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Photoreduction of 4-substituted nitrobenzenes by amines

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The reduction of several nitrobenzenes bearing electron-donor and electron-withdrawing substituents in the 4-position by triethylamine in acetonitrile was studied by cyclic voltammetry, EPR spectroscopy, and steady-state photolysis. The electrochemical reduction of nitro compounds showed a reversible cathodic wave corresponding to one electron transfer, and forms the nitrobenzene radical anion. The reduction potentials were well correlated with the hyperfine nitrogen coupling constants of the radical anion and with the donor-acceptor characteristics of the 4-substituent. The photoreduction of nitro compounds in the presence of triethylamine gave the nitrobenzene radical anion. EPR spin trapping experiments showed that the α-aminoethyl radical is formed only in the photolysis of nitrobenzenes with electron-donating substituents. These compounds in the presence of the amine were efficient photoinitiators of the methyl methacrylate polymerization. The polymerization rate increases with the amine concentration reaching a constant value. Similar behaviour was observed for the photobleaching quantum yield. These results indicate that the photobleaching and the reaction that leads to radicals able to add to the monomer come from the interaction of the triplet state of the nitro compound with the amine followed by proton transfer within the geminate ion pair giving the neutral radicals. In the absence of monomer, nitrosobenzene appeared to be the primary product. The polymerization in the presence of electron-withdrawing substituted nitrobenzenes was negligible. This is in agreement with the lack of α-aminoalkyl radical formation.

Introduction

Photoreactions of nitro aromatic compounds have been the subject of several studies. In recent years the photoreduction of nitrobenzenes[1–8] and nitronaphthalenes[9–13] by amines has received special attention. Photoreactions are very dependent on the structure of the amine and on the solvent. The photoreaction of 1-methoxy nitronaphthalene[9] and methoxy nitrobenzenes[5–7] with methylamine and n-hexylamine leads to the replacement of the methoxy substituent. While Bunce *et al.*[11] found that the photoirradiation of 1-methoxy-4-nitronaphthalene in the presence of primary amines causes the replacement of the nitro group, and secondary amines give methoxy displacement and substitution. Electron spin resonance and laser flash photolysis studies on the interaction of nitrobenzenes and nitronaphthalenes with amines showed that the reaction involves the lowest electronic triplet state of the nitro compound.[7,11,13,14] Radical ions are formed in an electron transfer reaction. Although, with ethyl glycinate and primary alkylamines has been proposed that the reaction proceeds through a S_{N2} reaction from the triplet state of the nitro compound.[11,15] More recently, Görner[16] has reported that the triplet quenching of nitronaphthalenes by triethylamine and diethylamine in acetonitrile involves a two-step process. The nitro and amine ion radicals are formed by electron transfer from the amine, and the neutral protonated nitrobenzene radical is formed by the reaction of nitronaphthalene ground state and the α-amino radical originated from the amine cation radical. In benzene, the neutral radicals are produced inside the geminate radical ion pair. Nitrosonaphthalene is the major product. Initial electron transfer followed by proton transfer also has been reported for the photoreduction of nitrobenzylidene malonic derivatives with triethylamine in benzene.[17] However, most of these studies on the reduction of nitro compounds by amines concern to alkoxy nitro aromatic compounds. Because of the presence of the charge transfer intermediate, the quenching mechanism and the production of radicals in these reactions are also expected to be strongly dependent on the electron donor-acceptor characteristics of substituents on the aromatic ring.

Aromatic nitro compounds in the presence of tertiary amines behave as efficient photoinitiators of the polymerization of methacrylic and acrylic monomers.[18–20] Costela *et al.*[21] have examined the photopolymerization activity of 4-nitroaniline in the presence of tertiary amines. These studies suggest that the photoreduction takes place by an electron transfer process from the amine to the aromatic compound followed by a proton transfer process generating the α-amine radical that initiates the polymerization. In a previous work using EPR spectroscopy we directly observed the nitroaniline and the amine neutral radicals.[22]

In the present work, we studied the photoreduction by triethylamine of several nitrobenzenes with electron-donor and electron-withdrawing substituents in the 4-position in acetonitrile. The aim of this work is to obtain information on the effect of the 4-substitution in the photoreduction mechanism of these compounds, and on their efficiency as photoinitiators of the methyl methacrylate polymerization. Electrochemical reduction also was carried out with several nitrobenzenes bearing different substituents in the 4-position.

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Experimental

Nitrobenzenes (Aldrich) were purified by recrystallization. Triethylamine (TEA) from Aldrich was vacuum distilled before use. Methyl methacrylate (MMA) from Fluka was purified by washing with 10% NaOH solution and then distilled under vacuum. Nitrosobenzene (NB), 2-methyl-2-nitrosopropane, and 3,5-dibromo-4-nitrosobenzene sulfonic acid from Sigma were used as received.

