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FLASH PHOTOLYSIS OF 2,4,6-TRINITROTOLUENE SOLUTIONS

K. Suryanarayanan, et al

Picatinny Arsenal
Dover, New Jersey

November 1972

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OF
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K. SURYANARAYANAN
C. CAPELLOS

NOVEMBER 1972

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13. ABSTRACT

Flash photolysis of aerated 2,4,6-trinitrotoluene (TNT) solutions indicates a photochemically induced isomerization leading to the aci-nitro isomer (AH) of TNT with an absorption maximum of 460 nm in nonpolar solvents, or the anion (A^-) of the aci-nitro isomer of TNT, with absorption maxima at 500, 540, and 630 nm in polar liquid media.

The pK of the acid-base equilibrium $AH \rightleftharpoons A^- + H^+$ was measured and found to be equal to -0.93. Both species, AH and A^-, have transient existence, and their identification was based on the detailed spectroscopic and kinetic studies presented here.

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Polar and nonpolar solvents						
Intramolecular proton transfer reaction						
Acid base equilibrium						
Flash photolysis						
Singlet and triplet excited states						
UV and visible light						
Negative ion						

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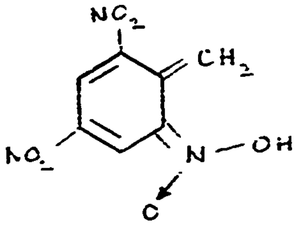
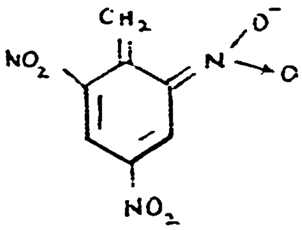
ABSTRACT

Flash photolysis of aerated 2,4,6-trinitrotoluene (TNT) solutions indicates a photochemically induced isomerization leading to the aci-nitro isomer



(AH)

with an absorption maximum of 460 nm in nonpolar solvents, or the anion



(A^-)

of the aci-nitro isomer, with absorption maxima at 500, 540, and 630 nm in polar liquid media.

The pK of the acid-base equilibrium $AH \rightleftharpoons A^- + H^+$ was measured and found to be equal to -0.93. Both species, AH and A^-, have transient existence, and their identification was based on the detailed spectroscopic and kinetic studies presented here.

INTRODUCTION

Photochromism and the necessary molecular structural requirement for this phenomenon has been studied extensively (Ref 1 through 5). Solutions of 2-nitro- and 2,4- as well as 2,6-dinitrotoluenes have been reported to exhibit phototropic activity when exposed to ultraviolet light (Ref 5 through 9). The transient species responsible for the photochromic behavior of these nitroderivatives of toluene have been well characterized by flash photolysis studies (Ref 6 through 9). The mechanism of photochromism in these compounds is due to an intramolecular proton transfer from the methyl group to one of the ortho-nitro groups.

This report presents evidence that TNT also exhibits photochromic behavior induced by electronic excitation resulting in the aci-nitro transient isomer (AH) in nonpolar media, or its conjugate anion (A^-) in polar solvents, respectively.

EXPERIMENTAL

The flash photolysis system used in this work consisted of a Xenon Corporation Model-A high energy photolysing micropulser. Two sets of lamps, one with a flash duration of 25 μsec (C = 10 μf, 500 J delivery at 10 kV), the other one with 50 μsec (C = 20 μf, 1000 J delivery at 10 kV), were used. The lamps were actually charged to a maximum of 8 kV. The analyzing light (1000 W high pressure Xe-Hg lamp) passed through a 11.7 cm cell, a light baffle to reduce scattered light, and eventually into a Bausch and Lomb monochromator; ultimately it was picked up by the photocathode of an Amperex XP 1003 photomultiplier, and the resulting signal was displayed in a Tektronix 564B storage oscilloscope. The absorption spectra of the transient species reported here were obtained by pulsing the solution with a 25 or 50 μsec flash of light and measuring the maximum transient absorption at the end of the flash at preselected wavelengths.

Degassing of the solutions were done by helium flushing in a deaeration flask which was attached to the optical cell. Presaturation of helium with the vapors of the solvent was considered essential in order to avoid concentration changes during the deaeration procedure. The efficiency of degassing by this method had been established earlier (Ref 10).

The TNT anion was produced by reaction of TNT with Na, in vacuo,in tetrahydrofuran (THF). Solution of 1 mM TNT and Na were kept in different arms of the glass vessel during evacuation. Afterwards, they were brought into contact in a controlled fashion to generate the anion.

The solvents used were spectrograde. TNT was purified by successive recrystallizations from ethanol until the gas chromatogram of the sample showed no detectable amounts of impurities. Fisher ACS reagent H_2SO_4 was used. The concentration of TNT in various solutions was $\sim 10^{-3}$M.

In salt effect experiments, the solutions flashed were contained in a cell which was jacketed with a concentrated solution of LiCl to make sure that no direct excitation of LiCl would take place in the experimental solutions.

RESULTS AND DISCUSSION

Spectroscopic Studies

Figure 1 shows the absorption spectrum of the transient species formed in aerated flash photolyzed solutions of TNT in cyclohexane and benzene.

When TNT is flash photolyzed in highly acidic aqueous solutions, a transient species is formed with the same spectral profile (Fig 2) as in Fig 1, but with a blue shifted maximum.

In polar solvents, however, flash photolysis of TNT leads to a different transient with an absorption spectrum shown in Fig 3. This spectrum is identical with the absorption spectrum of the TNT negative ion (Fig 4), formed chemically in THF with Na metal, in vacuo.

The formation and decay of the transient species discussed above are not affected by the presence of molecular oxygen.

