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Redox Photochromism in a Heteroatomic Polycyclic Quinone

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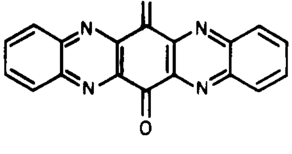
Visible-light irradiation of the yellow 5,7,12,14-tetraazapentacene-6,13-quinone (1) in acidic, alcoholic solvents leads to a blue doubly reduced salt 3. Upon exposure to an oxidant (air or H_2SO_4), the photoproduct 3 is reconverted ultimately to 1. Excited-state properties of 1, together with its cyclic voltammetric characterization, are presented. Multiple recycling between the oxidation levels of the compounds, giving rise to yellow or blue absorption bands, is possible, although degradation of the quinone eventually occurs. 1 is useful as a reduction photocatalyst responsive to visible light.

Our interests in visible light induced photochemistry[1] and in photoredox reactions of polycyclic aromatic hydrocarbons and their derivatives[2] have led us to explore a new photochromic process occurring upon excitation with visible light of a pentacyclic heteroatom-containing quinone. Although redox reactions can profoundly change the conjugation in arenes, and hence their absorption spectra, recent monographs[3] on photochromism do not discuss separately redox photochromism for, indeed, relatively few examples are known. This deficiency is not attributable to a lack of photochemical reductions but rather to the usual thermal irreversibility of such photochemical processes. A key criterion for redox photochromism is therfore a closely balanced equilibrium between the reduced and oxidized forms of the photoactive molecule.

Introduction

Primarily because of the importance of quinones in the dye industry, the photoreactions of quinones have been studied extensively.[4] Although they can react by many pathways, e.g., dimerization, [2 + 2] cyclizations with olefins, etc., all but photoreduction occur with very low quantum yield in dilute solution. This highly efficient photoreduction (typically, quantum yields approach unity[4]) derives from the exceptionally strong oxidizing power of photoexcited quinones. Although the mechanism for the reduction may involve either hydrogen abstraction or sequential electron and proton transfer (and is probably not generalizable for the entire family of quinones), photoexcited quinones rival the halogen atoms in their oxidizing power. The excited state of anthraquinone is estimated, for example, to abstract hydrogen atoms with a facility between that of chlorine and fluorine atoms.[5]

The thermal reversibility of this photoreduction can be estimated by electrochemical redox potentials. Here, too, extensive data on the family are available.[6,7] In general, the reduction potential becomes more negative with ring homologation, for example, in the series benzoquinone, naphthoquinone, anthraquinone. Since as a family these couples are nearly ideally reversible, we believed our best chance for reoxidation of a photoreduced quinone without an applied bias lay with polycyclic quinones. This, together with the observation that acidic solutions of 5,7,12,14-tetraazapentacene-6,13-quinone[8] (1) which became intensely blue when stored on a window sill faded when stored in a drawer, led us to more closely investigate the photoredox chemistry of this compound (a quinazolinophenazinedione).



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Results

When a suspension of quinone 1 (λ_{max} 342, 360, 380 nm) in aqueous or alcoholic 0.1 M H_2SO_4 was exposed to visible light, an intense blue color appeared (λ_{max} 630 nm). This

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(2) Fox, M. A.; Nobs, F. J.; Voynick, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 4036.

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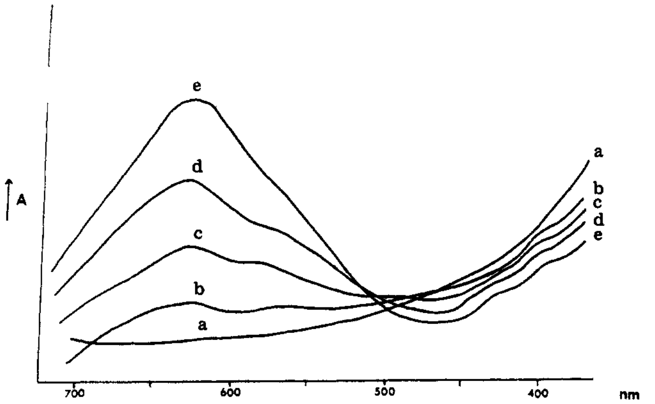
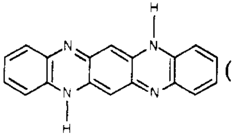


Figure 1. Visible absorption spectrum of the photolysis mixture obtained from the irradiation of quinone 1 (saturated solution of 1 in 0.1 M ethanolic H_2SO_4). Irradiation of 3-mL ampule at 350 ± 20 nm. Irradiation times: curve a = 0 min; b = 2 min; c = 4 min; d = 5 min; e = 7 min.

