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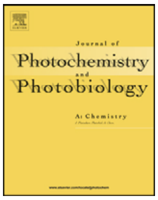

Short Note

Photoinduced intramolecular charge shift reaction in ammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate adducts

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ABSTRACT

Ammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate adducts were synthesized and characterized by using different protonated amines as counter-ion: NH_4^+, $(CH_3{-}CH_2{-})_2NH_2^+$, $(CH_3{-}CH_2{-}CH_2)NH_3^+$, $(CH_3{-}CH_2{-}CH_2{-}CH_2{-})NH_3^+$ and $(CH_3{-}CH_2{-})_3NH^+$. A photochemical process was observed under ultraviolet (λ_{exc}, 254 nm) or solar irradiation, both in solid state and in solution: DMSO, acetone or acetonitrile. 3,5-Dinitrobenzene and carboxylate groups, separated by an N-benzylamide bridge, are present in these adducts, acting as electron acceptor and electron donor, respectively. Spectroscopic analyses (NMR, IR and UV–vis) suggest a photoinduced intramolecular electron transfer. A first-order photochemical kinetics was proposed in DMSO/(n-propylammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate) solution; such behavior was similar for all adducts studied, probably due to total salt dissociation in solution. In the solid state, however, electron transfer process efficiency is directly proportional to Lewis base (amine) strength of the adduct counter-ion. Decarboxylation is observed after the irradiation process, giving rise to a σ-adduct intermediate, and subsequent formation of benzaldehyde and 3,5-dinitrobenzamide degradation products.

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1. Introduction

The electron transfer (ET) mechanism is a very common event related to photoinduced processes. Charge transfer (or electron donor–acceptor) complexes (CTC) have been extensively studied in fields from ranging biological to materials science [1–3]. Normally, CTC formation occurs through electron transfer between vacated HOMO or LUMO orbitals of the donor and acceptor groups [4]. Intramolecular CTC should occur when a molecule presents the following fundamentals: an electron donor group (D), an electron acceptor group (A) and a bridge (B) bonding these two groups through σ and/or π bonds [4,5]. In specific cases, D or A (or both) can be charged, given a long-lived charge migration species. The charge transfer process observed in 9-arylacridinium ions has been described as an interesting example [6,7].

$$D - B - A \xrightarrow{h\nu} (D - B - A)^* \rightarrow \overset{+\cdot}{D} - B - \overset{-\cdot}{A}$$

It has been proposed that the size and nature of the bridge may control the ET energy, intra- or intermolecular spatial interaction, environment arrangement and state of the process (solid and/or solvated) [8,9]. Thus, a large amount of information on the ET process has been described, regarding distance dependence, symmetric effects, configuration and energetics of the bridge. In solution, the solvent plays a role in the ET process due to polarity variation following the electron transfer between species involved [4].

Aromatic nucleophilic substitution reactions have been frequently studied in the presence of a dinitrobenzene electron acceptor system [10,11]. A CTC intermediate has been proposed in such reaction mechanisms, formed through a single electron transfer (SET). In a simplified fashion, we can state that CTC stability involving nitro-aromatic compounds can be controlled by the nucleophilicity of the electron donor group, in which strong nucleophilic groups such as OH^-, CN^- and MeO^-, promote an intermediate CTC formation, but the equilibrium is displaced to nucleophilic substitution products [10,11]. In the presence of amines, CTC formation is favored due to the weak nucleophilic nature of the amine [12,13]. In other cases, the CTC only can be obtained under excitation energy such as UV light [1–5,14–20].

Herein, we report the synthesis of stable organic salts derived from N-(3,5-dinitrobenzoyl)-α-phenylglycine (**DNP**) and some amines [21]. These adducts contain electron donor and acceptor groups bonded through an N-benzylamide bridge, as displayed in Scheme 1.

