TIME-RESOLVED SPECTROSCOPY AND CHEMICAL REACTIVITY OF ENERGETIC TRANSIENT SPECIES OF NITROAROMATICS*

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Summary

Electronic excitation of symmetric trinitrobenzene (TNB) in aerated protic solvents generates a transient species the yield of which is a function of the oxygen concentration. Spectroscopic and kinetic data suggest the formation of a complex between TNB and oxygen. Electronic excitation of symmetric 2,4,6-trinitrotoluene (TNT) indicates a photochemically induced isomerization leading to an *aci*-quinoid transient in non-polar solvents or the 2,4,6-trinitrobenzyl anion in polar solvents. In the gas phase, electronic excitation of TNT generates the 2,4,6-trinitrobenzyl radical. This species is also formed from electronically excited TNT, 2,4,6-trinitrobenzyl chloride and hexanitrobibenzyl in 1,4-dioxane at room temperature and in ether–isopentane–ethanol at 77 K. Nanosecond laser time-resolved spectroscopy studies of mononitronaphthalenes and dinitronaphthalenes in non-polar and polar solvents indicate that the lowest triplet excited states of these compounds behave like n,π^* states in non-polar media, while in polar solvents the n,π^* character of these states is reduced with a simultaneous increase in their charge transfer character. In the case of 1,4-dinitronaphthalene, owing to the symmetry of nitro substitution, the triplet state retains its n,π^* character even in polar solvents.

1. Introduction

The initiation of exothermic decompositions in energetic materials such as symmetric trinitrotoluene (TNT) is probably due to the initial formation of energetic transients, *e.g.* electronically or vibrationally excited states, ionic species or free radicals. The stimuli which can cause such an event can be a shock, a thermal stimulus or a light pulse.

In the present paper data are presented on the spectroscopy and chemical reactivity of ionic species, free radicals and electronically excited states of nitroaromatics formed via electronic excitation of the parent molecules. Throughout this work the notations TNB and TNT refer to the symmetric forms of trinitrobenzene and trinitrotoluene respectively.

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2. Experimental details

All solvents used in this work were spectrograde quality. The TNB, TNT and nitronaphthalenes reported on here were purified by successive recrystallizations from ethanol or n-hexane followed by sublimation under vacuum until the gas chromatogram of the sample showed that the impurity level was below 0.001%. Deaeration of the solutions was performed by flushing with argon or helium for 30 min in a flask attached to the optical cell. Electronic excitation of liquid and gaseous samples of TNB and TNT was achieved with the flash photolysis system described earlier [1]. Spectroscopic and kinetic studies of nitronaphthalenes in the nanosecond range were performed with a ruby laser nanosecond kinetic spectrophotometer as described in detail previously [2]. Most of the kinetic data presented here were analyzed with a Nova 840 computer. The kinetic oscilloscope traces were analyzed for first-order or second-order plots, and the result was displayed on a 4010 Tektronix terminal with the use of graphics subroutines. After determining the order of the reaction, the least-squares line was plotted; the rate constants were calculated from the slope of this line.

3. Results and discussion

3.1. Energetic transients formed from electronically excited trinitrobenzene

Electronic excitation of TNB in aerated polar solvents with appreciable proton affinity such as iso-C_3H_7OH and CH_3OH results in the formation of a transient species with absorption maxima at 430 and 510 nm (Fig. 1). The yield of this species is a function of the O_2 concentration, and its rates of formation and decay are viscosity and temperature dependent. In CH_3OH the transient is
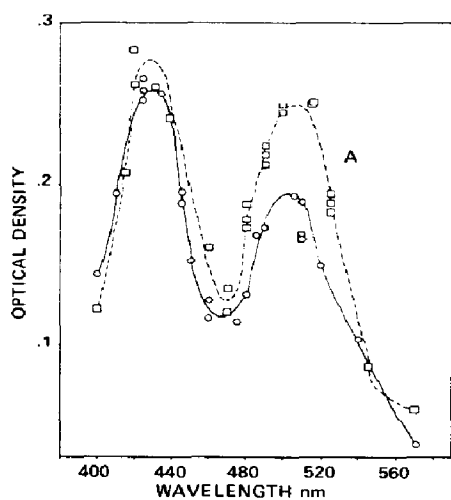

Fig. 1. Absorption spectra of the transient species formed in aerated flash-photolyzed TNB solution: spectrum A, iso-C_3H_7OH medium; spectrum B, CH_3OH medium.

