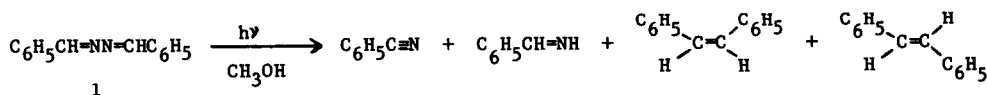EXCITED STATES IN BENZALAZINE PHOTOCHEMISTRY[1]

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During the past several years we have been investigating the photochemistry of benzalazine

(1). These efforts, which to date primarily have been concerned with product identification[3] and

mechanistic interpretation[4], recently have led to a detailed scheme for understanding the photo-

chemical reactions of this compound[5]. We have now investigated the nature of the excited states

$$C_6H_5CH=NN=CHC_6H_5 \xrightarrow[CH_3OH]{h\nu} C_6H_5C\equiv N + C_6H_5CH=NH + \underset{H}{\overset{C_6H_5}{}}C=C\underset{H}{\overset{C_6H_5}{}} + \underset{H}{\overset{C_6H_5}{}}C=C\underset{C_6H_5}{\overset{H}{}}$$

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involved in this benzalazine (1) photoreaction and can report that there are two such states par-

ticipating in this process. The total quantum yield for reaction of these two species is quite

low (Φ disappearance of 1 = 0.00036). The existence of this low quantum yield when combined with

the intense absorption of benzalazine (1) between 300 and 400 nm accounts to a large extent for

the reported effectiveness of 1 as an ultra-violet absorber[6].

The quantum yields, using three different filters, for the disappearance of benzalazine

(1) as well as the appearance of the photoproducts benzonitrile, benzaldimine (isolated as benzal-

dehyde), and cis- and trans-stilbene are shown in Table I. Each reaction was conducted with 1.00

mmol of benzalazine (1) in 400 ml of methanol under nitrogen with a 450-W Hanovia high-pressure

mercury-vapor lamp. Potassium ferrioxalate actinometry was employed[7] and the reaction products

were isolated by column chromatography of the reaction mixtures on Florisil using solutions of

ether and hexane as the eluents.

The addition of various quantities of piperylene to the irradiation mixture (Table II) has a

quenching effect on the reaction process. The Stern-Volmer plot of the reciprocal of the quantum

yield vs. quencher concentration (Figure I) shows a linear behavior at low piperylene concentra-

TABLE I.   QUANTUM YIELDS FOR BENZALAZINE PHOTOREACTION[a]

	$\Phi_{disappearance}$	$\Phi_{benzonitrile}$	$\Phi^b_{benzaldehyde}$	$\Phi^c_{stilbenes}$
Filter I[d]	3.6×10^{-4}	1.5×10^{-4}	1.7×10^{-4}	$6. \times 10^{-6}$
Filter II[e]	3.6×10^{-4}	1.9×10^{-4}	1.8×10^{-4}	$4. \times 10^{-6}$
Filter III[f]	1.1×10^{-4}	0.6×10^{-4}	0.6×10^{-4}	$2. \times 10^{-6}$

a) all reactions in methanol; b) benzaldehyde isolated is assumed to be equal to benzaldimine formed; c) the quantum yield for the two stilbenes is combined since they interconvert photochemically; d) light absorbed between 205 and 350 nm; e) light absorbed between 258 and 350 nm; f) light absorbed between 300 and 350 nm.

tions which falls off around 0.1 molar piperylene again to become essentially linear and horizontal at higher concentrations. The response of excited benzalazine (1) to the presence of various concentrations of piperylene shows that a fraction of the benzalazine (1) excited states are capable of being quenched by piperylene while a certain percentage are not effected by the presence of this quenching agent.

