Nanosecond Laser Photolysis of Acetophenone in Organic Solvents

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Summary Transient absorption spectra observed in solutions of acetophenone in several organic solvents by laser photolysis at 265 and 353 nm were shown to be due to the triplet state and the ketyl radical; the corresponding rate constants of triplet decay were measured.

WE report results of a study on the primary transient species formed in the photoreduction of acetophenone, using a *Q*-switched Nd laser with frequency converters as excitation light source and a rapid spectrophotometric detection system for the spectral observation of the transients. The time resolution is with this method sufficient to make possible the study of decay processes of the triplet state even under conditions where they undergo rapid chemical reactions such as hydrogen abstraction from the solvent. Porter and Topp[1] recently used this technique to measure the triplet decay of benzophenone in various organic solvents.

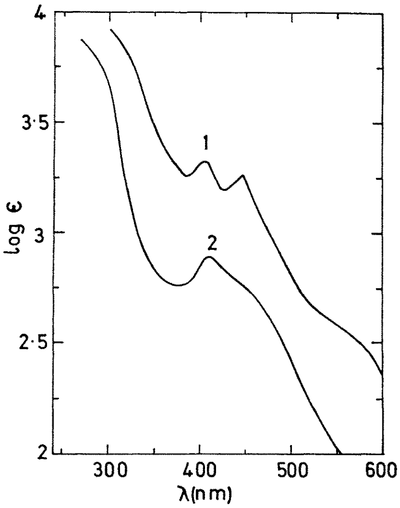

FIGURE 1. *Transient absorption spectra of acetophenone in cyclohexane, observed after laser excitation:* (1) *triplet absorption* (*measured at the end of the laser pulse*), (2) *ketyl radical absorption* (*measured* 1·4 *μs after the pulse*).

The laser (Compagnie Générale d'Electricité, type VD 231) was used at a maximum output of 25 J per pulse at 1058 nm (halfwidth 30 ns); K.D.P. crystals converted part of this energy to the wavelengths 265 or 353 nm. The laser beam was condensed on a 4 mm high, 7 mm wide surface of a 10 mm square silica cell containing the solution to be studied. Transient light-absorption changes were measured photoelectrically in a crossed-beam arrangement over a 3 mm wide section of the irradiated part of the solution using a xenon flash lamp as monitoring light source.

Laser excitation at 265 or 353 nm of degassed or aerated solutions of acetophenone in cyclohexane (0·002—0·006 M at 265 nm, 0·1—0·2 M at 353 nm) produced a transient absorption, shown in Figure 1 (curve 1) as it appears at the end of the laser pulse. The intermediate responsible for this spectrum was quenched by O_2 and piperylene; the quenching rate constants were $2{\cdot}0 \times 10^9$ and $2{\cdot}4 \times 10^9$ $M^{-1} s^{-1}$, respectively. On laser excitation at 353 nm of acetophenone in solutions containing naphthalene, a transient spectrum was observed, identified as being due to triplet naphthalene. Since naphthalene does not absorb at 353 nm this result indicates that the triplet is formed by energy transfer from triplet acetophenone. These different quenching experiments are convincing evidence that the spectrum given in Figure 1 (curve 1) is due to triplet acetophenone. Laser excitation of acetophenone in ethanol gave a spectrum shown in Figure 2 (curve 1). This spectrum agrees reasonably well with a spectrum found in EPA at 77 K by flash excitation, and which was attributed to the acetophenone triplet.[2]

In degassed solutions a slowly disappearing absorption of low intensity remained at the end of the triplet decay; this absorption did not show up in aerated solutions. The spectrum of the long-lasting absorption, recorded 1·4 μs after laser excitation, is shown in Figures 1 and 2 (curves 2). Laser excitation of acetophenone in toluene and isopropyl alcohol produced the same types of transient spectra as those found in cyclohexane and ethanol. In benzene solutions, irradiated at 353 nm, the acetophenone triplet appeared; however, in this solvent only a very weak absorption remained at the end of the triplet decay, too small to allow a determination of its structure. On the basis of these findings, and by analogy with previous results reported for benzophenone,[3] the residual spectrum

