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ENERGETIC TRANSIENT SPECIES FORMED VIA ELECTRONIC EXCITATION OF--ETC(U)
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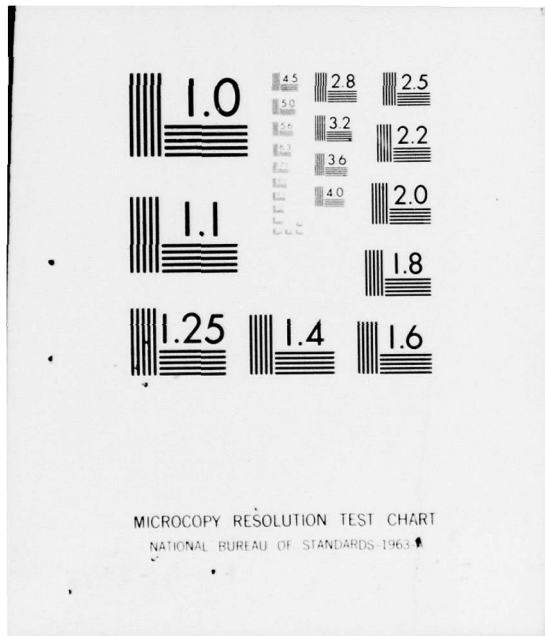
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ENERGETIC TRANSIENT SPECIES FORMED
VIA ELECTRONIC EXCITATION OF S-TNB AND S-TNT, (U)

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INTRODUCTION: The initiation of exothermic explosive decompositions in materials, such as, s-TNT² (2,4,6-trinitrotoluene) is probably due to the initial formation of energetic transients, like electronically or vibrationally excited states, ionic species or free radicals. The stimuli which can cause such an event can be an electronic, shock wave or thermal pulse. So far, there has been no information in the literature pertaining to the formation and reactivity of these energetic transients in secondary explosives.

In the present paper data are presented on the spectroscopy and chemical reactivity of ionic species, electronically excited states and free radicals of nitro aromatics formed via electronic excitation of the parent molecules. Furthermore, it was discovered in the present work, that formation of the TNT anion, $(C_6H_2^{\ominus})(NO_2)_3CH_2^{\ominus}$, (B^{\ominus}) , in molten TNT by additives such as $(CH_3)_4NB_3H_8$, known as QMB₃, NaOH, and NaI lead to deflagration of TNT. These additives sensitized TNT to impact and differential scanning calorimetry yielded data which are consistent with the sensitization of TNT by these additives.

It was also discovered in this work that TNT can be sensitized by additives such as benzoquinone and tetraethyl lead. It is believed that these additives abstract a hydrogen atom from the methyl group of TNT during thermal excitation to form the radical $(C_6H_2)(NO_2)_3CH_2^{\bullet}$, (B^{\bullet}) . Work is in progress for the formation and detection of this radical in electronically excited TNT in the gas phase at 215°C.

¹Formerly known as: K. Suryanarayanan. ²Throughout this report the notations TNB and TNT refer to the symmetric form.

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EXPERIMENTAL

All solvents used in this work were spectrograde quality. TNB, TNT and the nitronaphthalenes reported 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 done by argon or helium flushing for 30 minutes in a flask attached to the optical cell. Electronic excitation of liquid and gaseous samples of TNB and TNT was achieved with a flash photolysis system which has been 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 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 square line was plotted from the slope of which the rate constants were calculated.

RESULTS AND DISCUSSION

I. Energetic Transients Formed From Electronically Excited TNB

Electronic excitation of TNB in aerated polar solvents with appreciable proton affinity, such as, i-PrOH (A) and MeOH (B) results in the formation of a transient species with absorption maxima at 430 and 510 nm (Fig 1).