Cyclic voltammetry (CV) was carried out using a Weenking POS 88 instrument with a Kipp Zenen BD93 recorder, in acetonitrile solution (1 mM), under nitrogen atmosphere, using three-electrode cells. The tetrabutylamonium perchlorate (0.01 M) was used as supporting electrolyte. A mercury-dropping electrode was used as the working electrode, a platinum wire as the auxiliary electrode, and saturated calomel (SCE) as the reference electrode. The CV experiments were carried out at 25 °C employing a sweep rate that varied from 100 to 1000 mV s^{-1}.

EPR spectra were recorded in X band (9.85 GHz) using a Bruker ECS 106 spectrometer with a rectangular cavity and 50 KHz field modulation at room temperature. Other conditions of measurements were as follows: power, 20.1 mW, and attenation, 10.0 dB; modulation amplitude, 0.49 G; receiver gain, 1×10^5; conversion time, 40.96 ms; time constant, 81 ms. Each spectrum was recorded with 15 scans. DPPH (α,α′-diphenyl-β-picrylhydrazyl radical) was employed as reference for spectrum calibration. The radical anions were generated by electrolytic reduction "*in situ*" at room temperature. Also, the radicals were generated "*in situ*" in the cavity *via* a photo-induced electron transfer between the nitro compounds and triethylamine in deoxygenated acetonitrile solution. Samples were irradiated with light from 250 W medium-pressure mercury lamp with cut-off filters (Schott) to isolate the 366 nm line. The hyperfine splitting constants were estimated to be accurate within 0.05 G. Simulation of the EPR spectra was achieved with a program WINEPR Simfonia 1.25 version.

Spin trapping techniques, in conjunction with EPR spectroscopy, were used to obtain information on radicals present in low steady-state concentration. Nitrosobenzene, 2-methyl-2-nitrosopropane, and 3,5-dibromo-4-nitrosobenzene sulfonic acid were used as spin traps. The concentration of nitroso compounds was 100 mM.

^{1}H NMR spectra were obtained with a Brucker Avance 400 MHz spectrometer. Spectra were recorded in deuterated acetonitrile, and the chemical shifts (in ppm) are informed with respect to Me_4Si.

The photobleaching of nitrobenzenes by amines was evaluated in acetonitrile degassed solutions from the change in the near-UV absorption band. The solutions were irradiated at 360 nm with a Photon Technology International irradiation system comprising a 150 W xenon lamp and a monochromator (PTI-102). The rate of the reaction was measured after the decrease of the absorbance of the nitro compound at different irradiation times. The photoreaction quantum yield was determined taking Aberchrome 540 as reference.[23] Absorption spectra were recorded with a Hewlett-Packard 6453E diode array spectrophotometer.

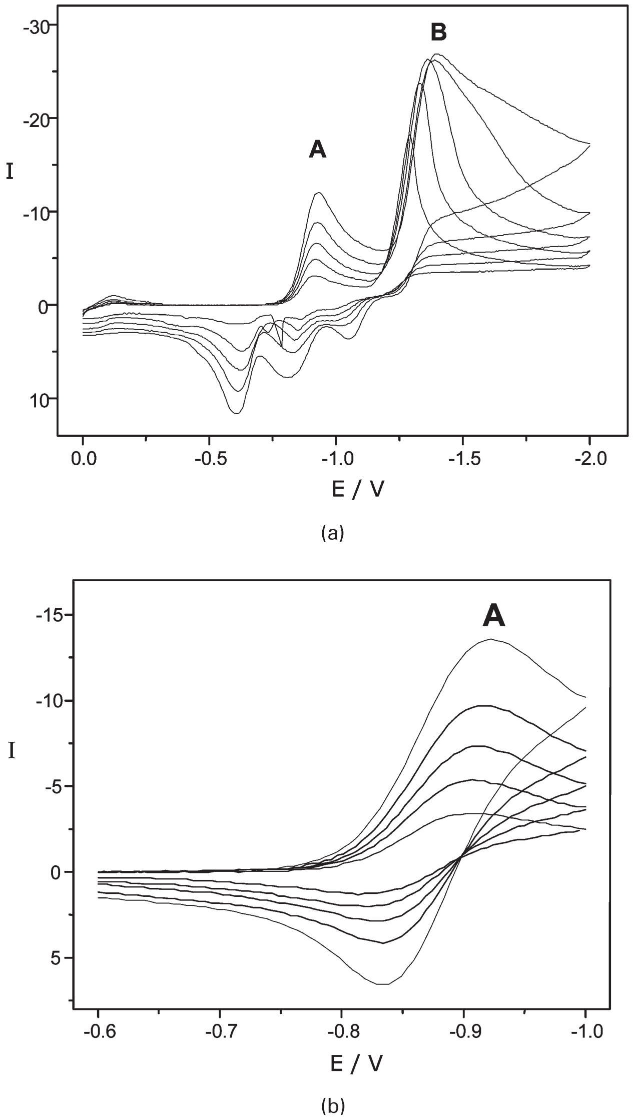
Polymerization rates (R_p) were measured dilatometrically in oxygen-free solutions. All measurements were carried out at 25 °C, in solutions containing equal volumes of MMA and acetonitrile. Irradiations were carried out using a medium-pressure mercury lamp (Black-Ray) with cut-off filters (Schott) of 366 nm. Low absorbance of the initiator (0.2) was used to avoid the generation of inhomogeneous free radical distribution.[24]

