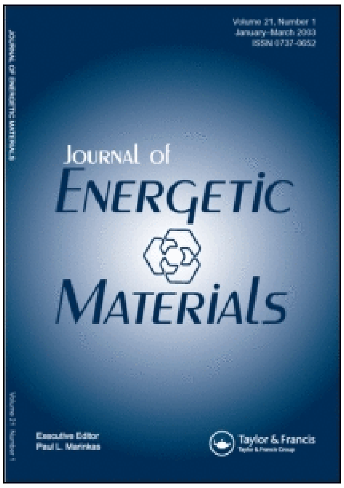

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ON THE PHOTOCHEMICAL PHENOMENON IN TATB

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ABSTRACT

TATB (1,3,5 triaminotrinitrobenzene) is a yellow compound that slowly changes to green upon exposure to sunlight. IR, UV-Visible, and ESCA data pertaining to this phenomenon are presented. It is shown that various types of irradiation can induce NO_2 loss, radical formation, or secondary amine production in TATB. Molecular orbital calculations are used to dispute the previously assigned structure of the radical in irradiated TATB.

INTRODUCTION

TATB (1,3,5 triaminotrinitrobenzene, Figure 1B) is an explosive that is of interest because of its high resistance to initiation. One curious property of this yellow material is a surface color change to green upon prolonged exposure to sunlight. The study of this problem is complicated by the low solubility of

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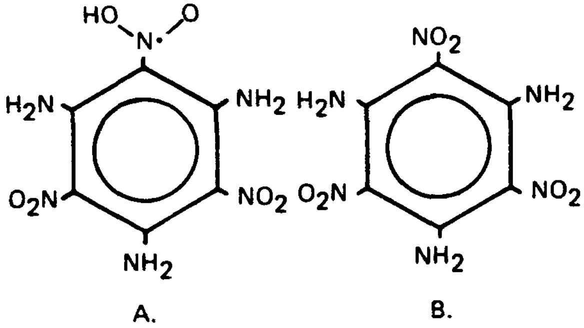

A.

B.

FIGURE 1
A) Postulated radical structure. B) TATB.

TATB in all known solvents (maximum solubility 10^{-4}M in DMSO). Nonetheless, work is in progress to understand this phenomenon, and this report summarizes the results of the investigation thus far.

A few articles have appeared describing irradiation phenomena in TATB. Sharma, Owens, et al. published XPS studies on TATB before and after UV irradiation in vacuo; the results indicated partial NO_2 loss after UV exposure.[1,2] No mention was made of a color change. Britt et al. described ESR experiments where exhaustively UV-photolyzed TATB was extracted with DMSO or DMF; the resulting solution gave a complex ESR spectrum that corresponds to a single free radical species.[3] The radical is reported to be remarkably persistent in the solid state, showing no evidence of decay after two years at ambient temperature (25°C) and open to the air. The authors claim that free radical production is accompanied by the development of the green color, and a structure for the radical (Figure 1A) is proposed.

MOLECULAR ORBITAL CALCULATIONS

We had some doubts that the molecule in Figure 1A was the correct structure for the observed free radical, and so we obtained the actual experimental ESR spectrum from Professor Britt for examination. The spectrum is complex to a degree that a structural assignment cannot be deduced from it alone with any confidence. It was decided to test the coupling constants provided in Britt's paper, which should describe the experimental ESR spectrum, by entering them into a computer simulation program. A spectrum with over 1000 lines was obtained, and it was necessary to use a data reduction routine to generate a plot with approximately the same resolution as the experimental spectrum. The experimental plot and the computer-generated plot were superimposed, showing a vague but inconclusive match. Although this result points out some error in the assignment of coupling constants, it does not eliminate 1A as a possible structure for the observed radical. We desired to confirm or refute the structure of 1A, and decided to pursue a calculational approach.