formed with a half-life of 25 μs, while in iso-C_3H_7OH its half-growth time is 60 μs. The decay of the transient obeys second-order kinetics and the k/ε values in iso-C_3H_7OH were

$$k/\varepsilon_{430} = 1.26 \times 10^{-4}\ s^{-1}\ cm$$

and

$$k/\varepsilon_{515} = 1.22 \times 10^{-4}\ s^{-1}\ cm$$

indicating that both absorption maxima are attributable to only one transient species. It is important to emphasize that this transient is not formed in CH_3CN which is a polar solvent without appreciable proton affinity.
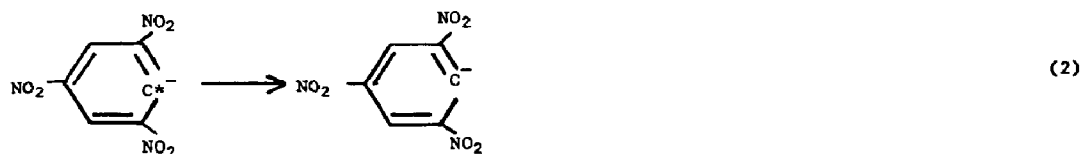
3.2. Assignment of the transient and mechanism

CH_3OH is a molecule with large proton affinity. A proton transfer mechanism such as

(1)

TNB*

ground state   electronically excited   deprotonated TNB*
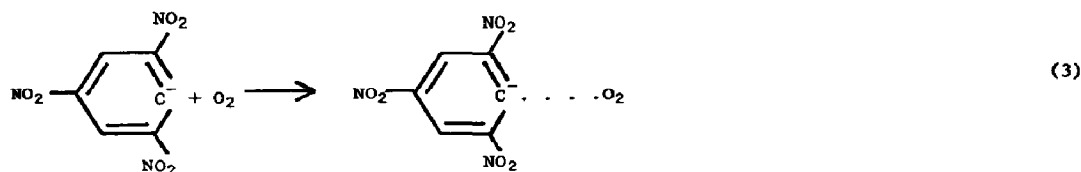   state
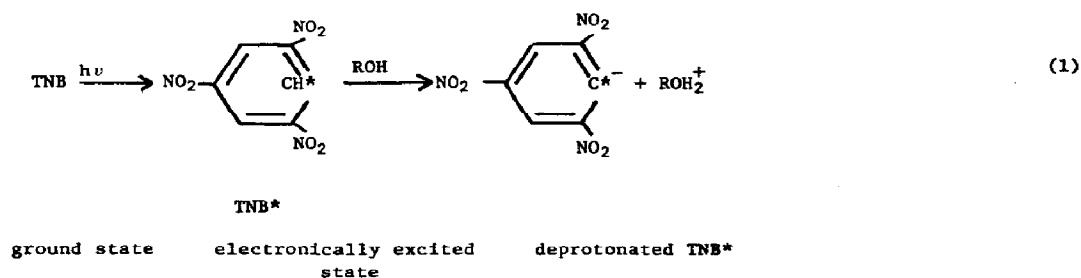
is very probably involved in the photochemical generation of the transient.

The deprotonated form of TNB* decays to generate the negative ion of TNB:

(2)

It is further proposed that TNB⁻ interacts with molecular oxygen to form the transient charge transfer complex $TNB^- \cdots O_2$:

(3)
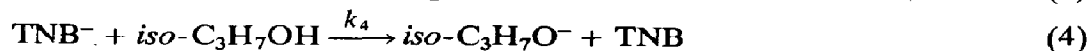
In order to probe further into the polar nature of the proposed mechanism which leads to the formation of $TNB^- \cdots O_2$, the effect of H_2SO_4 on the formation of this species was studied. The presence of acid affects not only the formation of $TNB^- \cdots O_2$ but also its decay, by changing the order of decay from second order

when there is no acid to pseudofirst order in the presence of concentrations of H_2SO_4 (1.3×10^{-4} M) that are relatively large compared with the estimated small concentration of $TNB^- \cdots O_2$ (about 10^{-6} M). The effect of the acid strongly supports reactions (1) and (2) and the following neutralization reaction:

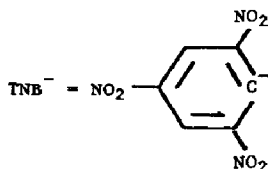$$TNB^- \cdots O_2 + H^+ \rightarrow product$$

The proton transfer mechanism (reaction (1)), assisted by polar solvents with relatively high proton affinities, is further supported by the fact that a similar type of dissociation has been proposed [3] for ground state TNB in polar media with high proton affinities. It is conceivable that the protons in TNB are acidic because of the substantial electronegative character of the nitro groups. Furthermore, in the excited state the protons would be expected to be even more acidic owing to intramolecular charge transfer from the aromatic moiety to the nitro group during photoexcitation. However, even in the excited state the removal of a proton requires extra energy which is furnished by the proton affinity of the CH_3OH molecule. The acidic behavior of excited TNB seems to be analogous to that of the triplets of ketones and quinones having hydroxy and amino substituents [4].