Results and discussion

Cyclic voltammetry

The reduction of 4-nitrobenzenes at 25 °C in acetonitrile was followed by cyclic voltammetry in the potential range of 0.0 to −2.0 V. Typical cyclic voltammograms for 4-nitroacetophenone are presented in Fig. 1a. All voltammograms exhibit two cathodic waves, **A** and **B**, in the range of −0.6 V to −2.0 V. The general pattern of the voltammogram was studied as a function of the sweep rate and switching potential. The wave **A** shows the main characteristics of a reversible one-electron transfer (Fig. 1b). On the reverse scan the reduction wave shows an anodic counterpart, and the reduction and oxidation peaks are independent on the scan rate. When the potential scan is reversed before peak B, the intensity ratio i_{pA}/i_{pC} has a value close to unity. The ratio $i_{pC}/v^{1/2}$ is constant as expected in a diffusion controlled process. The anodic–cathodic peak potential difference within each couple is ~60 mV. Thus, wave A can be unambiguously assigned to an one-electron charge transfer, leading to a relatively stable anion-radical. The wave **B** does not have an anodic counterpart, even at high scan rates. This behaviour suggests an irreversible charge transfer.

Values of the cathodic potential peak for several 4-substituted nitrobenzenes are given in Table 1. These values are very similar to the half-wave potential previously obtained by polarographic experiments.[25] Compounds with electron-withdrawing substituents in the 4-position are easily reduced, while electron-donor substituted compounds gave more negative



(a)

(b)

Fig. 1 Cyclic voltammograms of 4-nitroacetophenone at different scan rates, in acetonitrile at 25 °C, SCE as reference electrode. Scan rates from the top: 2; 1; 0.5; 0.25; and 0.1 V s^{-1}. (a) Potential range from 0 to −2.0 V; (b) Potential range from −0.6 to −1.0 V.

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Table 1 Voltammetric cathodic potentials (E_{pc}), and nitrogen coupling constants (a_N).

4-Substituent	Wave A Ep_C/V	a_N/G (electrochemical EPR)
CN	0.87	6.3
$COCH_3$	0.91	6.6
$COOCH_3$	0.96	7.73
$CONH_2$	0.98	8.15
CH_3	1.20	10.79
OCH_3	1.24	11.34
NH_2	1.37	12.32

potential. The reduction potential potted against the σ_p Hammett parameter has a good linear correlation with a correlation coefficient of 0.998. The slope corresponds to a ρ value of 0.39, reflecting stabilization of the anion radical by partial transfer of negative charge from the substituent to the radical site.

EPR experiments showed that the radical anion formed at the cationic first potential redox in the electrochemical reduction "*in situ*" is the nitro centered anion radical. Fig. 2a shows the EPR spectrum obtained for 4-nitroanisole. This spectrum is superimposable with the simulated spectrum, Fig. 2b. The values of the nitrogen coupling constant (a_N) for several 4-substituted nitrobenzenes are summarised in Table 1. Lower values of a_N are found for compounds with lower reduction potential. Compounds with electron-donating substituents are increased in a_N and the electron attracting ones cause a decrease. This behaviour is reasonable if it is assumed that the effect of the substituent group on the over-all electron distribution is reflected in the distribution of the unpaired electron. The nitro group becomes more deficient of unpaired electron density as the 4-substituent is made more electron attracting. This is supported by the fact that a_N values correlate very well with the reduction potential ($r = 0.99$), yielding a high ρ negative value of -12.5.