The value of a splitting constant in ESR is proportional to the amount of unpaired electron spin density on the splitting atom. Without going into more detail, we will state that it is possible to start with a postulated radical structure, calculate values of spin density from quantum mechanics, and use these values to predict the appearance of the radical's ESR spectrum. This approach has been successfully used to predict ESR spectra for a number of nitroaromatic anions.[4,5] Because of the necessary assumptions that are made in order to perform calculations on such a large molecule, one cannot expect the result to be superimposable upon the experimental ESR spectrum. On the other hand, molecular orbital computations can be confidently applied to predict the general appearance of an ESR spectrum, so that gross differences between a theoretically generated spectrum and the experimental spectrum will point to an incorrectly assigned radical structure.

Calculation on TATB

The initial task undertaken was an INDO (Intermediate Neglect of Differential Overlap) energy-level calculation on TATB, using structural parameters taken from the TATB crystal structure.[6] To simplify the calculation, the structure was assumed to be planar, and bond distances were normalized. This adjustment was expected to have very little impact on the calculation, and in fact, we found good agreement between our results and earlier work.[2] Both studies show a series of closely spaced levels near the valence region (Figure 2), with the highest occupied molecular orbitals localized largely on the nitro groups. Following this result, electron density maps of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were prepared. These maps showed one symmetric nodal plane in the HOMO

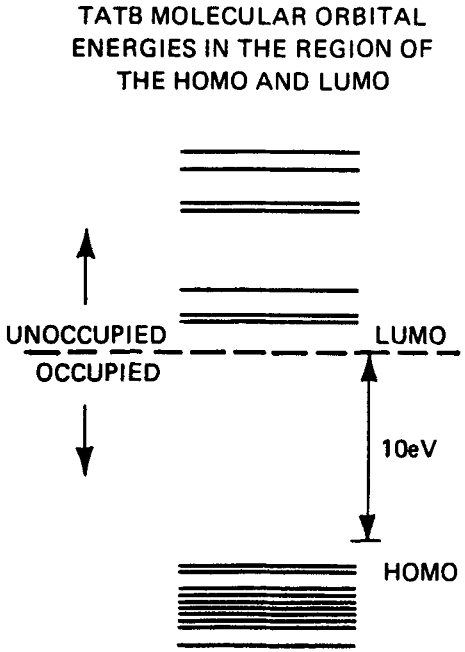

FIGURE 2.
INDO-calculated eigenvalues for TATB.

and two in the LUMO, features that parallel the known characteristics of benzene. The INDO approach was clearly yielding credible results, and it was deemed appropriate to move on to the theoretical treatment of the 1A structure.

Calculation on the 1A Radical Structure

After the molecular orbitals of the 1A molecule were derived via the INDO technique, the HOMO was singled out for special examination since it will contain the unpaired electron in this radical compound. As mentioned above, the distribution of this lone electron over the molecule is directly related to the ESR spectrum. A two-dimensional model of this distribution is provided by an electron density map (Figure 3), which represents a planar cross-section of the HOMO taken above and parallel to the plane of the carbon ring. It is immediately seen that the unpaired electron resides primarily on the NO_2H group. One would, therefore, expect that the ESR spectrum of radical 1A will have one very large coupling constant (due to the N of the NO_2H group) that will

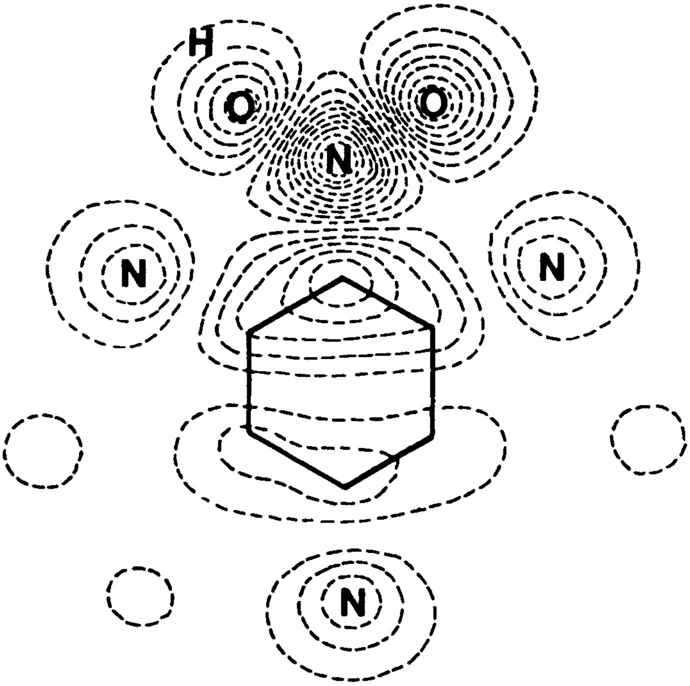

FIGURE 3.
INDO-calculated electron density map for the HOMO of the 1A radical.

