with TNM. Preparative runs initially established that the isolatable products after silica column workup were α- and β-nitronaphthalene in a ratio between 4 and 7, significantly lower than the ratios found for other reaction modes, like nitration by nitronium ion, nitrogen dioxide, or coupling between radical cation and nitrogen dioxide.[4] Pentane fractionation (see the Experimental Section) of the crude product mixture separated the products into (1) a pentane-soluble mixture of α- and β-nitronaphthalene in the ratio of 19.4:1 (5% yield) and (2) a dichloromethane-soluble mixture of addition products (eq 20, 35% yield). The latter fraction displayed an NMR spectrum of high complexity, revealing that naphthalene and its nitro isomers could be present only in amounts of <5%. The region between 5.0 and 6.8 ppm showed a complex pattern of signals that is ascribed to vinylic, allylic, and benzylic protons of the adducts (four isomers possible; benzylic protons α to NO_2 or $C(NO_2)_3$ in anthracene 9,10-adducts[25] appear at 6.41 and 6.26 ppm, respectively, whereas adducts from 4-methylanisole showed[28] olefinic resonances in the 5–6.5-ppm region). Integration of aromatic and vinylic/allylic/benzylic signals gave a ratio of ca. 1.3, as compared to the expected 1.00 for adducts. Upon GLC analysis this mixture gave naphthalene (20%) and nitronaphthalenes (80%) with an α/β ratio of 3.2. Small-scale experiments (Table III) revealed a consistent pattern with respect to the workup procedure employed: with only an extraction/water wash procedure the GLC analysis showed a relatively high α/β ratio and also indicated that starting material was present, whereas after column workup the α/β ratio was lower and most of the naphthalene had disappeared. This indicates that the adducts of eq 20 are analyzed by GLC as their nitroform elimination products but that also elimination, as exemplified in eq 21, can take place with formation of trinitromethyl nitrite and naphthalene.[51] Workup by column chromatography causes elimination of nitroform and results in a mixture of nitronaphthalenes.[52]



(20)



(21)

In line with this reasoning, photolysis in the presence of a hindered base, like 2,6-di-*tert*-butylpyridine (DTBPy) or pentaisopropylguanidine, directly gave a mixture of nitronaphthalenes with a very low α/β ratio (≈1.5) which did not change upon column workup (Table III). The same result was obtained when tetrabutylammonium nitrite was used as the base. These experiments represent cases with a minimum of nitrogen dioxide nitration (the base slows down this process by scavenging any acid present and/or formed in the reaction) and a maximum of adduct

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(47) The $E°(NO_2/NO_2^-)$ value in a dipolar aprotic solvent is around 0.9 V (NHE), whereas the substrates used in photonitrations have $E°(ArH^{\bullet+}/ArH) > 1.45$ V. This means that the corresponding outer-sphere ET rate constants are estimated to be $>10^7$ M^{-1} s^{-1}.

(48) Squadrito, G. L.; Fronczek, F. R.; Wathins, S. F.; Church, D. F.; Pryor, W. A. *J. Org. Chem.* **1990**, *55*, 4322.

(49) Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 4289. Dietz, R.; Larcombe, B. E. *J. Chem. Soc. B* **1970**, 1369.

(50) In some cases, $ArNO_2$ yields in Table II exceed 100%, but we do not think these numbers are significant in view of the complexity of the ArH/TNM system and the possibility of other thermal nitration reactions occurring.

(51) Because of the reaction of eq 21, it was not possible to verify the α/β ratio of 3.2 obtained by GLC analysis of the adduct mixture by NMR spectral analysis of the latter.

(52) The relatively low yields of nitro substitution products and modest material balances are presumably due to the fact that the adducts are not completely decomposed on the column but instead are retained and/or converted to compounds that are not eluted (e.g., carboxylic acids). Small amounts of olefinic products, possibly derivatives of binaphthalene, were also detected (NMR) besides the adducts.

Table III. Photolysis of Naphthalene/Tetranitromethane Solutions in Dichloromethane at 25 °C, Using Filtered Light (cutoff at λ < 435 nm), Unless Otherwise Stated

[Naph], M	[TNM], M	light period, h	Naph recovered, %	$ArNO_2$ yield, %	α/β ratio	remark
0.39	1.55	48	2	32	3.5	isolated yields
0.55	0.99	67	2	36	4.1	isolated yields
0.50	1.25	60	4	24	7.2	isolated yields
0.40	1.00	20	22	14	5.8	BW[b]
			24	22	5.0	AW[c]
0.40	1.00	48	5	22	7.5	BW
			3	35	4.2	AW
0.68	2.05	5[a]	2	15	6.2	BW
			1	35	2.5	AW
0.68	1.52	20	19	15	6.1	BW
			14	35	2.3	AW
0.82	2.10	40	7	32	7.5	BW
			2	71	4.3	AW
0.10	0.20	40	16	11	3.6	BW
			17	48	3.8	AW
0.10	0.25	60	6	21	7.0	BW
			0.6	26	4.0	AW
0.25	0.63	60	12	29	10.0	BW
			0.2	40	4.3	AW
0.50	1.25	60	3.4	41	8.9	BW
			0	54	3.8	AW
1.00	2.50	60	4.4	2.7	8.2	BW
			0.6	40	4.1	AW
0.68	2.05	5[a]	28	17	1.2	BW; [DTBPy] = 0.68 M
			37	17	1.2	AW
0.68	0.52	20	42	17	1.4	BW; [DTBPy] = 0.68 M
			49	17	1.4	AW
0.41	1.04	40	27	39	1.4	BW; [DTBPy] = 0.16 M
			23	24	1.0	AW
0.68	1.52	20	31	16	1.1	AW; [Bu_4NNO_2] = 0.68 M
0.68	0.68	20	67	7	1.7	AW; pentaisopropylguanidine = 0.34 M
0.40	1.01	60	0	35	3.5	methyl naphthoate 1%, $MeOH/CH_2Cl_2$ 92/6 (v/v)
0.40	1.80	60	0	34	2.4	methyl naphthoate 1%, MeOH as solvent

[a] "UV" light. [b] BW = before workup. [c] AW = after workup.

formation. However, the base causes elimination of nitroform from the latter during photolysis and thus a mixture of nitronaphthalenes results.

