Photochemical Decomposition of 2,4,6-Trinitrotoluene and Related Compounds in Ethers†

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(Received: March 19, 1981; In Final Form: July 14, 1981)

Photochemical and thermochemical decomposition has long been a crucial problem in transport and storage of propellants and explosives. This EPR investigation of the photochemical decomposition of 2,4,6-trinitrotoluene (TNT) and related compounds in ethers was designed to identify radicals produced in the initial phases and compare them with those produced in neat photochemical and thermochemical decomposition. Three radical types from nitroaromatic species have been identified: the radical anion, the hydrogen-acceptor radical, and the solvent-adduct radical. These observations support a mechanism advanced by Cowley and Sutcliffe for photochemical decomposition of nitrobenzene and chlorinated nitrobenzenes in ethers for TNT and related compounds. The radicals identified in this paper from the photochemical decomposition of TNT in ether solvents match neither spectra produced from thermoochemical decomposition of neat TNT nor spectra produced from photochemical decomposition of neat TNT.

Introduction

Photochemical and thermochemical decomposition of explosives and propellants has long been of interest to the scientific and military community. Determination of the mechanisms of these decompositions and identification of intermediates is crucial to providing methods to slow or eliminate these processes.

This paper will focus on the initial phases of photochemical decomposition of 2,4,6-trinitrotoluene (TNT) and related nitroaromatics in ethers. Our study was initiated to aid in identification of radicals which are produced during irradiation and thermolysis of TNT.

The literature contains many studies of photochemical decomposition of nitroaromatics in solution. Two specific kinds of solvents can be identified: those with hydrogen atoms which apparently are abstractable by excited nitroaromatics such as ethers or alcohols,13,14 and those which apparently are inert during at least the early phases of the photochemical reaction.15-24 Lagercrantz and Yhland25 and Ward26 were the first to use electron paramagnetic resonance (EPR) to observe production of radicals from photochemical reaction of nitrobenzene in ethers. Ward's interpretation of the spectra was later corrected by Cowley and Sutcliffe,27 and Janzen and Gerloch.28 Wang and Wan further investigated nitroaromatic photochemical decomposition in ethers.29 Suryanarayanan and Capello30 did extensive studies on photochemical decomposition of TNT and other compounds in apparently inert solvents such as benzene and acetonitrile.

There have also been many studies of radicals produced from nitroaromatics by electrochemical and chemical means. EPR parameters have been reported for radicals produced from nitrobenzene,23,27 the dihydrobenzenes,23,30 the nitrobenzenes,31,32 the dinitrotoluenes,33 TNT,34 and s-trinitrotoluene.5-36 Most of the radicals produced in these systems have been the radical anions of the parent species, although other types of radicals have been observed. Two important aspects of the earlier work are pertinent to our study: (1) the large solvent dependence of the EPR parameters for the radical anions;5 (2) the presence in some solvent systems of only one large nitrogen coupling for the radical anion of molecules such as s-trinitrobenzene which appears to have more than one

†A preliminary report of this work was presented at the 197th National Meeting of the American Chemical Society, Houston, TX, March 1980.

equivalent nitrogen.\textsuperscript{35,37}

Our work described here extends that previously reported by others in two ways. (1) We have produced and identified radicals from TNT photochemical decomposition which have not been previously reported. (2) We have provided evidence that the photochemical decomposition mechanism of nitrobenzene and chloronitrobenzenes proposed by Cowley and Sutcliffe\textsuperscript{10} is valid for TNT and for related systems as well.

Experimental Section

All compounds except the class 1 explosives were obtained commercially and used without further purification if no EPR signal was observed before irradiation. In cases where a signal was observed in unirradiated samples, the compounds were purified by recrystallization. Trinitrobenzene was provided by R. N. Rogers of the Los Alamos Scientific Laboratory. Trinitrotoluene\textsuperscript{42} and methyl-deuterated trinitrotoluene\textsuperscript{46} were prepared by using previously reported procedures.

Dioxane (reagent grade) was passed through an activated silica-gel column to remove any impurities. Other ether solvents were reagent grade and were used without further purification. The pure solvents produced no EPR signals when irradiated in the same manner as the nitroaromatic samples.

All EPR spectra were obtained with a Varian E109 spectrometer operated in first-derivative mode with a field-frequency lock accessory controlling the magnetic field. A TE102 rectangular cavity fitted with a light transmitting grid was used. All samples were 0.30 mL and were contained in 3-mm cylindrical quartz EPR tubes. All spectra were obtained at 0.2-G modulation amplitude, a modulation frequency of 100 kHz, and an incident microwave power of 6 mW. The field-frequency lock accessory was operated in the locked mode in conjunction with a Hewlett-Packard electronic counter 5245M and frequency counter 5266A to compare the signal from the accessory's internal solid DPPH standard to that from solid DPPH placed directly in the sample cavity. The observed magnetic field offset between these two DPPH signals was then used to compare the magnetic field for the center of sample EPR spectra to the field for solid DPPH. Sample g factors were then calculated, assuming a g factor of 2.0036 for DPPH.

