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Laser Flash Photolysis Study of the Reaction of 1*H*-Benz[*f*]indane-1,2,3-trione with Olefins

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A fotoquímica de 1*H*-benz*[f]*indano-1,2,3-triona (**1**) em presença de olefinas, em solução de benzeno e a temperatura ambiente, foi examinada empregando a técnica de fotólise por pulso de laser. O estado excitado triplete de **1** ($\tau = 3\,\mu$s, $\lambda = 460$ e 490 nm, em benzeno) é suprimido por olefinas contendo hidrogênio alílico com constantes de velocidade variando de 10^5 L mol^{-1}s^{-1} (para 1,5-hexadieno) a 10^9 L mol^{-1}s^{-1} (para 2,5-dimethyl-2,4-hexadieno). A comparação entre a reatividade de **1** com a de 1,2,3-indanotriona (**2**) mostra que um mesmo mecanismo de supressão está operando nos dois casos, o qual envolve, essencialmente, o estado excitado triplete de energia mais baixa da tricetona vicinal cíclica com característica n,π*.

The photochemistry of 1*H*-benz*[f]*indane-1,2,3-trione (**1**) in the presence of olefins has been examined in benzene solution at room temperature by laser flash photolysis. The triplet excited state of **1** ($\tau = 3\,\mu$s, $\lambda = 460$ and 490 nm, in benzene) is quenched by olefins containing allylic hydrogen with rate constants ranging from 10^5 L mol^{-1}s^{-1} (for 1,5-hexadiene) to 10^9 L mol^{-1}s^{-1} (for 2,5-dimethyl-2,4-hexadiene). A comparison of the reactivity of **1** with that of 1,2,3-indantrione (**2**) shows that a similar mechanism for the quenching by olefins is operating for the two cyclic vicinal triketones and involves essentially the lowest triplet excited state of n,π* character.

Keywords: cyclic vicinal triketone, laser flash photolysis, triplet state

Introduction

It is well known that the reactivity towards hydrogen donors of aromatic ketones having triplet excited state with π,π* character is much lower than that for an n π* triplet. This is easily explainable since n,π* excitation implies a considerable increase in the eletrophilicity of the carbonyl oxygen, resulting in its ability to participate in hydrogen abstraction reactions, either intramolecular (Norrish Type II reaction) or intermolecularly (carbonyl photoreduction through hydrogen abstraction of an hydrogen atom from suitable hydrogen donors). Higher reactivity for the n,π* triplet excited state of aromatic ketones when compared to a π,π* state is also observed in photocycloaddition reactions (Patternò-Büchi reaction), in which a carbonyl adds to an olefin forming a 1,4-biradical, which ultimately results in oxetane formation. Aromatic ketones have n,π* and π,π* excited states very close in energy (ΔE between 12 and 21 kJ mol^{-1}). Due to this, small structural changes, as for example the introduction of an electron-donating substituent such as a

methoxy group, may switch the electronic configuration of their T_1 and T_2 states. Similar behavior is observed upon change in the solvent polarity.[1-3]

In a recent publication we show that, for the cyclic vicinal triketone 1,2,3-indantrione, substitution by a methoxy group does not affect its reactivity towards olefins.[4] In this case, a difference of ~84 kJ mol^{-1} between the lowest triplet excited state (T_1), of n,π* character, and T_2, of π,π* nature,[5] does not allow an inversion of these two states by simply introducing a methoxy group in the aromatic ring.[4]

In this work we show results of a study of the photochemical behavior of 1*H*-benz*[f]* indane-1,2,3-trione (**1**) in the presence of olefins containing allylic hydrogen employing the laser flash photolysis technique. This study is aimed to extend our knowledge of the photochemistry

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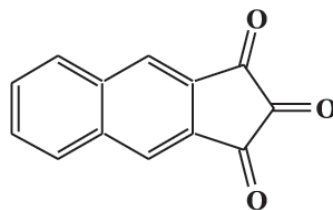
of cyclic vicinal tricarbonyl compounds by investigating the effect of the presence of a naphthalene ring upon their reactivity.

