Charge-transfer Interactions in the Intramolecular Quenching of Carbonyl Triplets by β-Aryl Substituents

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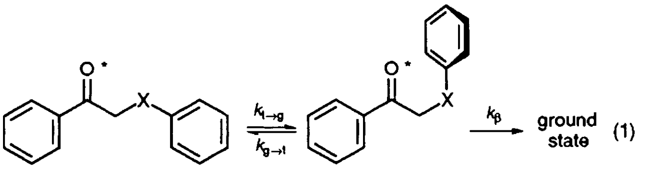
The triplet decay rates of ten β-aryl-4-methoxypropiophenone derivatives in methanol, acetonitrile, toluene and isooctane solution at 21 °C correlate with σ^+ substituent constants ($\rho^+ = -1.8 \pm 0.2$), indicating that charge-transfer exciplex interactions between the aryl group (donor) and the carbonyl group (acceptor) play a dominant role in the intramolecular β-aryl quenching of carbonyl n,π* triplets.

The intramolecular quenching of carbonyl triplets by β-aryl substituents is a well-known phenomenon[1,2] which plays an important role in the photochemistry of lignin-rich woodpulps[3] and which has been exploited for the photostabilization of polymers[4] and to probe the effects of organized media such as liquid crystals,[5] cyclodextrins[6] and zeolites[7] on the conformational mobility of solutes. It is well established that the extremely short triplet lifetimes of β-phenyl ketones such as **1a**[1] and **1b**[2] in fluid solution are due to efficient quenching of the carbonyl n,π* triplet by through-space interactions with the β-phenyl ring. For this to occur, the molecule must be able to adopt a *gauche* conformation which allows overlap between the β-phenyl π-system and the carbonyl oxygen n-orbital [see eqn. (1)].[1d]

Table 1 Triplet lifetimes of ketones **2a–j** in deoxygenated solution at 21 ± 1 °C

	τ_T/ns[a]			
Ketone (X)	MeOH	MeCN	MePh	OCT
2a (4-OMe)[b]	8 ± 2	3 ± 2	3 ± 2	4 ± 2
2b (4-Me)	49	9	11	11
2c (4-C-C_6H_{11})	57	12	13	11
2d (H)	225	49	60	57
2e (4-Cl)	225	52	54	50
2f (4-Br)	263	65	58	56
2g (3-CF_3)	1080	530	620	550
2h (4-CF_3)	2580	1000	1030	1160
2i (4-CN)	2050	700	590	[d]
2j [3,5-$(CF_3)_2$]	10300	3060	2650	1830
$\rho^+ (r^2)$[c]	−1.8 ± 0.2 (0.987)	−1.9 ± 0.2 (0.968)	−1.8 ± 0.2 (0.961)	−1.8 ± 0.4 (0.940)

[a] Lifetimes are considered accurate to ±10% or less, unless otherwise noted. [b] Determined by Stern–Volmer quenching using 1-methylnaphthalene as acceptor.[1f,11] Lifetimes calculated from $k_q\tau$ values (59.4, 29.1, 22.5 and 51 $dm^3\ mol^{-1}$ for MeOH, MeCN, MePh and OCT, respectively), using quenching rate constants tabulated in Ref. 12. [c] Errors are reported as ±2σ. [d] Insoluble.



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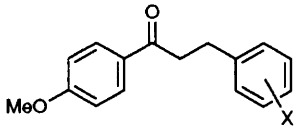
a; X = CH_2
b; X = O

The deactivation process has been proposed to involve charge-transfer (exciplex) interactions between the aryl and carbonyl groups,[1f] because the triplet decay rate of **1a** is decreased slightly in derivatives bearing electron-withdrawing substituents on the β-phenyl ring, and arenes are known to quench carbonyl triplets intermolecularly (with rate constants in the 10^4–10^7 $dm^3\ mol^{-1}\ s^{-1}$ range).[8] The intermolecular quenching process correlates with σ+ values for electron-rich arenes and has been proposed to involve exciplex intermediates, although such intermediates have been detected directly only in the quenching of cyclohexanone triplets by substituted benzenes.[9] In contrast to intermolecular cases, the effect of (β-aryl) substituents on the triplet decay rate of **1a** is very slight,[1f] leading to the suggestion that in β-aryl ketones with lowest n,π* triplet states, the rate-determining step for triplet decay in fluid solution is formation of the *gauche*-quenching geometry.

We have synthesized the series of β-aryl-4-methoxypropiophenones **2a–j**,† and determined their triplet lifetimes in a series of solvents at room temperature using nanosecond laser flash photolysis (NLFP) techniques. The triplet lifetime of **2d** is known to be substantially longer than that of **1a** in solution at room temperature.[1e,f] In this case, the lowest triplet is the π,π* state; β-phenyl quenching in **2d** is thought to involve thermal activation to the n,π* triplet which is 2–3 kcal mol^{-1} higher in energy (1 cal = 4.184 J).[1f] Thus, the rate-determining step for triplet decay in these compounds is the β-phenyl quenching process, and not the conformational motions involved in assuming the quenching geometry. It would therefore be expected that the triplet lifetimes of these compounds should be much more sensitive to substituents on the β-phenyl ring than is the case with the parent compound **1a**, and hence afford a better indication of the role of charge-transfer interactions in the quenching process.



