solvents, but their τ data do indicate that k_R may reach its diffusion limit in solvents of high viscosity.

Hagemann and Schwartz studied the pulse radiolyses of benzyl chloride in cyclohexane and obtained $\epsilon_B = 12000\ M^{-1}\ cm^{-1}$ and $k_R = 2 \times 10^9\ M^{-1}\ sec^{-1}$.[18] Then Burkhart obtained $k_R \simeq 1.8 \times 10^9$ in benzene and $2.0 \times 10^9\ M^{-1}\ sec^{-1}$ in cyclohexane by the rotating sector method on the reaction of triethyl phosphite and benzyl mercaptan.[19] Although the last two reports agree on $k_R \simeq 2 \times 10^9\ M^{-1}\ sec^{-1}$ for cyclohexane, we believe the Hagemann and Schwartz value of k_R (and ϵ_B) may be high. This is because their yield of product, based on hydrogen chloride rather than on B species, could be low, and because the decay of B, possibly enhanced by the presence of other reactive species such as cyclohexyl, hydrogen, unsaturates, etc., could be high.

We are left with a factor of 3 discrepancy between our k_R and Burkhart's,[19] which we cannot explain. As pointed out above and also in connection with the evaluation of ϵ_B, the errors in flash photolysis generally lead to overestimates of k_R and ϵ_B. We would be reluctant, therefore, to revise our k_R upward. In the same vein, if ϵ_B was actually 10 times larger than our value of $1500\ M^{-1}\ cm^{-1}$, as some authors claim,[2b] then k_R would have been *ca.* $7 \times 10^9\ M^{-1}\ sec^{-1}$. Since this "high" figure corresponds to the calculated diffusion-controlled limit for B,[19b] it is less likely to be correct.

Since they were first detected, interest in isoelectronic benzyl, phenoxyl, and anilino radicals has evolved on many fronts.[5,20,21] By now their chemical and electron spin resonance properties are quite familiar,[22] but beyond simple recognition, there has often been disagreement in their physical description. The summary in Table III does not, of course, disclose the sort of discrepancies which we have pointed out in detail with respect to ϵ_B and k_R(B). These inconsistencies are not uncommon in the work on radicals, the more so when different research groups and/or techniques are used.[2b,11,23] For this reason, we emphasize that some of the figures of Table III may not be final, but we believe that, at least with respect to B, their margin of uncertainty has been considerably reduced.

Table III. Properties of Radicals at ~25°

	λ, nm	ϵ, M^{-1} cm^{-1}	$k_R \times 10^9$ $M^{-1}\ sec^{-1}$	Solvent
$C_6H_5CH_2\cdot$	318	$1500^{a,b}$	0.68^b	CH_3OH
$C_6H_5NH\cdot$	308^c	4700^c	1.5^c	H_2O
$C_6H_5O\cdot$	330^d	3800^d	$1.4^{d,e}$	H_2O

[a] Reference 2b. [b] This work. [c] Reference 20. [d] Reference 21. [e] Discrepancies in this figure are found in ref 20–23, because of the confusion of $2k_R/\epsilon$ with k_R/ϵ and possibly because of arithmetic errors. From ref 20 and 21b, we calculate a mean value of $k_R/\epsilon = (3.65 \pm 0.75) \times 10^5$. Using $\epsilon = 3800 \pm 800$ (ref 21a), we calculate $k_R = 1.4 \pm 0.6 \times 10^9\ M^{-1}\ sec^{-1}$. Reference 23 also reports $k_R = 6.3 \pm 2.5 \times 10^8\ M^{-1}\ sec^{-1}$ in C_6H_6 and $k_R = 5.5 \pm 2.2 \times 10^7\ M^{-1}\ sec^{-1}$ in chlorobenzene.

Acknowledgment. We are grateful to Dr. W. G. Brennan for assistance with the computer fits to eq 6 and 7.

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Reaction of Formazan with Singlet Oxygen[1a]

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Abstract: Singlet molecular oxygen reacts with 1,3,5-triphenylformazan to yield benzoic acid, benzene, phenol, and the tetrazolium cation. Oxidation by singlet oxygen, produced chemically or with a sensitizer of low triplet energy, results in degradative oxidation of formazan. Under both conditions benzene and benzoic acid are produced; in addition phenol is a product of the photochemical reaction. When a sensitizer of high triplet energy is used, the formation of 2,3,5-triphenyltetrazolium, the nondegradative oxidation product of the formazan, is also observed. A mechanism is suggested for these reactions.