Experimental

Materials

The solvents, from Aldrich Chemical Co., were used as received. The olefins cyclohexene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, 1,5-cyclooctadiene, 2,5-dimethyl-2,4-hexadiene, 2,5-dimetil-1,5-hexadiene, 1,5-hexadiene, 2,4,4-trimethyl-1-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, 2-carene, 3-carene, ethyl vinyl ether, *n*-butyl vinyl ether, *trans*-1,3-pentadiene, *trans*-*β*-methylstyrene, *cis*-stilbene and *trans*-stilbene were purchased from Aldrich and were purified when necessary (purity <99%). 1*H*-Benz[*f*]indane-1,2,3-trione was prepared by vacuum sublimation of 2,2-dihydroxy-1*H*-benz[*f*]indene-1,2-dione (Aldrich) at 120-130 ºC.[5] After preparation, the green crystals were kept in sealed ampoules under reduced pressure.

General techniques

UV-visible spectra were recorded with a Varian Cary 3E spectrophotometer. Laser flash photolysis (LFP) experiments were carried out on Edinburgh Analytical Instruments LP900. Samples were contained in a 10 mm x10 mm cell made from Suprasil quartz tubing and were deaerated by bubbling oxygen-free nitrogen for 20 min. The samples were irradiated with a Nd/YAG Surelite laser, using the third harmonic (λ = 355 nm, ~5 ns, 40 mJ/pulse). The concentration of triketone was chosen in order to give an absorption at the wavelength of excitation (355 nm) of ~0.3. Stock solutions of quenchers in the same solvent employed in sample preparation were prepared so that it was only necessary to add microliter volumes to the sample cell in order to obtain appropriate concentrations of the quencher. All experiments were carried out using benzene as solvent.

Results and Discussion

Laser excitation (355 nm) of 1*H*-benz[*f*]indane-1,2,3-trione in benzene solution leads to the formation of a transient, which shows absorption maxima at 460 and 490 nm (Figure 1). This transient decays by first order kinetics with a second-order contribution and shows an apparent lifetime of 3 μs (see inset in Figure 1). Second-order contribution is not uncommon in the decay of aromatic
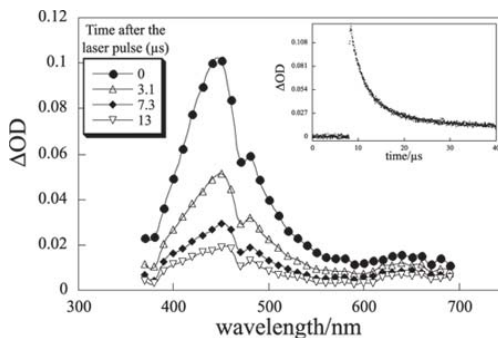

Figure 1. Transient absorption spectrum obtained on 355 nm excitation of 1*H*-benz[*f*]indane-1,2,3-trione (**1**) in benzene. *Inset:* decay for this transient monitored at 460 nm.

ketones, being related to a triplet-triplet annihilation process.

The above transient was quenched by 1,3-cyclohexadiene (E_T = 219 kJ mol^{-1})[6] with k_q = 3.0 x 10^8 L mol^{-1}s^{-1}, following equation 1:[7]

$$k_{obs} = k_0 + k_q[Q] \tag{1}$$

where: k_0 is the triplet decay rate constant in the absence of quencher; k_q is the triplet decay rate constant in the presence of the quencher and [Q] is the quencher concentration.
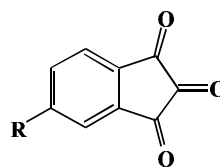
2 R=H
3 R=OMe