Kinetic Studies

Table 1 shows the order and rate constants for the decay of the transient species formed in various solvent media. As indicated by the k values shown in Table 1, the optical transitions shown in Fig 3 originate from the same transient species.

Assignment of Transients and Mechanism

In order to establish whether the transient species formed in flash photolyzed polar solutions of TNT is negatively charged, salt effect experiments were carried out (Fig 5). Because of the extremely low solubility of TNT in water, the experiment was performed in methanol; LiCl was used for varying the ionic strength of the medium (Ref 11).

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

$$\log k = \log k_o + 2A\, Z_A Z_B \,(u^{1/2}/1 + u^{1/2}) \qquad (1)$$

where k is the rate constant at ionic strength u ; k_o is the rate constant at infinite dilution; the constant $A = 1.825 \times 10^6\ (DT)^{-3/2}$ and $Z_A Z_B$ represent the charges on the reacting ions. For methanol at $T = 298^oK$, the static dielectric constant, D, = 32.63. The value of A is calculated to be 1.9. Therefore equation 1 is assuming the following form:

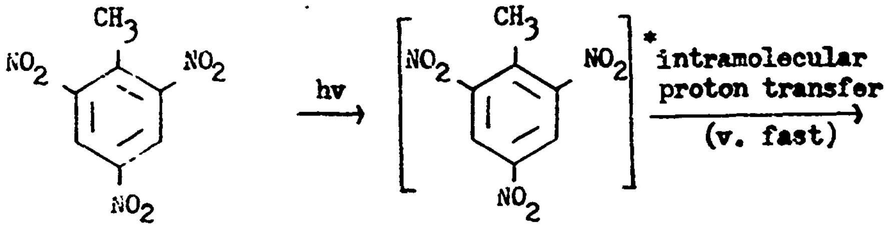
$$\log k = \log k_0 + 3.8\, Z_A Z_B \left(\mu^{1/2}/1 + \mu^{1/2}\right) \qquad (2)$$

Plotting the data according to equation 2, the amount of negative charge of the TNT transient species formed in polar media was found to be equal to -1 (Fig 5).

It should be emphasized at this point that the negative ion of TNT formed photolytically in polar solvents is not produced through a biphotonic process, as indicated by the linear dependence of the $O.D._{initial}$ vs the square of the charging voltage.

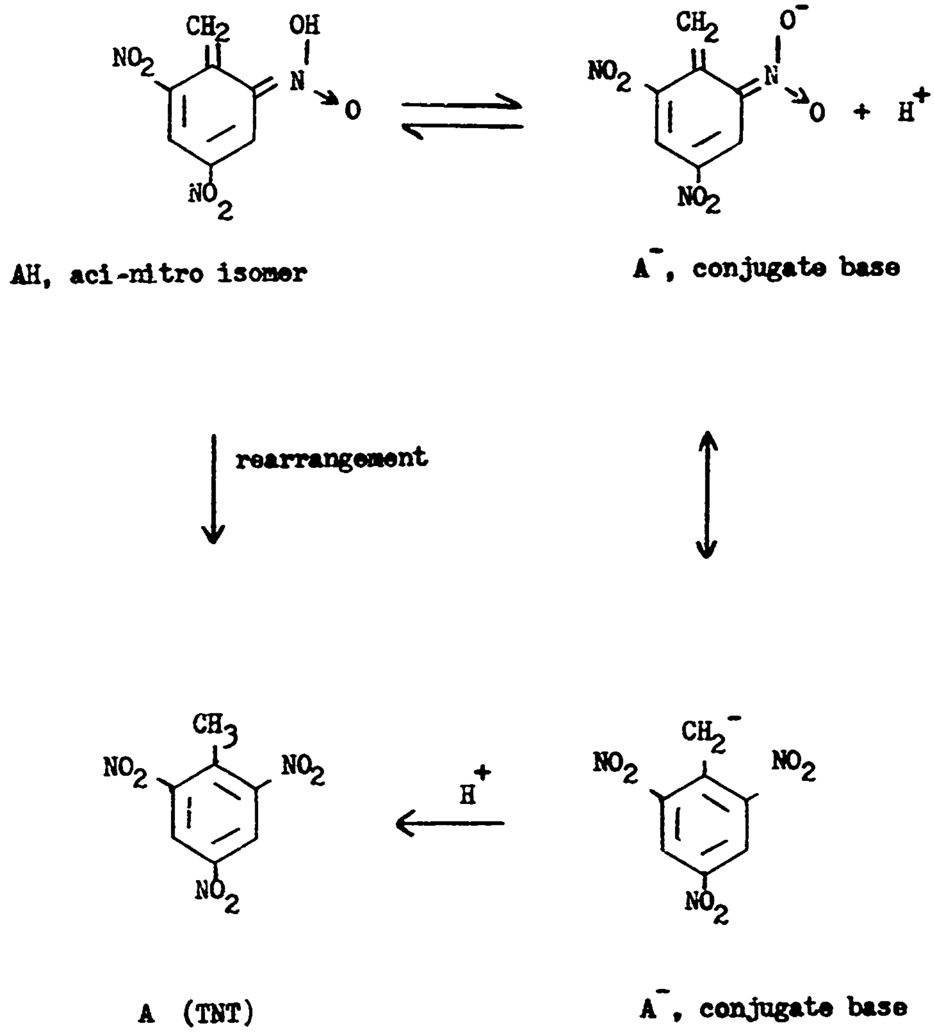
As shown earlier (Ref 5 through 9), ortho-nitrotoluene, 2,4- and 2,6-dinitrotoluenes, exhibit photochromism, which was attributed to an intramolecular proton transfer reaction from the methyl group of their nitro forms to one of the ortho-nitro groups, to yield the aci-nitro isomer which is in equilibrium with their conjugate bases in the proper pH range.