Table I. Absorption and Fluorescence Spectra of Compounds Related to 1

compd	absorption maxima, nm	fluorescence emission maxima, nm
1	343, 360, 380	405, 430, 455
yellow product (2)	400, 430	460, 485
blue product (3)	630	none below 700
 (5)	578	640

conversion can be followed by absorption spectroscopy under more dilute conditions, and a typical reaction profile is shown in Figure 1. Time evolution of product, along with potassium ferrioxalate actinometry[9] for excitation at 350 ± 30 nm, allows calculation of the quantum yields for disappearance of 1 ($\Phi_d = 0.40 \pm 0.10$) and appearance of product ($\Phi = 0.20 \pm 0.10$). The absence of an isosbestic point in Figure 1 and the inequality of these two quantum yields indicates that 1 is not converted directly to product; i.e., the reaction proceeds through some other species. If the intense blue solution is covered with foil to eliminate exposure to light, the original yellow color slowly reappears. Thin-layer chromatography indicates the presence of quinone 1 and a new species. Upon exposure of the yellow solid mixture to oxygen and chromatography on silica gel, quinone 1 was recovered essentially quantitatively (>95%). A comparison of the absorption and fluorescence spectra of 1 and the yellow product mixture is shown in Table I. Although both the yellow product (2) and blue product (3) could be recovered if the chromatography were conducted under an inert atmosphere, neither compound was sufficiently soluble to allow normal NMR structural analysis.[11] Neither compound 3, a nonsublimable powder, nor compound 2 melted below 400 °C.

The reversion of blue product, ultimately to quinone, occurred in alcoholic sulfuric acid both in the presence and absence of oxygen, although somewhat more slowly in the latter case. A sealed ampule containing the acidic ethanolic solution of 1 could be cycled from yellow-to-blue-to-yellow at least five times (less than 10% loss of quinone). Repeated cycling of aqueous acid does result in eventual loss of quinone. Chromatographic analysis of the product indicates production of an inseparable complex mixture, elemental analysis of which indicates incorporation of oxygen. Although blue color was observed when HCl was used as the acid, the color did not fade in the absence of air as it did when sulfuric acid was used.

Table II. Effect of Solvent and Acid on the Rate of Product Formation[a]

solvent	acid or salt[b]	relative rate
H_2O	H_2SO_4	0.74
CH_3OH	H_2SO_4	1.20
CH_3CH_2OH	H_2SO_4	1.00
CH_3CH_2OH	$NaHSO_4$	0.95
CH_3CH_2OH	HCl	1.08
CH_3CH_2OH	HNO_3	1.00
CH_3CH_2OH	HOAc	0.00
CH_3CH_2OH	$(NH_4)_2SO_4$	0.00
CH_3CH_2OH	NaCl	0.00
CH_3CH_2OH	Na_2SO_4	0.00
$(CH_3)_2CHOH$	H_2SO_4	0.31
$(CH_3)_3COH$	H_2SO_4	0.00

[a] Suspension of 1 in acid/solvent mixture; irradiation source 350-nm phosphorcoated low-pressure mercury vapor lamps; irradiation period 0-30 min. [b] 1 M acid or buffer, room temperature.

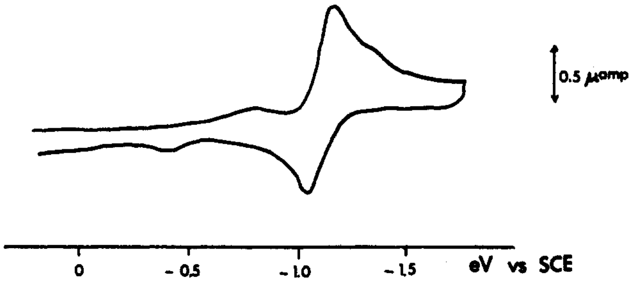


Figure 2. Cyclic voltammogram of quinone 1 (saturated CH_3CN, 0.1 M tetrabutylammonium perchlorate, room temperature, scan rate 100 mV/s).

