

IMPURITY FLUORESCENCE IN THE IRRADIATION OF BENZOPHENONE AND ITS DERIVATIVES

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Summary

Irradiation of benzophenone or its derivatives in the presence of molecules with abstractable hydrogen atoms gives rise to trace levels of impurities. Even when the concentration of these impurities is too low to permit detection in the UV spectrum of the sample, its intense and short-lived fluorescence is prominent. The intensity of its emission (*i.e.* its concentration) is not related in any simple manner to the concentration of abstractable hydrogen or to the extent of exposure to light.

1. Introduction

Benzophenone has been a prototype for many photochemical and photophysical studies of $n\pi^*$ triplet processes. In many respects it is a well-behaved molecule. Yet over the past 15 years there have been recurring reports [1 - 7] of an elusive impurity produced on irradiation of benzophenone in the presence of molecules with abstractable hydrogen atoms. The most recent and also the most thorough study has been that of Chilton *et al.* [8] who, on the basis of nuclear magnetic resonance evidence, have assigned the isobenzpinacol structure shown in Fig. 1 to this light-absorbing transient (LAT). According to Chilton *et al.* the absorption spectrum of the LAT could not be fully resolved, but it appeared to be blue shifted from the $(n-\pi)^*$ absorption of benzophenone in cyclohexane solution.

2. Investigation and discussion

We would like to report that this photogenerated impurity is intensely fluorescent. Although solutions of benzophenone in carbon tetrachloride (CCl_4) show no sign of emission other than that of ketone phosphorescence (and thermally activated delayed fluorescence) [9] even after prolonged ir-

radiation, solutions containing benzophenone or its derivatives and a source of abstractable hydrogen atoms give evidence of a new impurity fluorescence after even short exposure to light.

This new emission shows up in two ways.

(1) The steady state emission spectrum shows distortions at the blue end of the spectrum which can become quite severe*. An example is given in Fig. 2 which shows the spectrum of a mixture of benzophenone (1×10^{-3} M) and *n*-hexane (0.26 M) in CCl_4 . This sample was occasionally exposed to light in the course of lifetime measurements and its luminescence spectrum was run several times. None the less the new impurity emission is clearly present.

It is difficult to resolve this spectrum rigorously into its components. We made an attempt to do so by assuming that the intensity at wavelengths above 500 nm is entirely due to the benzophenone phosphorescence. The resulting (uncorrected) emission spectrum has λ_{max} at 400 nm and, like the absorption of the LAT, is sharply blue shifted from the benzophenone phosphorescence.

(2) The second kind of evidence about the nature of the luminescent impurity comes from emission decay experiments. During our experiments we discovered that no combination of excitation and emission filters could

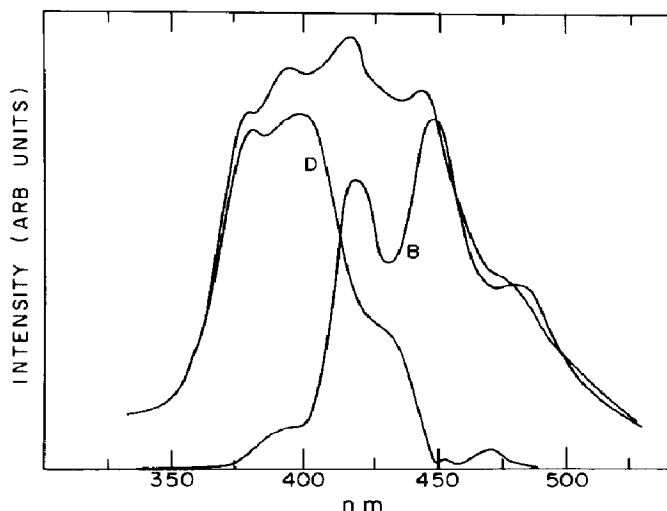
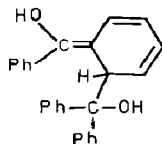


Fig. 1. The structure of the LAT as suggested by Chilton *et al.* [8].

Fig. 2. The emission spectrum of benzophenone (1×10^{-3} M) in CCl_4 containing 0.26 M *n*-hexane after several exposures to UV light ($\lambda_{\text{ex}} = 325$ nm). Also shown are the phosphorescence spectrum (B) of benzophenone in CCl_4 and the difference spectrum (D) obtained by subtracting spectrum B from the total emission after arbitrarily normalizing the spectra at 480 nm.