The dye-sensitized photooxidation of organic compounds is of interest because it underlies phenomena of great biological importance. Early investigators showed the participation in these reactions of long-lived metastable excited states of the sensitizing dye, and supposed the formation of a dye–peroxide complex as a reaction intermediate.[2,3] Subsequent studies, however, showed that electronically excited (singlet)

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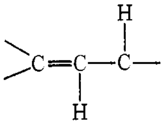
oxygen is probably a reactive oxidizing intermediate.[4,5] Singlet oxygen was identified as a product of microwave discharge and of the reaction of sodium hypochlorite with hydrogen peroxide. Up to 65% of the oxygen generated in solution is then in the $^1\Delta$ state.[6]

Most studies have shown that the products of reaction with "chemically-generated" singlet oxygen are identical with those produced by photochemical reaction,[4,5,7] but this is not always the case.[2] In the photosensitized oxidation of cholest-4-en-3β-ol the distribution of products is dependent on the particular sensitizer used;[8] the reason for this observation is still not entirely clear.[9]

A wide range of substrates for photooxidation have been studied, and by a suitable choice of substrate this reaction has been used, *e.g.*, to synthesize compounds of biological importance,[9,10] and to study enzyme action by means of selective destruction of specific amino acid residues.[11,12]

Typical monoolefin substrates for the study of oxidation with singlet oxygen include compounds containing allylic bonds (i) and the N-disubstituted enamine (ii)



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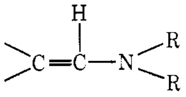

ii

groupings. We have chosen to investigate the reactivity of an air-stable compound containing the sequence >C=NNH—, the nitrogen analog of an allylic system, a grouping which has not hitherto been used as a substrate. We have found 1,3,5-triphenylformazan to be an efficient acceptor of excited oxygen. The products of its reaction with chemically and photochemically generated singlet oxygen are identical when Methylene Blue is used as the sensitizer, and differ from those produced either by slow air or by chemical oxidation (*e.g.*, by hydrogen peroxide or by hypochlorite alone). The high reactivity of the formazan and the fact that it absorbs visible light enabled us to perform a kinetic study and allowed us to establish directly the ratio of the rate constants for the various steps of a proposed reaction mechanism both for the photochemical and for the dark (chemical) reaction.

Experimental Section

Materials. 1,3,5-Triphenylformazan (hereafter referred to as formazan and 1,3-diphenyl-5-(α-naphthyl)formazan (hereafter referred to as naphthylformazan) were obtained from Mann Research Laboratories. After recrystallization from acetone–water, both had mp 173°, consistent with their literature values,[13] and showed single spots with thin layer chromatography. They were used without further purification.

Methylene Blue and Eosin Y were both histological grade, obtained from Fisher and Allied Chemical, respectively. H_2O_2 was Fisher Certified ACS grade (30%) solution. NaOCl was Matheson Coleman and Bell reagent grade (5%). The mixtures of oxygen and nitrogen were prepared by Matheson. For quantitative product determinations, the ethanol was distilled and the middle third fraction used as the solvent.

Procedure. Freshly prepared solutions of formazan in ethanol have a maximum in absorption at 489 nm (ϵ 1.72 × 10^4 l. mol^{-1} cm^{-1}). The products of its oxidation do not absorb in the visible, so the decrease in absorption of an appropriately diluted solution was used to measure the quantum yield of oxidation. Methylene Blue in ethanol has a maximum absorption at 657 nm. Mixtures of Methylene Blue and formazan show no indication either of complex formation or of anaerobic photoreduction of dye by the formazan. Both compounds are individually quite stable in air-saturated ethanolic solutions shielded from light, but each undergoes a slow dark autooxidation when mixed together. The maximum rate of this dark autooxidation is slower by a factor of 30 than the sensitized photooxidation and was corrected for when appropriate. The formazan is stable in ethanol–peroxide and ethanol–basic peroxide solutions for periods much longer than those required for appreciable chemical oxidations to take place.