We recapitulate the most important features of the photonitration of naphthalene. After the initial photochemical event to give the triad of eq 6, trinitromethanide attacks naphthalene radical cation at the position of highest charge density, the α position.[53] The preference for this regioselectivity has been amply demonstrated for other naphthalene radical cation/nucleophile combinations,[54] the α/β ratio being >20 (anodic oxidation in CH_2Cl_2 at ambient temperature) and 28 [reaction between $(Naph)_2^{\bullet+}$ and acetate ion in CH_2Cl_2 at −77 °C] for acetoxylation and 6–9 (anodic oxidation in CH_2Cl_2 at ambient temperature) and 15 [reaction between $(Naph)_2^{\bullet+}$ and cyanide ion in CH_2Cl_2 at −77 °C] for cyanation; in the cases of trifluoroacetoxylation and chlorination, only the α isomer was detectable. The 1-(trinitromethyl)naphthalenyl radical is then attacked by NO_2 at either the 2- or 4-position, a reaction that is not expected to display any significant selectivity. Elimination of nitroform finally generates nitronaphthalenes with a low α/β ratio, ≈1.5, the value obtained on photolysis in the presence of a hindered base or nitrite.

Parallel to the addition/elimination process occurs slow nitration by NO_2, a reaction that is expected[35c] to give an α/β ratio of 20–25. The NO_2 is formed either by leakage from the triad or from the photochemical step of eq 15. We detect this reaction in a high α/β ratio in the fraction of nitronaphthalenes that is already present before workup (extractable into pentane). It accounts for ca. 14% of the total nitration product.[55] Finally, we also detect one product derived from trinitromethylation, namely methyl 1-naphthoate (for a more detailed treatment of this reaction, see below), when photolysis is carried out in the presence of methanol (Table III). 1-(Trinitromethyl)naphthalene can be formed by either substitution (eq 7 and 8) or addition/elimination (eqs 12–15).

Table IV. Photolysis of 1-Methoxynaphthalene/Tetranitromethane Solutions in Dichloromethane at 25 °C, Using Filtered Light (cutoff at λ < 435 nm), Unless Otherwise Stated[a]

]1-MON], M	]TNM], M	light period, h	1-MON recovered, %	1-MON-NO_2, %	4-/2- ratio	4-MNN[b] yield, %
0.43	0.53	4.5	8	58	7.1	3
0.75	0.93	20[c]	1	47	6.6	5
0.43	0.53	2[d]	<1	67	6.8	6
0.43	0.53	4.5[e]	4	42	5.9	3
0.43	0.53	1	39	44	7.6	1
		2	27	53	7.9	2
		3	14	70	7.8	3
		3.5	11	73	7.4	5
		20	0	72	7.0	5
0.10	0.15	8	1	77	7.6	3
0.43	0.53	3	0	55	6.8	5[f]
0.43	0.53	3[g]	20	34	5.0	2[h]
0.43	0.53	3[i]	10	47	5.1	2[j]

[a] Yields "after workup" (see Experimental Section). [b] 4-Methoxy-1-naphthonitrile. [c] Preparative run; the yield of 4-methoxy-1-naphthoic acid was 9%. [d] "UV" light. [e] Light with cutoff at λ < 530 nm. [f] The yield of 4-methoxynaphthoic acid was 7%. [g] [DTBPy] = 0.21 M. [h] The yield of 4-methoxy-1-naphthoic acid was 5%. [i]]Bu_4NNO_2] = 0.17 M. [j] The yield of 4-methoxy-1-naphthoic acid was 4%.

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[53] Steenken, S.; Warren, C. J.; Gilbert, B. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 335. The excess charge at the α position of the naphthalene radical cation is 0.181 and at the β position it is 0.069.

[54] Acetoxylation: Eberson, L.; Helgée, B. *Acta Chem. Scand., Ser. B* **1978**, *32*, 157. Fritz, H. P.; Ecker, P. *Chem. Ber.* **1981**, *114*, 3643. Trifluoroacetoxylation: Kremer, H.-J. Thesis. Technical University of Munich, 1976. Kreh, R. P.; Tadros, M. E.; Hand, H. M.; Cockerham, M. P.; Smith, E. K. *J. Appl. Electrochem.* **1986**, *16*, 440. Chlorination: Ellis, S. R.; Pletcher, D.; Brooks, W. N.; Healy, K. P. *J. Appl. Electrochem.* **1983**, *13*, 735. Cyanation: Eberson, L.; Helgée, B. *Chem. Scr.* **1974**, *5*, 47. Fritz, H. P.; Ecker, P. *Chem. Ber.* **1981**, *114*, 3643.

