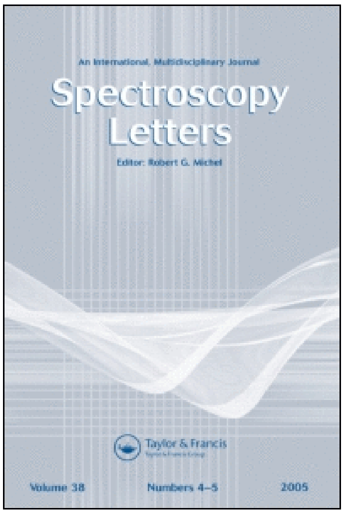

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REVERSIBLE PHOTOISOMERIZATION OF β-METHYL-β-NITROSTYRENE: THE ROLE OF TRIETHYLAMINE.

KEY WORDS: EPR , Photoisomerization, radical, nitrostyrene

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ABSTRACT

The photolysis of *trans*-β-nitro-βmethylstyrene in acetonitrile solution gives the cis-isomer with a quantum yield of 0.8. Addition of triethylamine to the system leads to a small decrease in the photoisomerization quantum yield and the appearance of a strong EPR signal. This signal remains for several hours at the end of the irradiation. It is demonstrated that the EPR signal is associated to an intermediary produced during the triethylamine catalyzed thermal back formation of the *trans* isomer. This intermediary bears an unpaired electron mostly associated to the nitro group and suggest that the thermal back reaction takes place by an initial electron transfer from the amine to the nitro group, leading to a long lived zwitterionic biradical.

INTRODUCTION

β-nitro-methylstyrenes are a family of compounds with particular properties due to the conjugation between the nitro group and the aromatic moiety mediated by the presence of the vinyl double bond. These compounds possess interesting chemical and biological properties. In particular, it has been reported that they stimulate the nervous central system, inhibit bacterial growth, and present cytototic and antitumoral effects in rats (1,2). Their one electron electrochemical reduction in aprotic solvents leads to the formation of the corresponding radical anions that are stable in the absence of oxygen (3). The electron paramagnetic spectra of these ions indicate that, although the unpaired electron is mainly attached to the intro group, it is delocalized over all the aliphatic and aromatic Π system.

Trans-β-nitro-β-methylstyrenes presents a strong absorbing band in the near UV (ca 300 nm). Excitation in this band leads to very low fluorescence (4) indicative of a very short singlet lifetime. This could indicate the presence of favored intersystem crossing and / or internal conversion processes, or the occurrence of an efficient chemical deactivation pathway. A possible efficient deactivation pathway could be the *trans*-cis isomerization (5,6). The cis-isomer thermally reverts to the *trans*-isomer in a process that is catalyzed by trialkylamines (6). The mechanism of this process, as well as the role of the amines in the photoisomerization process, has not been evaluated.

EXPERIMENTAL

Materials: *Trans*-β-methyl-β-nitrostyrene was prepared according to previous procedures. Triethylamine was used after distillation under reduced pressure. The other reagents were used after routine purification. The concentration of the reactants usually was 1×10^{-3} M. The solutions (i.e., acetonitrile) were flushed with nitrogen before the irradiation.

Measurements: The solutions for EPR investigations were placed in a test tube in the dark or diffuse light and degassed by bubbling with argon for 20 minutes. The solutions were then transferred to a 0.1 mm quartz EPR flat cell and again deoxygenated by a slow stream of argon. The cell was introduced into a 4101 STE/8219 cavity of an ER 100D spectrometer equipped with BST 100/700 BHN12 accessory for variable temperature control. The samples were irradiated in the cavity with a Hanovia 977B0090-1000-W mercury-xenon lamp in a model LH 51H Schoeffel lamp housing. The light was focused through quartz lenses and filtered by appropriate Corning or Oriel glass filters. The spectra were calibrated by DPPH (α,α'-diphenyl-β-picrylhydrazyl). EPR spectra were simulated using a Rochester University program.

UV spectra for determining isomerization rates were recorded on a Shimadzu UV-160 spectrophotometer. Quantum yields were determined by irradiating samples in Pyrex test tubes in a merry-go-round apparatus. The incident light intensities were measured by using the Reinecke'salt actinometer. All irradiation was conducted in a Rayonet photoreactor equipped with 300 nm lamps.