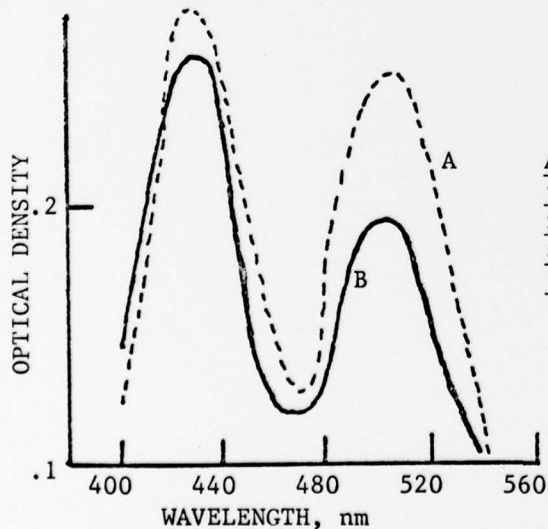


Fig. 1

Absorption spectrum of the transient species formed in flash-photolyzed aerated TNB solutions in (A) i-PrOH medium (B) methanol medium

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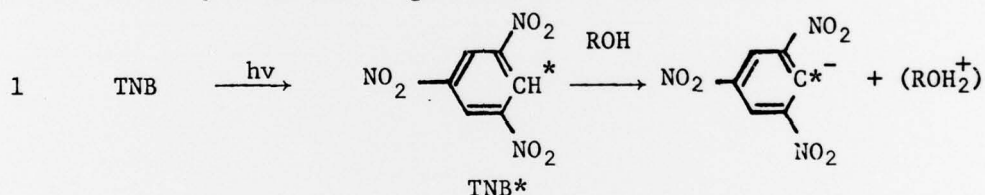
The yield of this species is a function of oxygen concentration, and its rate of formation and decay is viscosity and temperature dependent. In methanol it grows with a half-life of 25 μ sec, while in *i*-PrOH its half-growth time is 60 μ sec. Its decay obeys second order kinetics and the k/ϵ values in *i*-PrOH were found as follows:

$$k/\epsilon_{430} = 1.26 \times 10^{-4} \text{ and } k/\epsilon_{515} = 1.22 \times 10^{-4} \text{ sec}^{-1} \text{ cm}$$

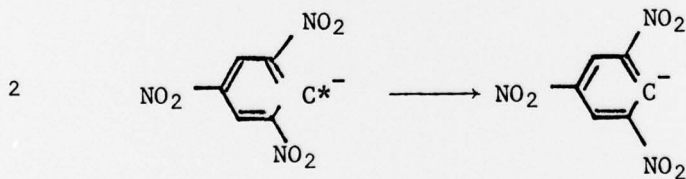
indicating that both absorption maxima are attributed to only one transient species. It is important to emphasize that this transient is not formed in CH_3CN which is a polar solvent without appreciable proton affinity.

Assignment of the Transient and Mechanism

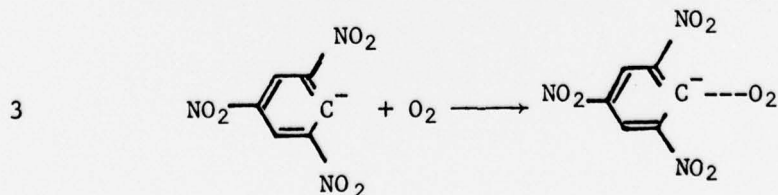
Methanol is a molecule with large proton affinity. A proton ejection mechanism as shown in reaction 1 is very likely to be involved in the photochemical generation of the transient:



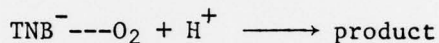
The deprotonated form of TNB* decays to generate the negative ion of TNB:



It is further proposed that TNB^{\ominus} interacts with molecular oxygen to form the transient charge transfer complex $\text{TNB}^{\ominus} \cdots \text{O}_2$, as shown below:

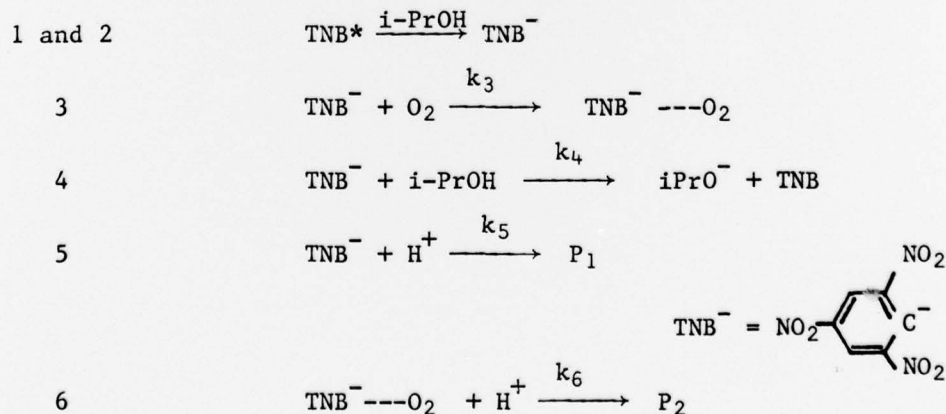


In order to probe further into the polar nature of the proposed mechanism which leads to the formation of $\text{TNB}^{\text{---}}\text{O}_2$, the effect of sulfuric acid on the formation of this species was studied. The presence of acid affects not only the formation of $\text{TNB}^{\text{---}}\text{O}_2$, but also its decay, by changing the order of decay, namely, from second order when there is no acid, to pseudofirst order in presence of relatively large concentrations of H_2SO_4 (1.3×10^{-4} M) as compared to the estimated small concentration of $\text{TNB}^{\text{---}}\text{O}_2$ (about 10^{-6} M). The effect of the acid strongly supports reactions 1 and 2 and the following neutralization reaction:



The proton ejection mechanism, reaction 1, assisted by polar solvents with relatively high proton affinity, 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 affinity. It is conceivable that the protons in TNB are acidic because of the large electronegative character of the nitro groups. Furthermore, in the excited state, the protons would be expected to be even more acidic due to intramolecular charge transfer from the aromatic moiety to the nitro group during photoexcitation. However, even in the excited state the removal of proton requires extra energy which is furnished by the proton affinity of the methanol 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 $\text{TNB}^{\text{---}}\text{O}_2$ in acidic solutions (2.1×10^{-5} M H_2SO_4) of TNB in *i*-PROH, the following reaction scheme was considered:



where P_1 and P_2 are products. The first half-life for the decay of $\text{TNB}^{\text{---}}\text{O}_2$ in aerated i-PrOH in the absence of added acid is 2.5 milliseconds. However, in solutions of TNB in aerated i-PrOH containing 2.1×10^{-5} M H_2SO_4 , the first half-life for the decay of this transient species is 500 microseconds. Hence, in acidified solutions, the fate of $\text{TNB}^{\text{---}}\text{O}_2$ is solely controlled via 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 due to reactions 3, 4, and 5. Consequently, the rate determining step for the formation of $\text{TNB}^{\text{---}}\text{O}_2$ would depend on the relative reactivity and concentration of oxygen as compared to those for i-PrOH and H^+ . Setting $(\text{TNB}^-) = (X)$ and $(\text{TNB}^{\text{---}}\text{O}_2) = (Y)$, the following integrated equation was obtained:

$$7 \quad (Y) = (X'_0) [1 - e^{-(k_3 + k_4)t}] e^{-k_6 t}$$

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 Eq. 7, the simplifying assumption $k_5 = k_6$ was made. Substitution of (Y) by $(\text{O.D.})_Y / \epsilon_Y l$ into Eq. 7 leads to the expression

$$8 \quad (\text{O.D.})_Y = \epsilon_Y l (X'_0) e^{-k_6 t}$$

since the term $1 - \exp \{-(k_3 + k_4)t\}$, describing the growth of $\text{TNB}^{\text{---}}\text{O}_2$, becomes practically unity after 300 μsec as the data indicate. Equation 8, describing the decay of $\text{TNB}^{\text{---}}\text{O}_2$, yielded a linear plot. From the plot, the following values were obtained:

$$k_6 = 2.1 \times 10^7 \text{M}^{-1} \text{sec}^{-1}$$

$$\text{intercept} = \epsilon_Y l (X'_0) = 0.26$$

The term $1 - ((\text{O.D.})_Y e^{k_6 t} / \text{intercept})$ describes the kinetic behavior of $\text{TNB}^{\text{---}}\text{O}_2$, during the growth period. This term plotted on semilog paper versus t gave a linear plot from the slope of which the value of $k' = k_3 + k_4 = 1.2 \times 10^4 \text{sec}^{-1}$ was obtained for the disappearance of TNB^- by reaction with both oxygen and i-PrOH.

Efforts 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 (about $2000 \text{M}^{-1} \text{cm}^{-1}$) of the species (5).