[55] If NO_2 nitration is assumed to give an α/β ratio of 25 and the addition/elimination reaction 1.5, the average α/β ratio of 4.0 after workup in the reactions without added hindered base means that NO_2 nitration accounts for ca. 10% of the nitration products.

Table V. Formation of 4-Methoxynaphthoic Acid or Esters Thereof during Photolysis of 1-MON/Tetranitromethane in Dichloromethane at 25 °C

[1-MON], M	[TNM], M	period of irradiation, h	additive[a] (vol %)	recovered 1-MON, %	yield of ArCOOH/ester,[b] %	yield of $ArNO_2$, % (4-/2-)
0.77	1.03	16	none		5.5[c,d]	not detected
0.41	0.51	4	none[e]	0	5[c]	71 (6.7)
0.16	0.20	16	MeOH (84)	0	30	20 (5.0)
0.16	0.20	8[f]	EtOH (8)	1	31	12 (5.0)
0.16	0.20	8[f]	PrOH (11)	0	47	13 (5.8)
0.40	0.51	2	MeOH (6)	40	4	32 (7.9)
		4	MeOH (6)	42	6	36 (8.0)
		4 + 16 (dark)	MeOH (6)	4	28	29 (7.1)
		4 + 100 (dark)	MeOH (6)	0	47[g]	15 (5.9)

[a] The concentration of the alcohol is given as vol % of the total solvent mixture. [b] The ester isolated corresponded to the alcohol added. [c] Acid. [d] Preparative run, aimed at isolating a sample of the acid. [e] In this run, the dichloromethane had been presaturated with water. [f] "UV" light. [g] In addition, a 10% yield of the acid was obtained.

Photonitration of 1-Methoxynaphthalene (1-MON). As judged by its $E°(ArH^{•+}/ArH)$ value, 1.23 V (Ag/AgCl) in acetonitrile and 1.28 V (Ag/AgCl) in dichloromethane[56] (see the Experimental Section), 1-MON is ca. 0.7 V easier to oxidize than naphthalene, and it should be correspondingly more reactive toward electrophiles. Its reactivity toward NO_2 should therefore be high,[11] which was experimentally confirmed. The reaction with NO_2 reached 50% conversion in 5 min at the 0.05 M concentration level of both reactants. In the presence of an excess of DTBPy, no NO_2 nitration occurred during the first 10 min.

Preparative photolysis experiments of 1-MON/TNM solutions in dichloromethane showed that high yields of nitration products, a mixture of 4- and 2-nitro-1-methoxynaphthalene, were obtained. These experiments, as well as small-scale runs, are reported in Table IV. Under the conditions used the substrate was essentially consumed after 100 min. There was a tendency for obtaining higher yields of nitro products at lower concentrations of 1-MON/TNM. We then monitored (Figure 3) the production of NO_2 from the photolysis of 1-MON/TNM under conditions identical with those used in Figure 1. In agreement with the higher reactivity of 1-MON toward NO_2, $[NO_2]$ increased at a lower level (4–5 times lower) than in the naphthalene case (Figure 1) and reached a maximum after ca. 40 min. After 60 min, when the substrate was consumed to ca. 70%, $[NO_2]$ again increased to a constant level which lasted until at least 920 min, when the experiment was discontinued. We ascribe the first part of the curve to production of NO_2 via photolysis, its leakage into the solution, and its consumption by reaction with 1-MON in the thermal process. As [1-MON] decreases below a certain level, its nitration products take over CT complex formation with TNM and the photochemical NO_2 production again speeds up. Finally, $[NO_2]$ reaches a constant level because of the very low reactivity of 1-MON nitro products toward NO_2 (cf. Figure 1). The nitration products of 1-MON do form CT complexes with TNM, as shown by a strong increase in absorbance upon addition of TNM (0.46 M) to 4-nitro-1-methoxynaphthalene (0.14 M) in dichloromethane (ΔAbs = 1.8, 1.2, 0.9, and 0.5 at 460, 470, 480, and 490 nm, respectively).

The ratio between 4- and 2-nitro isomer from MON varies in the range between 4 and 11 in a way that is not yet possible to connect to the various nitration modes. Nitration by NO_2 displays a 4-/2-nitro isomer ratio of 6.1, whereas a lower ratio, 4.1, is observed when NO_2 nitration is suppressed during photolysis (by nitrite ion or DTBPy; Table IV). Injector nitration gives a low ratio, 1.1, while nitronium ion nitration gives a ratio of 1.7. In these respects, 1-MON resembles naphthalene, although with smaller total variation. Since we know relatively little about the new nitration mode(s) induced by HNO_2, it is yet too early to try to explain these small differences.

Of considerable interest was the finding that a solid inevitably precipitated in 1-MON/TNM solutions during or after photolysis. This compound was identified as 4-methoxynaphthoic acid and its yield generally was in the range of 0.5–10%. In principle, it is not difficult to explain how such a compound is formed, since acidic hydrolysis of (trinitromethyl)arenes has been shown to give the corresponding carboxylic acids in a number of cases.[26,28] However, in our case [and presumably one literature case, formation of 3-methyl-4-methoxybenzoic acid from 2-methyl-4-(trinitromethyl)anisole[26]] no water had been added to the system, nor could any of the reactants adventitiously contain so much water.