The chemical oxidations were performed in 25-ml test tubes at initial peroxide concentrations of 0.17 *M*. The alkaline hypochlorite solutions were injected into the bottom of the rapidly stirred formazan–peroxide solutions through a 22-gauge hypodermic needle. Chlorine generated *in situ* from acid hypochlorite oxidized formazan to its tetrazolium salt. Under the alkaline conditions normally used, no tetrazolium salt formation was observed. The absence of chlorine formation is also seen from observation that addition of hypochlorite to an initially alkaline solution of formazan and peroxide did not change the observed yield. For "yield" determinations (*vide infra*), no more than 10% of the formazan was oxidized.

The Methylene Blue sensitized oxidations were performed in an optical cell 1 cm in path length, having provisions for bubbling mixtures of oxygen and nitrogen through the solutions prior to and during the course of the reaction. The solutions were irradiated using a 500-W TDC slide projector at a distance of 10 cm from the cell. For quantum yield determinations, a Bausch and Lomb interference filter, transmitting maximally at 657 nm, was inserted between the slide projector and the cell. The intensity of the radiation was determined with a calibrated thermopile (Eppley Laboratories, 16 junction bismuth–silver, 3M black coating).

For the identification and separation of the products of oxidation, reactions were carried out in a flask provided with a condenser. After the chemical reaction was completed, the solution was distilled, and spectra of succeeding fractions of the distillate (benzene) were determined. The alkaline residue was evaporated to dryness under vacuum, acidified, and serially extracted with cyclohexane. Absorption spectra were determined, and the melting point of the purified (sublimed) benzoic acid was determined (112°). Recovery experiments, carried out in a fashion identical with that outlined above on a mixture of 20 μmol each of benzene and benzoic acid, gave 89 and 91% recovery, respectively. In the case of dye-sensitized reactions the irradiated solution was diluted with an equal volume of water, made about 3 m*M* in NaOH, and distilled. Fractions of the distillate were examined spectroscopically. The ethanolic fractions contained benzene, and succeeding fractions, obtained by steam distillation, contained phenol. Distillation was discontinued when the absorbance of the distillate became negligible. The residue was diluted, acidified, and extracted with ether. The extracts contained benzoic acid (identified by its ir and uv spectra). Control experiments, using a mixture of 20 μmol each of authentic benzene, benzoic acid, and phenol indicated 94, 87, and 93% recovery, respectively.

To determine the amounts of formazans oxidized to tetrazolium, the oxidized solutions were diluted with 0.1 *N* NaOH, and an excess of $Na_2S_2O_4$ was added. The resultant formazan was extracted with cyclohexane and examined spectrophotometrically. Control experiments noted quantitative production of formazan from the tetrazolium salt.

Calculation of Reaction Parameter. The quantum yield of the photochemical reaction was calculated using the following formula

$$\Phi = \frac{-\mathrm{d}[\mathrm{S}]}{\mathrm{d}t}\,\frac{lv}{I_0a(1 - 10^{\epsilon cl})}$$

which is equal to moles of formazan oxidized per einstein absorbed.

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Table I. Products of Oxidation of Formazans with Singlet Oxygen[a]

Method of oxidn	F or NF oxidized, μmol	Products identified, μmol B or N	Benzoic acid	Phenol	Tetrazolium
OCl^-/H_2O_2	19.5 (F)	15.7 (B)	17.5	None	Trace
28.5 μM MB	19.6 (F)	15.9 (B)	15.2	5.2	Ne[a]
150 μM MB	30.0 (NF)	15.4 (B) + 14.1 (N)	Ne	Ne	Ne
150 μM MB	19.6 (F)	17.8 (B)	16.5	4.5	Trace
51 μM Eosin Y	25.0 (F)	8.8 (B)	6.8	3.4	16.2

[a] Abbreviations: F = formazan; NF = naphthylformazan; B = benzene; N = naphthalene; MB = Methylene Blue; Ne = not examined.