In order to evaluate the kinetic data showing the growth and decay of $TNB^- \cdots O_2$ in acidic solutions (2.1×10^{-5} M H_2SO_4) of TNB in iso-C_3H_7OH, the following reaction scheme was considered:

$$TNB^* \xrightarrow{iso\text{-}C_3H_7OH} TNB^- \qquad\qquad (1) \text{ and } (2)$$

$$TNB^- + O_2 \xrightarrow{k_3} TNB^- \cdots O_2 \qquad\qquad (3)$$

$$TNB^- + iso\text{-}C_3H_7OH \xrightarrow{k_4} iso\text{-}C_3H_7O^- + TNB \qquad\qquad (4)$$

$$TNB^- + H^+ \xrightarrow{k_5} P_1 \qquad\qquad (5)$$

$$TNB^- \cdots O_2 + H^+ \xrightarrow{k_6} P_2 \qquad\qquad (6)$$

where

and P_1 and P_2 are products. The first half-life for the decay of $TNB^- \cdots O_2$ in aerated iso-C_3H_7OH in the absence of added acid is 2.5 ms. However, in solutions of TNB in aerated iso-C_3H_7OH containing 2.1×10^{-5} M H_2SO_4, the first half-life for the decay of this transient species is 500μs. Hence, in acidified solutions, the fate of $TNB^- \cdots O_2$ is solely controlled by reaction (6).

Experimental evidence indicates that the rate of formation of TNB^- through reactions (1) and (2) exceeds by far the rate of its disappearance through reactions (3) - (5). Consequently, the rate-determining step for the formation of $TNB^- \cdots O_2$ will depend on the relative reactivity and concentration of O_2 rather

than on those of iso-C_3H_7OH and H^+. By setting $[TNB^-] = [X]$ and $[TNB^- \cdots O_2] = [Y]$, the following integrated equation was obtained:

$$[Y] = [X]_0' \, [1 - \exp\{-(k_3' + k_4')t\}] \exp(-k_6't) \tag{7}$$

where $[X]_0' = [X]_0 k_3'/(k_3' + k_4)$ and primes refer to pseudofirst-order rate constants ($[X]_0 = [X]$ at the end of the flash). In deriving eqn. (7), the simplifying assumption $k_5' = k_6'$ was made. Substitution for $[Y]$ by $OD_Y/\varepsilon_Y l$, where OD_Y denotes the optical density of Y, in eqn. (7) leads to the expression

$$OD_Y = \varepsilon_Y l \, [X]_0' \exp(-k_6't) \tag{8}$$

since the term $1 - \exp\{-(k_3' + k_4')t\}$, which describes the growth of $TNB^- \cdots O_2$, becomes practically unity after $300 \, \mu s$, as the data indicate. Equation (8), which describes the decay of $TNB^- \cdots O_2$, yielded a linear plot. From the plot, the following values were obtained:

$$k_6 = 2.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$\text{intercept} = \varepsilon_Y l \, [X]_0' = 0.26$$

The term $1 - \{OD_Y \exp(k_6't)/\text{intercept}\}$ describes the kinetic behavior of $TNB^- \cdots O_2$ during the growth period. This term, when plotted on semilogarithmic paper as a function of t, gave a linear plot from the slope of which $k' = k_3' + k_4' = 1.2 \times 10^4 \text{ s}^{-1}$ was obtained for the disappearance of TNB^- by reaction with both O_2 and iso-C_3H_7OH.

Attempts to observe TNB^- directly by flash photolysis in aerated or deaerated solutions of TNB in alcohols, in the wavelength region 260 - 700 nm, were unsuccessful because of the low extinction coefficient [5] of the species.

3.3. Energetic transients formed from electronically excited trinitrotoluene

Electronic excitation of TNT in aerated non-polar solvents such as benzene or cyclohexane results in the formation of a transient species, designated here as species BH, with an absorption maximum at 460 nm as shown in Fig. 2. This species decays in cyclohexane with a first-order rate constant $k = 1.04 \times 10^3 \text{ s}^{-1}$.

In polar solvents, however, electronic excitation of TNT generates the transient absorption shown in Fig. 3. The rate constants for the decay of the transient absorption in CH_3OH at 500 and 630 nm were found to be equal within experimental error:

$$k_{500} = 1.61 \text{ s}^{-1} \qquad k_{540} = 1.86 \text{ s}^{-1} \qquad k_{630} = 1.74 \text{ s}^{-1}$$

