The Detection of Transients in Thiocarbonyl Flash Photolysis

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Summary Short-lived transient species have been observed following laser photolysis of thiobenzophenone and Michler's thione and have been tentatively assigned to the triplet state of these compounds.

Valuable information has recently been derived from an investigation of the emission properties of a number of thiocarbonyl compounds in rigid matrix at 77 K.[1,2] No emission was observed in fluid media at room temperature. Using the ns flash photolysis technique, we have observed short-lived transient species from two of these compounds at room temperature. The evidence suggests that these short-lived absorptions are attributable to the triplet state of these compounds.

The ns flash photolysis apparatus was basically that described by Porter and Topp.[3] The second harmonic (347 nm) of the ruby laser was used for excitation. Changes in optical density were measured photoelectrically using a pulsed xenon arc lamp as a pseudo-continuous monitoring source.

Laser photolysis of thiobenzophenone† and Michler's thione in cyclohexane gave rise to short-lived transient species. The species from thiobenzophenone absorbed in the region 400—600 nm (the wavelength accessible to the apparatus) with a maximum at about 475 nm, while that from Michler's thione was shown to absorb in the region from 470 to *ca* 520 nm (it was only possible to investigate this region due to the ground state absorption of this compound).

In both thiobenzophenone and Michler's thione the transient absorption decayed by first order kinetics and was dependent on the concentration of the thione. Self-quenching rate constants of $4{\cdot}2 \times 10^9$ M^{-1} s^{-1} for thiobenzophenone and $2{\cdot}9 \times 10^9$ M^{-1} s^{-1} for Michler's thione were obtained, while extrapolation to infinite dilution gave unimolecular decay constants of $6{\cdot}9 \times 10^5$ s^{-1} and $1{\cdot}4 \times 10^6$ s^{-1}, respectively. The rate of decay of absorption was constant, within experimental error, throughout the wavelength region investigated indicating that only one short-lived species was present.

The addition of increasing concentrations of cyclooctatetraene (COT) lead to kinetic quenching of the species from both thioketones. From a least-squares analysis, quenching rate constants of $7{\cdot}0 \times 10^8$ M^{-1} s^{-1} for thiobenzophenone and $6{\cdot}7 \times 10^8$ M^{-1} s^{-1} for Michler's thione were obtained. On the other hand, the rate of decay of thiobenzophenone was unaffected by the presence of 5×10^{-3} M naphthalene and on monitoring at 425 nm, no absorption attributable to triplet naphthalene was observed, indicating that no energy transfer was taking place. Similarly, the species from Michler's thione was unchanged in the presence of 10^{-2} M biacetyl. These results indicate that the transient does not originate from the corresponding ketone.

The evidence presented here indicates that the species observed in each thioketone is to be attributed to the triplet state. The observed self-quenching of these species rather excludes the possibility that it is due to an excimer. The rather inefficient quenching by COT may be an indication that the quenching is chemical in nature, although, since the triplet level of COT is not known, energy transfer may be energetically unfavourable for the low lying triplet states of these compounds.[1,2] Nevertheless, it has been shown that COT quenches the phosphorescence of both thiobenzophenone and Michler's thione[1,2] providing strong evidence that the above assignment is correct.

The dependence of the observed rate constant on the initial concentration of the thioketone implies the existence of an interaction of a molecule in the triplet state with one in the ground state. The formation of the disulphide as the major product of the photoreduction of both thiobenzophenone[4] and Michler's thione[1] is consistent with this suggestion. The resultant 2,3-dithiatetramethylene could be reduced to the disulphide or revert to starting material. The existence of an excimer in Michler's thione has recently been established from emission and absorption spectroscopy at 77 K.[2]

We have also shown that the rate of decay of the transient absorption is faster in isopropyl alcohol than cyclohexane ($1{\cdot}7 \times 10^7$ s^{-1} and $6{\cdot}9 \times 10^5$ s^{-1}, respectively). Reduction of the lifetime in hydrogen donating solvents is characteristic of (n,π^*) states. Further evidence that the absorptions observed here are due to (n,π^*) triplet states originates from the fact that both thioketones emit from this state.

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† Due to its susceptibility to oxidation, thiobenzophenone was kept in a nitrogen atmosphere. All solutions were thoroughly degassed using the freeze-pump-thaw technique.

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