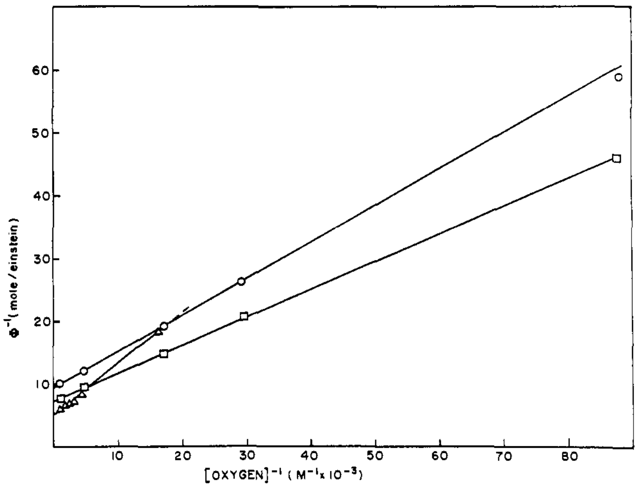

Figure 1. Methylene Blue (MB) sensitized oxidation of formazan (F) as a function of oxygen concentration. F 0.227 mM: dye 20 μM(○), 2.0 μM(□). F 2.27 mM: dye 20 μ M(△).

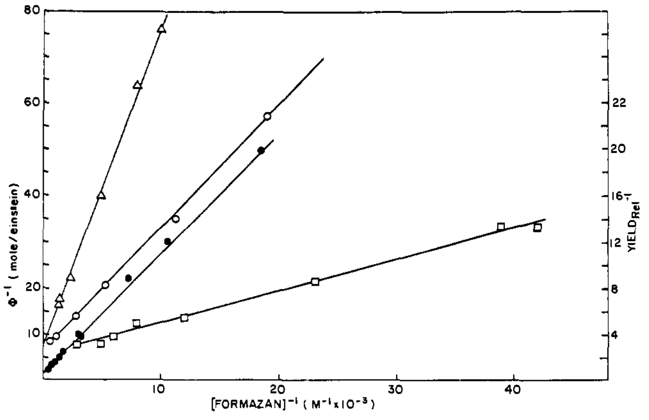

Figure 2. Methylene Blue sensitized and chemical oxidation of formazan as a function of formazan concentration in ethanol. Oxygen concentration 0.227 mM. □, ○, and △ represent Methylene Blue concentrations at 4.0, 66.5, and 200 μM, respectively. ●: chemical oxidation by $NaOCl–H_2O_2$.

I_0 is the intensity of incident light (in einsteins cm^{-2} sec^{-1}), ϵ the extinction coefficient of the sensitizer (l. mol^{-1} cm^{-1}), c the concentration of the sensitizer (mol l.$^{-1}$), l the depth of cell used (= 1 cm), a the area of cell irradiated (= 4.3 cm^2), [S] the concentration of formazan (mol l.$^{-1}$), and v the volume of solution irradiated (0.021 l.).

For the dark oxidation of formazan by hypochlorite-generated singlet oxygen the data were treated as follows: yield = moles formazan oxidized per mole of hypochlorite used; yield$_{max}$ = maximum yield, obtained at [S] where yield is independent of S; yield$_{rel}$ = yield/yield$_{max}$.

Results

The maximum quantum yield obtained for the oxidation of 1,3,5-triphenylformazan as sensitized by Methylene Blue is 0.16 mol of formazan oxidized per einstein 657 nm absorbed. Using a 500-W projector at a distance of 10 cm with a Corning CS 2-70 glass cut-off filter, about 10% of the formazan is oxidized in 1 min of illumination. In the absence of sensitizing dye there is no bleaching of formazan. In the complete absence of oxygen, there is no evidence of interaction between triplet sensitizer (either Eosin Y or Methylene Blue) and formazan.

The quantum yield of photooxidation is independent of oxygen at oxygen concentrations greater than 4 × 10^{-4} M and is independent of substrate at substrate concentration above 10^{-3} M. The oxygen and substrate dependence of the quantum yield form straight lines when treated as inverse relationships, as illustrated in Figures 1 and 2. Figure 2 also includes a plot of the extent of formazan oxidation by chemically generated singlet oxygen; again there is a straight-line dependence of the inverse parameters. Hypochlorite alone oxidizes formazan to the tetrazolium chloride; at the highest concentration of hypochlorite used this product represents 0.1% of the singlet oxygen products. A tenfold increase in H_2O_2 concentration decreases the dark formazan oxidation by a factor of 3 but has no effect on the photosensitized reaction rate.