II. Spectroscopy and Chemical Reactivity of Electronically Excited States of Nitroaromatics

A series of mono and dinitronaphthalenes (NO₂N and DNO₂N) was studied, in polar and nonpolar 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-, and 2-nitronaphthalenes as well as 1,2-, 1,4- and 1,8-dinitronaphthalenes were obtained in nonpolar and polar solvents. 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 (6) and the values are reported in Table 1.

Table 1

Values of Dipole Moments of T₁, T_n and Ground States
of Nitronaphthalenes

	μ_g	T ₁	T _n	$\Delta\mu_{T_1 \rightarrow T_n}$
1-NO ₂ N	4.04	5.24	9.74	4.5
2-NO ₂ N	4.4	5.7	11.9	6.2
1,2-DNO ₂ N	6.5	7.1	10.4	3.3
1,8-DNO ₂ N	7.7	9.6	11.0	1.4

The extent of spectral shifts, lifetimes, 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 nonpolar solvents, while in polar media the n- π^* character of these states is reduced with a simultaneous increase in their intramolecular charge transfer character (2,7). In the case of 1,4-dinitronaphthalene (7b), however, owing to the symmetry of nitrosubstitution, there is lack of spectral shift and the triplet excited state retains its n- π^* character even in polar media.

Table 2
Spectroscopic and Kinetic Data of Nitronaphthalene Triplets

Compound	T ₁ -T _n Abs. Max. in Hex- ane (nm)	Red Shift in Etha- nol (nm)	Triplet Mean- life (μs) in		Reaction Rate Constant (M ⁻¹ sec ⁻¹) of the Triplet With								
			Hex- ane nol	Etha- nol	Pure Solvent		Oxygen in		H ⁺	Et ₃ N	NaOH	Et ₃ N	Bu ₃ SnH
					(x10 ⁵)	(x10 ⁴)	Hex- ane nol (x10 ⁹)	Etha- nol (x10 ⁹)					
1-NO ₂ N	525	55	0.93	4.9	1.4	1.2	1.3	3.3	1.8	1.7	2.8	-	
2-NO ₂ N	425	45	0.53	1.7	2.5	3.5	1.7	1.6	88	12	6.4	0.4	
1,2-DNO ₂ N	490	60	1.0	4.3	1.3	1.3	1.9	3.3	0.17	7.9	5.2	3.4	
1,4-DNO ₂ N	545	No Shift	4.6	4.8	0.29	1.2	1.7	2.0	0.003	15	3.0	3.8	
1,8-DNO ₂ N	550	40	2.5	5.3	0.52	1.1	0.81	2.1	2.5	5.0	4.6	1.6	

III. Energetic Transients Formed From Electronically Excited TNT

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

In aerated polar solvents like methanol or acetonitrile, flash photolysis of TNT leads to a different transient with absorption maxima at 500, 540, and 630 nm, as illustrated in Figure 2, B.

