

Solvent Dependence of the Triplet Reactivity of Pivalophenone as Evidenced by Laser Flash Photolysis

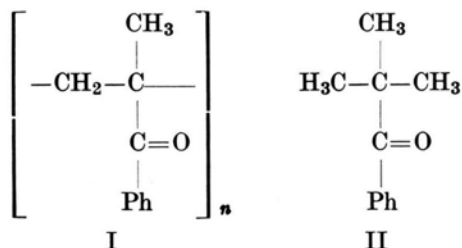
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Phenyl-*t*-butylketone (pivalophenone) was irradiated in mixtures of benzene and 2-propanol with 25 ns flashes of 347.1 nm light. Triplet lifetimes were measured by monitoring the decay of the T-T-absorption. 2-propanol exerts a significant stabilizing influence upon the triplet lifetime and lowers the triplet reactivity probably due to a $n, \pi^* \rightarrow \pi, \pi^*$ inversion of the lowest triplet state.

During a recent investigation [1] of the primary events during the photolysis of poly(phenylisopropenylketone) I and its model compound phenyl-*t*-butyl ketone II (pivalophenone) in benzene solution it turned out that



α -cleavage was the dominant chemical route of triplet deactivation in both cases. However, triplets of I were found to decay appreciably faster (about 4 times) than those of II, which was assumed being due to a strong interaction of triplet excited carbonyl groups of I with unexcited neighboring base units. Upon investigating in benzene solution the reaction of triplets of I and II with 2-propanol a relatively low reactivity of triplets of II was revealed. This finding was explained by assuming that molecules of I are preferentially solvated by

benzene molecules. Thus, alcohol molecules are prevented to interact strongly with I but are permitted to attack occasionally excited moieties of I. On the other hand it was assumed that 2-propanol is capable of interacting significantly with either the ground state or the excited state of molecules of II. This paper reports results which yield clear evidence for an interaction between II and 2-propanol. Pivalophenone (2.6×10^{-3} mol/l) was irradiated with 25 ns flashes of 347.1 nm light produced by a frequency doubled ruby laser (Korad model K1QS2) in Ar-saturated solutions as described before [2].

Solvent mixtures containing benzene and 2-propanol at various ratios were used. The decay of the T-T absorption formed during the flash was monitored at the wave lengths 320 and 460 nm. Triplet decay rate constants k_T are plotted as a function of solvent composition in Figure 1. It can

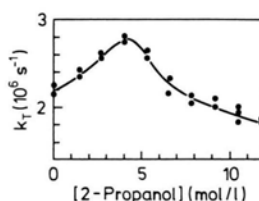


Fig. 1. The triplet decay rate constant as a function of the solvent composition. Pivalophenone (2.6×10^{-3} mol/l) in Ar-saturated mixtures of benzene and 2-propanol.

be seen that k_T increases with increasing 2-propanol content at relatively low alcohol concentrations but decreases after passing a maximum as the 2-propanol concentration is increased further. These results indicate that at low concentrations of 2-propanol the latter reacts with triplets of II relatively effectively ($k = 1.6 \times 10^5$ l/mol s). However, the triplet lifetime is increasing again as 2-propanol is becoming the major constituent of the solvent mixture, indicating that the triplet state is stabilized as the polarity of the solvent system is increased. It appears to be feasible to explain these results by an $n, \pi^* \rightarrow \pi, \pi^*$ inversion of the lowest excited triplet state with increasing 2-propanol content in analogy to the explanation presented for the diminution of the reactivity and the efficiency of photo reduction of carbonyl triplet states in other systems [3, 4].

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