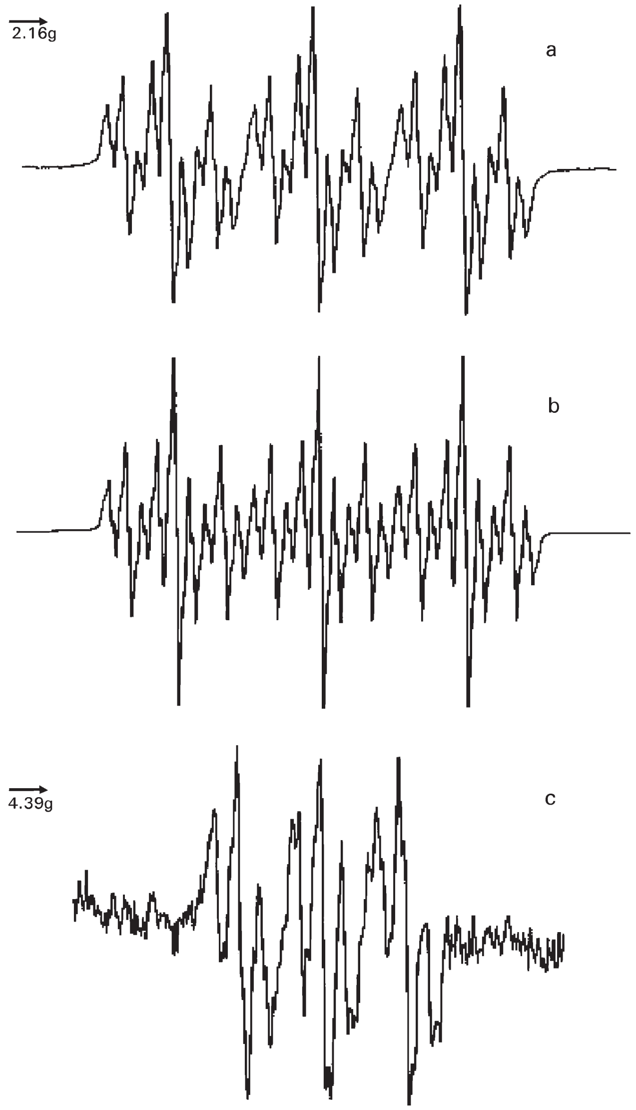
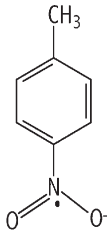


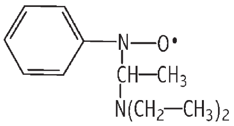
Fig. 2 EPR spectra of the radical anion of 4-nitroanisole in acetonitrile at 25 °C, when is generated: (a) by electrochemical reduction; (b) simulated spectrum of the radical anion, with linewidth of 0.4 G and ratio Lorentzian/Gaussian of 0.4; (c) photochemically in the presence of 0.1 M TEA.

Photoreduction in the presence of triethylamine

When solutions of substituted 4-nitrobenzenes in acetonitrile were irradiated with wavelength of 360 nm at 25 °C in acetonitrile in the EPR cavity any radicals could be detected. However, when nitrobenzenes were irradiated in the presence of TEA it was generated a strong EPR spectrum that persits at least 30 seg. Fig. 2c shows the spectrum generated upon irradiation of 4-nitroanisole in the presence of TEA. The hyperfine splitting constants are $a_N = 11.8$ gauss, $a_{2H} = 1.4$ gauss, $a_{2H} = 4.2$ gauss, and $a_{3H} = 0.40$ gauss. The simulated spectrum, with linewidth of 0.4 gauss, is similar to the observed spectrum, and similar to that electrochemically generated, Fig. 2. Thus, the intermediate is assigned to the nitrobenzene radical anion, Structure 1. The EPR spectrum obtained in the irradiation of 4-nitrotoluene in acetonitrile also gave the signal corresponding to the nitrobenzene radical anion. The EPR spectrum of the 4-nitroveratrole irradiated in the presence of TEA or piperidine also shows the presence of the nitrobenzene radical anion.[4]



On the other hand, the addition of nitrosobenzene (NB) to a solution containing 4-nitroanisole and TEA produced an EPR detectable free radical. The EPR spectrum, Fig. 3, $g = 2.0137 \pm 0.0002$, of 4-nitroanisole indicates that the hyperfine splitting includes the hyperfine interaction with one hydrogen atom and two nitrogen atoms, as consequence of the formation of a NB-TEA adduct. The values of coupling constants are as follows: $a_N = 10.7$ G ($NO^{\bullet}$), $a_H = 14.4$ G, $a_{2H} = 1.1$ G, and $a_{3H} = 3.85$ G. This spectrum is in excellent agreement with the simulated spectrum (linewidth 0.7), and is assigned to Structure 2, showing the presence of the α-aminoethyl radical.



The spectrum of the α-aminoethyl radical also was observed with other spin trapping, such as 3,5-dibromo-4-nitrobenzene sulfonic, and 2-methyl-2-nitrosopropane. The presence of the α-aminoalkyl radical was previously showed in the photolysis of the 4-nitroaniline in the presence of TEA.[22] Although, in this case the protonated nitrobenzene radical also was observed.

On the other hand, when nitrobenzenes bearing an electron-withdrawing substituent in the 4-position in the presence of