dominate the spectrum. However, such a distinctive coupling is not observed in the experimental spectrum; in fact, its gross appearance is indicative of a number of comparable coupling constants. This large discrepancy between theoretical and actual spectra does not support 1A as the correct structure of the radical in irradiated TATB.

UV-VISIBLE SPECTROSCOPY

The UV-visible spectrum of TATB in DMSO solution shows two absorptions: a major absorption over the 290-435 nm range with a maximum at 360 nm, and a less intense, well-defined band at 270 nm. A similar spectrum is obtained for solid TATB with photoacoustic spectroscopy, although the peaks appear flattened and slightly broader. When a solid TATB sample was irradiated with a solar simulator lamp, the photoacoustic UV-visible spectrum of the resulting green material shows two additional absorptions: an intense broad band over the 575-850 nm range centered at 670 nm, and a small well-defined band in the 505-545 nm range. The overall appearance of the spectrum is one of two broad absorptions, with a valley in the 475-575 nm region. The material thus absorbs all wavelengths except those in the green region, resulting in a green appearance. As irradiation proceeds, the two broad, featureless absorptions overlap and engulf the entire visible spectrum; it is not surprising that exhaustive irradiation eventually causes green TATB to darken to greenish-black.

IR AND RAMAN RESULTS

There is virtually no difference between the transmission infrared spectrum (KBr pellet) of yellow and green (irradiated) TATB. However, if only the surface is analyzed (either by diffuse reflectance IR or photoacoustic IR), the difference spectrum between green and yellow TATB shows a peak at 3431 cm^{-1}, which is attributed to a secondary amine in the green material. To conclude that there is a one-to-one relationship between the color change and secondary amine production is unwarranted at this time; it is possible that we are observing an unrelated side reaction that occurs to a limited extent. Nonetheless, the IR result is thus far the only structural evidence pertaining to a chemical change that accompanies the irradiation phenomenon.

A similar pair of surface IR analyses (done before and after irradiation) was performed on the chlorinated derivative shown in Figure 4. Irradiation of this yellow compound caused its surface to darken only slightly and did not produce a green color. A reflectance IR taken after irradiation showed reduced intensity in all peaks, but yielded no other useful information. We are currently investigating the photochemical behavior of other nitroanilines.

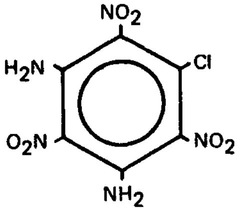

FIGURE 4
Chlorinated derivative of TATB.

An attempt was made to obtain Laser Raman data on yellow TATB. At the laser's wavelength of 514.5 nm, the power going into the sample was found to be too high, resulting in a darkening of the sample and meaningless data. The future availability of dye lasers will make this experiment feasible; differences between the Raman spectra of yellow and green TATB are expected to complement the structural information obtained from IR.

ESCA RESULTS

Samples of TATB were examined with ESCA before and after irradiation with a solar simulator lamp. There appeared to be a slight reduction in the NO_2-type nitrogen signal after irradiation, but the change was almost negligible. This result differs from the Sharma, Owens, et al.[2] work where UV irradiation produced a pronounced reduction in the same signal. The discrepancy can be rationalized by considering the difference in radiation sources; the higher energy of the UV lamp may be inducing NO_2 losses or transformations unattainable with the solar lamp.

SUMMARY

Solar radiation induces a surface color change in TATB, from yellow to green. Radical formation and secondary amine production accompany this transformation; NO_2 loss probably does not occur except under harsher UV photolysis. A previously proposed structure for the radiation-generated radical is not supported by INDO calculations, and the assignment of this species remains unresolved.

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