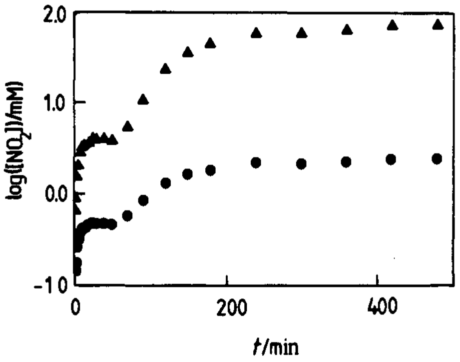

Figure 3. Time development of log ($[NO_2]$/mM) (●, actual concentration; ▲, computed[20] total $[NO_2]$) in a solution of 1-methoxynaphthalene (0.43 M) and tetranitromethane (0.85 M) in dichloromethane at 25 °C upon irradiation with filtered light (cutoff <435 nm).

Table V lists a series of experiments showing the influence of additives on the yield of carboxylic acid or derivatives thereof. No increase in yield was noticed upon working with water-saturated dichloromethane as solvent, whereas addition of alcohols considerably enhanced the yields of the corresponding esters. The last experiment of Table V reveals another remarkable feature of 1-MON/TNM/alcohol photolysis, namely that the production of the methyl ester can be initiated by a relatively short photolysis period, followed by a dark reaction during an extended period.

We assume that proton-carrying species other than water might be responsible for this facile "hydrolysis". Nitrous acid, necessarily formed in trinitromethylation via eq 8, is a likely candidate as a proton source. One way to achieve this transformation might be a photochemical nitro/nitrito rearrangement of the aryltrinitromethane (cf. eq 9), followed by loss of NO + NO_2 to give $ArCO{-}NO_2$. Further reaction with nitrous acid or an alcohol would produce ArCOOH or its ester, respectively. The relatively high yields of esters obtained indicate that the alcohol must have further beneficial effects on some step(s) of the reaction mechanism.

Table VI shows that nitration of 1-MON can be initiated by light (8–60 min), followed by a longer, dark period during which the yield of nitration products increased by a factor of up to 3. The same holds for 1,4-dimethoxybenzene *but not for naphthalene*. The dark nitration reaction was traced to the influence of nitrous acid which initiates/catalyzes nitration of reactive substrates, like

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[56] An $E_{1/2}$ value for oxidation of 1-MON has been determined to be 1.38 V vs SCE in acetonitrile/Pr_4NClO_4 (0.1 M): Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* **1967**, *32*, 1322.

Table VI. Light-*Initiated* Nitration of Aromatic Substrates (ArH) in Tetranitromethane/Dichloromethane Solutions at 25 °C ([ArH] = 0.41 M, [TNM] = 0.62 M)

substrate	period of irradiation, h	dark period, h	recovered ArH, %	yield of $ArNO_2$, %
none	1[a]	1	100	0
none	2[a,b]	1	98	1.7
1-MON	0.13		55	5
	0.13	20	49	15
1-MON	0.27		53	10
	0.27	20	25	28
1-MON	0.50		51	16
	0.50	60	36	46
1-MON	1		77	17
	1	60	30	47
1-MON	1		49	25
	1	60	11	59
1-MON		240	100	0
naphthalene	1.50		100	0
	1.50	180	100	0
1,4-DMB	0.50		67	9
	0.50	20	71	10
1,2-DMB	1		62	6
	1	180	54	11

[a] 1-MON added *after* the irradiation period. [b] "UV" light.

Table VII. Dark Nitration of Aromatic Substrates (ArH) by Nitrous Acid/Tetranitromethane in Dichloromethane at 25 °C ([ArH] = 0.41 M, [TNM] = 1.03 M, $[Bu_4NNO_2]$ = 0.091 M, [TFA] = 0.083 mM)

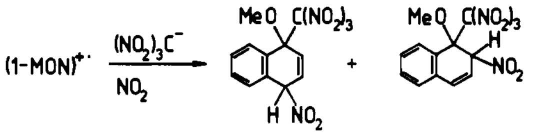
substrate	reaction period, h	recovered ArH, %	yield of $ArNO_2$, %	4-/2- ratio	acid,[a] %	4-MNN yield,[b] %
1-MON	20	47	11		3	
1-MON	20[c]	52	10		5	
1-MON	20[d]	48	12		4	
1-MON	20[e]	41	13		3	
1-MON	60	81	13	6.7	+	1.1
1-MON	20	84	15	7.2	+[f]	<0.4
	100	57	31		7	
1-MON[g]	20	87	3	6.0	+[f]	1.3
	100	57	21		1.5	
1-MON[h]	20	100	<0.1			1.1
	100	83	0			<0.4
1-MON[i]	20	102	<0.1			<0.4
	100	100	<0.1			<0.4
1-MON[j]	20	99	6	5.1	+[f]	0.6
naphthalene	20	99	<1			
1,4-DMB	20	43	20			
1,2-DMB	20		8			
anisole	40	100				

[a] 4-Methoxynaphthoic acid: "+" means that some acid had precipitated after the run. [b] 4-MNN = 4-methoxy-1-naphthonitrile. [c] With 5 mol % HNO_2. [d] With 10 mol % HNO_2. [e] With 15 mol % HNO_2. [f] After standing for 7 days in the dark. [g] TFA left out. [h] Bu_4NNO_2 left out. [i] TNM left out. [j] All concentrations are five times lower.

1-MON and 1,4-dimethoxybenzene, in combination with TNM (Table VII). As little as 5 mol % of HNO_2 with respect to ArH caused dark nitration to occur. Naphthalene and anisole were not influenced by this reagent. Importantly, 4-methoxy-1-naphthoic acid is a product in the dark reaction effected upon 1-MON by HNO_2/TNM. Thus this combination is capable of acting as a trinitromethylating agent.