Samples were irradiated with an Oriel 1000-W Hg(Xe) high-pressure arc source. Narrow band-pass filters with maximum transmission wavelengths of 200, 250, 300, and 350 nm were used in some experiments to determine which wavelengths were most effective in causing the photochemical decomposition. The lamp was located 37 cm from the sample cavity and the light was collimated on the cavity.

The Varian variable temperature controller maintained a sample temperature of 25.0 ± 0.5 °C during irradiation. The sample temperature was set by placing a thermocouple attached to a Doric Tendricator at the sample location with the arc source on. All experiments were performed with a sample concentration of 0.10 M. Unfiltered light from the arc source was used except for specific experiments designed to study wavelength effects. Samples were irradiated until the initial radical produced had started to decay. Spectra were irradiated until the initial radical produced had started to decay. Spectra were taken every few minutes during this time and for a few minutes after the irradiation had ceased. One experiment made with a degassed sample of TNT in dioxane showed no apparent difference from the nondegassed experiments.

Spectral simulations were carried out with a Fortran program kindly provided by Dr. Ira B. Goldberg of Rockwell International. The program is capable of simulating multiple radicals and a large number of hyperfine couplings for each radical. Parameters used in the simulations were first measured from the experimental spectra and then modified to give the best overall spectral fit between the simulated and observed spectra. It should be pointed out that, while many of the reported coupling constants for different hydrogens in a molecule are identical, they could be varied by up to 0.2 G and still obtain a good fit with the experimental spectrum.

Results

Several different radical species are produced from photochemical and thermochemical decomposition of TNT. Figure 1 shows spectra of the initial radicals observed in three photolyses and a thermochemical experiment.\textsuperscript{39} In each case, other radical species are formed as these radicals disappear. Figures 2 and 3 show the time evolution (all on the same intensity scale) of the TNT radicals produced during and after irradiation at 25 °C in
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Figure 2. Photolysis of TNT in dioxane. EPR spectra were taken before (A), during (B–E), and immediately after (F) irradiation with a xenon lamp. All spectra were recorded at a 90-s sweep rate and are all of the same relative intensities.

Figure 3. Photolysis of TNT in diethyl ether. EPR spectra were taken before (A) and during (B–E) irradiation with a xenon lamp. Spectra were taken as described in Figure 2.

dioxane and diethyl ether, respectively. It is clear that the two initial spectra are different, although the spectrum at 25 min in diethyl ether looks similar to the initial spectrum in dioxane, especially in the wings. The initial spectrum in dioxane and the 25-min spectrum in diethyl ether can be best simulated as the radical anion of TNT. This simulated spectrum is compared with the experimental spectrum for the initial radical in dioxane in Figure 4, where a good fit is obtained. Table I lists the hyperfine splitting constants and g values for TNT radical anions observed in a variety of ethers. In all solvents except diethyl ether, the radical anion is observed as the first radical present. The similarity of the EPR parameters suggests that the species are the same in each solvent. The hyperfine splitting constants are somewhat different from those of related radical anions produced electrochemically, however, a substantial solvent dependence for these species has been noted by others.

The initial radical observed in diethyl ether is best simulated by a species which has one extra hydrogen coupling of the same magnitude as the other five hydrogens in the molecule. The comparison between the observed spectrum and a simulation for this species is given in Figure 5. Coupling constants and number of equivalent nuclei were determined to be $a_{1N} = 15.4$ G and $a_{1H} = 2.3$ G. The g value was measured to be 2.0051. This radical has been tentatively identified as the radical formed by a hydrogen-atom transfer from the solvent to the nitro group of the nitroaromatics. The larger nitrogen coupling and the smaller hydrogen couplings as compared with the radical anion indicate that it is a different species from those seen in other ethers. In addition, the extra hydrogen coupling of 2.3 G is of the correct magnitude to be a hydrogen attached directly to a nitro-group oxygen.

