

Short Communication

The Photochemistry of Decafluorobenzophenone: dependence on concentration and light intensity

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Decafluorobenzophenone in isopropyl alcohol has been recommended as an actinometer [1]. However, it was recently shown by Schaffner *et al.* [2] to be unsuitable, even in degassed solutions. For this reason and since no further details of concentration and intensity of irradiation were given for this photoreaction, an examination with respect to these variables seemed to be of interest. First experiments made it clear that oxygen-containing solutions follow a quite complex mechanism. Similar to benzophenone [3] the photoreaction is not reproducible under these conditions and therefore is not at all suitable for actinometry. For this reason only degassed solutions were examined further with our graphical and numerical methods [4 - 6].

Table 1 demonstrates the dependence of the photoreaction at an irradiation wavelength of 313 nm on concentration. With increasing concentration the photoreaction becomes more and more complex, shown by the increasing number of linearly independent reaction steps. For various concentrations extinction (*E*)-diagrams and extinction-difference-quotiential (*EDQ*) diagrams* are outlined in Figs. 1 and 2 to illustrate this behaviour. These diagrams [4, 5] give the possibility of distinguishing between the number of linearly independent reaction steps** and thus giving information on the reaction procedure. Although at very dilute solutions ($10^{-5} M$) the photoreaction is nearly uniform up to a conversion rate of approximately 95%, the photoreaction is definitely unsuitable for actinometry under the conditions mentioned in ref. 1. At 313 nm photolysis the by-products [2] absorb only at high concentration at the irradiation wavelength. Therefore

* The diagrams are calculated and plotted by programs KINET and EDQDQ-PLOT written for a CDC 3300 at the Computing Center of the university and a HP 9820 by G. Gauglitz.

** Linear *E* diagrams prove a uniform reaction ($s = 1$), whereas linear *EDQ*-2-diagrams result for $s = 2$ during the total reaction. Recently a new type of diagram (*EDQ*-3-) [8] has been developed giving a straight plot for $s = 3$. s is the number of linearly independent reaction steps.

TABLE 1

Decafluorobenzophenone, dependence of the photoreaction on concentration and irradiation wavelength

Sample	Concentration $\times 10^5$ (M)	$I_0 \times 10^9$ [Einst/cm ² s]	E-diag.*	EDQ-2-diag.*	EDQ-3-diag.	Comments
1	4.95	1.6	1 a			uniform photo-reaction until 90 - 95% conversion
2	6.44	1.6	1 a			
3	8.90	1.6	1 a			
4	9.0		similar to 1 c	2 c		irradiation at 254 nm
5	9.48	1.6	1 b			$s = 1$ until 80% conversion, in total: two linear independent reaction steps
6	10.0	1.6	1 b			
7	11.0		complex			irradiation at 254 nm
8	14.5	1.6	1 c	2 c		$s = 2$ two linear independent steps
9	515.0	1.6	1 d	2 d	linear	$s = 3$ three linear independent reaction steps

* Numbers refer to the graphs in Figs. 1 and 2.

in very dilute solutions these products influence the reaction procedure only after extremely long irradiation times [see Figs. 1 (a) and 1 (b)]; whereas for the irradiation at 254 nm, the photoreaction is complicated even in dilute solutions (consecutive decomposition of the main products) [2].

By solving the differential equation for the rate law further proof for an assumed mechanism can be found. This can be easily done for simple mechanisms according to refs. 4 and 6 by "formal integration" of the rate law. Since at the dilute solutions the photoreaction appeared to be non-complex and uniform for nearly the total reaction time using light of 313 nm, an evaluation according to the simple mechanism $A \xrightarrow{h\nu} B$ was tried. Using