As a key to determining the mode of attack of singlet oxygen in the $>C=NNH-$ bond grouping, we attempted to identify the products of formazan oxidation as well as possible. As shown in Table I, two of the products of both the Methylene Blue sensitized and the dark chemical oxidation are identical: per mole of formazan 1 mol each of benzene and benzoic acid is obtained. If, after photochemical oxidation, the solution is made basic, phenol is recovered. In the dark chemical oxidation, not a trace of phenol is found, but such solutions yield trace amounts of p-nitroaniline (identified spectrophotometrically after column chromatography). When α-naphthylformazan is used as a substrate, naphthalene as well as benzene is formed. Table I indicates that the sum of the moles of naphthalene and benzene produced equals the moles of α-naphthylformazan oxidized.

Photosensitized oxidation of formazan with Eosin Y yields considerable amounts of the tetrazolium salt as a product, whereas Methylene Blue yields almost none.

Discussion

The photosensitized oxidation of the substrate may be described by a kinetic scheme such as the following.

$$D + h\nu \xrightarrow{k_1} D^*$$

$$D^* \xrightarrow{k_2} D$$

$$D^* \xrightarrow{k_3} D'$$

$$D' + S \xrightarrow{k_4} D + S$$

$$D' \xrightarrow{k_5} D$$

$$D' + O_2 \xrightarrow{k_6} D + O_2^*$$

$$D' + D \xrightarrow{k_7} 2\,D$$

$$O_2^* \xrightarrow{k_8} O_2$$

$$O_2^* + D \xrightarrow{k_9} O_2 + D$$

$$O_2^* + S \xrightarrow{k_{10}} \text{products}$$

In the usual fashion D, D*, and D′ are used to designate the ground, first excited singlet, and metastable excited states of the dye, respectively, and O_2 and O_2^* designate the ground (triplet) and electronically excited (singlet) states of oxygen. S denotes the substrate, formazan. The following rate equation describes these reaction steps.

$$\Phi^{-1} = k' \frac{\frac{k_5}{k_6} + \frac{k_7}{k_6}[D] + \frac{k_4}{k_6}[S] + [O_2]}{[O_2]} \times \frac{\frac{k_8}{k_{10}} + \frac{k_9}{k_{10}}[D] + [S]}{[S]}$$

or

$$\Phi^{-1} = k' \frac{\alpha + [O_2]}{[O_2]} \frac{\beta + [S]}{[S]} = k' \frac{\delta}{[O_2]} + \frac{k_4[S]}{k_6[O_2]}\left(1 + \frac{\beta}{[S]}\right)$$

where

$$\alpha = \frac{k_5}{k_6} + \frac{k_7}{k_6}[D] + \frac{k_4}{k_6}[S]$$

$$\beta = \frac{k_8}{k_{10}} + \frac{k_9}{k_{10}}[D]$$

$$\delta = \frac{k_5}{k_6} + \frac{k_7}{k_6}[D] + [O_2]$$

$$k' = (k_2 + k_3)/k_3$$

The value of α may be determined as a function of [D] and [S] from the slopes and intercepts of plots such as those illustrated in Figure 1. Although the rate equation does not predict linearity between ϕ^{-1} and $[S]^{-1}$, this is in fact observed (Figure 2), since at the substrate concentrations used $k_4[S]/k_6 \ll \delta\beta/[S]$. Because $k_4\beta/k_6 \ll \delta$, β may be evaluated as the ratio of the slope and intercept of data plotted as in Figure 2. The ratio $k_3/(k_2 + k_3)$ is evaluated from the observed quantum yield and that calculated using the above-determined values of α and β.

For the reaction of formazan with chemically generated singlet oxygen, only steps 8 and 10 are operative, and the rate equation becomes

$$\text{yield} = \frac{\text{mol of formazan oxidized}}{\text{mol of hypochlorite used}} = k_a \frac{[S]}{(k_8/k_{10}) + [S]} = k_a \frac{[S]}{\gamma + [S]}$$

where k_a is the number of moles of singlet oxygen produced per mole of hypochlorite used, and $\gamma = k_8/k_{10}$. The values obtained for α, β, and γ are summarized in Table II. From these data we calculate the following values for the ratios of the rate constants of the photochemical reaction.