Similar types of reactions could explain the formation of the TNT negative ion and the aci-nitro isomer during the photochemical excitation of TNT as shown by the following reaction scheme:



A
(TNT)

A*, singlet or
triplet excited
state


AH, aci-nitro isomer
A⁻, conjugate base
rearrangement
H⁺
A (TNT)
A⁻, conjugate base

This reaction scheme can be written in the following simplified form

$$A \xrightarrow{h\nu} A^* \longrightarrow AH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^- + H^+ \qquad (3)$$

$$A^- + H^+ \xrightarrow{k_4} A \qquad (4)$$

$$AH \xrightarrow[\text{Rearrangement}]{k_5} A \qquad (5)$$

Species AH is formed in the flash photolysis of TNT in hydrocarbons (Fig 1) or in highly acidic media (Fig 2), in the pH region shown in Fig 6. The observed blue shift of the maximum absorption of the aci-nitro form (AH), with increasing polarity of the solvent (hydrocarbon → acidic aqueous solutions) indicates that this is probably an $n \rightarrow \pi^*$ transition. A shift of this magnitude is not unusual for this type of transition (Ref 12). Adding acetonitrile in solutions of TNT in benzene changes the nature of the transient species from the aci-nitro isomer (AH) in pure benzene to its conjugate base (A^-) in mixtures of benzene and acetonitrile (Fig 7).

The pK for the acid-base equilibrium $AH \rightleftharpoons A^- + H^+$ was obtained by measuring the initial yield of the aci-nitro form (AH), generated by the flash, as a function of pH (Fig 6). This value was found to be equal to -0.93.

As shown in Fig 6, the yield of the AH form starts decreasing at concentrations of H_2SO_4 equal to or higher than 14M (pH = -1.14). Absorption spectra of TNT solutions indicate that this decrease is not due to protonation of the ground state TNT. It probably can be attributed to protonation of electronically excited TNT, which is not expected to lead to the formation of the aci-nitro form (AH).

Figure 8 shows the effect of pH on the lifetime of AH. At 12M H_2SO_4 (pH = -1.08) the rate constant for the decay of AH is equal to 0.37×10^3 sec^{-1}. This value probably is equal to the rate constant for fading (reaction 5). Increasing the pH results in shortening the lifetime of AH. This effect could be explained by assuming that in this pH region AH is, through reaction 3, converted to A^-, which reacts very rapidly to regenerate A. Using the experimentally determined rate constant $K = 5 \times 10^6$ $M^{-1}sec^{-1}$ (in methanol) for the reaction $A^- + H^+ \rightarrow$ products, the half-life of A^- at 6M H_2SO_4 is calculated to be 23 nanoseconds, which is well below the time resolution of the flash photolysis equipment used for the present work.

Observation of A^- in neutral aqueous solutions was not possible because although TNT is soluble in highly acidic aqueous solutions (Ref 13), it has an extremely low solubility in neutral aqueous solutions.

The pK values for the acid-base equilibrium, $AH \rightleftharpoons A^- + H^+$ in the case of 2-nitrotoluene and 2,4- as well as 2,6-dinitrotoluenes have been reported to be 3.7 (Ref 8), 1.1 (Ref 7), and 1.8 (Ref 9), respectively. These pK values, compared with the corresponding pK for TNT determined in this work, demonstrate clearly that the acid strength of the aci -nitro isomer increases with the increasing number of nitro groups.

CONCLUSION

Flash photolysis of TNT solutions in the microsecond range indicates a photochemically induced isomerization which involves an intramolecular proton transfer from the methyl group to one of its ortho-nitrogroups. It is demonstrated in the present work that the photochemically induced isomerization can lead to ionization of TNT in polar media.

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TABLE 1

Transient kinetics of flash photolyzed TNT

Solvent	Reaction Studied			Wavelength at which the decay of AH or A^- was studied(nm)
	$AH \xrightarrow{R} A$ k, sec^{-1}	$A^- + Solvent \rightarrow P$ pseudo first order k, sec^{-1}	$A^- + H^+ \rightarrow P'$ k, M^{-1} sec^{-1}	
Methanol (aerated)		1.61		500
"		1.86		540
"		1.74		630
Methanol (aerated) + 4.4×10^{-5}M H_2SO_4			5.0×10^6	
Acetonitrile (aerated)		0.44		500
i-PrOH (aerated)+ 1.83×10^{-5}M H_2SO_4			4.6×10^7	
Cyclohexane (aerated)	1.04×10^3			445
Water containing 12M H_2SO_4 (aerated)	0.37×10^3			420