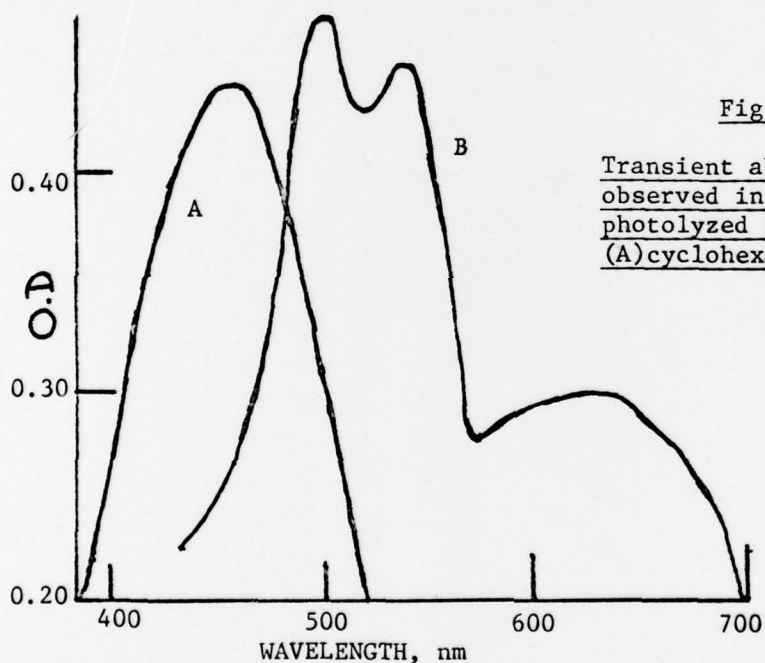


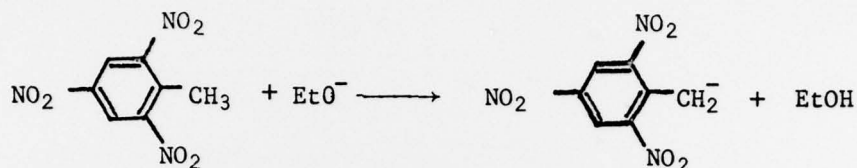
Fig. 2

Transient absorption spectra
observed in aerated flash-
photolyzed solutions of TNT
(A)cyclohexane (B) methanol

The rate constants for the decay of the transient absorption in methanol at these wavelengths were found to be equal within experimental error;

$$k_{500} = 1.61, k_{540} = 1.86 \text{ and } k_{630} = 1.74 \text{ sec}^{-1}$$

which indicates that these transitions originate from the same transient species. This species has an absorption spectrum which is closely in agreement with the spectrum of 2,4,6-trinitrobenzyl anion (8) formed by the reaction



and will be designated as B^- .

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

A. Salt Effect Studies

The Bronsted-Bjerrum theory of ionic reactions combined with the extended Debye-Huckel theory (9) leads to the following relationship

$$9 \quad \log k = \log k_o + 2AZ_A Z_B [\mu^{1/2}/(1 + \mu^{1/2})]$$

where k is the rate constant at ionic strength μ and k_o is the rate constant at infinite dilution. The constant A is given by Eq. 10

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

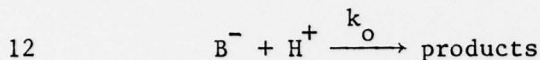
where Z_A , Z_B represent the charges on the reacting ions, and D is the static dielectric constant.

For most cases reported in the literature Eq. 9 was applied to ionic reactions in aqueous solutions. Dainton and coworkers demonstrated, however, that by using LiCl to vary the ionic strength of the solution, Eq. 9 could also be applicable to ionic reactions in methanol (10).

At 298°K the static dielectric constant of methanol is $D = 32.63$ and the constant A calculated from Eq. 10 becomes 1.9. Then Eq. 9 assumes the following form:

$$11 \quad \log k = \log k_o + 3.8Z_A Z_B [\mu^{1/2}/(1 + \mu^{1/2})]$$

Because of the limiting solubility of TNT in neutral water (11), reaction 12 was studied in methanol:



where H^+ represents the acid added before the flash ($4.4 \times 10^{-5} \text{ M H}_2\text{SO}_4$).

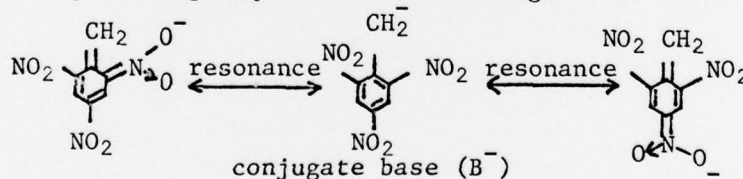
The neutralization reaction 12 was followed by time-resolved absorption spectroscopy at 540 nm where B^- absorbs strongly. The rate constant measured for this reaction was equal to $k_0 = 5.0 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$. Subsequently the rate constant k of reaction 12 was determined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

B. 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, $\tau_{\text{BH}} = 1/k_1 = 0.96 \times 10^{-3} \text{ sec}$; in methanol, $\tau_{\text{B}^-} = 1/k_2 = 0.575 \text{ sec}$) were found to be unaffected by the presence of oxygen.

Their assignment to electronically excited states of TNT can also be excluded because their lifetimes are extremely large as compared with the values reported (12) for the electronically excited states of nitroaromatics, and furthermore, molecular oxygen would be expected to quench excited states (12).