RESULTS

Irradiation of *trans*-β-nitro-β-methylstyrene (BNMS) with a light of 300 nm reduces the absorbance at 304 nm due to the *trans*-compound, and increases the absorbance at 282 nm. This can be attributed to the formation of the cis-isomer. Since the absorption of the cis-isomer at 304 nm is negligible, the decrease in absorbance at this wavelength can be directly related to the disappearance of the *trans* compound. The *trans*-isomer quantum yield consumption was evaluated as 0.8, indicating that the chemical pathway is the main decay process of the excited molecules. In the presence of triethylamine (up to 0.1 M) the photoconsumption quantum yield of the BNMS reduces to ca. 0.65.

As previously postulated (6), one of the main products of BNMS photolysis is the cis-isomer. This is confirmed by the increase in the absorbance at 304 nm associated to the dark incubation of the photolyzed samples at 40 °C, particularly in the presence of TEA.

Photolysis of BNMS in the EPR cavity does not produce any significant free radical signal. On the other hand, when the photolysis is carried out in the presence of TEA (0.1

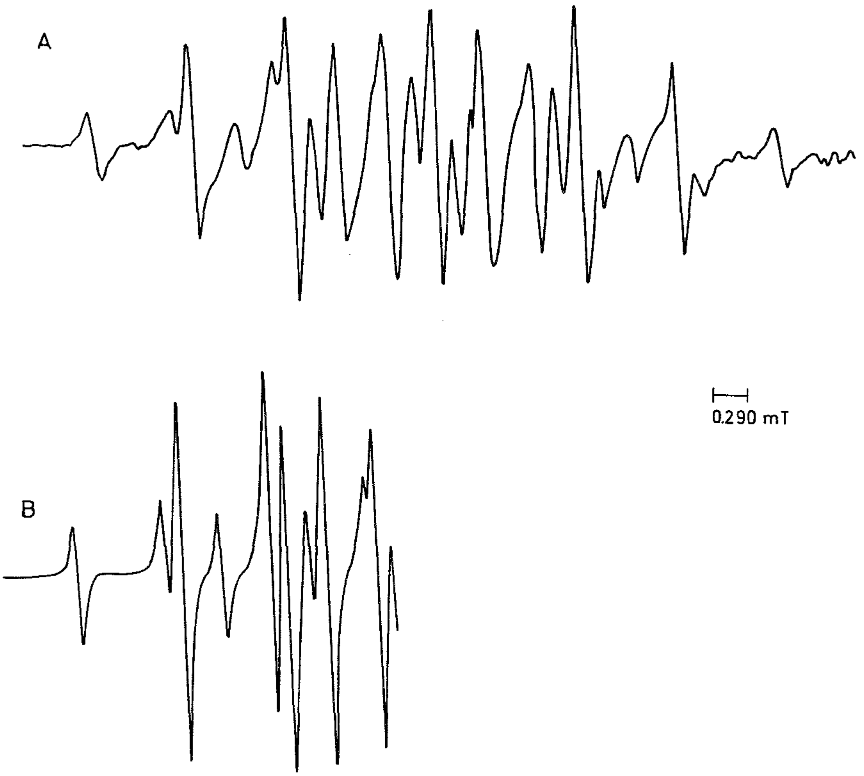

FIG. 1 (A) EPR Experimental Spectrum of the *trans*-β-methyl-β-nitrostyrene (BNMS); (B) Computer Simulation of the Same Spectrum

M) a persistent EPR signal is observed (Fig. 1) that remains a long time in the dark, after shutting-off the light. The EPR spectrum consists of a hyperfine splitting with the following constants:

$$a_N = 1.7 \text{ mT}, \; a_{3H} = 1.3 \text{ mT}, \; a_H = 1.0 \text{ mT}$$

The back formation of the *trans*-compound from the photochemical produced cis-isomer is catalyzed by TEA. This process produces a strong EPR signal identical to that observed when the photolysis is carried out in the presence of amine. This signal disappears in the presence of oxygen.

DISCUSSION

The large isomerization quantum yields observed in the photolysis of BNMS indicates that even in the presence of amines, the main process can be considered to be a simple *trans*-cis isomerization, such as:

trans-BNMS + hν -----> cis-BNMS

The photochemistry can be considered to take place in a simple elementary step, without formation of stable intermediates of free radical character. This process takes place independently of the presence of amines. In fact, the small reduction in quantum yield observed in the presence of amines can be ascribed to some catalyzed back reaction.