which indicates that these transitions originate from the same transient species. This species has an absorption spectrum which is very similar to the spectrum of the 2,4,6-trinitrobenzyl anion [6] formed by the reaction
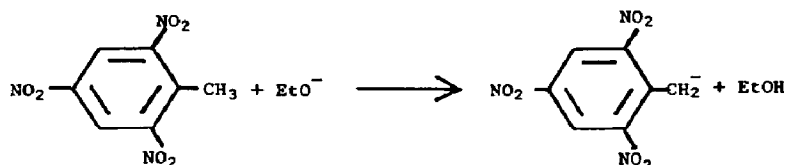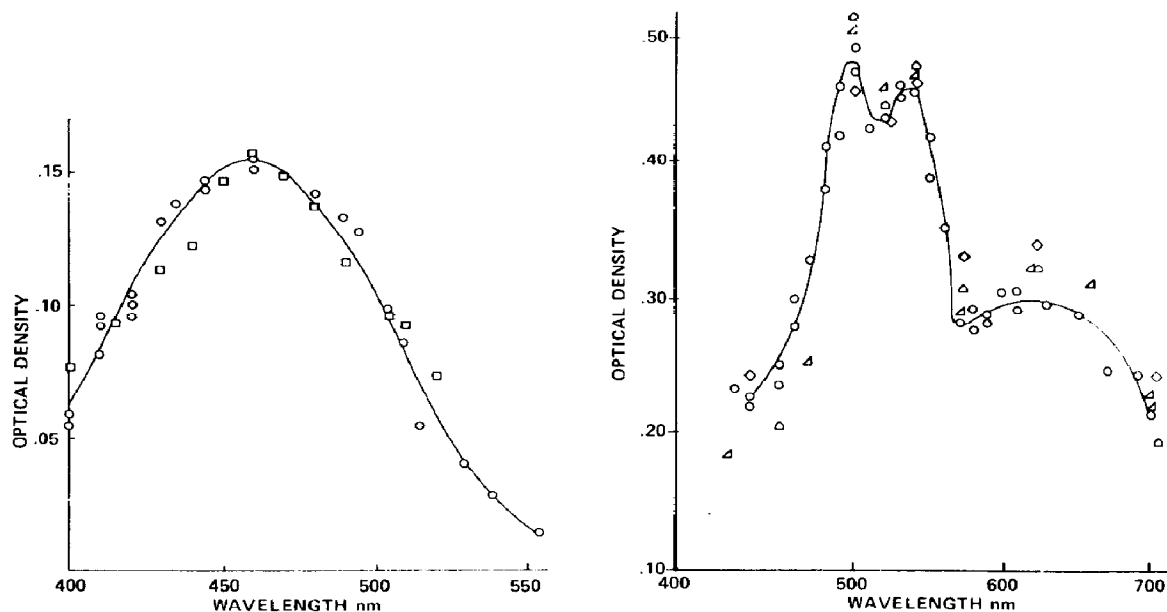

and will be designated B^-.

Fig. 2. Absorption spectrum of the transient species formed in an aerated flash-photolyzed solution of 1 mM TNT: O, in cyclohexane; □, in benzene.

Fig. 3. Absorption spectrum of the transient species formed in aerated flash-photolyzed solutions of TNT in polar solvents: O, CH_3OH; △, CH_3CN; ◊, CH_3OH with 4.4×10^{-5} M H_2SO_4 and 235 mM LiCl; △, iso-C_3H_7OH.

In order to substantiate further the possibility, based on spectral similarities, that the transient species B^- formed photolytically in polar solutions of TNT is negatively charged, salt-effect experiments were carried out.

3.4. Salt-effect studies

The Brønsted–Bjerrum theory of ionic reactions combined with the extended Debye–Hückel theory [7] leads to the following relationship:

$$\log k = \log k_0 + 2AZ_AZ_B\frac{\mu^{1/2}}{1+\mu^{1/2}} \tag{9}$$

where k is the rate constant at ionic strength μ and k_0 is the rate constant at infinite dilution. The constant A is given by the following equation:

$$A = 1.825 \times 10^6 (DT)^{-3/2} \tag{10}$$

In these equations, Z_A and Z_B represent the charges on the reacting ions, T (K) is the temperature and D is the static dielectric constant.

For most cases reported in the literature eqn. (9) has been applied to ionic reactions in aqueous solutions. Buxton et al. [8] have demonstrated, however, that by using LiCl to vary the ionic strength of the solution eqn. (9) can also be applicable to ionic reactions in CH_3OH.

At 298 K the static dielectric constant D of CH_3OH is 32.63 and the constant A calculated from eqn. (10) becomes 1.9. Then eqn. (9) assumes the following form:

$$\log k = \log k_0 + 3.8Z_AZ_B \frac{\mu^{1/2}}{1+\mu^{1/2}} \tag{11}$$

Because of the limited solubility of TNT in neutral water [9], the following reaction in CH_3OH was studied:

$$B^- + H^+ \xrightarrow{k_0} \text{products} \tag{12}$$

where H^+ represents the acid added before the flash $(4.4 \times 10^{-5}$ M $H_2SO_4)$.