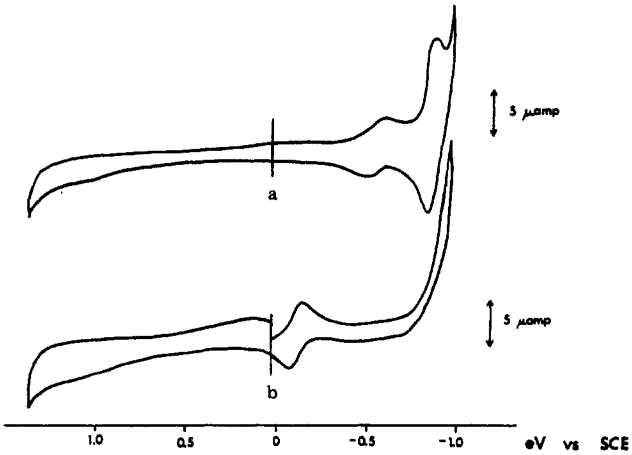


Figure 3. Cyclic voltammogram of photolysis mixture from quinone 1 in acidic methanol (methanol, 1 M H_2SO_4, 0.1 M Na_2SO_4, room temperature, scan rate 100 mV/s); (a) immediately after photolysis; (b) sample from a after the addition of *p*-benzoquinone.

The relative rates of production of blue product in varying solvent and acid conditions are listed in Table II. In the absence of acid or in ether solvents, no blue coloration can be observed.

Cyclic voltammetry of 1 revealed a reversible wave ($E_{1/2}$ = −1.10 eV vs. SCE; Figure 2). Cyclic voltammetry of the blue product mixture gives rise to the curve shown in

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[9] Hatchard, C. G.; Parker, C. A.; *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

[10] Eistert, B.; Fink, H.; Werner, H.-K. *Justus Liebigs Ann. Chem.* **1962**, *657*, 131.

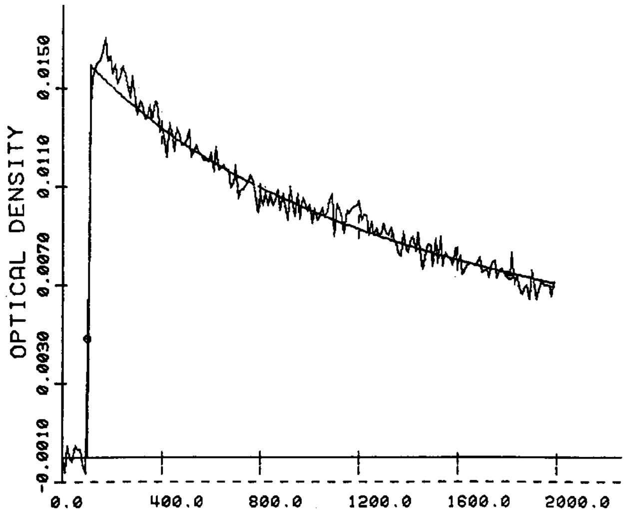


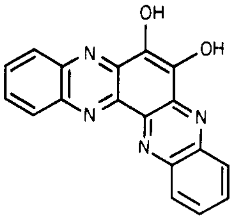
Figure 4. Second-order fit of the decay of the transient formed by flash photolysis of 1 in 0.1 M ethanolic H_2SO_4: smooth curve, computer fit for second-order decay; rough curve, observed decay of the transient.

Figure 3. Addition of *p*-benzoquinone alters the curves as shown (Figure 3) and causes immediate fading of the blue color. When the potential in an electrochemical cell containing a methanolic suspension of 1 and Na_2SO_4 was held at −0.75 eV vs. SCE by a potentiostat, a weak anodic current (5 μA) could be observed. If the thermostatted cell was irradiated inside the cavity of a circular array of phosphor-coated low-pressure mercury arcs, the current grew slowly over a period of 10 min, reaching a maximum value of about 0.3 mA as the solution became intensely blue. Upon treatment with a dilute solution of *p*-benzoquinone, the blue color faded immediately and the "photocurrent" disappeared.

If quinone 1 was suspended in a 0.1 M solution of *p*-benzoquinone in acidic ethanol and irradiated at wavelengths greater than 400 nm (conditions under which benzoquinone light absorption is negligible), no blue color developed but a clean conversion to hydroquinone was observed.

Flash excitation (λ_{ex} 337 nm) of a filtered suspension of 1 in ethanolic 0.1 M H_2SO_4 gave rise to a transient absorption at 390 nm with a half-life of 1.5 msec. Decay of the transient was second order (Figure 4). This may be attributed either to a radical formed by hydrogen abstraction or by sequential electron and proton transfer or to a long-lived triplet. A time-resolved spectrum shows this transient fading as 2 and then 3 are sequentially formed.

No blue color developed when 4,[10] the reduced form of an isomer of 1, was irradiated with visible light in 1 M ethanolic H_2SO_4.