Another series of experiments showing the role of thermal nitration processes during photolysis of ArH/TNM solutions is listed in Table VIII. Here a solution of ArH/TNM (naphthalene, 1-methylnaphthalene, anisole) was irradiated for a certain period of time and 1-MON was then added to the resulting solution in the dark. In all cases nitration of 1-MON took place, showing the presence of one or several thermally active nitration agents that have been formed during the photolysis period.

Summarizing, the photolysis of 1-MON/TNM occurs via a blend of photochemical and thermal reactions. As for naphthalene (and presumably most other substrates), the initial step consists of excitation of the CT complex to give the triad, from which the first intermediate appears. For the radical cation of a methoxy-substituted aromatic compound one would expect[28] the most reactive positions to be the 1- (ipso to MeO), 4-, and 2-positions, in that order. Ipso attack produces an intermediate radical which gives addition product(s) as shown in eq 22. These addition product(s) can only eliminate nitroform since the HNO_2 elimination pathway is excluded, and thus will ultimately give 4- and 2-nitro isomers of 1-MON. Attack by trinitromethanide on the 4-position will give addition product(s), both of which lead to 4-(trinitromethyl)-1-methoxynaphthalene (eq 23) by elimination of HNO_2. The "hydrolysis" of the latter compound will take place according to an as yet unknown mechanism. Nitration of 1-MON will be caused either by the NO_2 formed, by addition/elimination of products formed by initial trinitromethanide attack on the 2- or 4-position of $1\text{-MON}^{\bullet+}$, or by the thermal HNO_2/TNM pathway.



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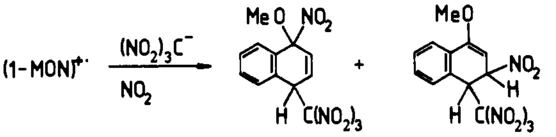

(23)

Conclusions

We summarize our experience with photolysis of naphthalene or 1-methoxynaphthalene together with TNM in dichloromethane in the following way:

(1) For a less reactive substrate, such as naphthalene, photochemical excitation of the substrate/TNM CT complex produces a triad from which one or several adducts are formed via trinitromethanide attack upon the radical cation, followed by reaction of the intermediate neutral radical with NO_2. Some NO_2 leaks

Table VIII. Photolysis of an ArH/TNM Solution in Dichloromethane Solution, Followed by Dark Reaction with 1-MON (Temperature 25 °C)

[ArH], M	[TNM], M	light period, h	ArH recovered, %	$ArNO_2$ yield, %	α/β ratio	1-MON recovered, %	1-MON-NO_2 yield, %	4-/2- ratio
				ArH = Naphthalene				
0.44	0.44	1	90	1	2.8	98	1	
0.44	0.44	3	84	4	3.2	88	7	5.2
0.44	0.44	20	41	26	2.7	92	6	6.0
0.50	1.25	20	21	31	2.2	63	9	5.0
0.50	3.00	20	25	37	1.9	48	19	7.4
0.41	1.04	48	7[a]	29	5.0	53	55	7.2
			1[b]	26	1.9	42	27	7.0
				ArH = 1-Methylnaphthalene				
0.41	1.04	20	18[a]	23		39	74	3.6
			3[b]	8		27	25	7.3
				ArH = Anisole				
0.41	1.04	20	31[a]	11		54	47	4.4
			24[b]	6	54	20	5.3	

[a] Before workup (see Experimental Section). [b] After workup (see Experimental Section).

into the solution and can cause thermal nitration according to a well-known mechanism.

(2) Our original aim to find an independent way to study α/β nitro isomer ratios from the $ArH^{\bullet+}/NO_2$ coupling reaction has been thwarted by the differing reaction modes induced by light in naphthalene/TNM solutions in dichloromethane.

(3) For more reactive substrates, such as 1-methoxynaphthalene, again photochemical initiation is needed. However, in this case the production of NO_2 and HNO_2 is more dominant, meaning that nitration/trinitromethylation will take place largely via thermal nitration reactions by NO_2 and/or HNO_2/TNM. We cannot exclude the possibility that trinitromethyl nitrite can be formed and react in thermal reactions.

(4) The system ArH/TNM/$h\nu$ has turned out to be immensely complex, no doubt with additional surprises to be unravelled as exploration of its fascinating chemistry continues.

Experimental Section

Materials. Naphthalene, 1-methoxynaphthalene, 1,2- and 1,4-dimethoxybenzene, anisole, 4-methoxy-1-naphthaldehyde, 4-methoxy-1-naphthonitrile, tetranitromethane, tris(4-bromophenyl)aminium hexachloroantimonate, and 2,6-di-*tert*-butylpyridine were obtained from Aldrich-Chemie (Steinheim, Germany) and pentaisopropylguanidine from Merck AG (Darmstadt, Germany). Tetrabutylammonium nitrite and 1-nitro-2,5-dimethylbenzene were purchased from Fluka AG (Buchs, Switzerland) and 4-nitro-1-methoxynaphthalene from Janssen Chimica (Beerse, Belgium). Acetonitrile (UVASOL quality (Merck)) and dichloromethane ("zur Rückstandsanalyse") were from Merck AG, whereas tris(4-tolyl)amine was available from other work.[41] Tetrabutylammonium trinitromethanide was prepared according to a literature method[57] and recrystallized from methanol/water. 4-Methoxynaphthoic acid was prepared by permanganate oxidation of 4-methoxynaphthaldehyde. Tetrabutylammonium hexafluorophosphate was from Aldrich and was recrystallized twice from ethyl acetate/cyclohexane. The nitro derivatives of naphthalene were available from previous work,[35c] and 1-methoxy-2-nitronaphthalene was obtained by nitration of 1-MON by nitric acid. Dinitrogen tetroxide solutions in dichloromethane were prepared as before from lead(II) nitrate.[35c]

Instrumentation. The UV–vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer, equipped with the HP 89500 UV/VIS ChemStation. Stopped-flow kinetic measurements were performed at 20.0 °C, using the Rapid Kinetics Spectrometer Accessory (Model RX.1000, cell path 2 mm) from Applied Photophysics, Leatherhead, England, in conjunction with the HP 8452A instrument. Kinetic runs and data treatment were performed by the HP 89512 UV/VIS Kinetics Software.