The neutralization reaction (12) was followed by time-resolved absorption spectroscopy at 540 nm where B^- absorbs strongly. The rate constant measured for this reaction was $k_0 = 5.0 \times 10^6$ dm^3 mol^{-1} s^{-1}. Subsequently, the rate constant k of reaction (12) was determined as a function of the ionic strength, which was varied with LiCl, and the data were plotted according to eqn. (11). From the slope of the resulting linear plot, the negative charge on B^- was found to be equal to unity.

3.5. Assignment of the transient species BH and B⁻

The species BH and B^- cannot be attributed to a free-radical type of species because their lifetimes (in cyclohexane, $\tau_{BH} = 1/k_1 = 0.96 \times 10^{-3}$ s; in CH_3OH, $\tau_{B^-} = 1/k_2 = 0.575$ s) were found to be unaffected by the presence of oxygen.

The assignment of these species to electronically excited states of TNT can also be excluded because their lifetimes are extremely large compared with the values reported [10] for the electronically excited states of nitroaromatics and, furthermore, because O_2 would be expected to quench excited states [11].

The transient species B^-, having an absorption spectrum closely in agreement with that of the 2,4,6-trinitrobenzyl anion [6] and possessing a charge equal to -1, is assigned to the following species:
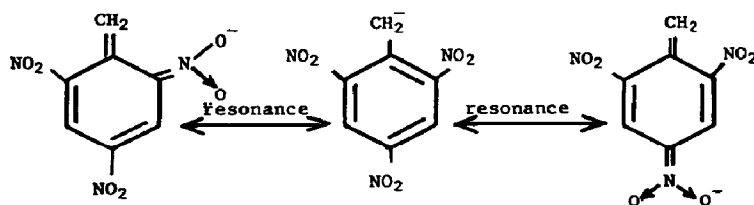

conjugate base (B⁻)

This structure is consistent with participation of the conjugate base in the photochromic mechanism of o-nitrotoluene and o-dinitrotoluene [12 - 14]. According to this structure the conjugate base B^- is not paramagnetic and oxygen would not be expected to affect its lifetime; this agrees with experimental observations.

The spectroscopic evidence [11] which indicates that increasing polarity of the solvent converts BH to B^- seems to be in agreement with the aci-quinoid

and the conjugate base mechanism suggested by Wettermark and coworkers [12 - 14] to explain the photochromic activity of nitrotoluenes. It should be realized, of course, that, while the polarity of the solvent is necessary for the stabilization by solvation of the species B⁻, the basicity of the solvent is also expected to facilitate the dissociation of BH [14].

Additional evidence supporting the assignment of the species BH to the *aci*-quinoid isomer

(BH)
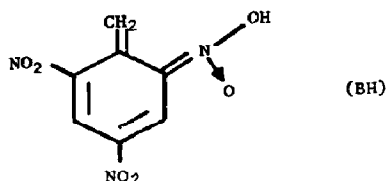
is obtained by comparing the absorption spectrum of the species BH (Fig. 2) with those reported earlier [12 - 14] for the *aci*-quinoid isomer of 2-nitrotoluene, 2,4-dinitrotoluene and 2,6-dinitrotoluene. The comparison shows spectral similarities and a red shift with increasing number of nitro substitutions, which is consistent with the absorption maximum of BH at 460 nm.

Furthermore, the half-life $t_{1/2} = 0.69 \times 10^{-3}$ s of BH in cyclohexane is in fair agreement with the half-life $t_{1/2} = 1.1 \times 10^{-3}$ s for the rearrangement or fading reaction of the *aci*-quinoid isomer of 2-nitrotoluene [12]:

aci-quinoid isomer   2-nitrotoluene
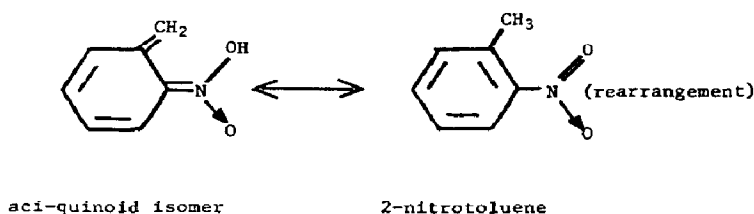
The similarity of the half-lives is not surprising, since the fading reaction represents an intramolecular proton transfer reaction which is not expected to be strongly influenced by the solvent medium.