A recent study of the low lying electronic states and photophysical aspects of 1*H*-benz[*f*]indane-1,2,3-trione (**1**), carried out using absorption, emission and excitation spectra in various solvents, at different temperatures, showed that **1** exhibits n,π* phosphorescence at 77 K and an unusual n,π* fluorescence at room temperature.[5] From this study, a value of 172 kJ mol^{-1} for the lowest triplet excited state of **1** and of n,π* character, in methylcyclohexane, was obtained.[5] Thus, the quite fast rate constant quenching process is not consistent with an energy transfer process from triplet **1** to the conjugated diene, due to the high endothermicity of this process (in excess of 50 kJ mol^{-1}). This can be associated with a

quenching process involving a small amount of the triplet hydrate derived from **1** and produced through an excited state photoaquation equilibrium. Similar behavior, *i.e.*, large quenching rate constants for cyclic vicinal triketones of low triplet energy by 1,3-cyclohexadiene, was previously observed for 1,2,3-indanetrione (**2**, R=H) and its 5-methoxy derivative **3**, R=OMe.[4,8]

To further confirm the triplet nature of the transient observed in Figure 1, quenching experiments employing β-carotene were undertaken. β-Carotene shows triplet energy of 79 kJ mol[-1][9] and has intersystem crossing quantum yield of essentially zero.[10] Thus, β-carotene triplet can only be formed through an energy transfer process from a suitable triplet donor. Since β-carotene has a characteristic triplet-triplet absorption showing a sharp peak at 520 nm, the quenching process of **1** by this polyene could be easily monitored either by following the mono-exponential decay of the triplet of **1**, at 460 or 490 nm, or following the mono-exponential growth of the β-carotene triplet at 520 nm. In both cases a diffusion-controlled rate constant ($k_q = 5.0 \times 10^9$ L mol^{-1}s[-1]) in benzene was obtained, which enables us to confirm the triplet nature of the transient obtained upon laser excitation of **1**. Figure 2 shows the triplet-triplet absorption spectrum for β-carotene obtained by energy transfer from 1*H*-benz[*f*]indane-1,2,3-trione (**1**) in benzene.
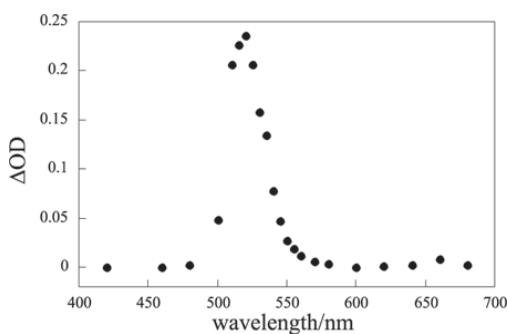

Figure 2 – Triplet-triplet absorption spectrum for β-carotene obtained by energy transfer from 1*H*-benz[*f*]indane-1,2,3-trione (**1**) in benzene.

Addition of olefins containing allylic hydrogen to a benzene solution containing **1** led to a shortening of its triplet lifetime. The triplet decay for **1** in the presence of these quenchers followed clean pseudo-first order kinetics (k_{obs}). Figure 3 shows representative Stern-Volmer plots using equation 1 for the quenching by 1,5-hexadiene, 2,4,4-trimethyl-1-pentene, 2-carene and 3-carene. The rate constants obtained are included in Table 1.
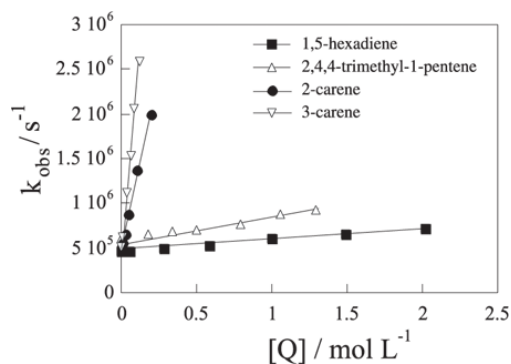

Figure 3. Representative quenching plots for the triplet state of 1*H*-benz[*f*]indane-1,2,3-trione (**1**) by olefins in benzene (λ_{exc}=355 nm, λ_{mon}=460 nm).