NMR spectra were recorded on a Nicolet 300-MHz instrument, chemical shifts being given with respect to tetramethylsilane. GLC analyses were performed on a Hewlett Packard 5790A instrument, using a 5% NPGS on Chromosorb W 2 m × 3 mm column, a Varian 1400 instrument with the same column, and/or a Varian 3450 instrument with a 25 m OV-1701 capillary column. On these GLC instruments, the injector chamber temperature was 250 °C. GLC/MS analyses were carried out in the EI mode (70 eV) on a Finnigan 4021 or JEOL JMS-SX 102 mass spectrometer.

Cyclic voltammetry was performed on a BAS-100 Electrochemical Analyzer with a platinum button working electrode, an Ag/AgCl reference electrode, and a Pt wire counterelectrode. ESR spectra were recorded on a Bruker ER-200D SRC instrument.

Measurement of $[NO_2]$ during Photolysis of Tetranitromethane/Naphthalene or Tetranitromethane/1-Methoxynaphthalene in Dichloromethane. A solution (0.30 mL) of tetranitromethane (0.85 M) and naphthalene or 1-methoxynaphthalene (0.43 M) was placed in a quartz tube and irradiated by filtered light (cutoff <435 nm). The tube was withdrawn for ESR analysis after appropriate periods, $[NO_2]$ being determined by relating the height of the sample signal to that of a solution of known $[NO_2]$.

Kinetic Measurements. The rate constant of the reaction between TNM and nitrite ion was measured at 20.0 °C by monitoring the decrease in absorbance at 410 nm in a dichloromethane solution, the $[TNM]/[Bu_4NNO_2]$ ratio being >100 and [TNM] in the range of 0.2–0.6 M. Good first-order kinetics were observed and an average value of the second-order rate constant = 2.5 (5) × 10^{-3} M^{-1} s^{-1} was obtained. Similar runs with tetrabutylammonium nitrate (20 mM) instead of the nitrite and TNM (0.65 M), monitored at 410 nm, showed biphasic behavior with a first, rather rapid reaction ($k \approx 0.07$ min^{-1}), an inflection point, and a second, slow process ($k \approx 0.003$ min^{-1}); the resulting solution had attained a yellow color after 20 h.

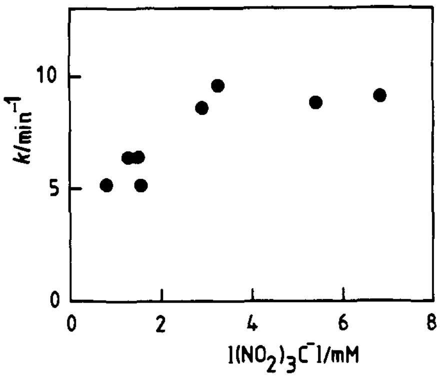

Figure 4. Plot of the pseudo-first-order rate constant of the reaction between trinitromethanide ion and $TBPA^{\bullet+}$ in dichloromethane at 20.0 °C. $[TBPA^{\bullet+}]$ = 0.162 mM.

The kinetics of the reaction between TNM and tris(4-tolyl)amine in dichloromethane at 20.0 °C were monitored at the developing maximum of the radical cation (676 nm) under pseudo-first-order conditions with tris(4-tolyl)amine in excess. Runs at three levels of $[Ar_3N]$ gave good first-order behavior, the average second-order rate constant coming out at 0.44 (2) M^{-1} s^{-1}.

The kinetics of the reaction between tetrabutylammonium trinitromethanide and tris(4-bromophenyl)aminium hexachloroantimonate in acetonitrile at 20.0 °C were monitored at the 702-nm maximum of the radical cation under pseudo-first-order conditions, with the trinitromethanide salt in excess at the 1–5 mM concentration level. The kinetics did not exhibit ideal first-order behavior but resembled a blend of first- and zero-order kinetics, with the characteristic break in the absorbance–time curve when the reaction had reached the end absorbance. The rate constants from such runs were estimated from their well-reproducible half-lives, and an average value of $\tau_{1/2}$ = 18 (1) min was obtained, corresponding to a second-order rate constant of 0.38 M^{-1} s^{-1}. Rate constants of this reaction in dichloromethane were obtained by using the stopped-flow technique (see above), the decay of $TBPA^{\bullet+}$ being monitored at 728 nm. Good first-order kinetics were obeyed and the resulting rate constants showed saturation behavior (Figure 4), levelling out at about 9 min^{-1} at $[Bu_4NC(NO_2)_3] \approx 3$ mM with $[TBPA^{\bullet+}SbCl_6^-]$ = 0.16 mM. It was therefore not obvious how to compare rate constants between the two solvents,[58] and thus the procedure indicated in Figure 2 was adopted to demonstrate the large reactivity difference. Under these conditions, the reactivity ratio was $>10^3$.

