PHOTOCHEMISTRY OF AZO COMPOUNDS. II.

EFFECT OF KETONIC SENSITIZERS ON PHOTOREDUCTION OF

4-DIETHYLAMINO-4'-NITROAZOBENZENE

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In an earlier paper (1) it was shown that the photoreduction of 4-diethylamino-4'-nitroazobenzene (I) in alcoholic media occurred, with low quantum efficiency, to produce hydrazo compound II.
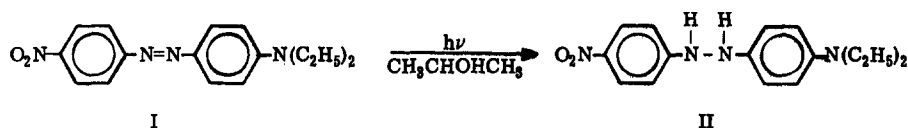
Benzene and naphthalene were inefficient sensitizers of this reaction. We report here the effect of ketonic sensitizers and the mechanism of sensitization.

Quantum yields for hydrogen abstraction by I were low, both in the absence of sensitizers and in the presence of hydrocarbon sensitizers. However, acetone and benzophenone efficiently sensitized the photoreduction of I in the presence of hydrogen donors (benzhydrol or isopropanol). Fluoren-9-one did not significantly increase the quantum yield for the photoreduction of I. The absence of a dark reaction following partial photodegradation under degassed conditions in the presence of either hydrocarbon or ketonic sensitizers showed that photoisomerization was not important. The results of these experiments are given in Table I.

TABLE I

Quantum Yields Obtained in the Photolysis of I Under Various Conditions[a]

Solvent	Additive Compound	Concn, Moles/L.	Wavelength, Nm	Intensity[b]	Φ_D (12)
Isopropanol	None	-----	366[c]	9.8×10^{-7}	1.4×10^{-4}
Isopropanol	Benzophenone	0.55	366	4.8×10^{-6}	0.051
Isopropanol	Benzophenone	0.55	366	1.9×10^{-6}	0.056
Isopropanol	Fluoren-9-one	0.025	366	4.8×10^{-6}	$<1 \times 10^{-4}$
Isopropanol	Acetone	2.7	254	4.5×10^{-7}	0.08
Acetone	None	-----	254	4.5×10^{-7}	5.7×10^{-4}
Benzene	Fluoren-9-one	0.025	366	4.8×10^{-6}	$<1 \times 10^{-4}$
Benzene	Benzophenone Benzhydrol	0.55 0.00	366	4.8×10^{-6}	9×10^{-3}
Benzene	Benzophenone Benzhydrol	0.55 0.54	366	4.8×10^{-6}	0.17
Benzene	Benzophenone Benzhydrol	0.55 0.54	366	4.8×10^{-8}	0.17[d]

(a) Concentration of I was $2.2 - 2.6 \times 10^{-4}$ moles/liter.

(b) Incident light intensity in Einsteins/minute.

(c) A Hanovia 325-watt, medium-pressure mercury arc and Corning glass filter kit 7-83 were used in
the experiments with 366-nm light. All experiments were run under degassed conditions in 1-cm ^{2}
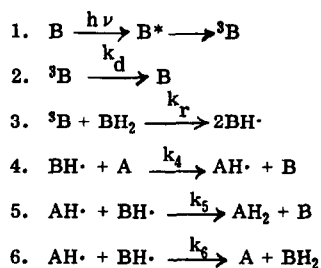pyrex or quartz cells.

(d) Concentration of I was 2.2×10^{-5} moles/liter.

In addition to those results reported in Table I, data obtained for the reduction of I in the presence
of benzophenone(B)/benzhydrol(BH$_2$) demonstrated that the rate of reduction was first order in light
intensity and was dependent on the concentration of benzyhydrol. The Stern-Volmer equation was obeyed.
A linear relationship existed between $1/\Phi_D$ and $1/BH_2$ for benzhydrol concentrations from 0.54 to 0.01

mole/liter. An intercept of 5.4 and a slope of 0.27 were obtained.

Two possible mechanisms could account for the effect of acetone and benzophenone on the reduction of I: (1) energy transfer from the excited triplet state of the ketone to a reactive triplet level of I which was not populated by direct absorption and (2) transfer of a hydrogen atom from a ketyl radical (formed by hydrogen abstraction from the solvent by ketone triplet) to the ground state of I. The latter process is important in the photoreduction of other compounds (2-5). A mechanism involving triplet-triplet energy transfer to I does not appear to be important in view of the following considerations: From the known rate constant for hydrogen abstraction from isopropanol by benzophenone triplet (1.28×10^6 $M^{-1}sec^{-1}$) (6), and the assumption that energy transfer proceeds at a diffusion-controlled rate ($k_d = 3.2 \times 10^9$ $M^{-1}sec^{-1}$ in isopropanol) (6), it is estimated that, at 2×10^{-4} $\underline{M}$ concentrations of I, no more than 5% of the initially formed triplets can undergo energy transfer. Therefore, hydrogen abstraction to generate the ketyl radical should be the major process. Both benzene (E_t 85, Φ_{IC} .24) and naphthalene (E_t 61, Φ_{IC} .39) were inefficient sensitizers compared to acetone (E_t 70, $\Phi_{IC}=1$) and benzophenone (E_t 69, $\Phi_{IC}=1$)(1). In addition, a tenfold decrease in the concentration of I had no measurable effect on the photoreduction quantum yield (the rate is zero order in I over this concentration range).

The major reaction resulting in the photodegradation of I is hydrogen atom transfer from ketyl radical to the azo linkage of the ground-state azo compound. A mechanistic scheme which is consistent with the observed results is as follows:

1. $B \xrightarrow{h\nu} B^* \longrightarrow {}^3B$

2. ${}^3B \xrightarrow{k_d} B$

3. ${}^3B + BH_2 \xrightarrow{k_r} 2BH\cdot$

4. $BH\cdot + A \xrightarrow{k_4} AH\cdot + B$

5. $AH\cdot + BH\cdot \xrightarrow{k_5} AH_2 + B$

6. $AH\cdot + BH\cdot \xrightarrow{k_6} A + BH_2$

where B = benzophenone and A = azo compound

Chain transfer of the hydrazyl radical (AH·) with benzhydrol (BH$_2$) and termination by combination of two ketyl radicals are precluded by the first-order dependence on light intensity. From the above scheme the following equation is obtained, predicting a linear relationship between $1/\Phi_D$ and $1/BH_2$.

$$\frac{1}{\Phi_D} = \left(\frac{k_5 + k_6}{k_5}\right) + \left(\frac{k_5 + k_6}{k_5}\right) \frac{k_d}{k_r[BH_2]}$$

The slope-to-intercept ratio (k_d/k_r) of 0.05 is in excellent agreement with that reported previously (7, 8) for the reduction of benzophenone in the presence of benzhydrol. The inclusion of reaction 6 accounts for quantum yields for the reduction of I which are less than the quantum yield for reduction of benzophenone. From the value of 5.4 obtained for the intercept, it was found that the rate of interaction of ketyl radical with hydrazyl radical to give I and benzhydrol is 4.4 times greater than the rate of formation of hydrazo compound II and benzophenone.

The inefficiency of fluoren-9-one in promoting photoreduction in isopropanol is consistent with the known inefficiency of hydrogen abstraction by fluorenone triplet (10, 11). The absence of a pronounced effect of fluoren-9-one on the photoreduction gives further evidence against a sensitization by an energy transfer mechanism.

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12. Φ_D is the overall quantum yield for the initial 10% degradation of I.