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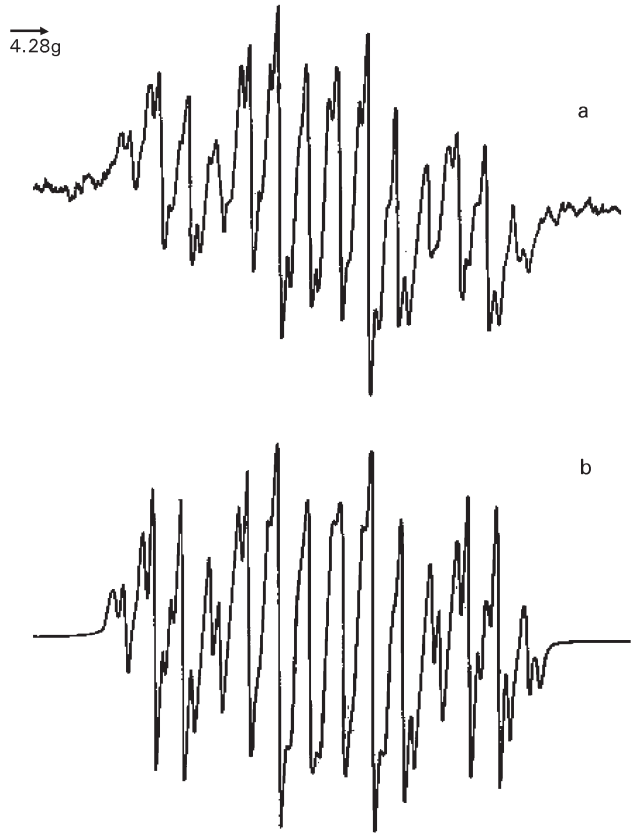


Fig. 3 Effect of nitrosobenzene addition on the EPR spectrum of 4-nitroanisole irradiated in the presence of 0.1 M TEA in acetonitrile at 25 °C. (a) Experimental spectrum; (b) simulated EPR spectrum; linewidth, 0.48 gauss, and Lorentzian/Gaussian ratio of 0.4.

TEA were irradiated in the EPR cavity the spectra corresponding to the nitrobenzene radical anion were obtained. The spectrum of 4-nitroacetophenone consists of three line groups in the hyperfine structure with $a_N = 7.02$ gauss, $a_H = 2.95$ gauss, $a_{2H} = 0.88$ gauss, $a_{3H} = 0.66$ gauss, Fig. 4. The simulation (linewidth 0.48 gauss) of this spectrum corresponds to the nitrobenzene radical anion and is almost the same as that obtained by electrochemical measurements. Similarly, the EPR spectrum of the nitrobenzene radical anion was observed in the photolysis of all nitrobenzenes with electron-withdrawing substituents in the 4-position in the presence of TEA. However, for these compounds the α-aminoethyl radical could not be observed with any spin trapping.

It is well accepted that the photoreduction of nitro aromatic compounds by tertiary amines in organic media takes place through electron transfer from the amine to the electronically excited nitro compound forming a charge transfer intermediate.[17,26,27] The main decomposition steps of this intermediate are the back electron transfer, the dissociation into separated radical ions, and the proton transfer to form neutral radicals, Scheme 1.

Time-resolved spectroscopic studies on the photoreduction of nitronaphthalenes and 4-nitroveratrole by amines have showed that the reaction proceeds *via* the excited triplet state.[8,16,28] The EPR results obtained in this work with nitrobenzenes bearing electron-donating substituents at the 4-position are consistent with the mechanism depicted in Scheme 1. The EPR experiments show the presence of the separated radical ions. The proton transfer within the geminate radical anion pair is evidenced by spin trapping experiments that show the presence of the carbon center α-amino radical. The fact that no EPR signal arising from the nitrobenzene neutral radical could be detected under our experimental conditions suggests that this radical has a much shorter lifetime than the anion

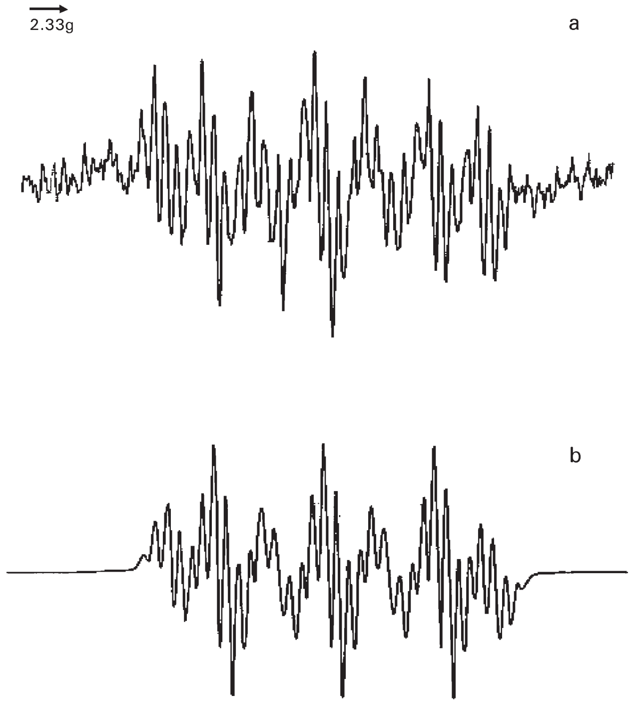
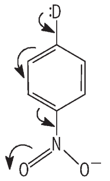
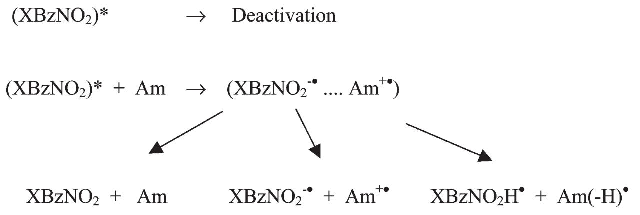