TABLE II.   PIPERYLENE QUENCHING OF BENZALAZINE PHOTOREACTION[a]

Piperylene Concentration	0.000	0.001	0.010	0.025	0.050	0.075	0.100	0.200	0.500
$\Phi_{disappearance} \times 10^4$	3.6	3.0	2.9	2.6	2.2	2.0	1.7	1.7	1.7

a) in methanol with light from 258-350 nm

FIGURE I.   QUENCHING OF BENZALAZINE BY PIPERYLENE (STERN-VOLMER PLOT)
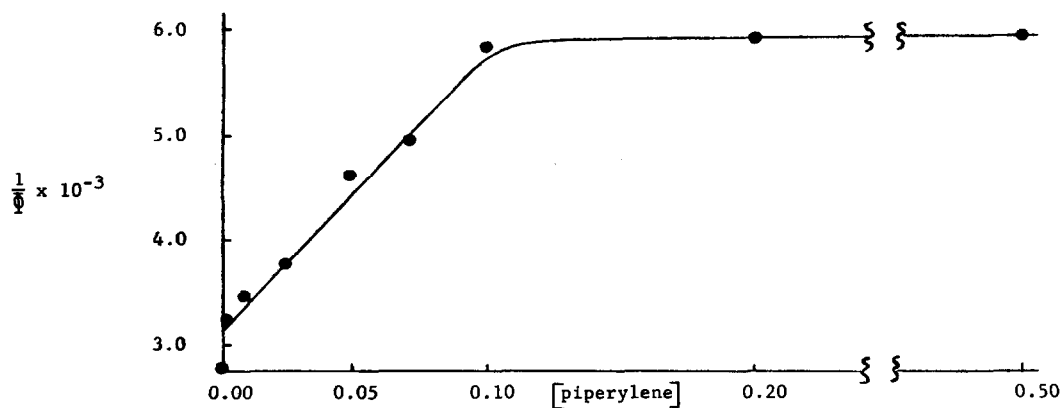
The interpretation of the results from these quenching studies is clouded by the fact that it has not yet been possible to determine the triplet energy for benzalazine (1); thus, the possibility (or even probability) exists that the transfer of excitation from benzalazine (1) to piperylene is not diffusion controlled. The determination of rate constants based on the assumption of diffusion control, a normal procedure, is not justified under the present conditions.

Even though diffusion control cannot be assumed, the Stern-Volmer treatment (Figure 1) of the quenching experiments clearly indicates the formation of two reactive excited states from the photolysis of benzalazine (1). One of these is quenchable and one is non-quenchable. The non-quenchable excited state appears to be that one responsible for the formation of benzonitrile and benzaldimine since the chemical yield of these products actually rises when the piperylene is added to the reaction mixture (Table III) while the quantum yields are essentially unchanged. The quenchable excited state appears to be responsible, at least in part, for the stilbene forming reaction and for a previously noted[5] reaction which leads from excited benzalazine to a non-isolable product. In the presence of sufficiently high concentrations (greater than 0.1 molar) of piperylene, stilbene formation is reduced while the amount of starting material accounted for increases by a considerable extent (Table III).

TABLE III.   PRODUCT YIELDS FROM PHOTOLYSIS OF BENZALAZINE[b]

Piperylene Concentration	Benzonitrile	Benzaldehyde	Stilbenes	Starting Material Accounted For
0.0 molar	52%	51%	1.0%	53%
0.1 molar	71%	71%	0.4%[a]	71%
0.2 molar	71%	71%	0.3%[a]	71%

a) by uv analysis only due to extremely small amount formed; b)in MeOH with 258-350 nm filter.

Although the evidence for the existence of at least two excited states in benzalazine (1) photochemistry is clear, the nature of these two states is obscure. Perhaps the most reasonable proposal is that the quenchable excited state is a triplet while the non-quenchable excited state is a singlet. Although this appears to be the most reasonable explanation, at present, this assignment cannot be made with certainty on the basis of the present information. Further investigations are in progress to determine, if possible, the exact identity of the reactive excited states formed from benzalazine (1) photolysis.

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