NOTE:
R : Rearrangement
P and P': Products

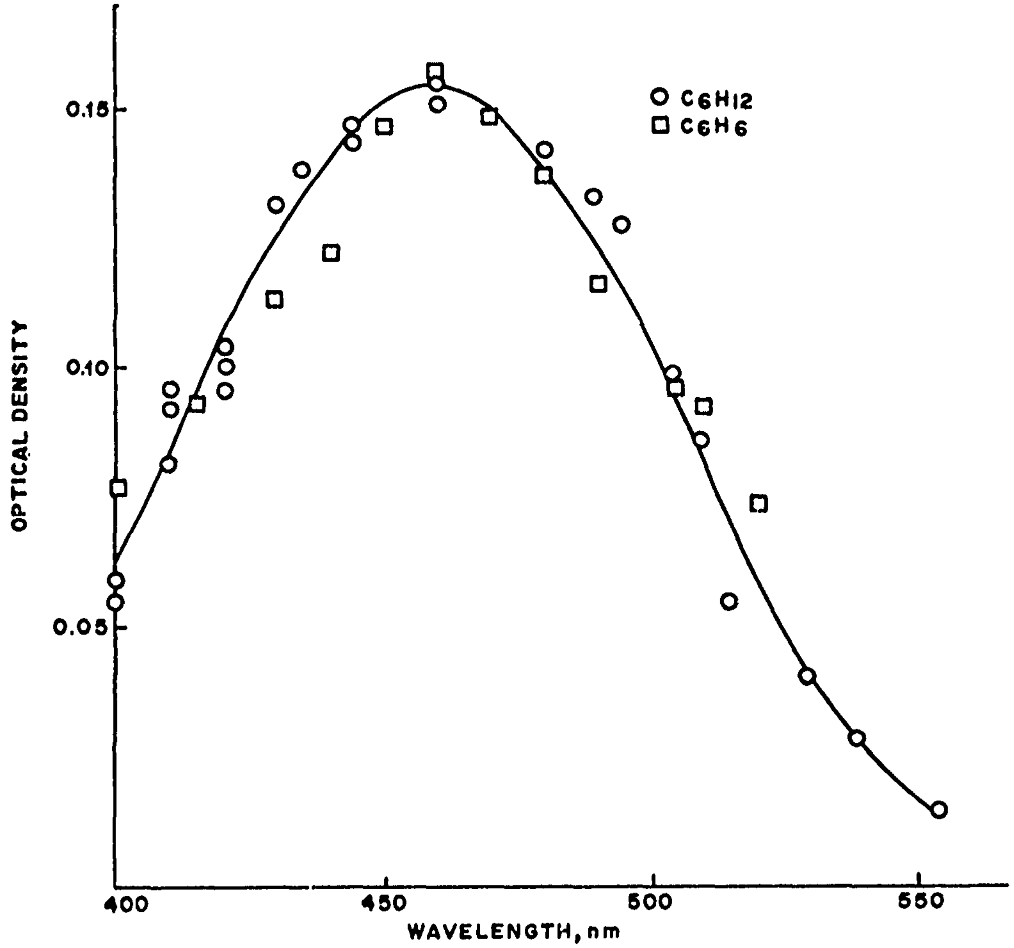


Fig 1 Absorption spectrum of the transient species formed in aerated flash photolyzed solution of 10^{-3}M TNT in cyclohexane (o) and benzene (□)

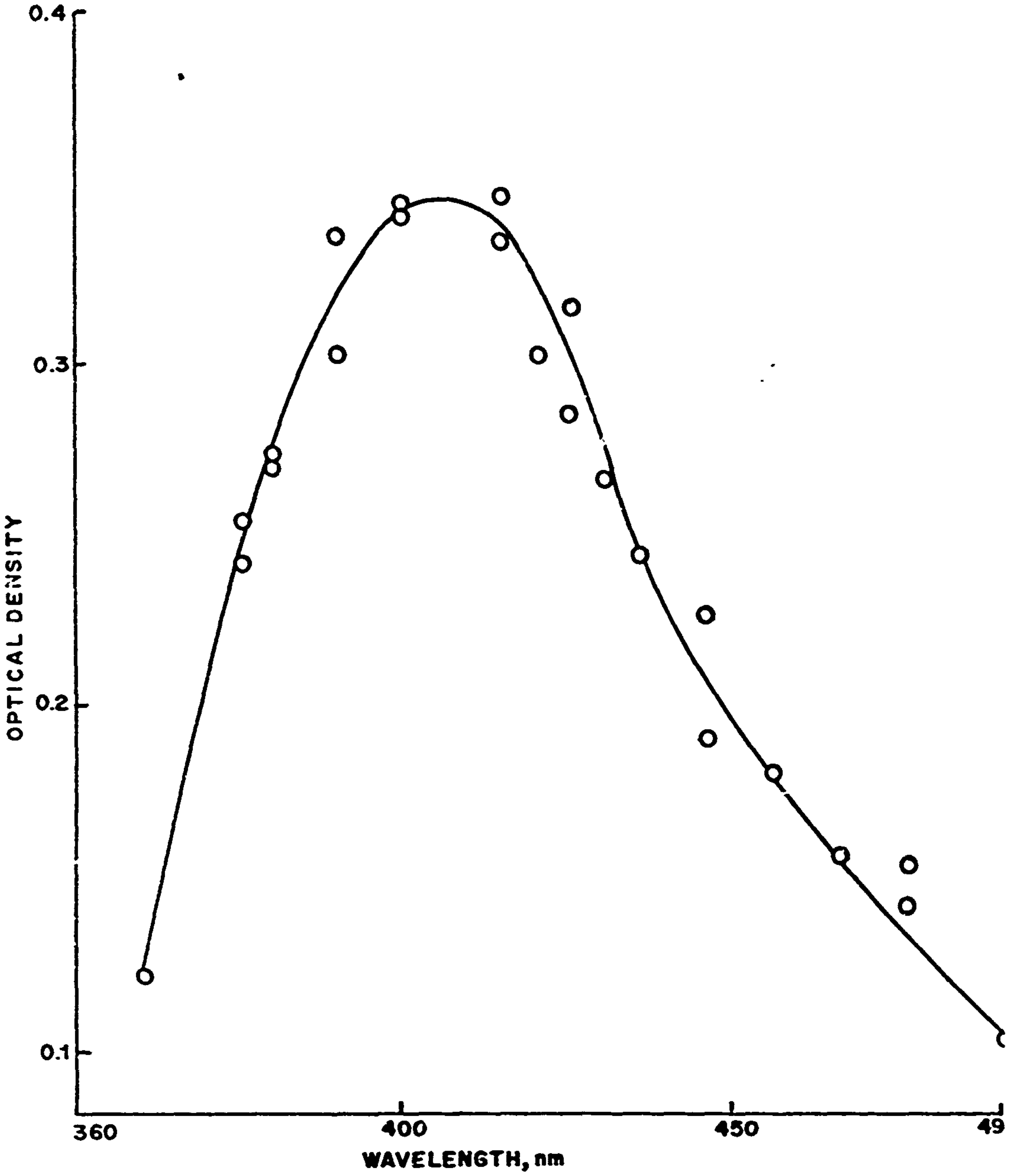


Fig 2 Absorption spectrum of the transient species formed in aerated flash photolyzed solutions of TNT in water containing 12M H_2SO_4