Fig. 4 EPR spectra of 4-nitroacetophenone irradiated in the presence of 0.1 M TEA in acetonitrile at 25 °C. (a) Experimental spectrum; (b) simulated EPR spectrum; linewidth, 0.48 gauss, and Lorentzian/Gaussian ratio of 0.4.

radical observed in the EPR experiments. Probably fast radical–radical termination is the main reaction of these species. On the other hand, experiments with electron-withdrawing substituted nitrobenzenes did not show evidence of the α-aminoalkyl radical formation. The favourable proton transfer within the geminate ion pair in nitrobenzenes with electron-donating substituents could be explained in terms of a increased charge density on the nitro group, Structure 3.



Our previous studies with 4-nitroaniline and TEA are in agreement with the present results. The intermediate observed in the EPR experiments was the protonated nitrobenzene radical.[22] The strong electron-donor character of the amine 4-substituent could increase the rate of the proton transfer process. The formation of protonated nitrobenzene radical has been proposed in the photolysis of aromatic nitro compounds in the presence of TEA, however the mechanism depends on the solvent and the nature of the nitro compound. Evidence for the formation of the protonated neutral nitrobenzene radical was shown by the photoreduction of 1- and 2-nitronaphthalenes and 1-methoxy-4-nitronaphthalene by TEA in benzene, and in acetonitrile.[16] However, in acetonitrile it was postulated that



Scheme 1

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the protonated radical is formed in a secondary delayed step.[13] In the photolysis of 4-nitroveratrole in acetonitrile was suggested the formation of the protonated radical inside the initial ion pair.[8]

Photobleaching of 4-nitroanisole by TEA

The photobleaching of nitrobenzenes with electron-donating substituents in the 4-position is promoted by TEA. No reaction was observed in the dark. The absorption of the longest wavelength band of the 4-nitroanisole decreased, a new absorption appeared in the region 260–300 nm with an isobestic point at 290 nm, and no absorption was observed at wavelengths longer than 320 nm. The consumption of the nitro compound was evaluated in argon-saturated acetonitrile in the presence of different amine concentrations by following the decrease in the absorbance at the longer absorption band. In this region was observed a clean photobleaching with up to 80% disappearance of the nitro compound. The extent of the chromophore loss increases with the amine concentration, reaching a constant value, Fig. 5. Values of 0.032 and 0.007 were obtained for the maximum photobleaching quantum yield of 4-nitroanisole and 4-nitrotoluene, respectively.

If the photoconsumption quantum yield is due to the interaction of the triplet state of the nitro compound with the amine, the photobleaching quantum yield will be proportional to the fraction of triplet states that are deactivated by the amine according to eqn. (1),

$$\phi_{\text{bleach}} \approx \frac{k_q[\text{TEA}]}{\sum k + k_q[\text{TEA}]} \qquad (1)$$

where k_q is the rate constant for the triplet quenching by the amine. The plot of $1/\phi_{\text{bleach}}$ as function of 1/[TEA] is shown in the insert of Fig. 5. The near-linearity of this plot suggests that the consumption comes from the interaction of the triplet excited state with the amine, and any process of the singlet can be considered as negligible. The Gibbs free energy change for the electron transfer process, ΔG°, can be calculated from the redox potentials of the donor E_{D/D^+} and acceptor E_{A/A^-}, and the energy E^* of the excited state involved, using the Rehm–Weller equation,[29]

$$\Delta G^\circ = E_{D/D^+} - E_{A/A^-} - E^* - C \qquad (2)$$

where C is the Coulombic energy term, for which −0.06 eV has been calculated in acetonitrile for unitary charges.[30] Taking the measured redox potential of 4-nitroanisole (Table 1), the TEA oxidation potential in acetonitrile as 0.95 eV,[31] and the reported value of 60 kcal/mol for the energy of the 4-nitroanisole triplet[32] one obtains a negative ΔG° value of −0.35 V. This value implies a quenching rate constant that is nearly diffusion-controlled.[30] From the high reduction potential of 4-nitrotoluene one expects a large value for the quenching rate constant by TEA. A value of k_q of 1.4×10^9 M^{-1} s^{-1} has been reported by the triplet quenching of 4-nitroveratrole in acetonitrile.[8]

The evolution of the main reaction products in the photolysis of 4-nitroanisole in the presence of TEA was monitored directly by ^{1}H NMR spectroscopy at different irradiation times. Nitrosobenzene appeared to be the main primary product (singlet at δ 3.9 for three protons, doublet at δ 7.06 for two protons, and doublet at δ 8.2 for two protons). These experiments indicate that neither photofragmentation nor stable photosubstitution products are formed. Only photoreduction products are observed in acetonitrile. Nitrosobenzene has been identified in the photolysis of various nitroaromatic compounds, and is proposed to be formed by the decomposition of the coupling product of the α-aminoalkyl and nitro protonated radicals.[13,26,33]

Photoinitiation mechanism

Studies of the MMA polymerization rates photoinitiated by nitrobenzenes in acetonitrile as solvent were carried out using irradiation of 360 nm. The irradiation of nitrobenzenes alone or the nitro compounds with electron-withdrawing substituent in the 4-position in the presence of TEA did not lead to the MMA polymerization. However, the irradiation of nitrobenzenes with electron donor substituents in the presence of TEA efficiently activated the polymerization of MMA.