2. Experimental

All organic reagents and solvents were purchased from Sigma Aldrich or Acros. UV–vis and kinetic experiments were carried out in DMSO, previously dried in the presence of calcium hydride and

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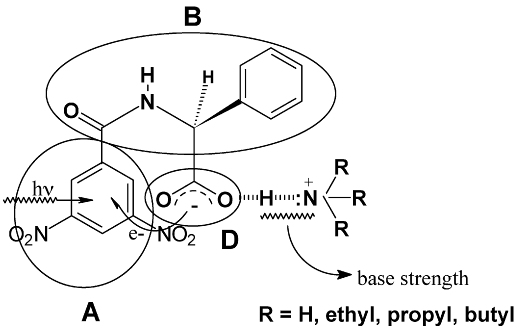


Scheme 1. Ammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate adduct structure.

distilled under vacuum. Nuclear magnetic resonance spectra ^{1}H NMR and ^{13}C NMR were recorded in a Varian Unity Plus (300 MHz) spectrometer using acetone-d_6, DMSO-d_6, or $CDCl_3$ as solvent. UV–vis spectra were registered in a Varian Cary 50 (Xenon lamp) or PerkinElmer Lambda 6 (tungsten and deuterium lamp) spectrophotometers in the 190–900 nm region, in the presence of the solvent as background. All measurements were registered in 3 mL quartz cuvettes. Infrared spectra were registered using a Bruker FTIR (model IFS66) (1% sample KBr pallets). The decomposition point was determined on Electrothermal 9100 melting point equipment. Elemental analyses were performed in Carlo Erba (model EA 1110) equipment. Gas chromatogram/mass spectra were taken (Shimadzu model QP5050) with a 30-m capillary column, using a 60–200 °C temperature range (10 °C min^{-1}). Comparisons with authentic sample were performed to identify reaction products and reagents and confirmed by GC/MS. Photoinduced reaction experiments were carried out in a black box. All measurements in solution samples were performed in 3 mL quartz cuvettes using a 6-W UV lamp (low pressure Hg, $\lambda = 254$ nm) as radiation source. Solid state sample measurements were performed in round pastil shape containing **DNP** salts powder under direct irradiation. Syntheses of adducts are described in the Supplementary data.

3. Results and discussion

The respective ammonium salts were synthesized by **DNP**/amine acid–base reaction, in diethyl ether medium: NH_4^+ (**ADNP**), $(CH_3{-}CH_2{-})_2NH_2^+$ (**DDNP**), $(CH_3{-}CH_2{-}CH_2{-})NH_3^+$ (**PDNP**), $(CH_3{-}CH_2{-}CH_2{-}CH_2{-})NH_3^+$ (**BDNP**) and $(CH_3{-}CH_2{-})_3NH^+$ (**TDNP**). Satisfactory yields were observed in the synthesis of the related salts and the respective decomposition temperatures demonstrate a thermal stability below 130 °C (Table 1).

UV irradiation (λ_{exc}, 254 nm) of the related adducts, at the π-π* transition region of the aromatic groups ($\lambda \sim 260$ nm), both in solution (DMSO, acetonitrile and acetone) and solid state, causes a color change from white to purple (Fig. 1), given rise to two new bands at $\lambda = 406$ and 555 nm, and a shoulder at $\lambda = 640$ nm, thereby indicating a photochemical phenomenon. **DNP** and its respective ester (methyl N-(3,5-dinitrobenzoyl)-α-phenylglycinate) are not photosensitive, indicating that the photoinduced process should not occur through the unpaired electrons of the amide nitrogen [19,20] or between aromatic groups of the **DNP** structure. Therefore, the ET process probably occurs between the carboxylate (donor) and 3,5-dinitrobenzene (acceptor) groups (Scheme 1), in which the N-benzylamide bridge must support the necessary conformation for the photoinduced ET. The photochemical effect occurring in the solid state strongly indicates an intramolecular effect [4].

Table 1
Reaction yields, melting and decomposition points for **DNP** and respective salts.

Entry	Compound	Yield (%)	Decomposition temperature (°C)
1	**DNP**	88	211–213[a]
2	**ADNP**	93	189
3	**DDNP**	74	170
4	**PDNP**	89	180
5	**BDNP**	84	175
6	**TDNP**	66	140

[a] Melting point.