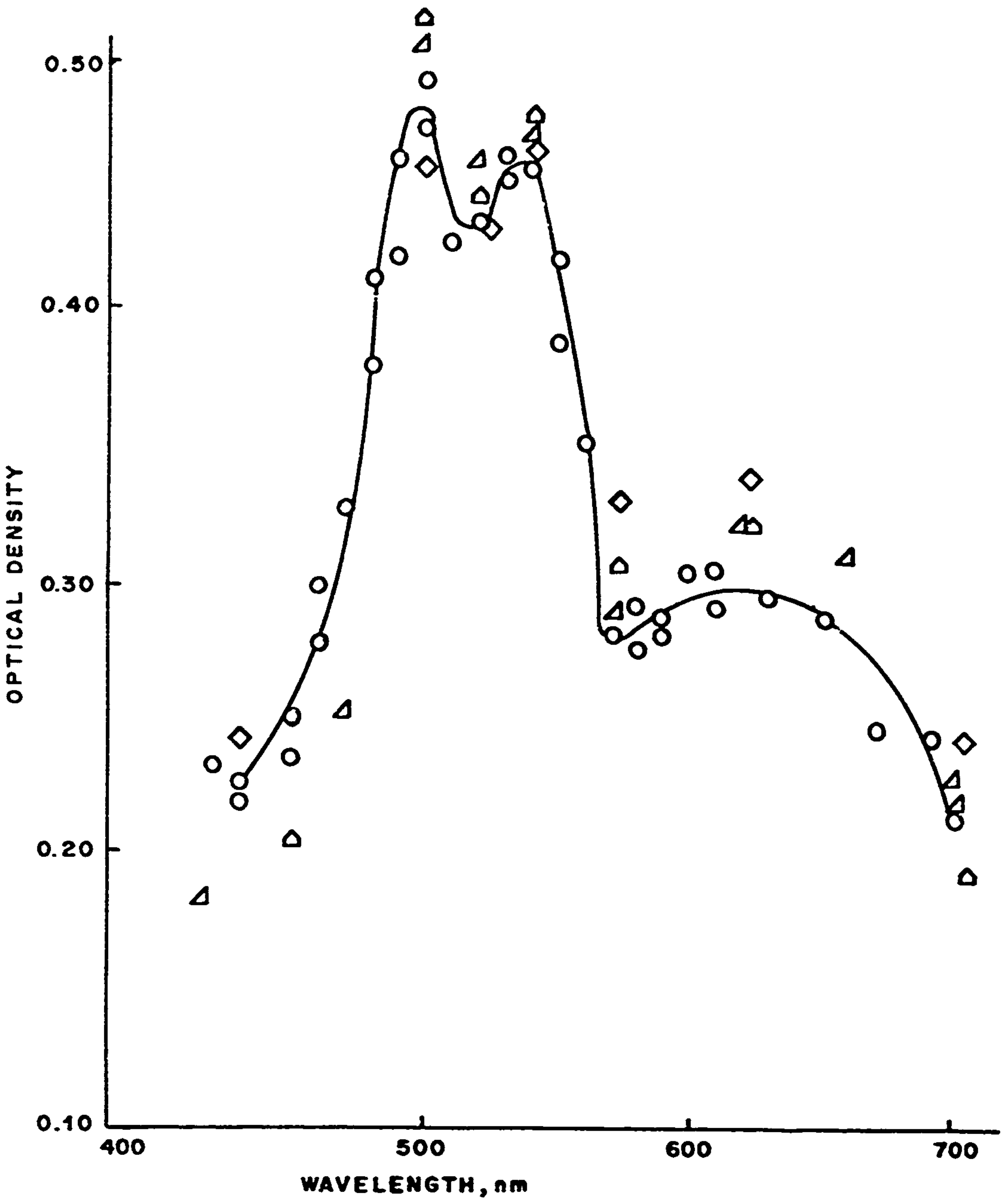


Fig 3 Absorption spectrum of the transient species formed in aerated flash photolyzed solutions of TNT in polar solvents: (o) methanol, (⊿) acetonitrile, (◇) methanol with 4.4 x 10^{-5}M H_2SO_4 and 235 mM LiCl, and (△) isopropyl alcohol with 1.83 x 10^{-5}M H_2SO_4 and 45 mM LiCl

