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EFFECTS OF SOLVENT ON TRANSIENTS AND ON QUANTUM YIELDS IN PHOTOREDUCTION OF KETONES

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We have reported (1) that photoreduction of benzophenone by 2-propanol, with ultraviolet light filtered through Pyrex, proceeds more rapidly in a 1 M solution of 2-propanol in benzene or in isooctane than in undiluted 2-propanol. This effect is noteworthy and is advantageous when the procedure is used synthetically for the photooxidation of an alcohol, since the alcohol need not be present in excess over that required for photoreduction of the ketone (1). We wish to report a more quantitative examination of this effect.

Quantum yields for photoreduction of 0.1 M benzophenone by 2-propanol were determined as a function of concentration of the alcohol in benzene with a ferrioxalate (2) actinometer. Solutions were degassed and irradiated under argon at 313 mμ with an Osram S-P200 lamp, Bausch and Lomb grating monochromater, light intensity ~ 10^{16} quanta cm^{-1} sec^{-1}. Aliquots were diluted with 2-propanol and allowed to stand overnight, and residual benzophenone was determined at and near 334 mμ. Conversions of benzophenone were 20 ± 3% in 13 M to 0.1 M 2-propanol, and 9% in 0.05 M alcohol. Some results are given in Table 1.

Table 1

Photoreduction of 0.1 M Benzophenone by 2-Propanol in Benzene.

2-Propanol M	φ	2-Propanol M	φ
13 (neat)	1.16	0.50	1.41
5.0	1.32	0.27	1.16
3.0	1.71	0.10	0.71
1.0	1.57	0.05	0.45
0.7	1.60		

The quantum yield for photoreduction with monochromatic light <u>increases</u> as the concentration of 2-propanol <u>decreases</u> from 13 <u>M</u> to 3 <u>M</u> and remains higher than in pure 2-propanol down to 0.3 <u>M</u> 2-propanol in benzene. A plot of $1/\varphi$ vs 1/(2-propanol) may be constructed and is linear at concentrations of 3 <u>M</u> and lower; extrapolation to $1/C = 0$ leads to a theoretical limiting value of $\varphi = 1.9$, 60% greater than the value (1.16) actually measured in neat 2-propanol. This extrapolated value would have physical significance only if the system behaved at high concentration of alcohol in the same way as it behaves in dilute solutions of alcohol in benzene, which, in fact, it does not.

The overall quantum yields for photoreduction of 0.1 <u>M</u> benzophenone in neat 2-propanol decreased substantially with extent of reaction, from 1.12 at 18% reduction to 0.79 at 37% reduction. The absorbances of the solutions increased markedly with time of irradiation as has been noted (3,4). Absorbance at λ_{max} rose from 1.61 at 334 mμ initially, to 2.57 at 328 mμ after irradiation for 65 minutes. Shaking with air or long standing is required to show the decreased absorbance due to photoreduction, on which the calculations of rates and quantum yields are based. At 1 <u>M</u> 2-propanol in benzene the quantum yield is higher and the absorbance decreases from the start of irradiation, but some absorbing transient is still detected. However, dilution of the 2-propanol with an equal amount of water leads to increase in absorbance similar to that in 2-propanol, and to no increase in quantum yield.

High quantum yields for photoreduction of 0.1 <u>M</u> benzophenone in undiluted 2-propanol, $\varphi \sim 1.9$, have been observed at low light intensity (5), $\sim 10^{13}$ quanta cm^2 sec^{-1}. Quantum yields have been found to be lower at high light intensity, and quenching of the ketone triplet by free radical intermediates has been proposed (6). This may well have occurred at the very high light intensities of those experiments. Erratic results, quantum yields of 1.4 ± 0.4 for photoreduction of benzophenone in undiluted 2-propanol, have been described (7). It is very unlikely that the variations in quantum yield with extent of reaction and on dilution with hydrocarbon, which we observe at essentially constant light intensity, can result from quenching by short-lived intermediates, radicals or triplets.

We conclude that the effects are in large part related to the properties of a relatively long-lived transient. It is formed from light-produced radicals, more rapidly and growing to higher concentration at higher light intensities when the rate of its formation may more greatly exceed the rate of its thermal decomposition. The transient absorbs light and acts as an internal mask, and it may also be a quencher for triplets. It is present to a larger extent in neat and aqueous alcoholic solutions; it is formed less or is less persistent in hydrocarbon media and the latter lead to increased quantum yields. The light absorbing transient, discussed for many years (3), has not been isolated. It appears to be a labile radical coupling product, that from para-para coupling of two benzophenone-ketyl radicals (8), or that from para-alpha coupling of benzophenone-ketyl and 2-hydroxy-2-propyl radicals (9).

Other systems show similar effects of medium on quantum yield. The rate of photoreduction of benzophenone was 3 times greater in 0.5 M triethylamine in benzene than in undiluted amine (1). In this case too, a light absorbing transient has been observed during photoreduction in the neat amine (10). In the photoreduction of acetophenone by α-methylbenzyl alcohol the rate doubled as the neat (8.3 M) alcohol was diluted to 2 M in benzene (11). For this system too a light absorbing transient has been observed (12).

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