The spectra of several other nitroaromatics showed that the radical anions were generated during photolysis. Table II gives coupling constants and g values for these species. The radical anions of all of the multinitro species show only one large nitrogen coupling in each case. This has been observed previously and is an ion-pairing effect with the cation in the system. The other nitrogens in these systems generally have coupling constants of less than 0.3 G when

TABLE I: EPR Parameters from Photolysis of TNT in Ethers

<table>
<thead>
<tr>
<th>solvent</th>
<th>$a_{1N}$</th>
<th>$a_{1H}$</th>
<th>$a_{CH_2}$</th>
<th>g</th>
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<tbody>
<tr>
<td>dioxane</td>
<td>14.2</td>
<td>3.2</td>
<td>3.2</td>
<td>2.0050</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>13.6</td>
<td>3.2</td>
<td>3.2</td>
<td>2.0051</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>13.7</td>
<td>3.2</td>
<td>3.2</td>
<td>2.0050</td>
</tr>
<tr>
<td>glyme</td>
<td>14.2</td>
<td>3.2</td>
<td>3.2</td>
<td>2.0045</td>
</tr>
<tr>
<td>diglyme</td>
<td>14.2</td>
<td>3.2</td>
<td>3.2</td>
<td>2.0050</td>
</tr>
<tr>
<td>oxepane</td>
<td>13.6</td>
<td>3.3</td>
<td>3.3</td>
<td>2.0052</td>
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</tbody>
</table>
### Table II: EPR Parameters from Photolyses in Dioxane

<table>
<thead>
<tr>
<th>compd</th>
<th>$\alpha_N$</th>
<th>$\alpha_o$</th>
<th>$\alpha_m$</th>
<th>$\alpha_p$</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>picryl chloride</td>
<td>13.6</td>
<td>3.1 (2)</td>
<td></td>
<td></td>
<td>2.0047</td>
</tr>
<tr>
<td>m-dinitrobenzene</td>
<td>15.0</td>
<td>3.0 (2)</td>
<td>1.0</td>
<td>3.0</td>
<td>2.0047</td>
</tr>
<tr>
<td>s-trinitrobenzene</td>
<td>14.1</td>
<td>3.1 (2)</td>
<td></td>
<td>3.1</td>
<td>2.0047</td>
</tr>
<tr>
<td>2,4-dinitrotoluene</td>
<td>15.3</td>
<td>3.3 (2)</td>
<td>1.1</td>
<td>3.3 (3)$^b$</td>
<td>2.0046</td>
</tr>
<tr>
<td>methyl-deuterated TNT</td>
<td>14.2</td>
<td>3.0 (2)</td>
<td></td>
<td></td>
<td>2.0047</td>
</tr>
</tbody>
</table>

$^a$ Ortho, meta, and para notations refer to positions relative to the dominant N coupling. Numbers in parentheses refer to the number of couplings when greater than one. $^b$ Methyl-group hydrogens.

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**Figure 5.** The radical produced early in the photolysis of TNT in diethyl ether. The observed spectrum was recorded after 20-min continuous exposure with a mercury-xenon lamp. The simulation is for the neutral radical produced by transfer of a hydrogen atom from the solvent to the 4-nitro group of TNT.

**Figure 6.** The radical produced early in the photolysis of picryl chloride in dioxane. The observed spectrum was recorded after 2.7-min exposure. The simulation is for the radical anion of picryl chloride.

The nitrogen couplings are inequivalent.$^{35,37}$ These small nitrogen couplings were not observed in this work. Figures 6 and 7 show simulated and experimental spectra for picryl chloride and s-trinitrobenzene photolysis. Simulations were also attempted with more than one nitrogen coupling. In every case simulations based on only one observable nitrogen coupling provided the best match to experimental spectra. All of the radical anion spectra displayed apparently equivalent hydrogen couplings for all ring positions that are either ortho or para to the dominant N coupling. In addition, the methyl hydrogens produced couplings apparently equivalent to the ortho and para hydrogens. Only meta hydrogens (in molecules which have them) gave couplings substantially different from the other hydrogens. Longer photolysis of picryl chloride produced a spectrum which can be simulated as a species formed by loss of a chloride ion from the original radical anion. A
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Figure 9. The radical produced early in the photolysis of nitrobenzene in dioxane. The observed spectrum was recorded after 2.4 min. The simulation is for the radical produced by solvent addition to nitrobenzene, resulting in a 0.32-G proton splitting in addition to the original five protons in the molecule.