Cyclic Voltammetry. This was carried out on 1–4 mM solutions of the substrate in the appropriate solvent with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Tris(4-tolyl)amine was run in dichloromethane (with iR compensation) and showed E_{pa} = 925 mV and E_{pc} = 825 mV vs Ag/AgCl at a sweep rate of 20 mV s^{-1} [lit.[59] $E_{p/2}$ = 0.75 V vs SCE in acetonitrile/tetraethylammonium perchlorate (0.1 M)]. Tetranitromethane was run in acetonitrile and displayed a reduction peak at $E_{pc} \approx 0.0$ V vs Ag/AgCl (lit.[31] −0.15 V vs SCE) at sweep rates in the region of 100–1000 mV s^{-1}; oxidation peaks were seen at ≈1.3 and 1.9 V, presumably corresponding to oxidation of NO_2 and $(NO_2)_3C^-$, formed during reduction. Run by itself in acetonitrile, tetrabutylammonium trinitromethanide showed an oxidation peak at 1.98 V and two reduction peaks at ≈0.3 and −0.2 V at a sweep rate of 1600 mV s^{-1}. 1-Methoxynaphthalene was run in acetonitrile and exhibited reversible behavior upon anodic oxidation at sweep rates above 200 mV s^{-1}. At 200 mV s^{-1} the i_{pc}/i_{pa} ratio was 0.06 whereas at 20 V s^{-1} it was 0.20. The E_{pa} and E_{pc} values at 200 mV s^{-1} were 1.33 and 1.13 V, respectively. In dichloromethane, analogous behavior was observed.

General Procedure for Photochemical Nitrations. The light source was a vertically placed 250-W tungsten lamp, above which a combined IR filter and cooling plate (a flat, cylindrical glass cell of diameter 15 cm and thickness 5 cm through which a constant stream of cold water was maintained) was located. On top of the glass plate the cut-off filter (λ < 435 nm, <1% transmission at λ = 420 nm, <0.1% at λ < 405 nm) was placed, using black masking tape to prevent unfiltered light from passing. The samples to be irradiated, kept in small, closed Erlenmeyer flasks or

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[57] Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7880.

[58] In continuation of our interest in radical cation/nucleophile reaction mechanisms,[41] we plan to further study such reactions of trinitromethanide to get a more detailed understanding of its reactivity.

[59] Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087.

Table IX. Occurrence of "Injector Nitration" during GLC Analysis of Naphthalene and 1-Methoxynaphthalene in the Presence of Tetranitromethane

	yields with instrument 1,[b] %			yields with instrument 2,[c] %		
treatment[a]	ArH recovered	$ArNO_2$	4-MNN[d]	ArH recovered	$ArNO_2$	4-MNN[d]
			Naphthalene			
before TNM	100			100		
after TNM	≈100	0		70	1.0[e]	
after evap	≈100	0		84	0.4[e]	
after column	≈100	0		101	0	
			1-Methoxynaphthalene			
before TNM	100			100		
after TNM	76	0	<1	63	0.8[f]	7
after evap	94	0	<1	80	0.4[f]	6
after column	100	0	0	96	0	0

[a] See text. [b] HP 5830A GLC instrument, packed columns. [c] Varian 3400 GLC instrument, capillary column. [d] 4-Methoxynaphthonitrile. [e] In runs where nitronaphthalenes were formed, the α/β ratio was low, on the average 0.9 (lit.[45] value = 1.0). [f] In runs where 1-methoxynitronaphthalenes were formed, the 4–/2– ratio was low, on the average 1.1.

sample tubes, were placed on the filter and irradiated for the appropriate reaction period. This arrangement maintained the temperature of the photolyzed solution at 25 ± 1 °C. Occasionally, light from an ordinary 300-W "sun lamp" was used without the cut-off filter; these experiments have been referred to as utilizing "UV" light.

Small-Scale Photonitrations. The aromatic compound (0.25–1.0 mmol), internal standard, and additives, when appropriate (see tables and figures), were dissolved in dichloromethane and the required amount of TNM was finally added. After irradiation, the reaction mixture was diluted with dichloromethane and washed with water. GLC analysis at this stage has been referred to as "before workup" (BW) in Table IV. After the reaction mixture was dried by molecular sieves (3 Å) and evaporated at 30 °C for 10–20 min and the remaining material was passed through a short (7–8 cm) column (Silica Gel 60 from Merck AG, eluent pentane/dichloromethane 2/1), the fractions containing ArH and $ArNO_2$ were mixed and subjected to GLC analysis ["after workup" (AW) in Table IV]. Control experiments verified that the presence of the internal standard, 1-nitro-3,5-dimethylbenzene, had no effect upon the outcome of the reaction.

Preparative Photonitrations. The aromatic compound (1.0–5.0 mmol) and the appropriate additive were dissolved in dichloromethane, TNM was added, and the solution was irradiated for the time periods shown in the tables. The photolyzed solution was washed with water, dried, evaporated, and subjected to column chromatography, providing the pure compounds in isolated yields as given in the tables. When 1-MON was the substrate the precipitated 4-methoxy-1-naphthoic acid was collected by decantation or filtration followed by washing with dichloromethane/pentane 9/1. In a typical experiment, 5.7 mmol of 1-MON and 7.0 mmol of TNM in 6 mL of dichloromethane were irradiated for 16 h. Filtration provided 102 mg (0.50 mmol, 9%) of 4-methoxynaphthoic acid, identified by satisfactory spectral data (^1H and ^{13}C NMR, MS) and comparison with an authentic sample. Column chromatography on Silica Gel 60, using hexane/dichloromethane 2/1 as eluent, yielded 0.54 g (2.67 mmol, 47%) of a mixture of 2- and 4-nitro-1-methoxynaphthalene, followed by 50 mg (0.027 mmol, 5%) of 4-methoxynaphthonitrile (4-MNN), identified by comparison (^1H and ^{13}C NMR, MS) with an authentic specimen.