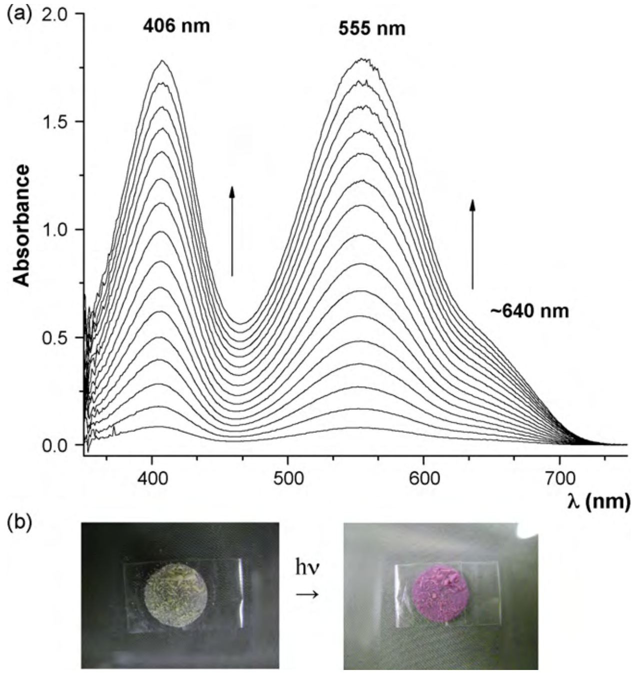


Fig. 1. (a) UV–vis spectrum of 5.0×10^{-3} mol L^{-1} **TDNP** (DMSO solution) acquired after successive UV (λ_{exc}, 254 nm) irradiations (5 min) in Ar atmosphere. (b) **TDNP** color change in solid state after 30 s of UV (λ_{exc}, 254 nm) irradiation.

The UV light irradiation of 5.0×10^{-3} mol L^{-1} **DNP** salt solutions (**PDNP**, **TDNP**, **DDNP**, **ADNP**, **BDNP**) dissolved in DMSO, at 5 min intervals and acquisition of the respective absorbance at 555 nm, reveals a similar kinetic behavior for CTC formation (Fig. 2), indicating a similar dissociation of the adducts studied in this medium. Therefore, in solution, the electron transfer should be occurring only in the anionic portion of the molecule.

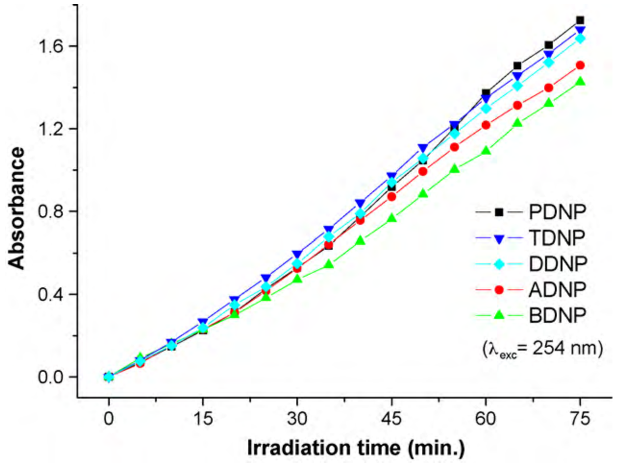


Fig. 2. Irradiation of 5.0×10^{-3} mol L^{-1} **DNP** salt solutions (**PDNP**, **TDNP**, **DDNP**, **ADNP**, **BDNP**) in DMSO at 5 min intervals ($\lambda_{exc} = 254$ nm) and data acquisition at 555 nm.

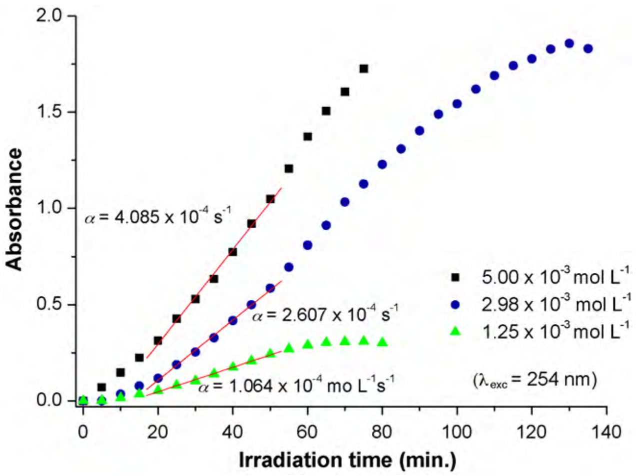
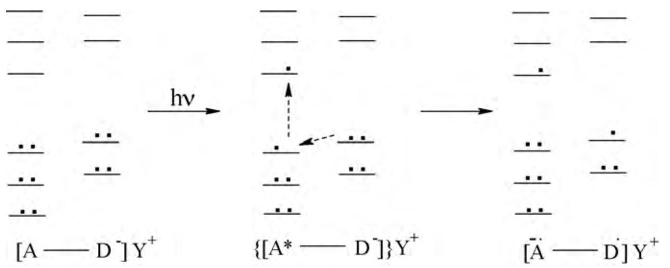


