The Behaviour of Benzophenone Triplets in Benzene

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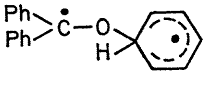
Summary Decay rates of benzophenone triplets have been measured using laser flash photolysis in highly purified benzene, [$^2H_6$]benzene, and hexafluorobenzene; the results indicate a very small deuterium isotope effect, and enhanced rate of decay in hexafluorobenzene, and are most consistent with reversible triplet addition to the ring as the process responsible for the short triplet lifetime.

THERE has been much discussion recently on the mechanism of deactivation of photoexcited ketones in benzene solution. It was originally observed that the quantum yield for the disappearance of Ph_2CO in benzene was $0 \pm 0{\cdot}05$ at 366 nm,[1] much less than in most solvents. This quantity has recently been redetermined as $0{\cdot}005 \pm 0{\cdot}001$.[2] However, two transients are clearly seen on flash photolysis of Ph_2CO in benzene.[3–5] The initial short-lived transient which decays by first-order kinetics is assumed to be the excited triplet state of Ph_2CO, from lifetime and quenching studies.[3–5] The long-lived transient, which decays by second-order kinetics, is assumed to be the ketyl radical $Ph_2\dot{C}OH$ by comparison of its absorption spectrum with that of $Ph_2\dot{C}OH$ formed on photoexcitation of Ph_2CO in the presence of good hydrogen donors.[3–5]

The lifetime of Ph_2CO triplets in benzene (10^{-5}–10^{-6} s)[3–9] is considerably shorter than the lifetime (*ca.* 10^{-3} s) in perfluorocarbons,[7,8] despite the low quantum yield for Ph_2CO disappearance. Four reasons for the short lifetime in benzene have been suggested: (a) quenching by impurities in the solvent, or by photoproducts;[3,7,10] (b) hydrogen abstraction from benzene, followed by reversal before phenyl and $Ph_2\dot{C}OH$ radicals escape from the solvent cage;[3,7,8] (c) charge-transfer interaction of ketone (as acceptor) and benzene (as donor);[3,8,11] (d) reversible formation of a diradical adduct (**1**).[5,9,12–14] We present evidence which strongly supports (d).


(1)

We have measured the decay characteristics of $^3Ph_2CO^*$ in benzene, [$^2H_6$]benzene, and hexafluorobenzene, using the technique of laser flash photolysis.[15] (Excitation at 347 nm; decay followed at 535 nm; flash lifetime 20 ns). Preliminary experiments[15] had been carried out with solvents which had not been purified extensively, and hence definite conclusions based on those results (Table) could not be drawn because of the possible role of quenching, even by trace impurities. The decay measurements have been repeated with 10^{-2} M-Ph_2CO in benzene, [$^2H_6$]benzene, and

TABLE

First-order decay rates of benzophenone triplets at room temperature

C_6H_6	C_6D_6	C_6F_6	Reference
$1\cdot0 \pm 0\cdot1 \times 10^5$ [a]	$0\cdot80 \pm 0\cdot14 \times 10^5$ [b]	$1\cdot4 \pm 0\cdot11 \times 10^6$ [c]	This work
$4\cdot0 \pm 0\cdot4 \times 10^5$	$2\cdot90 \pm 0\cdot30 \times 10^5$	$2\cdot3 \pm 0\cdot23 \times 10^6$	15
$1\cdot0 \pm 0\cdot5 \times 10^5$			3
$1\cdot0 \times 10^6$ [d]			8
$1\cdot8 \pm 0\cdot1 \times 10^5$			6
$1\cdot2 \times 10^5$ [e]			9
$0\cdot8 \pm 0\cdot1 \times 10^4$			5

[a] Average of three runs. [b] Average of two runs. [c] Average of four runs. [d] Extrapolated value from benzene quenching of Ph_2CO emission in perfluorodecalin at room temperature. [e] From phosphorescence quenching at room temperature.

hexafluorobenzene, all purified by the selective photochlorination procedure of Saltiel and Metts.[16] Benzene prepared in this way is of higher purity than that obtained by alternative procedures, as measured by the lowest observed rates of benzophenone triplet decay. The results are given in the Table, along with lifetimes of $^3Ph_2CO^*$ determined by other procedures. The strictly first-order decays observed in this study occur long after the decay of the flash. This was not the case with previous measurements using microsecond flashes,[3-6] which involved considerable error and correction due to the tail of the flash.

The small deuterium isotope effect (unity within experimental error) for triplet decay, in comparison with the very large isotope effects recently found for biphenyl formation[2,14] is inconsistent with postulate (b) involving hydrogen abstraction from benzene, a process that should show a large isotope effect owing to the high C–H bond dissociation energy of benzene. Other arguments against H-abstraction as an important process are given elsewhere.[13] The enhanced reactivity of hexafluorobenzene toward $^3Ph_2CO^*$, independent of the source and purity of the material, is inconsistent with (b) and (c). While charge transfer to ketone triplets may be significant with alkylbenzenes,[11] it is hardly expected to be important with benzenes containing strong electron-withdrawing groups. The most consistent interpretation of all the results is efficient formation of adducts of type (**1**), which subsequently decompose to ground-state benzophenone and benzene.[13] The inefficient reaction (Φ *ca.* 10^{-3})[2,14] which generates biphenyl and tetraphenylethylene glycol, may involve H-abstraction in competition with adduct formation,[5,14] although product formation *via* adduct (**1**)[13] has not been rigorously excluded.

Some evidence has recently been presented for a third transient on flash photolysis of Ph_2CO in benzene,[5] tentatively ascribed to a possible adduct of type (**1**). It has also been conclusively demonstrated that benzoyloxy radicals formed in the photochemical decomposition of benzoyl peroxide in benzene add reversibly to the benzene ring.[17]

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