Table II. Oxidation of Formazan

[D], $M \times 10^4$	[S], $M \times 10^4$	α, $M \times 10^5$	β, $M \times 10^4$	γ, $M \times 10^4$
0.20	20.0	24.9		
0.20	2.14	5.9		
0.02	2.14	5.9		
0	0	2.8	1.1	
0	Varied			11.1
2.0	Varied		13.0	

$k_6/k_5 = 2.6 \times 10^4$ l. mol^{-1} (efficiency of energy transfer to oxygen as compared to radiationless deactivation of mestastable dye)

$k_6/k_7 \geq 1.2$ (efficiency of energy transfer to oxygen as compared to self-quenching of mestastable dye)

$k_6/k_4 = 22.1$ (quenching of dye triplet by oxygen as compared with substrate quenching)

$k_{10}/k_9 = 0.17$ (light sensitized; reaction of oxygen singlet with substrate *vs.* quenching by dye)

$k_8/k_{10} = 1.3 \times 10^{-4}$ mol l.$^{-1}$ (light sensitized); 1.06×10^{-3} mol l.$^{-1}$ (dark reaction) (singlet decay *vs.* reaction with substrate)

$k_3/(k_2 + k_3) = 0.2$ (fraction of excited singlets which result in triplet formation)

Thus the value for k_8/k_{10} in the photosensitized reaction is tenfold smaller than that obtained for the oxidation with chemically generated singlet oxygen. For both the Rose Bengal sensitized and the chemical oxygenation of 2,5-dimethylfuran, $\gamma = 10^{-4}$ *M*.[14] However, in that study substrate dependence was not extrapolated to zero dye concentration, and therefore the true ratio of the reaction rate constants involved (k_8/k_{10}) in the photosensitized reaction may not have been determined. Assuming diffusion-controlled reaction rates, we calculate (from k_8/k_{10}) the minimum lifetimes of singlet oxygen as 0.14 and 1.2 μ sec (chemical and photochemical reactions, respectively) and (from k_4/k_6 and α) that of metastable excited Methylene Blue as 5.8 μsec. The lifetime calculated for Methylene Blue is in excellent agreement with the value (5.0 μsec) obtained previously for the same dye in a study of the photooxidation of histidine in aqueous solution at pH 9.[15]

Our value of 1.2 μsec for the minimum lifetime of O_2^* in ethanol is one-tenth that determined using carotene quenching[5,16] and one-sixth of the lifetime in methanol determined in a flash spectroscopic study.[17] It is longer than the one determined in water for the Rose Bengal, Methylene Blue, and proflavin sensitized photooxidation of amino acids.[15] The assumption of

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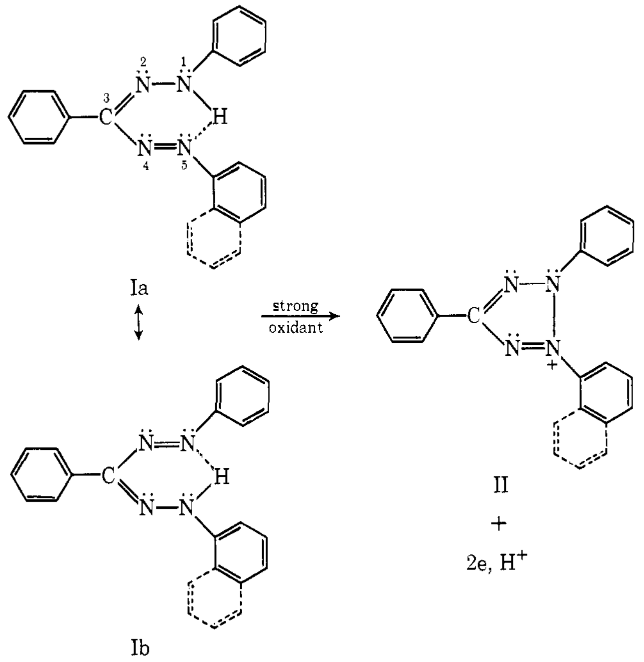
the 1:1 correspondence between collision frequency and oxidative reaction was perhaps not justified in that case, probably no more than 2% of collisions in the amino acid system resulting in reaction. The lifetime of O_2* in methanol is three times greater than that in water.[17] This fact cannot explain our observation that the lifetimes in the photochemical (ethanolic) and the chemical system (containing up to 10% water) differ by a factor of 10.