Fig. 3. Photoinduced reaction monitoring for **PDNP** solutions (1.25×10^{-3}, 2.98×10^{-3}, 5.0×10^{-3} mol L^{-1}) in DMSO: irradiation at 5 min intervals (λ_{exc} = 254 nm) at 555 nm.

Essays were performed to evaluate the kinetics of the colored intermediate in DMSO solution (Fig. 3). Three different concentrations of **PDNP** in DMSO (1.25, 2.98 and 5.00×10^{-3} mol L^{-1}) were irradiated (λ_{exc}, 254 nm) using the same procedure described in Fig. 2. Analysis of the linear coefficient of the curves and correlation of its respective values (1.064, 2.607 and 4.085×10^{-4}) indicates a first-order behavior for the photoinduced reaction. However, the colored intermediate undergoes a slow degradation, due absorbance decrease at the end of the irradiation time [22], what explains the shape and kinetics observed in the Fig. 3.

Therefore, an exciplex intramolecular photoinduced reaction mechanism should occur, involving an excited state, after UV irradiation of electrons of A (acceptor group, 3,5-dinitrobenzene) (Scheme 2). One electron is promoted to LUMO of A, followed by electron transfer from HOMO of D (donor group, carboxylate) to the vacant HOMO 1e- of A* and the CTC is formed [23–25]. Thus, we believe that both reaction partners (A and D) are built into one molecule, but barely interact. If an electron transfer from D to A is energetically feasible in the excited state, the product of such an intramolecular ET reaction is a charge-separated species: $D^{+\bullet}$–B–$A^{-\bullet}$. In the specific case of **DNP** salts, the D group is an anion



Scheme 2. Frontier molecular orbital of the photoinduced ET between nearly non-interacting D and A groups. Y$^+$ = ammonium counter-ion: in excitation of A (3,5-dinitrobenzene group), one electron is promoted to LUMO, followed by D (carboxylate group) ET to HOMO of A and the CTC is formed.

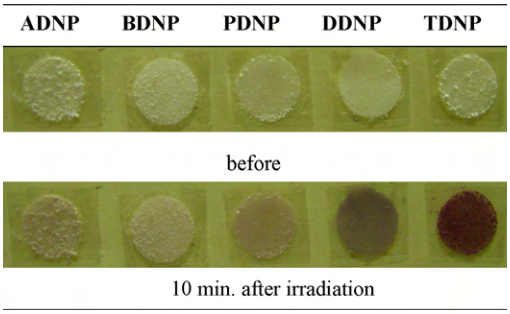
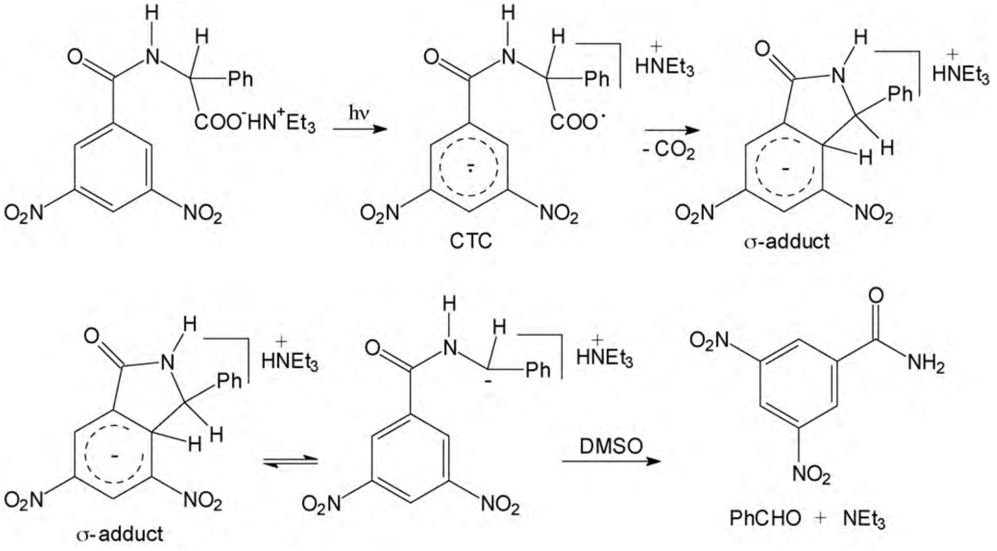


Fig. 4. Color change after 10 min irradiation (λ_{exc} = 254 nm) of: **ADNP**, **BDNP**, **PDNP**, **DDNP** and **TDNP** in solid state.

