Laser Flash Photolysis of 3-Phenylcyclopent-2-enone: Absorption Spectrum and Reactivity of its Triplet Excited State

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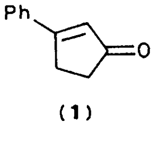
The triplet state of 3-phenylcyclopent-2-enone, formed upon pulsed laser excitation (308 nm; 15 ns pulse duration) in either cyclohexane or ethanol solution, is relatively long-lived at room temperature and is rapidly quenched by oxygen, piperylene, alkenes, and by its own ground state.

Although enones have played a central role in the development of organic photochemistry,[1,2] the properties of their excited states are still poorly understood in comparison to those of other classes of organic compounds, *e.g.* aromatic ketones, despite some very detailed flash photolysis studies especially by Bonneau and Schuster.[3—5] Our interest in inter- and intra-molecular cycloadditions of cyclopentenones[6,7] has prompted us to study the flash photolysis of 3-phenylcyclopent-2-enone (**1**). We report here that, unlike the other enones reported so far,[3—5] the triplet state of this compound is relatively long-lived in fluid solution at room temperature (between 1 and 20 μs, depending on conditions). This allows it to be conveniently monitored under photochemically relevant conditions, and we describe here its reactivity towards oxygen, piperylene, alkenes, and its own ground state.



(**1**)

Pulsed excimer laser (308 nm; 30 mJ; 15 ns) excitation of a degassed 1.0 mM cyclohexane solution of (**1**) yields a transient species (Figure 1), formed within 50 ns of the exciting flash, which decays by first-order kinetics with a lifetime of 2.9 μs at room temperature. The lifetime of the transient species is strongly dependent on the concentration of (**1**), indicating that a self-quenching process is occurring with a rate constant of 3×10^8 dm^3 mol^{-1} s^{-1}. Similar behaviour is observed for ethanol solution, the rate constant for self quenching being 2×10^8 dm^3 mol^{-1} s^{-1}. In aerated solutions the lifetime of the transient is markedly reduced, indicating a rate constant for quenching by oxygen of 2×10^9 and 1.2×10^9 dm^3 mol^{-1} s^{-1} for cyclohexane and ethanol solutions respectively. In degassed cyclohexane solution it is efficiently quenched by piperylene (3×10^9 dm^3 mol^{-1} s^{-1}) and by (*E*)-β-methylstyrene (2×10^9 dm^3 mol^{-1} s^{-1}) and less so by cyclohexene (1.1×10^7 dm^3 mol^{-1} s^{-1}) and 2,3-dimethylbut-2-ene (6×10^6 dm^3 mol^{-1} s^{-1}). The different rates obtained with these two sets of quenchers suggest that with piperylene and (*E*)-β-methylstyrene (E_T = 238 and 250 kJ mol^{-1} respectively[8,9]) quenching occurs *via* energy transfer whereas this is expected to be inefficient for the simple alkenes because of their higher E_T values and a chemical quenching mechanism is more likely. Further experiments will be required to demonstrate whether this is indeed the case. It may be noted however that the triplet states of these quenchers are expected to deactivate rapidly and hence are not expected to be observed under the present

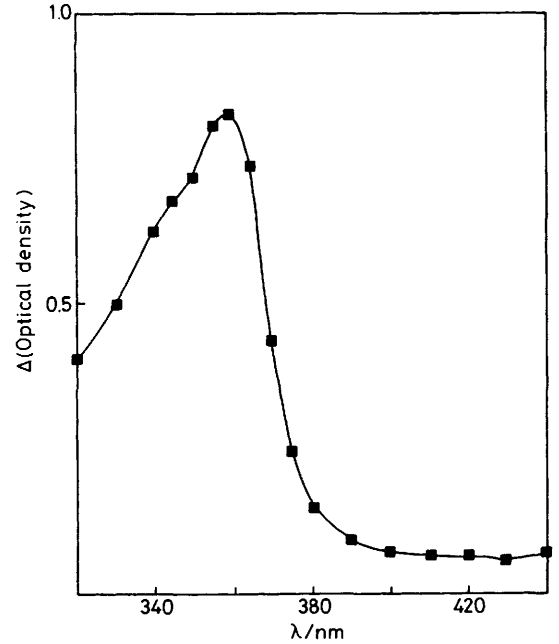


Figure 1. Absorption spectrum of the transient species recorded 500 ns after 308 nm laser pulse excitation of (1) in degassed cyclohexane solution. (Measurements at wavelengths out to 650 nm revealed no further absorption bands.)

flash photolysis conditions. By carrying out experiments in EPA [ether, isopentane, ethanol (5:5:2 v/v)] solution at temperatures down to 85 K, it has been possible to show that the species exhibiting the transient absorption has identical decay kinetics to those of the phosphorescence at 520 nm,[10] confirming that this transient is indeed the triplet excited state of (**1**).

The triplet state of (**1**) is considerably longer-lived than those formed from cyclopentenone itself or from simple cyclohexenones.[3—5] In the latter case a correlation has been found between the lifetime of the excited state and the rigidity of the enone. A long-lived transient formed from cycloheptenone has been assigned to a *trans*-cycloheptenone ground state.[11] In (**1**) twisting about the double bond must be difficult and conjugation with the phenyl group should stabilise the triplet state in its non-twisted geometry. The lack of evidence for efficient H-atom abstraction from either ethanol or cyclohexane at room temperature ($k_q < 10^4$ dm^3 mol^{-1} s^{-1}) is also consistent with an excited state having π–π^* rather than n–π^* character. Finally the observation that this excited state is quenched both by its ground state and by alkenes suggests a study to determine whether this species is the one responsible for the photocyclodimerisation and photocycloaddition reactions of (**1**), and such work is in progress at present.

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