TABLE III: EPR Parameters from Photoysis Solvent-Adduct Radicals in Dioxane

<table>
<thead>
<tr>
<th>compd</th>
<th>(a_{1N})</th>
<th>(a_{2N})</th>
<th>(a_{m})</th>
<th>(a_{P})</th>
<th>(a_{R})</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrobenzene</td>
<td>15.9</td>
<td>3.0</td>
<td>(2)</td>
<td>1.0</td>
<td>(2)</td>
<td>3.0</td>
</tr>
<tr>
<td>(\rho)-nitrotoluene</td>
<td>16.3</td>
<td>3.1</td>
<td>(2)</td>
<td>1.0</td>
<td>(2)</td>
<td>3.1 (3)</td>
</tr>
</tbody>
</table>

Comparison of the simulated and experimental spectra for this later radical is given in Figure 8. The coupling constants were measured to be \(a_{1N} = 9.0\) G, \(a_{2N} = 2.9\) G, and \(a_{M} = 0.6\) G. The measured \(g\) value was 2.0061.

In several cases, the initial spectrum could be ascribed to a species which contained a very small hydrogen coupling in addition to the other couplings in the molecule. This case in most readily observed for nitrobenzene, and its simulated vs. experimental spectra are given in Figure 9. Table III displays EPR parameters for radicals of this type, which have previously been identified as solvent-adduct radicals to the nitro group of the nitroaromatic. Studies done with deuterated solvents confirmed the involvement of the solvent species in this radical. The small additional hydrogen coupling is caused by the \(\beta\) hydrogen on the solvent part of the species.

Photolyses of TNT in dioxane using a series of band-pass filters confirmed the conclusion of other workers that the nitroaromatic species was absorbing the light as opposed to the solvent. The 250-nm band produced the greatest photodecomposition rate, and this wavelength is very close to the first absorption maximum of TNT.

**Discussion**

Observations of the radical anion (I), the hydrogen-adduct radical (II), and the solvent-adduct radical (III) during irradiation of the nitroaromatics in this study in ether solvents are consistent with the mechanism proposed by Cowley and Sutcliffe for photochemical decomposition of nitrobenzene and chloronitrobenzenes:

\[
\begin{align*}
\text{light} & \quad \text{ArNO}_2 \rightarrow \text{ArNO}_2^* \\
\text{ArNO}_2^* + \text{RH} & \rightarrow \text{ArNO}_2\text{H} + \text{R}^* \\
\text{ArNO}_2 + \text{R} & \rightarrow [\text{ArNO}_2^* \cdot \text{R}^*] \\
[\text{ArNO}_2^* \cdot \text{R}^*] & \rightarrow \text{ArNO}_2^- + \text{R}^+ \\
[\text{ArNO}_2^- \cdot \text{R}^+] & \rightarrow \text{ArN(O)R} \\
\end{align*}
\]

Step 1 summarizes light absorption by the nitroaromatic followed by intersystem crossing to the lowest triplet state \(T_1\). The nature of \(T_1\) \((\pi\pi^*\text{ or } \pi^*\pi)\) has not been firmly established, although Beltrop and Bunce have made an argument for a \(\pi^*\pi\) state based on both experimental and theoretical evidence. We have performed CNDO/S calculations on nitrobenzene, and these results indicate that \(T_1\) for nitrobenzene is a \(\pi^*\pi\) state in agreement with Beltrop and Bunce. The excited triplet then abstracts a hydrogen atom from the solvent as shown in step 2. The radical formed (II) can be observed if it does not react rapidly. Its reactions have been discussed by Cowley and Sutcliffe. Usually, however, subsequent steps 3-5 produce radical species very quickly whose spectra mask that of species II. The caged radical ion pair produced in step 3 can either combine chemically to form the solvent adduct (III) in step 5 or diffuse away to produce the radical anion (I). The observed radical species is determined by the relative rates of these processes, which themselves depend on solvent, temperature, and the nitroaromatic species itself.

Wong and Wan reported solvent-adduct radicals formed photochemically in some of the systems for which we conclude that the radical anion is the predominant species. Specifically, we have carefully searched without success for the additional splittings reported for \(s\)-trinitrobenzene irradiated in dioxane. These discrepancies could possibly be due to concentration effects, intensity effects, or the length of time that the sample was irradiated.

Our main goal has been to identify the early radicals produced in these systems in order to compare with radicals produced in the neat photochemical and thermochemical decompositions of pure TNT (without solvent). It is evident that the primary radicals in these latter experiments are not the radical anions or the hydrogen-adduct species. The mechanism proposed by Cowley and Sutcliffe for photochemical decomposition of nitrobenzene and related chloronitrobenzene in ethers is supported for TNT and related nitroaromatics by our work.

**Acknowledgment.** We thank Dr. Ira B. Goldberg of Rockwell International for donating the EPR simulation program. We additionally appreciate helpful comments and references from Professor E. G. Janzen of the University of Guelph in Ontario, Canada. The reviewer made numerous helpful suggestions. Finally, the expert typing of this manuscript by Mrs. Betty Darby is gratefully acknowledged.