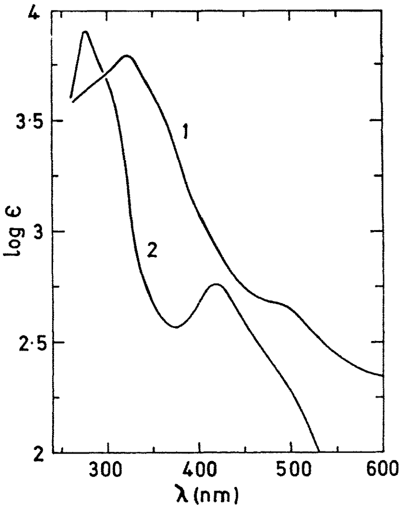

FIGURE 2. *Transient absorption spectra of acetophenone in ethanol, observed after laser excitation:* (1) *triplet absorption* (*measured at the end of the laser pulse*), (2) *ketyl radical absorption* (*measured* 1·4 *μs after the pulse*).

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may be assigned to the ketyl radical formed by hydrogen abstraction from the solvent.

The extinction coefficients of the triplet state given in the Figures were obtained by two alternative methods. One method consisted in determining the amount of triplet naphthalene formed by triplet energy transfer from acetophenone in 0·2 M-solutions of acetophenone in cyclohexane that were 0·01 M in naphthalene. On laser excitation at 353 nm the naphthalene triplet absorption appeared immediately after the pulse. Assuming that the triplet energy transfer from acetophenone to naphthalene were quantitative, the amount of donor triplet could be determined on the basis of the amount of acceptor triplet formed. In this determination a value of 22,600 M^{-1} cm^{-1} was used for the extinction coefficient of the naphthalene triplet at 413 nm.[4] Since this method was not suitable for measurements in the wavelength range of high acetophenone absorption, a second method based on triplet actinometry was used at wavelengths below 370 nm. Aerated solutions of acetophenone, benzophenone, and 1,2-benzanthracene at concentrations chosen such as to give equal optical densities at 265 nm were excited at this wavelength, and the respective triplet absorption intensities measured at the end of the laser pulse. From values for the triplet quantum yields[5,6] and the triplet extinction coefficients of benzophenone and 1,2-benzanthracene at the monitoring wavelengths (533 and 480 nm, respectively), the amount of triplet acetophenone formed could be evaluated after correction for variations in the laser output. In these determinations triplet extinction coefficients of the reference compounds were taken from data published by Land,[4] assuming that his values, given for benzene and cyclohexane solutions, are applicable also in ethanol.

The extinction coefficients for the ketyl radical given in the Figures were determined assuming that in cyclohexane and ethanol the triplet disappears exclusively to produce this radical.

Taking into account the uncertainties introduced by the different assumptions made in these determinations the error limits of the triplet and radical extinction coefficients were estimated to ± 40%.

The decay of the acetophenone triplet was found to be first-order in these different solvents; measured rate constants are given in the Table. The solvents are listed in the Table in decreasing order of hydrogen-donating efficiency.

Decay rate constants of the acetophenone triplet in organic solvents

Solvent	Rate constant (s^{-1})	Recording wavelength (nm)
Isopropyl alcohol ..	$9{\cdot}0 \times 10^6$	350
Ethanol	$7{\cdot}1 \times 10^6$	350
Cyclohexane	$4{\cdot}4 \times 10^6$	350
Toluene	$2{\cdot}2 \times 10^6$	380
Benzene	$3{\cdot}3 \times 10^5$	380

The expected correlation between this efficiency and the decay rate constant was previously observed by Porter and Topp in their study of benzophenone.

The rate constant found in benzene is in good agreement with the results from phosphorescence measurements obtained by Clark *et al.*[7] (3×10^5 s^{-1}). The rate constant obtained in isopropyl alcohol may be compared with results from indirect low-intensity studies. Recently, Lewis[8] presented a study of the photoreduction of acetophenone in isopropyl alcohol–benzene mixtures. From his results we extrapolate an overall rate constant of $9{\cdot}2 \times 10^6$ s^{-1} for the triplet decay, very close to the value given in the Table.

(*Received, March 17th,* 1971; *Com.* 331.)

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