The transient species B^- having an absorption spectrum closely in agreement with that of the 2,4,6-trinitrobenzyl anion (8) and possessing a charge equal to -1, is assigned to the following species:

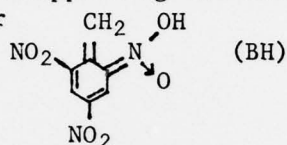


This structure is consistent with the conjugate base participating in the photochromic mechanism of ortho nitro and dinitrotoluenes (13). According to this structure the conjugate base B^- is not paramagnetic and oxygen would not be expected to affect its lifetime as shown to be the case experimentally.

The spectroscopic evidence 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 et al. (13) to explain the photochromic activity of nitrotoluenes.

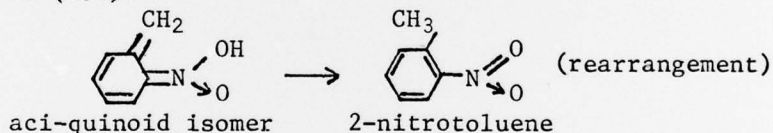
It should be realized, of course, that while the polarity of the solvent is necessary for the stabilization by solvation of the species B^- , the basicity of the solvent is also expected to facilitate the dissociation of BH (13c).

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



is obtained by comparing the absorption spectrum of the species BH (Fig 2, A) with those reported earlier (13) for the aci-quinoid isomer of 2-nitro and 2,4- and 2,6-dinitrotoluenes. 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 460nm.

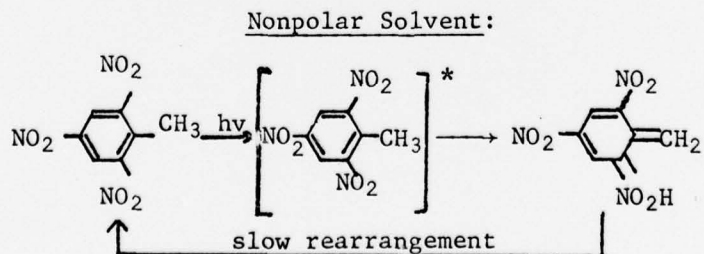
Furthermore, the half-life of BH in cyclohexane $t_{1/2} = 0.69 \times 10^{-3}$ sec is in fair agreement with the half-life $t_{1/2} = 1.1 \times 10^{-3}$ sec for the rearrangement or fading reaction of the aci-quinoid isomer of 2-nitrotoluene (13a):



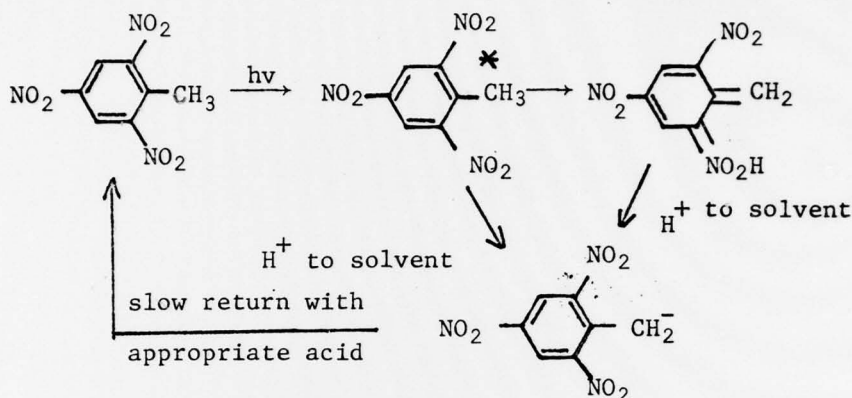
The similarity of the half-lives is not surprising, since the fading reaction represents an intramolecular proton transfer reaction which is not expected to be strongly influenced by the solvent medium.

C. Mechanism of the Photochromic Activity of TNT

Applying closely the mechanism suggested by Wettermark et al. (13) for the photochromism of mono and dinitrotoluenes to the case of TNT, the following mechanism can be proposed:



Polar and/or basic solvent:



SCHEME I

According to Scheme I, 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 nonpolar 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 species BH. Species B^- presumably regenerates TNT through proton abstraction from the solvent. Caldin et al. (14) and Blake et al. (15) have shown that 2,4,6-trinitrobenzyl anion decays in alkaline alcoholic solutions via 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 flash lamps. This implies that the yield of B^- is linearly proportional to the intensity of the excitation light.