Polymerization rates at several TEA concentrations employing 4-nitroanisole as photoinitiator were measured from the initial slope of the conversion *vs.* time plots. In all cases the conversion was lower than 10%. Fig. 6 shows that the polymerization rate increases with the amine concentration, reaching a maximum value at ~0.07 M amine. A similar behaviour was obtained for 4-nitrotoluene, but the maximum polymerization rate is 4 times lower than that obtained with 4-nitroanisole. Previous studies using 4-nitroaniline as photoinitiator showed a similar dependence of Rp with the amine concentration.[22]

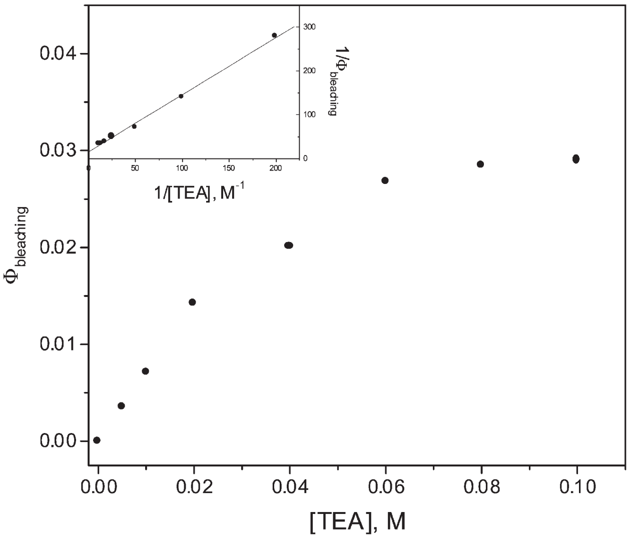

Fig. 5 Effect of TEA concentration on the 4-nitroanisole photobleaching quantum yield in acetonitrile. Insert: relation between inverse of photobleaching quantum yield and inverse of amine concentration according to eqn. (1).

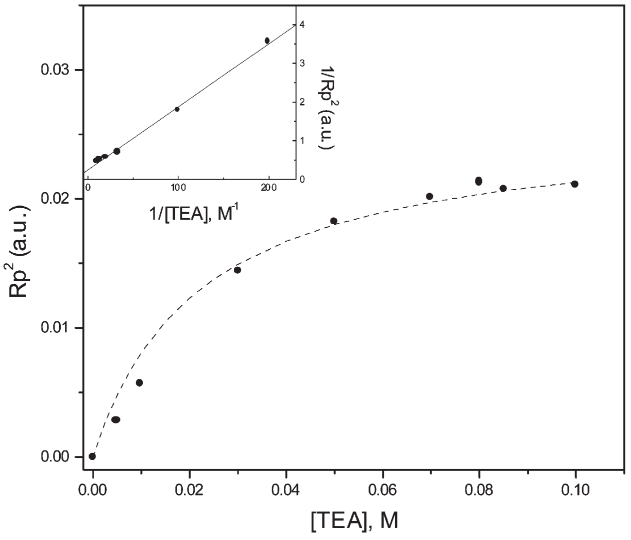

Fig. 6 Effect of the TEA concentration on the methyl methacrylate polymerization rate photoinitiated by 4-nitroanisole in monomer/acetonitrile (1/1). Insert: relation of polymerization rate and amine concentration according to eqn. (3).

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The increase of R_p with the amine concentration is in agreement with the increase of the fraction of triplet excited states that are deactivated by the amine. The polymerization rates will be related to the fraction of triplet quenched by the amine by eqn. (3),

$$f \approx \frac{k_q[\mathrm{TEA}]}{k_q[\mathrm{TEA}] + 1/\tau_T} \approx R_p^2 \qquad (3)$$

The linearity of $1/R_p{}^2$ *vs.* 1/[TEA] (see insert in Fig. 6) indicates that the active radicals come from the triplet interaction with the amine. The amine concentration required to reach the maxima MMA polymerization is similar to that necessary to reach the maximum bleaching of the nitro compound. This indicates that the photoreaction and the production of radicals that lead to polymerization come from the same precursor, the triplet excited state.

It is well known that amine neutral radicals produced in the interaction of triplet excited states with amines through an electron transfer process are the species responsible for photoinitiation in several polymerizations.[34] The fact that polymerization is not observed with 4-nitrobenzenes bearing electron withdrawing substituents in the 4-position is in agreement with the lack of α-aminoalkyl formation when these compounds are irradiated in the presence of TEA. Electron withdrawing substituents decrease the charge density at the N atom, then an unfavourable proton transfer within the geminate radical ion pair to give the neutral radicals is expected.