Table 1. Second order rate constants (k_q) for the quenching of 1*H*-benz[*f*]indane-1,2,3-trione triplet by olefins in benzene solution

Olefin	k_q naphthotrione[a]	k_q indanetrione[b]
cyclohexene	3.9×10^6	9.3×10^5
1,4-cyclohexadiene	3.3×10^5	1.4×10^{6c}
1,3-cyclohexadiene	3.0×10^8	4.0×10^8
1,5-cyclooctadiene	1.8×10^5	7.1×10^5
2,5-dimethyl-2,4-hexadiene	1.3×10^9	1.8×10^9
2,5-dimethy-1,5-hexadiene	3.1×10^5	4.8×10^5
1,5-hexadiene	1.3×10^5	1.6×10^5
2,4,4-trimethyl-1-pentene	2.5×10^5	3.1×10^5
2-methyl-1-butene	1.5×10^5	1.3×10^5
2-carene	7.8×10^6	1.0×10^7
3-carene	1.8×10^7	4.5×10^6
β-pinene	4.1×10^5	1.6×10^6
trans-1,3-pentadiene	3.0×10^7	1.3×10^7
trans-β-methylstyrene	9.9×10^6	8.3×10^6

[a] Estimated to be accurate to ± 10%; [b] from ref 4; [c] from ref. 8.

Laser flash photolysis of **1** in benzene (λ_{exc}=355 nm), in the presence of electron-rich olefins such as 2-methyl-2-butene, 2,3-dimethyl-2-butene or enol ethers, led to the observation of an intense signal with absorption maxima at the same wavelengths as those obtained for the triplet of **1**. Consequently, it was not possible to determine the corresponding quenching rate constants for these olefins due to the complexity of the kinetic traces obtained. This result fully agrees with the steady state photolysis of 1,2,3-indanetrione (**2**, R=H; E_T=176 kJ mol^{-1})[8] in the presence of electron rich olefins. UV irradiation of **2** in the presence of 2,3-diphenyl-1,4-dioxene[11] or *n*-butyl vinyl ether,[12] leads to the formation of the corresponding oxetanes, through a [$2\pi+2\pi$] photocycloaddition (Paternò-Büchi reaction). Laser flash photolysis studies of the photochemistry of **2** in benzene solution show that the mechanism for the reaction of its triplet with olefins involves only a partial

charge transfer complex in the quenching step.[4] Despite the fact that in the reactions of **1** with electron rich olefins, where the formation of products derived from a 1,4-biradical are expected, a long-lived new transient can be observed, which could not be assigned to an excited complex (if formed) or a 1,4-biradical, since short lifetimes are expected for these species.[13-15]

The photochemical reaction of carbonyl compounds with olefins containing allylic hydrogen may involve two competing processes: addition to give a 1,4-biradical or abstraction of an allylic hydrogen to give the semidione/ allylic radical, with the product distribution showing solvent, temperature and excited state dependence.[16,17] It has been postulated that both hydrogen abstraction and photocycloaddition are parallel processes that probably occur via the same intermediate, *i.e.*, an exciplex containing a partial charge transfer character.[18,19] In some cases, photochemical hydrogen abstractions and photo-cycloaddition can occur via a full electron transfer process. Electron spin resonance and laser flash photolysis studies have provided clear-cut evidence of the intermediates involved in these mechanisms.[20] For example, photolysis of **2** (R=H) with electron-rich olefins containing allylic hydrogen, such as 2-methyl-2-butene[11] or 2,3-dimethyl-2-butene,[21] results in the formation of products by hydrogen abstraction and photocycloaddition. For mono- or di-substituted olefins containing allylic hydrogen and which are not so electron-rich, such as 2,4,4-trimethyl-1-pentene,[11] 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene,[12] cyclohexene, 2-methyl-1-butene,[12] and 2,5-dimethyl-2,4-hexadiene,[12] the only products observed were those resulting from a hydrogen abstraction process. The magnitude of the rate constants shown in Table 1 (ranging from 10^5 to 10^7 L mol^{-1}s^{-1}) is consistent with a preferential mechanism involving an allylic hydrogen abstraction. It is expected that oxetane formation is favored when the olefin is a good quencher ($k_q > 10^7$ L mol^{-1}s^{-1}) of n,π^* states, with hydrogen abstraction starting to be competitive when $k_q < 10^7$ L mol^{-1}s^{-1}.[22] The quenching of mono- and di-carbonyl triplet compounds by olefins occurs preferentially by π-system interaction ($k_q > 10^6$ L mol^{-1}s^{-1}). When hydrogen abstraction competes with the cycloaddition mechanisms, the hydrogen abstraction product yield increases as a function of the presence of large substituents in the olefin (as for example the neopentyl group as in 2,4,4-trimethyl-1-pentene) or when the reaction is done in the presence of a highly strained cyclic olefin.[23-28] Even so, the increase in the yield of hydrogen abstraction products parallels the quenching rate constants, indicating that steric effects reduce the biradical formation and/or cyclization controlling the product distribution. However, previous studies on the reaction of cyclic vicinal tricarbonyl