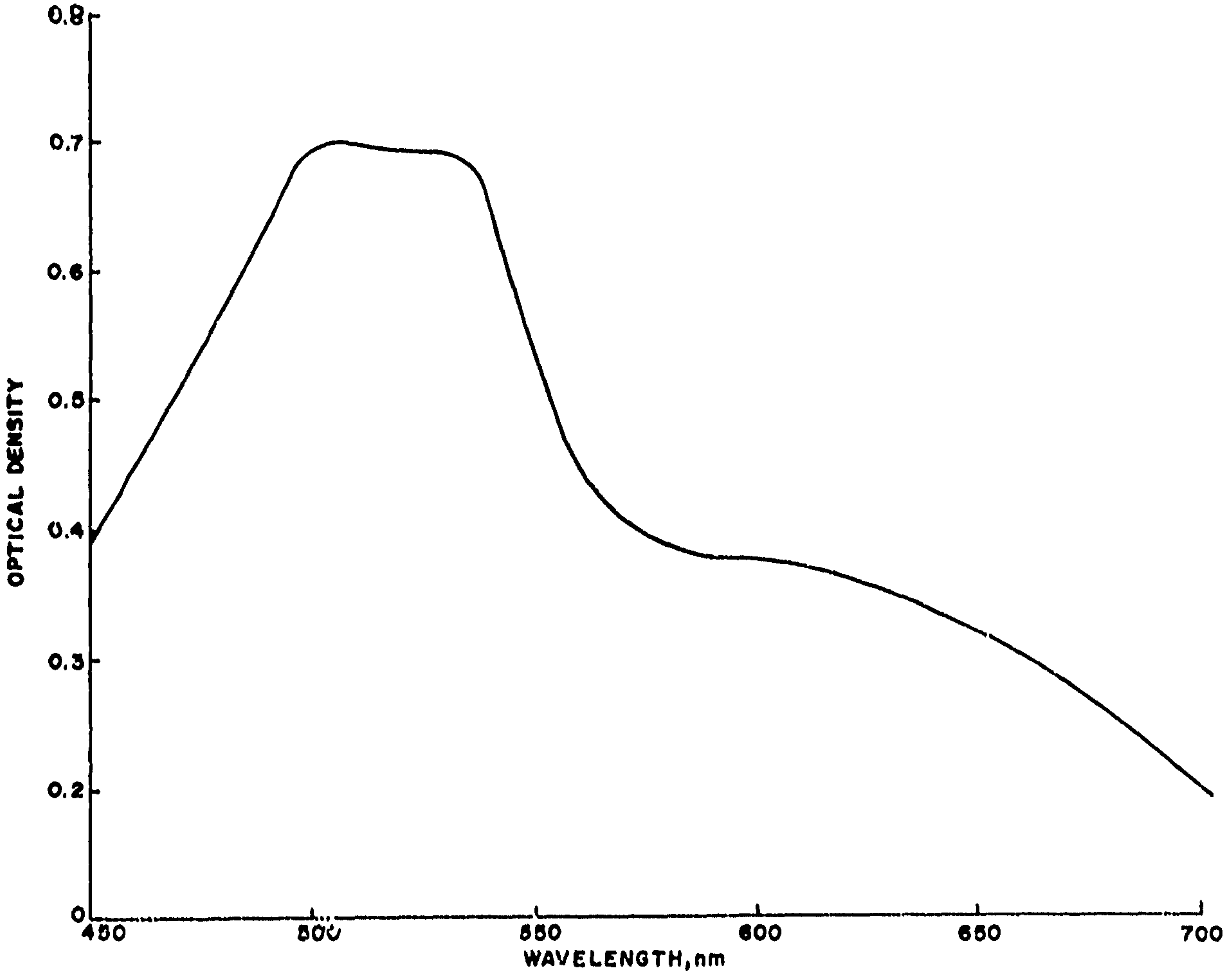
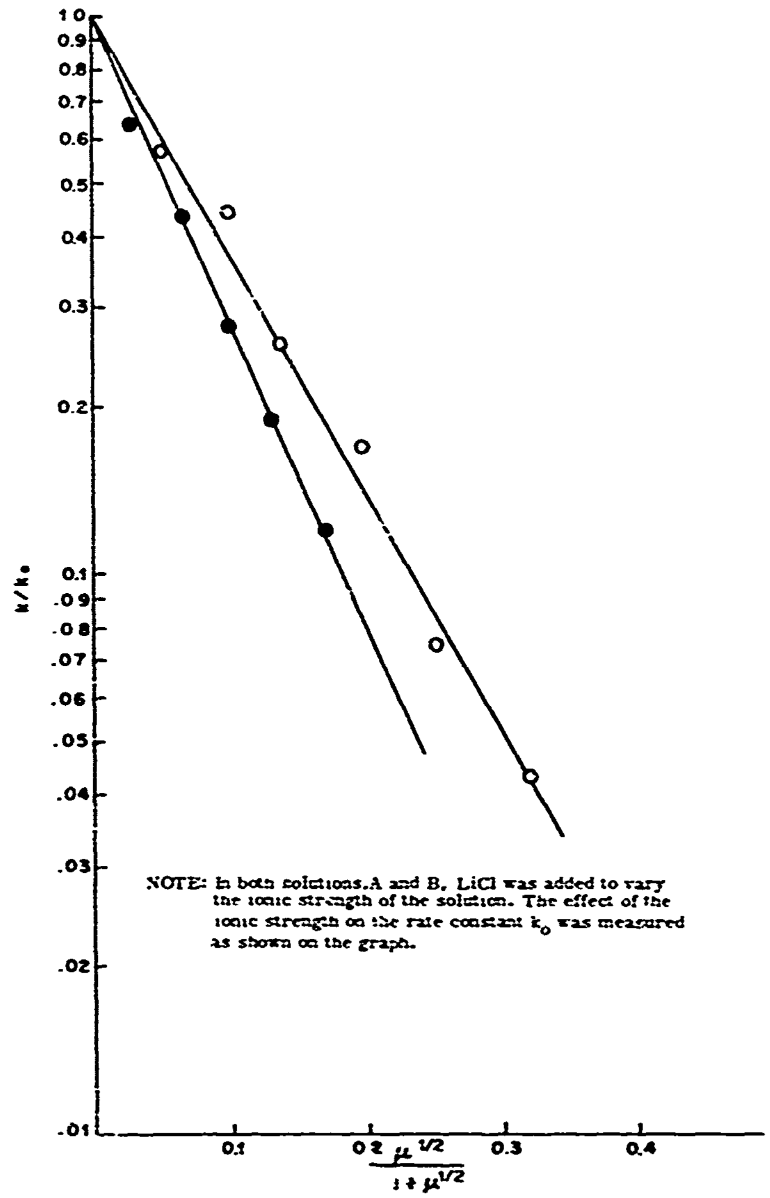


Fig 4 Absorption spectrum of the negative ion of TNT (TNT^-) formed chemically by reducing TNT with Na in deaerated THF



NOTE: In both solutions A and B, LiCl was added to vary the ionic strength of the solution. The effect of the ionic strength on the rate constant k_o was measured as shown on the graph.