(D^-) that becomes a radical ($D^\bullet$), after the ET process. Therefore, the radical anion $A^{-\bullet}$ is neutralized by the ammonium counter-ion (Y^+) and the electronic structure of the CTC ground state corresponds to a radical anion/radical/cation: $[A^{-\bullet}–D^\bullet]Y^+$ [4]. Such mechanism can be classified as a charge shift as proposed by Kakitami and Mataga [26].

In DMSO, the kinetics of the ET process was similar for all DNB salts studied. The counter-ion effect may be neglected likely due the complete dissociation of the salt in the solution. Different behavior was observed in the solid state and CTC formation was favored in the following order: **TDNP** > **DDNP** > **PDNP** > **BDNP** ≅ **ADNP** (Fig. 4). In the ammonium salt structure, the proton is disputed by the amine and carboxylate groups, which are two different bases



Scheme 3. Mechanism proposed to photodegradation of ammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate salts.

(Scheme 1). Therefore, the photoinduced process is favored in the presence of stronger Lewis bases (amines), releasing the carboxylate pair of electrons for the ET process. Amine basicity works as a HOMO energy modulator of the carboxylate group in the solid state (Scheme 2).

It was not observed reversibility after the photoinduced ET process, neither under visible light irradiation nor heating of the colored intermediate formed [18], therefore, the photochemical electron transfer process observed in **DNP** salts cannot be classified as a photochromic process [4]. Conventional techniques of analysis were used to evaluate the stability of the CTC intermediate and identify possible decomposition products. No spectral modification was observed for NMR analysis after several hours of irradiation probably due the low quantum yield and elevated extinction coefficient of the observed intermediate, however, the ^{1}H NMR and GC/MS analyses of a diluted DMSO-d$_6$/**TDNP** (3.0×10^{-3} mol L^{-1}) sample, irradiated for 9 h, made possible to identify benzaldehyde and 3,5-dinitrobenzamide decomposition products. IR analysis of **TDNP** (KBr pastille) irradiated in the solid state showed the appearance of a peak at 2337 cm^{-1}, characteristic for CO_2 asymmetric stretching, while the **TDNP** carboxylate group peaks at 1595 and 1390 cm^{-1} decrease. This is an important evidence about the formation of the carboxylate radical ($-CO_2^{\bullet}$), in agreement to the proposed photoinduced electron transfer between 3,5-dinitrobenzene and carboxylate groups. Therefore, the CTC intermediate should undergo decarboxylation, giving rise to a σ-adduct [10,11] (Scheme 3), followed by degradation to benzaldehyde and 3,5-dinitrobenzamide, in the presence of DMSO. This mechanism corroborates similar photodegradation mechanisms of α-aminoacids and α-aminoalcohols described in the literature [27,28].

Some studies involving structural modifications of the photoactive molecule (alkaline metal counter-ions and bridge structure), computational and ESR analysis, quantum yield and life time are in due course, which can give additional support to elucidate the photochemical mechanism.

4. Conclusion

In conclusion, a photochemical effect was observed for **DNP** ammonium salts both in the solid state and solution (polar solvents). A first-order photoinduced reaction mechanism involving an intramolecular ET process was proposed, with 3,5-dinitrobenzene as electron acceptor and the carboxylate group as electron donor. This behavior is ascribed to the favorable interaction between orbital energy levels of the donor and vacant acceptor* groups as well as N-benzylamide bridge. The CTC undergoes a slow process of decarboxylation followed by degradation to 3,5-dinitrobenzamide and benzaldehyde. To the best of our knowledge, this is the first example of photoinduced intramolecular ET between 3,5-dinitrobenzene and carboxylate groups.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.05.005.

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