3.6. Mechanism of the photochromic activity of trinitrotoluene

Applying closely the mechanism suggested by Wettermark and coworkers [12 - 14] for the photochromism of mononitrotoluenes and dinitrotoluenes to the case of TNT, the mechanism in Fig. 4 can be proposed. According to the scheme in Fig. 4, BH is formed through intramolecular proton transfer from the methyl group to one of the ortho nitro groups during the lifetime of the electronically excited TNT. In non-polar solvents, BH rearranges back to ground state TNT. In polar solvents, however, the only observable transient species is B⁻, and it is not known whether B⁻ is formed directly from electronically excited TNT or by rapid dissociation of the species BH. The species B⁻ presumably regenerates TNT through proton abstraction from the solvent. Caldin and Jackson [15]
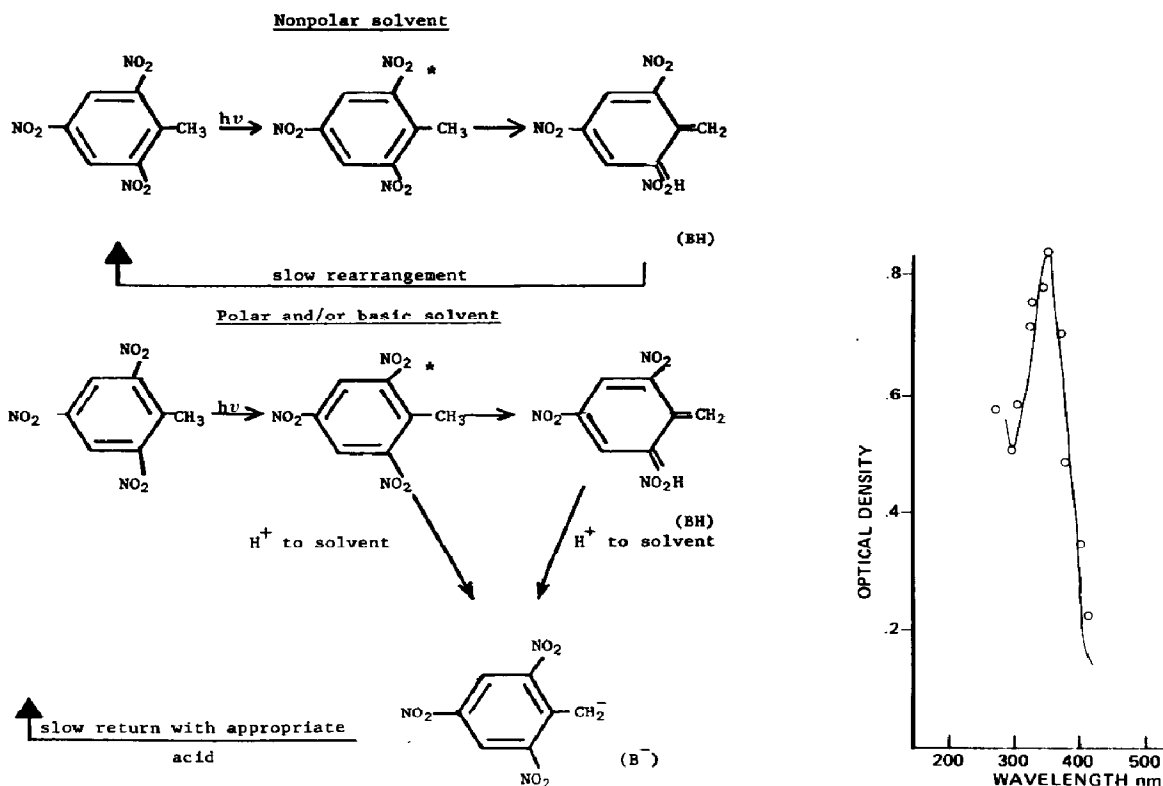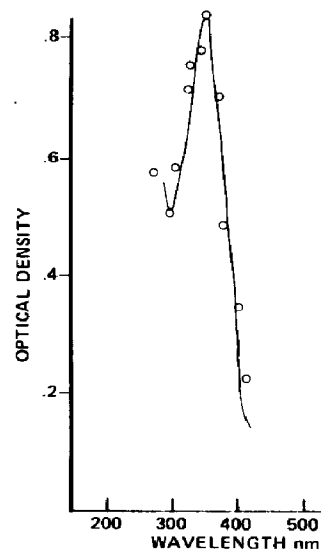
Fig. 4. Reaction scheme for the photochromism of TNT.

Fig. 5. Absorption spectrum of the transient species formed by the flash photolysis of TNT in the gas phase (215 °C; argon atmosphere at 600 mmHg).

and Blake *et al.* [16] have shown that the 2,4,6-trinitrobenzyl anion decays in alkaline alcoholic solutions via a proton abstraction reaction.

The biphotonic mechanism for the formation of B^- is excluded on the basis of experimental evidence showing that the optical density of B^- at the end of the flash is linearly proportional to the square of the charging voltage applied across the terminals of the flashlamps. This implies that the yield of B^- is linearly proportional to the intensity of the excitation light.