Fig 5 Effect of ionic strength on the rate constant of the reaction, $TNT^- + H^+ \xrightarrow{k_o}$ products; (○) 1 mM TNT in methanol containing 4.4×10^{-5}M H_2SO_4; k_o determined in this solution was equal to 5.0×10^6 M^{-1} sec^{-1} (●) 1mM TNT in isopropyl alcohol containing 1.83×10^{-5}M H_2SO_4; k_o determined in this case was equal to 4.6×10^7 M^{-1} sec^{-1}

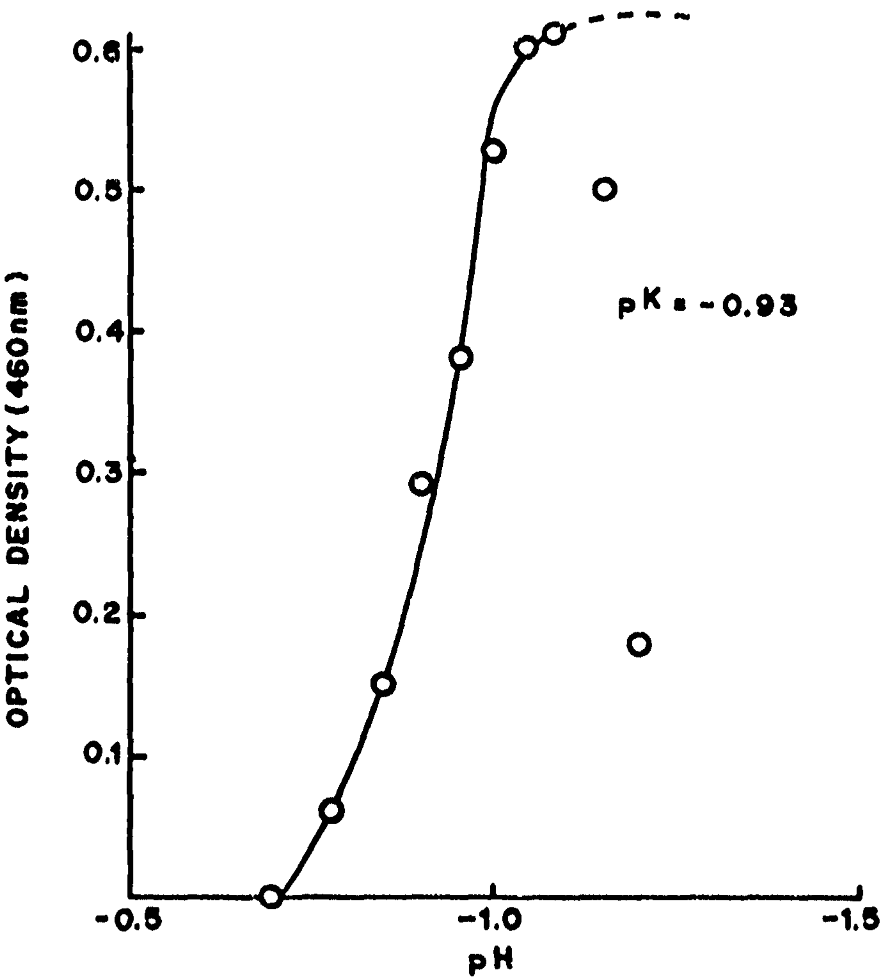


Fig 6 Initial absorption (O.D.$_{460\ nm}$) of the transient species formed in flash photolyzed solutions of TNT in water as a function of PH. The pK value determined from this plot was equal to -0.93