compounds with olefins show that electronic effects predominate over steric effects in the quenching process, with photocycloaddition products only starting to be formed when the ionization potential of the olefin approaches 8.7 eV.[4,11,21]

Monoketones containing a naphthalene chromophore show triplet energy around 55-59 kJ mol^{-1} and display very low reactivity towards hydrogen abstraction or photocycloaddition reaction,[22] which is due to the π,π^* character of their lowest triplet state. Recent spectroscopic work from Roy and co-workers[5] (see above) shows that 1*H*-benz*[f]*indane-1,2,3-trione (**1**) has a lowest singlet excited state containing 188 kJ mol^{-1} and showing n,π^* character. The phosphorescence emission observed was characteristic of a triplet excited state with n,π^* character, which shows E_T=168 kJ mol^{-1}. A second triplet excited state containing 213 kJ mol^{-1} and having π,π^* nature was also observed in these studies. Thus, the difference in energy between these two triplets of close to 46 kJ mol^{-1} would be sufficient to guarantee that the reactivity of the triplet of **1** is fully controlled by the vicinal tricarbonyl chromophore. To further confirm this reasoning, the rate constants obtained in this work for the quenching of 1*H*-benz*[f]*indane-1,2,3-trione (**1**) by olefins were plotted against those rate constants obtained for 1,2,3-indantrione (**2**) and reported in a recent work from our group[4] (Figure 4). This linear plot shows a slope of 0.89±0.08 (r=0.957), which is an indication that the quenching mechanism for **1** and **2** by olefins involves a triplet state of n,π^* nature in both cases.
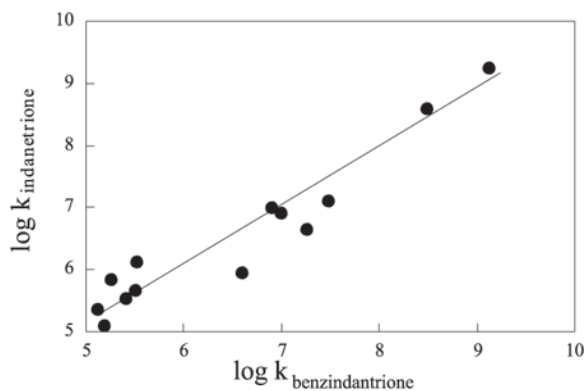

Figure 4. Plot of the correlation between quenching rate constants for triplet **1** and **2** (R=H) by olefins.

In conclusion, it has been demonstrated by laser flash photolysis studies that the photochemistry of 1*H*-benz*[f]*indane-1,2,3-trione (**1**) in the presence of olefins is controlled by the vicinal tricarbonyl group of nπ^* character, in spite the presence of the naphthalene moiety in the molecule.

Acknowledgements

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