3.7. The 2,4,6-trinitrobenzyl radical

Electronic excitation of TNT in the gas phase at 215 °C (in the presence of argon at 600 mmHg) leads to the formation of a transient species with the absorption spectrum shown in Fig. 5 and $t_{1/2} = 69$ s. O_2 and NO when used (at 600 mmHg) instead of argon were found to increase the yield and to reduce the lifetime of the transient: $t_{1/2}(\text{NO}) = 14$ s and $t_{1/2}(O_2) = 34$ s. The increased yield and shorter lifetime of this transient species in the presence of NO and O_2 are consistent with the assignment of this species to the 2,4,6-trinitrobenzyl free radical. Both NO and O_2 are expected to assist initially the formation of this

radical through hydrogen abstraction from the methyl group of the electronically or vibrationally excited TNT. Furthermore, when the radical is formed it is also expected to be scavenged by molecules such as NO and O_2.

The free radical B · is also formed from electronically excited TNT in 1,4-dioxane at room temperature and in 3-methylpentane at 77 K as shown in Figs. 6 and 7. The transient absorption in Fig. 6 with a maximum at 460 nm is attributed to the *aci*-form of TNT.

The assignment of the transient absorption (Fig. 6) to the 2,4,6-trinitro-benzyl radical was further supported by additional experimental evidence derived from flash-photolyzed solutions of 2,4,6-trinitrobenzyl chloride (TNT-Cl) and hexanitrobibenzyl (HNBB) in 1,4-dioxane as illustrated in Figs. 8 and 9. The spectral and lifetime similarities of the transient absorptions generated from electronically excited TNT, TNT-Cl and HNBB in 1,4-dioxane [17] strongly support the assignment of this absorption to the 2,4,6-trinitrobenzyl radical. Furthermore, it is interesting to note that the transient absorption (Fig. 6) assigned to the *aci*-form of TNT is almost absent from the spectra shown in Figs. 8 and 9. This is not surprising, since the molecules TNT-Cl and HNBB are not expected to form the *aci*-form of TNT.

Work is in progress to form the radical B · from electronically excited HNBB in the gas phase or in solid matrixes at 77 K. Furthermore, benzoquinone will be electronically excited in the gas phase in the presence of TNT. Electronically excited benzoquinone is expected to abstract a hydrogen atom from the methyl group of TNT and to yield the radical B · and the semiquinone radical C · which has an absorption maximum at 415 nm.
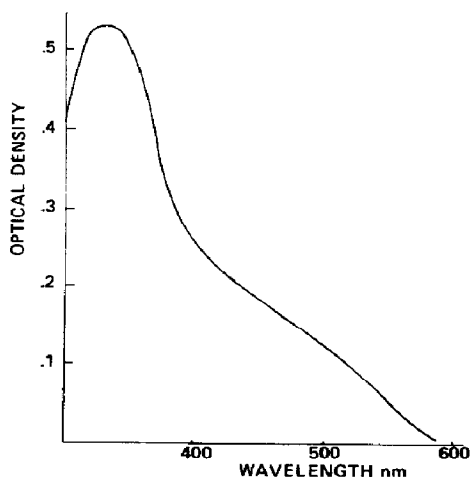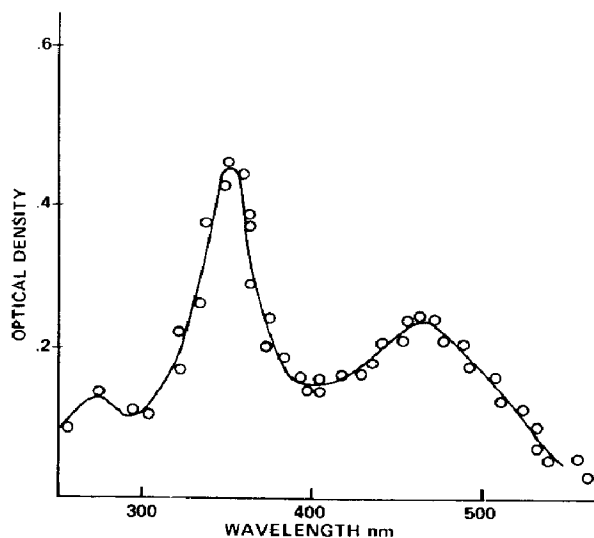

Fig. 6. Absorption spectrum of the transient species produced by the flash photolysis of TNT in 1,4-dioxane.