Acknowledgements

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References

1 J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. C*, 1968, 1467–1474.

2 R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, 1968, **90**, 1949–1952.

3 J. Cervelló, M. Figueredo, J. Marquet, M. Moreno-Mañas, J. Bertrán and J. M. Lluch, *Tetrahedon Lett.*, 1984, **25**, 4147–4150.

4 P. H. M. van Zeyl, A. M. J. van Eijk and C. A. G. O. Varma, *J. Photochem.*, 1985, **29**, 415–433.

5 A. Cantos, J. Marquet and M. Moreno-Mañas, *Tetrahedron*, 1988, **44**, 2607–2618.

6 A. M. J. van Eijk, A. H. Huizer, C. A. G. O. Varma and J. Marquet, *J. Am. Chem. Soc.*, 1989, **111**, 88–95.

7 A. Cantos, J. Marquet, M. Moreno-Mañas, A. González-Lafont, J. M. Lluch and J. Bertrán, *J. Org. Chem.*, 1990, **55**, 3303–3310.

8 R. González-Blanco, J. L. Bourdelande and J. Marquet, *J. Org. Chem.*, 1997, **62**, 6903–6910.

9 J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, **75**, 353–388.

10 K. Mutai and R. Nakagaki, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3663–3664.

11 N. J. Bunce, S. R. Cater, J. C. Scaiano and L. Johnston, *J. Org. Chem.*, 1987, **52**, 4214–4223.

12 T. Fournier, S. M. Tavender, W. A. Parker, G.. D. Scholes and D. Phillips, *J. Phys. Chem., A*, 1997, **101**, 5320–5326.

13 H. Görner and D. Döpp, *J. Chem. Soc., Perkin Trans. 2*, 2002, 120–125.

14 A. M. J. van Eijk, A. H. Huizer and C. A. G. O. Varma, *J.Photochem. Photobiol. A: Chem.*, 1991, **56**, 183–193.

15 A. Cantos, J. Marquet and M. Moreno-Mañas, *Tetrahedron Lett.*, 1989, **30**, 2423–2426.

16 H. Görner, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1778–1783.

17 F. M. Abd El Latif, M. A. Barsy, E. A. Rady, M. E. Hassan and M. A. El Maghraby, *J. Photochem. Photobiol. A: Chem.*, 1999, **121**, 111–117.

18 R. Sastre, M. Conde and J. L. Mateo, *J. Photochem. Photobiol., A: Chem.*, 1988, **44**, 111–122.

19 M. V. Encinas, A. M. Rufs, E. Norambuena and C. Giannotti, *J. Polym. Sci. A, Polym. Chem.*, 1997, **35**, 3095–3100.

20 A. Costela, I. García-Moreno, O. García and R. Sastre, *J. Photochem. Photobiol. A: Chem.*, 2000, **131**, 133–140.

21 A. Costela, I. García-Moreno, J. Dabrio and R. Sastre, *Macromol. Chem. Phys.*, 1997, **198**, 3787–3798.

22 M. V. Encinas, A. M. Rufs, E. Norambuena and C. Giannotti, *J. Polym. Sci. A, Polym. Chem.*, 2000, **38**, 2269–2273.

23 H. G. Heller and J. R. Loangan, *J. Chem. Soc., Perkin Trans. 2*, 1981, 341–343.

24 J. Alvarez, E. A. Lissi and M. V. Encinas, *J. Polym. Sci. A: Polym. Chem.*, 1998, **36**, 207–208.

25 A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, 1961, **83**, 1852–1860.

26 D. Dopp, D. Müller and K. H. Sailer, *Tetrahedron Lett.*, 1974, 2137–2140.

27 H. Görner, *Phys. Chem. Chem. Phys.*, 2002, **4**, 482–489.

28 A. M. J. Van Eijk, A. H. Huizer, C. A. G. O. Varma and J. Marquet, *J. Am. Chem. Soc.*, 1989, **111**, 89–95.

29 D. Rehm and A. Weller, *Ber. Bunsen-Ges. Phys. Chem.*, 1969, **73**, 834–839.

30 C. Porcal, S. G. Bertolotti, C. M. Previtali and M. V. Encinas, *Phys. Chem. Chem. Phys.*, 2003.

31 N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, 1968, **68**, 449–523.

32 J. S. Brinen and B. Singh, *J. Am. Chem. Soc.*, 1971, **93**, 6623–6629.

33 O. Massot, M. Mir, T. Parella, J. L. Bourdelande and J. Marquet, *Phys. Chem. Chem. Phys.*, 2002, **4**, 216–223.

34 E. A. Lissi and M. V. Encinas, in *Photochemistry and Photophysics*, ed. J. F. Rabek, CRC Press, Boca Raton, FL, 1991, vol. IV, p. 221–293.