2

a; X = 4-OMe
b; X = 4-Me
c; X = 4-c-C_6H_{11}
d; X = H
e; X = 4-Cl
f; X = 4-Br
g; X = 3-CF_3
h; X = 4-CF_3
i; X = 4-CN
j; X = 3,5-$(CF_3)_2$

NLFP experiments[10] were carried out using extensively deoxygenated, 0.005–0.02 mol dm^{-3} solutions of **2a–j** in methanol (MeOH), acetonitrile (MeCN), toluene (MePh), and isooctane (OCT), and a nitrogen laser (337 nm; 6 ns) whose beam was attenuated with neutral density filters. For **2b–j** (and **2a** in MeOH) clean first-order decay of the triplet state could be observed directly by monitoring the triplet-triplet absorption spectrum centred at 390 nm. Triplet lifetimes for **2a** in the aprotic solvents were estimated using the 1-methylnaphthalene (MN) probe method.[1f,11] Table 1 lists the lifetimes obtained for **2a–j** in each of the four solvents studied at 21 °C. Those of **2d** in MePh and MeOH and **2b** in MeCN and MeOH agree with those reported previously within experimental error.[1f,g] Self-quenching rate constants were estimated for **2g–j**, and vary within a range of 0.5–2 × 10^7 $dm^3\ mol^{-1}\ s^{-1}$.

In each solvent, the triplet lifetimes of the ten ketones vary over about three orders of magnitude throughout the series. The triplet decay rates in MeOH show an excellent correlation with σ^+ ($\rho^+ = -1.8 \pm 0.2$), verifying that intramolecular quenching of carbonyl triplets by β-aryl substituents involves strong charge-transfer interactions between the carbonyl (acceptor) and β-aryl ring (donor). Similar, but somewhat poorer, correlations were observed for the series of ketones in the other three solvents. The poorer correlations of the data for these solvents are due primarily to compound **2a**, in which the rate of intramolecular quenching is fast enough that conformational motions presumably contribute substantially to the rate of triplet decay. Interestingly, the ρ^+ value is solvent independent.

The results for **2a–j** are analogous to those reported previously for the intermolecular quenching of benzophenone triplets (BP) by electron-rich benzenes, whose rates also correlate with σ^+ ($\rho^+ = -2.7 \pm 1.0$).[8] One interesting difference between the inter- and intra-molecular quenching processes is that in the former, electron-poor arenes quench at

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† Ketones **2a–j** were prepared by catalytic hydrogenation of the corresponding chalcone derivative, which was prepared by condensation of 4-methoxyacetophenone with the corresponding substituted benzaldehyde. The compounds were recrystallized several times from ethanol or methanol and exhibited the following melting points (°C): 40.5–42 (**2a**), 63.5–65 (**2b**), 89–90 (**2c**), 95–97 (**2d**), 69–70 (**2e**), 99–101 (**2f**), 51.5–53 (**2g**), 62–64 (**2h**), 107–108.5 (**2i**), 65.5–67 (**2j**). The ^1H and ^{13}C NMR, infrared, and mass spectra and the parent ion exact mass were consistent with the proposed structure in each case. Details will be reported in a full paper.

faster rates than the correlation observed for electron-rich benzenes predicts.[8c] It was suggested that the nature of the quenching interaction is fundamentally different for electron-rich and electron-poor arenes; with the former, quenching occurs *via* an n-type exciplex which allows overlap of the arene π-system (donor) with the carbonyl n-orbital (acceptor). With electron-poor arenes, quenching was proposed to occur *via* a π-type exciplex which allows overlap of the arene π-system (acceptor) with the carbonyl π-system (donor).[8c] An analogous change in mechanism does not take place in the intramolecular quenching process in **2**, presumably because the molecule is unable to adopt the required geometry for efficient overlap between the β-aryl and carbonyl π-systems. Since **2g–j** are easily able to adopt a sandwich-like conformation which allows overlap between the two aryl rings, the present results suggest that the structure of the π-type exciplex involved in the intermolecular quenching of carbonyl n,π* triplets by electron-poor arenes is one in which π-overlap takes place specifically at the carbonyl group.

Further studies, to assess the effects of substituent and solvent on the energetics of β-aryl quenching in these compounds, are in progress.

We thank the NSERC (Canada) and the Canadian Mechanical and Chemimechanical Wood-Pulps Network of Centres of Excellence for financial support of this work.

Received, 12th February 1993; Com. 3/00861D

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