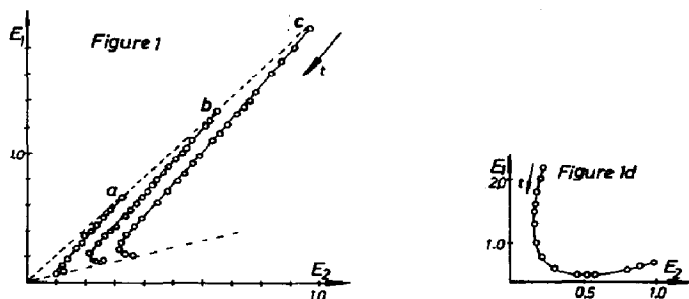


Fig. 1. E -diagram of decafluorobenzophenone in degassed isopropyl alcohol, irradiated at 313 nm. (a) - (c): E_1 : $\lambda = 248$ nm; E_2 : $\lambda = 263$ nm. (d). E_1 : $\lambda = 313$ nm and E_2 : $\lambda = 360$ nm (for clearness not all measured points are drawn).

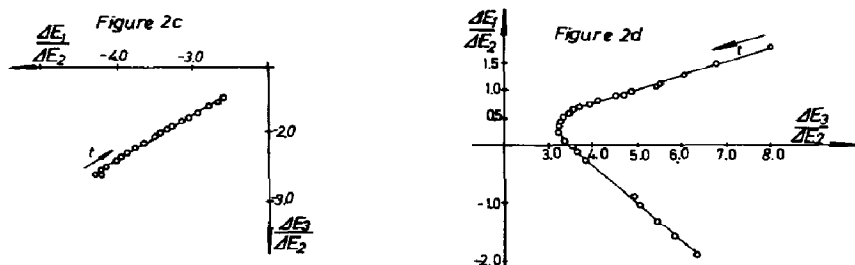


Fig. 2. EDQ -diagram for the photoreaction. (c) $\Delta E_1 = E_1(t) - E_1(t) = 0$: $\lambda = 235$ nm; ΔE_2 : $\lambda = 215$ nm; ΔE_3 : $\lambda = 248$ nm. (d) ΔE_1 : $\lambda = 340$ nm; ΔE_2 : $\lambda = 320$ nm; ΔE_3 : $\lambda = 313$ nm.

different observed wavelengths* a quantum yield of $\Phi^A = 0.78 \pm 0.04$ could be calculated for a lamp intensity of $I_0 = 1.6 \times 10^{-9}$ [Einstein/cm² s] (see Table 2). As the light intensity was reduced to $I_0 = 0.88 \times 10^{-9}$ [Einstein/cm² s] another quantum yield was obtained. Besides, using all observed wavelengths* for calculation, the computed values differed far more than the statistical ones. For these reasons the assumption of a simple photoreaction cannot be valid. Measurements with a special set up [7] showed that at low light intensities comparably fast dark reactions are measurable and influence the obtained absorbancy values. Under these conditions the photoreaction becomes irreproducible and dependent on light intensity — even at low concentrations.

Since the photoreaction of decafluorobenzophenone in isopropyl alcohol depends on light intensity, the substance cannot be recommended as an actinometer at any of the examined reaction conditions, not even in very dilute solutions.

* Although in principle the knowledge of the absorbancy depending on reaction time only at the wavelength of irradiation is necessary for the calculation of quantum yields for the assumed mechanism, the absorbancy changes at many wavelengths are measured and for each of them the quantum yield is calculated. These values must agree within error limits and a more precise value is obtained.

TABLE 2

Quantum yield in dependency of concentration and light intensity

$I_0 \times 10^9$ [Einst/cm ² s]	Concentration $\times 10^5$ (M)	quantum yield
1.6	6.44	0.77 ± 0.03
1.6	9.48	0.79 ± 0.03
0.88	6.44	for assumed simple mechanism
0.88	9.48	evaluation impossible

Experimental

Decafluorobenzophenone (EGA-Chemie) was sublimated *in vacuo* (m.p. 92 °C). The isopropyl alcohol had Uvasol-quality (Merck). The solutions were degassed by passing purified [9] nitrogen through the cells. The irradiation took place in sealed cells QS 211 (Hellma), using a stabilized DC-lamp (high-pressure Hg-lamp St 75, Hanau) and interference filters (Schott & Gen.). The intensities were determined according to the method of Harchard and Parker [10]. For absorbancy measurements a Zeiss PMQ II [7], a Zeiss DMR 21 [11] and a Cary 118C were used. The reference was double distilled water.

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