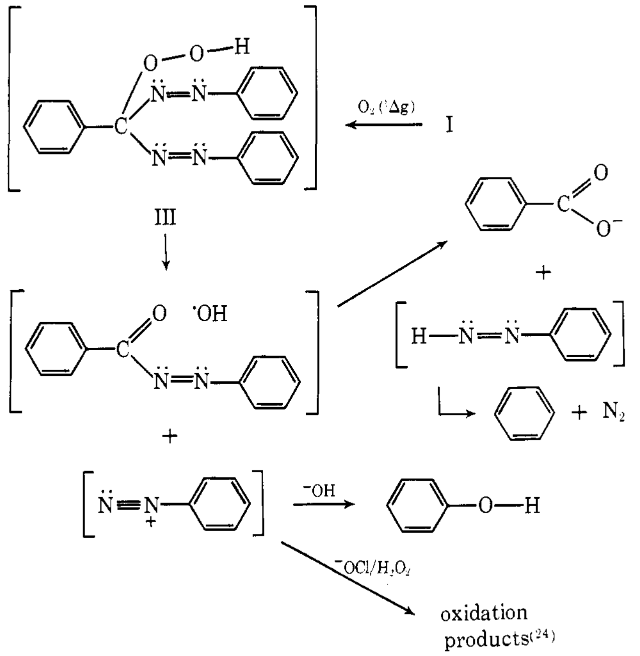
The fraction of excited singlet state dye molecules undergoing transition to the metastable state (0.2) is the same as that determined in the photoreduction of Methylene Blue.[18,19] The maximum ϕ of the reaction reported here does not reach this value because of the quenching reactions 4, 7, and 9. In contrast, in the xanthene-sensitized photooxidation of dimethylfuran such steps are unimportant.[20]

Two of the products formed in both the Methylene Blue photosensitized and the dark chemical reaction of singlet oxygen with formazan are identical: per mole of formazan oxidized, 1 mol each of benzene and benzoic acid is formed; presumably nitrogen is formed as well. The photochemical reaction yields 0.25 mol of phenol per mol of benzene. When the photooxidation is sensitized by a substance with higher triplet energy (Eosin Y), 75% of the molecules are oxidized to the tetrazolium compound and the remainder to benzene, benzoic acid, and phenol.

The reaction of formazans (I) with strong oxidizing agents (*e.g.*, nitrous fumes or PbO_2) results in the formation of the tetrazole ring (II). In fact, the general method of preparation of the tetrazolium salts is by the treatment of the formazans with strong oxidants.[13] In the oxidation of formazan by singlet oxygen generated either chemically or with Methylene Blue, there is no evidence of the formation of the tetrazolium cation (II). We, therefore, rule out simple H abstraction as the reaction mechanism. Chemically generated O_2* exists mostly in the $^1\Delta_g$ state,[21,22] and energy conservation permits only $^1\Delta_g$ to be generated by low triplet energy sensitizers such as Methylene Blue.[8] In this state, excited oxygen should act as a dienophile and undergo two-electron reactions.[7] The resulting hydroperoxides are stereospecific,[7,23] indicating the absence of a radical intermediate. Similarly, in our case, the observed formation of benzene and benzoic acid (and of phenol in the photochemical reaction) can be explained by the rearrangement of an intermediate azo hydroperoxide (Scheme I). Such rearrangements (*e.g.*, benzylazobenzene α-hydroperoxides) are well known.[25,26] We have been unable to identify the postulated hydroperoxide intermediate III. The low concentrations involved, the hydroxylic solvent used (precluding nmr study), and its apparent liability as compared with hydroperoxides of phenylhydrazones would preclude its observation.



Scheme I



The production of phenol (photosensitized reaction) and of nitroaniline (chemical oxidation) presumably occurs through hydrolysis and oxidation, respectively, of the diazonium cation. Such cations are known to be oxidized in alkaline media by a variety of oxidizing agents, including hydrogen peroxide. The initial products of such oxidations are the unstable aryl nitryl anilines, which rearrange to nitro aryl amines and other uncharacterized products.[26] In the photosensitized reaction, the absence of hydrogen peroxide permits the diazonium cation to hydrolyze to phenol.

The fact that naphthalene and benzene are formed in equimolar ratio from the photosensitized oxidation of naphthylformazan may be a consequence of resonance between the mesomeric forms Ia and Ib.[13]

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