Fig. 7. Absorption spectrum of the product formed by the photolysis of TNT in 3-methylpentane (77 K; instrument, Cary 14 spectrophotometer).
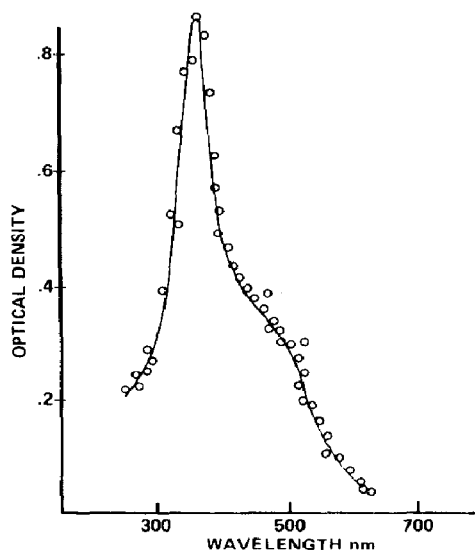
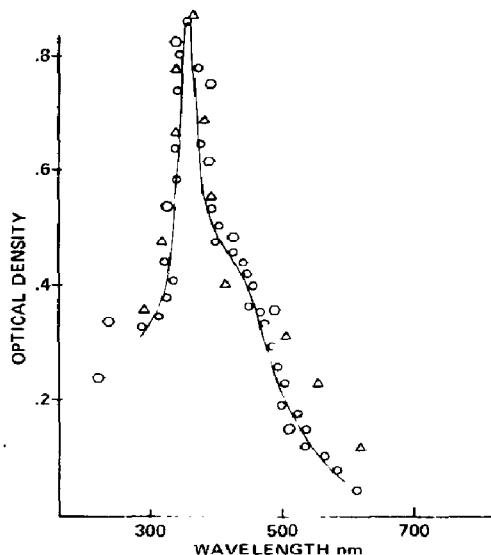Fig. 8. Absorption spectrum of the transient species produced by the flash photolysis of HNBB in 1,4-dioxane.

Fig. 9. Absorption spectrum of the transient species produced by the flash photolysis of TNT-Cl: △, in deaerated 1,4-dioxane; ○, in aerated 1,4-dioxane; ⬡, in benzene.

3.8. Spectroscopy and chemical reactivity of electronically excited states of nitroaromatics

A series of mononitronaphthalenes (NO_2N) and dinitronaphthalenes (DNO_2N) was studied, in polar and non-polar solvents, with a laser nanosecond kinetic spectrophotometer which was designed and assembled in our laboratory. Absorption spectra of the lowest triplet excited states of 1-nitronaphthalene and 2-nitronaphthalene as well as of 1,2-dinitronaphthalene, 1,4-dinitronaphthalene and 1,8-dinitronaphthalene in non-polar and polar solvents were obtained. The spectra were red shifted in polar solvents. From the spectral shifts, dipole moments of the lowest and upper triplet states of all the nitronaphthalenes studied in this work were calculated according to the method described earlier [18] and the values are reported in Table 1.

TABLE 1

Values of the dipole moments of the T_1, T_n and ground states of nitronaphthalenes

Compound	μ_g	μ_{T_1}	μ_{T_n}	$\Delta\mu_{T_1 \rightarrow T_n}$
1-NO_2N	4.04	5.24	9.74	4.5
2-NO_2N	4.4	5.7	11.9	6.2
1,2-DNO_2N	6.5	7.1	10.4	3.3
1,8-DNO_2N	7.7	9.6	11.0	1.4

TABLE 2

Spectroscopic and kinetic data of nitronaphthalene triplets

Compound	$T_1 \rightarrow T_n$ absorption maximum in hexane (nm)	Red shift in ethanol (nm)	Reaction rate constant (mol⁻¹ s⁻¹) of the triplet with the following systems									
			Triplet mean life (μs) in		Pure solvent		O_2 in		H^+ ($\times 10^7$)	NaOH ($\times 10^8$)	$(C_2H_5)_3N$ ($\times 10^9$)	$(C_4H_9)_3SnH$ ($\times 10^8$)
			Hexane	Ethanol	Hexane ($\times 10^5$)	Ethanol ($\times 10^4$)	Hexane ($\times 10^9$)	Ethanol ($\times 10^9$)				
1-NO₂N	525	55	0.93	4.9	1.4	1.2	1.3	3.3	1.8	1.7	2.8	—
2-NO₂N	425	45	0.53	1.7	2.5	3.5	1.7	1.6	88.0	12.0	6.4	0.4
1,2-DNO₂N	490	60	1.0	4.3	1.3	1.3	1.9	3.3	0.17	7.9	5.2	3.4
1,4-DNO₂N	545	No shift	4.6	4.8	0.29	1.2	1.7	2.0	0.003	15.0	3.0	3.8
1,8-DNO₂N	550	40	2.5	5.3	0.52	1.1	0.81	2.1	2.5	5.0	4.6	1.6

The extent of spectral shifts, lifetimes and quenching by oxygen and other data pertinent to the chemical reactivity of these triplet excited states are summarized in Table 2. These triplet states behave like n,π^* states in non-polar solvents, while in polar media the n,π^* character is reduced with a simultaneous increase in their intramolecular charge transfer character [2, 19, 20]. However, in the case of 1,4-dinitronaphthalene, owing to the symmetry of nitro substitution, there is no spectral shift and the triplet excited state retains its n,π^* character even in polar media [20].

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