D. Modification of Initiation Thresholds of TNT by Chemical Additives

During the course of the present studies it was discovered that TNT can be sensitized to impact and thermal decomposition by additives which form exothermically a charge transfer complex or salt in molten TNT through the initial formation of TNT anion, B^- . Such additives are NaOH, QMB₃ and NaI. These salts were isolated and

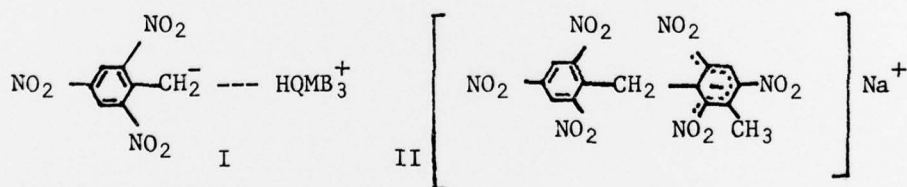
their sensitivity to thermal decomposition and impact were determined and listed in Table 3. Also listed in this table are the thermal and impact sensitivity of the physical mixtures of TNT with 5% W/W NaOH and QMB₃.

Table 3
Thermal and Impact Sensitivity Data

<u>Compound</u>	<u>DSC</u> <u>Exotherm</u> <u>Max. (° C)</u>	<u>* 50% Impact Value (cm)</u>
TNT	330	62 ± 2.59
TNT-QMB ₃ (5%) Phys. Mixt.	152	14.5 ± 1.04
TNT-NaOH Heterog. Mixture	100 (I peak) 151 (II peak)	- -
TNT - 7% NaI Phys. Mixt.	257	-
TNT - NaOH Complex (1:1)	272	50.9 ± 2.70
TNT - QMB ₃ Complex (1:1)	No Exotherm	No initiation up to 200 cm

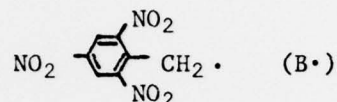
* Picatinny Arsenal unit with Type-12 Tool, sand paper and 2½ kg wt.

Absorption spectroscopic and ESCA studies resulted in the following assignment of the charge transfer complexes of TNT/QMB₃ (I) and TNT/NaOH (II).



Furthermore, it was also discovered that TNT can be sensitized by additives, such as, benzoquinone, , and tetraethyl lead, Pb(C₂H₅)₄.

DSC studies indicate that the exotherm appears at 274°C and 175°C for the mixtures TNT/Benzoquinone and TNT/Tetraethyl lead, respectively. The mechanism of sensitization, in this case, is attributed to the initial formation of the radical,



through hydrogen abstraction. Hydrogen abstraction by the benzoquinone is expected to lead to the semiquinone radical, $\text{HO} \text{---} \text{C}_6\text{H}_4 \text{---} \text{O}\cdot [\text{C}\cdot]$

while in the case of tetraethyl lead, ethane is expected to form since the hydrogen abstraction occurs by the ethyl radicals which are produced thermally from $\text{Pb}(\text{C}_2\text{H}_5)_4$.

Electronic excitation of TNT in the gas phase at 215°C (in the presence of 600mm argon) leads to the formation of a transient species with absorption maxima at 265 and 340 nm and $t_{1/2} = 69$ sec. Oxygen and NO used (at 400mm Hg) instead of argon were found to increase the yield and reduce the lifetime of the transient, $t_{1/2}(\text{NO}) = 14$ and $t_{1/2}(\text{O}_2) = 34$ sec. The increased yield and shorter lifetime of this transient species in the presence of NO and O₂ are consistent with the tentative assignment of this species to the free radical, B \cdot . Both NO and O₂ 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 O₂.

The results concerning the modification of initiation thresholds appear to be very promising, since eventual control of the sensitivity of explosives should contribute towards reducing pre-matures and vulnerability of munitions.

Work is in progress for the formation of the radical, B \cdot , from electronically excited HNBB (hexanitrobibenzyl, B-B) in the gas phase or solid matrices at 77°K. Furthermore, benzoquinone will be electronically excited in the gas phase in presence of TNT. Electronically excited benzoquinone is expected to abstract a hydrogen atom from the methyl group of TNT and yield the radical, B \cdot , and the semiquinone radical, C \cdot , which has absorption maximum at 415 nm.

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