*The emission spectra were run on an SLM model 4800 fluorescence spectrometer. The sample preparation was identical with that described by Winnik and Maharaj [10].

prevent the photomultiplier tube in our flash-emission apparatus from exposure to an intense and short-lived burst of light. Apart from possibly fatiguing the phototube, the source of this light and its emission seemed to have no effect on the triplet lifetime of the aromatic ketones in the sample. This led us to believe that the emission was due to an intense fluorescence from an impurity present in such low concentrations that it failed to quench significantly ketone triplets with lifetimes of the order of 100 - 200 μ s. Chilton *et al.* [8] have indicated that at higher concentrations the LAT is a powerful quencher of ketone triplet states.

We used the time-correlated single-photon counting technique both to measure the fluorescence lifetime of the impurity and to obtain the time-resolved emission spectrum of the mixture at short times. Figure 3 presents the resolved spectrum of the emission of the benzophenone derivative 1 (Fig. 4) (1.0×10^{-3} M in CCl_4) at a time within 7 ns of the exciting flash. This spectrum (uncorrected) resembles the impurity emission spectrum subtracted from the total emission spectrum in Fig. 2. In this instance the impurity emission decays exponentially with a lifetime in CCl_4 at 25 $^\circ\text{C}$ of 1.4 ns.

3. Conclusions

Irradiation of benzophenone and its derivatives in the presence of molecules with abstractable hydrogen atoms gives rise to trace levels of impurities. Even when the concentration of these impurities is too low to permit

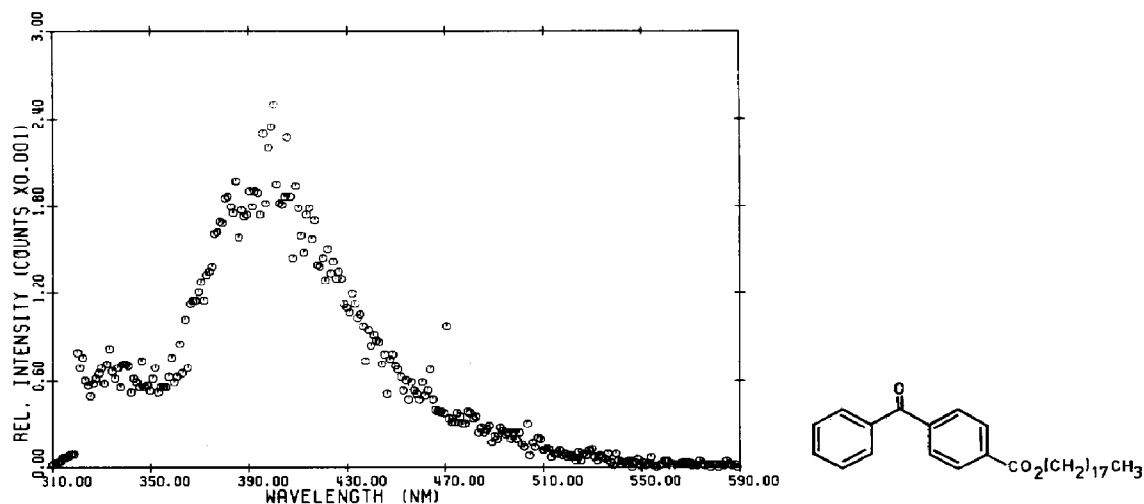


Fig. 3. The time-resolved emission spectrum of benzophenone-4- $\text{CO}_2(\text{CH}_2)_{17}\text{CH}_3$ (1×10^{-3} M) in CCl_4 after several exposures to UV light ($\lambda_{\text{ex}} = 313$ nm). This spectrum represents light emitted from the sample over the period from -1 to $+7$ ns from the exciting flash.

Fig. 4. The structure of derivative 1 of benzophenone.

detection in the UV spectrum of the sample, its intense and short-lived fluorescence is prominent. The intensity of its emission (*i.e.* its concentration) is not related in any simple manner to the concentration of abstractable hydrogen or to the extent of exposure to light. We would like therefore to advise caution in interpreting emission decay curves in the study of aromatic ketone photochemistry. The ubiquitous presence of photochemically generated impurity fluorescence makes analysis in the nanosecond time domain far more difficult than might initially be imagined.

Acknowledgment

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