

Formation of singlet oxygen during the decomposition of organic hydroperoxides in the presence of sulphur-containing compounds

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The decomposition of organic hydroperoxides (cumyl, tetralyl and *tert*-butyl) was investigated in the presence of sulphur-containing inhibitors: dithiophosphates; dithiocarbamates; dithiolates. The formation of singlet oxygen was established by chemical methods and chemiluminescence investigations.

Photophysical properties of benzil

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The two lowest electronic states S_1 and T_1 of benzil are of the n,π^* type and their energy difference is quite small (about 6 kcal mol^{-1}). Both fluorescence and phosphorescence are observed in fluid media at room temperature and the ratio of the two emissions depends on the temperature. To assess whether S_1 and T_1 are thermally equilibrated, lifetime and intensity measurements as functions of temperature were performed in benzene and cyclohexane. The data obtained indicate that both the intensity and the lifetime of phosphorescence decrease according to $\exp(-\Delta E/kT)$ while those of fluorescence are practically independent of T . These results rule out the hypothesis of thermal equilibration between S_1 and T_1 and suggest, rather, that T_1 decays via a temperature-activated path with a high pre-exponential factor (10^9 s^{-1}) that does not involve S_1 . This channel could involve direct deactivation to the ground state and could be favoured by large relative distortions of the relevant potential energy curves.