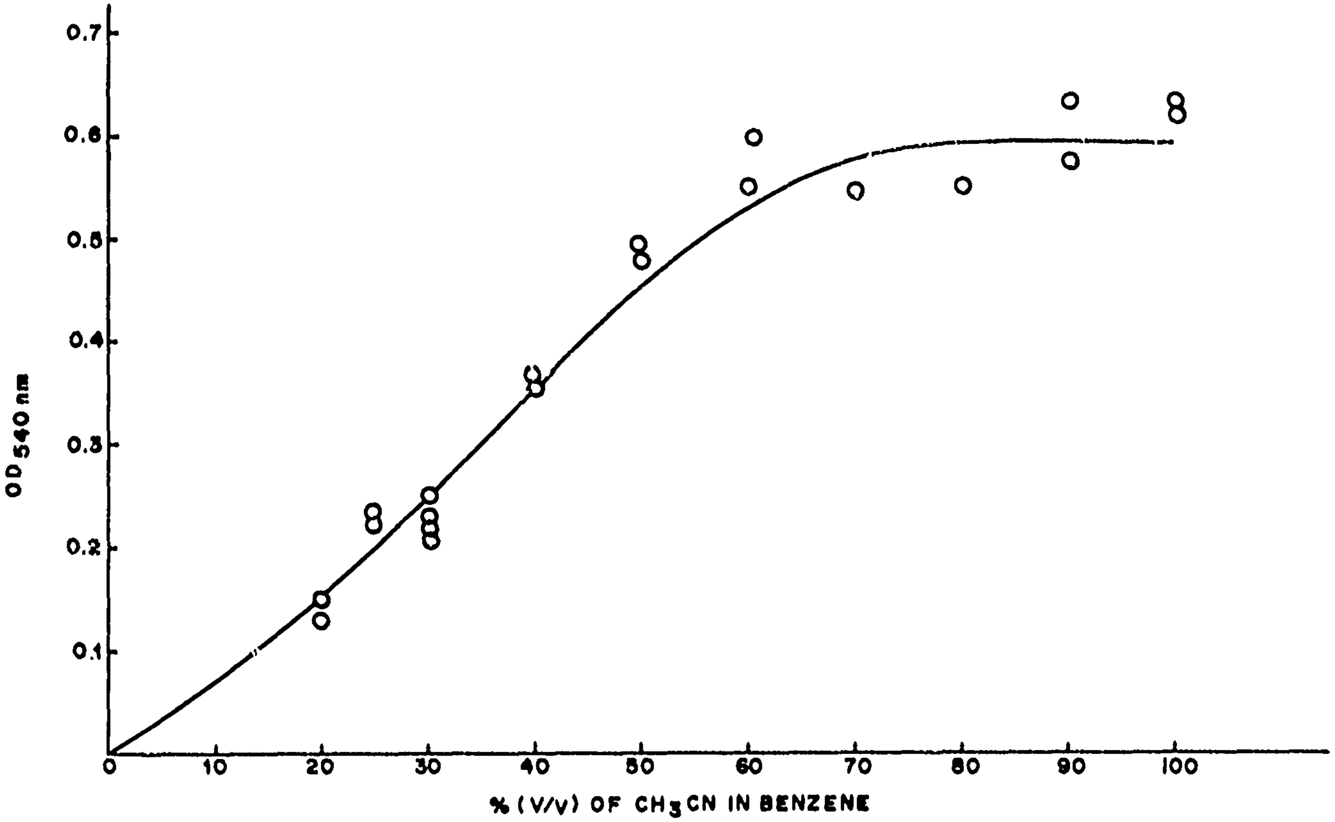


Fig 7 Formation of TNT$^-$ (determined by monitoring O.D.$_{\text{initial (540 nm)}}$) in flash photolysis of aerated solutions of TNT in benzene containing increasing amounts of acetonitrile

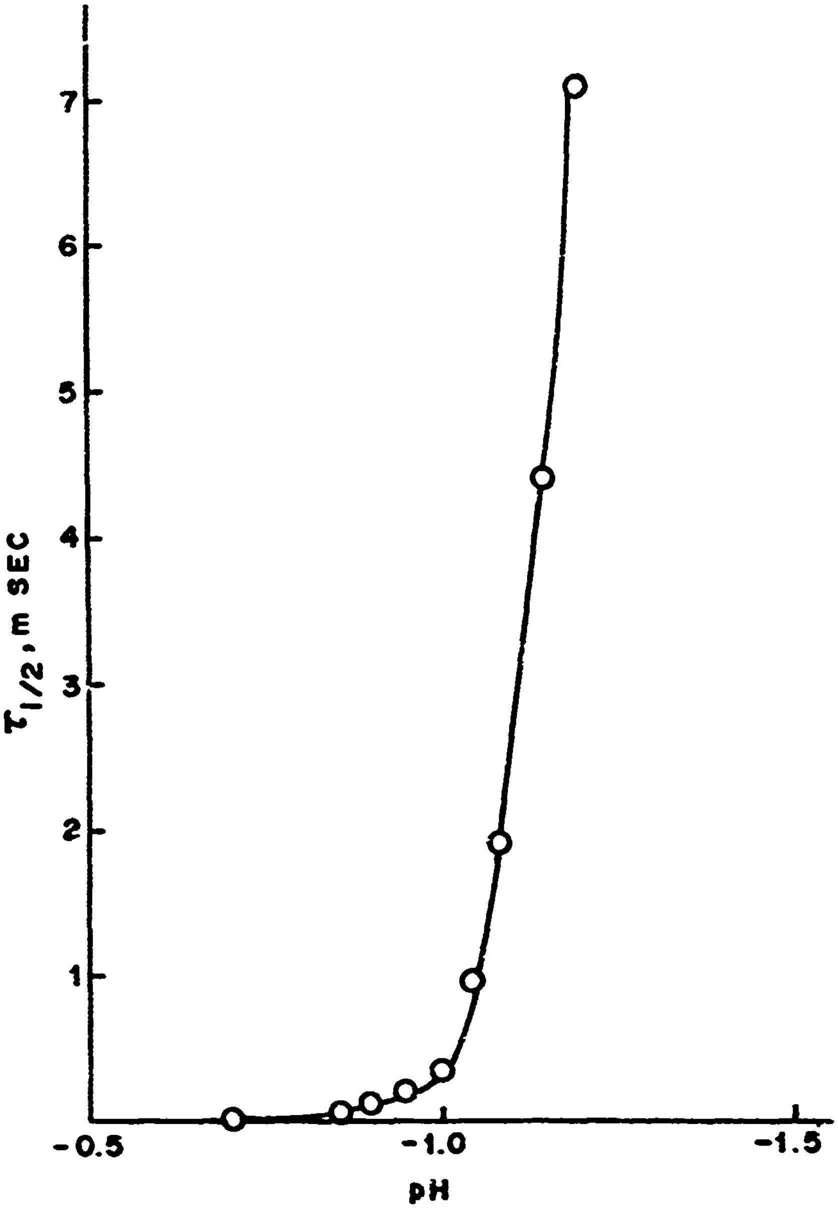


Fig 8 Effect of pH on the half-life of the transient species formed in flash photolyzed aerated solutions of TNT in acidic aqueous solutions