Preparation of Esters of 4-Methoxynaphthoic Acid. With use of the method described above and the concentrations given for the third experiment of Table VI, column chromatography (hexane/dichloromethane 2/1, order of elution 2- and 4-nitro derivative, followed by methyl 4-methoxy-1-naphthoate) provided a pure sample of the methyl ester, showing identical GLC retention time and NMR/mass spectra as a sample prepared by esterification of 1-methoxynaphthoic acid with methanol. Methyl 4-methoxy-1-naphthoate: ^1H NMR ($CDCl_3$) 3.97 (3 H, s), 4.04 (3 H, s), 6.79 (1 H, d), 7.51 (1 H, dt), 7.63 (1 H, dt), 8.26 (1 H, d), 8.33 (1 H, d), 9.03 (1 H, d). ^{13}C NMR ($CDCl_3$): 51.8, 55.6, 102.5, 118.8, 122.6, 125.5, 125.6, 125.7, 128.3, 132.8, 159.3. MS, m/z (rel intensity): 216 (68), 201 (4), 186 (18), 185 (100), 173 (8), 157 (26), 142 (16), 127 (22), 114 (60). The ethyl and propyl esters were characterized by their mass spectra.

Formation of Addition Products during Photonitration of Naphthalene. When naphthalene (0.5 M) was irradiated with a 3-fold excess of TNM in CD_2Cl_2 for 48 h, the ^1H NMR spectrum of the reaction mixture immediately after photolysis showed signals in the range of 5.0–6.8 ppm. These presumably originate from 1,2- and 1,4-addition products of the type shown in eq 20. In addition, signals in the aromatic region showed the presence of naphthalene and its two mononitro derivatives. Due to the complexity of this spectrum, it was not further analyzed and instead the following approach was used.

A solution of naphthalene (0.5 M) and TNM (1.0 M) in dichloromethane (4 mL) was irradiated for 100 h and evaporated and the residue extracted with 3 × 15 mL of pentane. The combined pentane extracts contained a 5% yield of α- and β-nitronaphthalene in a ratio of 19.4. The pentane-insoluble residue was extracted once with pentane/carbon tetrachloride (2:1) and the remaining oil was dissolved in a small volume of dichloromethane, followed by addition of cyclohexane. Upon evaporation of this suspension at 15 °C a slightly yellow crystal mass (yield ca. 35%) separated and was washed with carbon tetrachloride. Finally it was dissolved/evaporated twice in $CDCl_3$ to remove traces of protonated solvents. Redissolved in $CDCl_3$, the solid according to GLC analysis consisted of naphthalene and α- and β-nitronaphthalene in a ratio of 1.1:3.2:1.0, i.e., an α/β ratio of 3.2. However, compared to that of an authentic mixture of the above composition, the ^1H NMR spectrum showed large discrepancies. The spectrum contained a number of signals in the aromatic (8.0–7.0 ppm) as well as in the olefinic/allylic/benzylic (6.8–5.0 ppm) region, the ratio of the integrals of protons in these two regions being 1.3, fairly close to the ratio of 1.00 expected for addition products.

Light-Initiated Nitration of Aromatic Substrates. Solutions of 1-MON, TNM, and internal standard were photolyzed as above for a short period (see Table VII), a small sample was withdrawn for GLC analysis, and the remaining solution was kept in the dark for the period indicated in Table VII. For 1-MON and 1,2-dimethoxybenzene the yield of the nitro compounds increased by a factor of 2–3 during the dark period, while no dark reaction was observed in the corresponding experiments with naphthalene.

Dark Nitration of Aromatic Compounds by HNO_2/TNM. Employing the amounts required for the experiments of Table VIII, tetrabutylammonium nitrite was carefully weighed (hygroscopic!) into the sample tube, followed by the aromatic compound, internal standard, dichloromethane, TNM, and finally, carefully and dropwise, trifluoroacetic acid. The tubes were stoppered and kept in the dark for the appropriate reaction period.

Nitration of 1-MON by N_2O_4. Following the procedure described previously,[11] a solution of 1-MON, N_2O_4, and the internal standard was kept at 20 °C and samples withdrawn and analyzed (GLC) at intervals as shown in Figure 3.

Injector Nitration of Naphthalene and 1-MON by TNM. 1-MON (0.54 mmol) and internal standard were dissolved in 2 mL of dichloromethane in a sample tube covered by Al foil. GLC analysis (injector chamber kept at 250 °C) at this stage is equal to "before TNM" (Table IX; amount of 1-MON recovered defined as 100%). TNM (0.85 mmol) was then added and GLC analysis at this stage is equal to "after TNM". Shortly after the addition of TNM the solution was evaporated in the dark (GLC analysis "after evaporation") and the residue passed through a short column with pentane/dichloromethane 1/1 as the eluent. The fraction containing 1-MON and the internal standard was subjected to GLC analysis "after column". At this stage no TNM was present. The experiments with naphthalene were performed analogously. Yields from runs denoted "before workup" were corrected for injector nitration in the appropriate cases.

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