It has been postulated (6) that the thermal back isomerization of the cis compound, catalyzed by TEA, takes place through a zwitterionic biradical, as depicted in the scheme

$$\text{-CH=C(Me)NO}_2 + \text{TEA} \longrightarrow [\text{CH}_3\text{-CH}_2\text{-N(Et)}_2]^{\bullet+}[\ \text{CH=C(Me)NO}_2]^{\bullet-}$$

The results obtained in the present work demonstrate that a free radical species is involved as an intermediate in the process. However, the characteristics of the species detected (see Fig 1) seems to be incompatible with those expected for the nitrostyrene radical anion, because the hyperfine constants are bigger than the nitroaromatic ones. Furthermore, there is no evidence of the TEA derived radical cation.

A plausible explanation is that the initial electron transfer between the amine and the nitrostyrene derivative is followed by a proton transfer to give as an intermediate a radical such as:

$$[\ \text{CH-CH(Me)NO}_2]^{\bullet}$$

We attempt to produce this radical through the interaction of NO_2 and β- methyl styrene. Addition of NO_2 to β-methylstyrene produces a radical . He is particularly stable

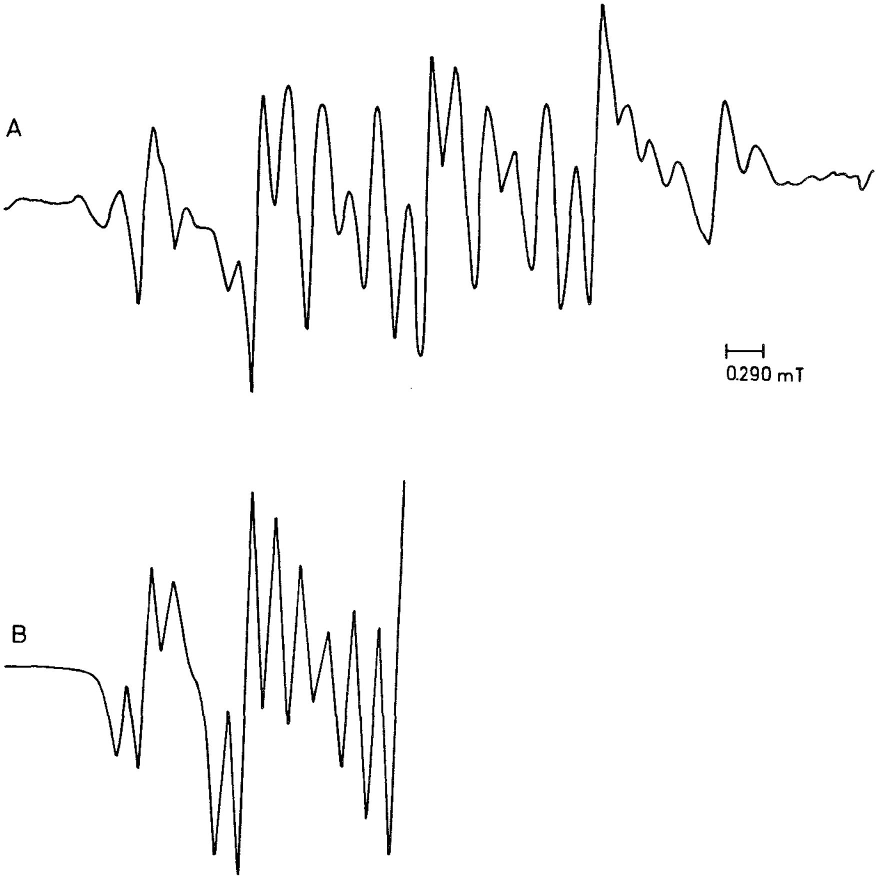

FIG. 2 (A) EPR Experimental Spectrum of the radical produces by the addition of NO_2 to the β-methylstyrene; (B) Computer Simulation of the Same Spectrum

in the presence of TEA. In fact, it could only be detected when the amine concentration is higher than 0.01M. The EPR spectrum of the radical obtained in the presence of TEA consists of 21 lines with the following constants: $a_N = 1.489$ mT, $a_{2H} = 1.01$ mT and $a_{2H} = 0.213$ mT (Fig 2). However, although this spectrum bears some similarity to that shown in Fig 1, both corresponds to different species.

In conclusion, we have shown that the photochemical isomerization *trans*- cis is not catalyzed by amines, the free radical species are intermediates in the TEA catalyzed back isomerization of cis-β-methyl-β-nitrostyrene. The free electrons are basically localized in the nitro styrene moiety, with TEA acting as a catalyser and / or stabilizer of the transient species. However, at present it is not possible to assign a structure to those intermediates.

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