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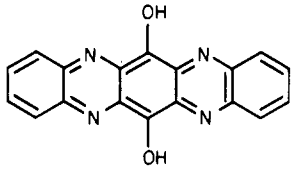
Discussion

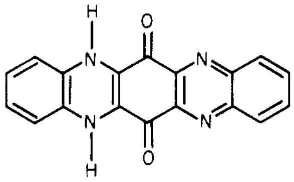
Formation of intense blue color upon irradiation of quinone 1 in the presence of acid probably results from photoreduction to a highly conjugated species which is protected from further redox chemistry by protonation. The absence of an isosbestic point, the inequality of the quantum yields for disappearance of 1 and appearance of blue color, and the isolation of a yellow compound different from, but reconvertible under oxidative conditions to, 1 indicate the involvement of at least one intermediate in the 1 → blue (3) interconversion (eq 1). Both the intermediate 2 and the final product 3 must be structurally related to 1, probably as different reduced forms of 1, for the reversion of 2 and 3 to 1 is nearly quantitative under oxidative conditions.

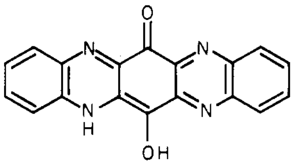
$$\underset{\text{yellow}}{1} \underset{[O]}{\overset{[H]}{\rightleftharpoons}} \underset{\text{yellow}}{2} \underset{[O]}{\overset{[H]}{\rightleftharpoons}} \underset{\text{blue}}{3} \tag{1}$$

In view of the extreme insolubility of 1–3 in any appropriate solvent and the difficulty in subliming or recrystallizing powders of 2 or 3,[11] we offer only tentative assignment of structure for these compounds. Elemental analysis of 2 shows it to be a monoreduced form of 1, i.e., 1·H_2. Of the possible tautomeric forms for 2 (2a–c), we prefer 2b because of an IR band at 1710 cm^{-1} and the color.[12] Tautomers 2a and 2c, having more extended conjugation, would be expected to closely resemble 5[8] or 6,[8] intensely violet-blue solids, in their absorption spectra.

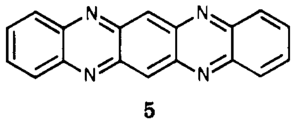


2a





2c



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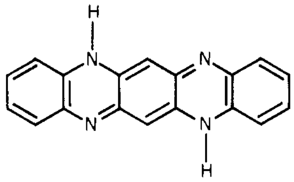

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Elemental analysis of 3 shows it to be a direduced, hydrated bis(sulfate salt) of 1. The absence of a carbonyl band in the IR spectrum of 3 and its intense blue color imply the structure shown (or one or its tautomers). Attempts to prepare neutral 3 by treatment of the diprotonated salt with dilute base were unsuccessful, a mixture of 2 and 1 being obtained even under degassed conditions. Indeed, the stability of 3 (salt) may be caused by its removal from neutral redox equilibria by protonation. Note in Table I that acetic acid and ammonium

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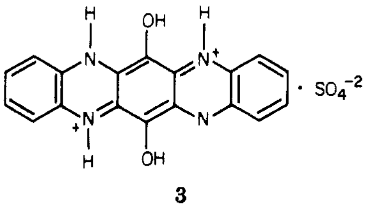
(11) The solubility of 1–3 in 1 M H_2SO_4 was less than 10^{-4} M, while those in acetonitrile and chloroform were, respectively, less than 10^{-5} and 10^{-6} M. We were therefore unable to obtain informative ^{13}C NMR spectra for these compounds. This insolubility also complicated crystal growth, and despite repeated attempts, we were unable to obtain crystals of sufficient size for X-ray analysis.

(12) These arguments assume the relative unimportance of hydrogen bonding. The real structure probably has significant inter- or intramolecular hydrogen bonding but maintains substantial C=O character.



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sulfate are ineffective in producing the blue compound.

By analogy with known chemistry of quinones, the photochemical reduction of 1 to 2 in alcoholic solvents is well precedented. If 2 exists as **2b**, a further photoreduction may be anticipated, perhaps with lower quantum efficiency, for the photochemical reduction of aminonaphthoquinones has been observed.[13] Protonation of the reduced product, as discussed above, leads to 3. While we are unsure about details of the mechanism,[4,14] the greater rates of reaction (Table I) in methanol and ethanol compared with that in water suggest that hydrogen atom abstraction may be more important than protonation. That the reaction rates are not monotonic in the series H_2O, MeOH, EtOH, *i*-PrOH may reflect relative hydrogen-abstraction ability in the series ($H_2O < CH_3OH < CH_3CH_2OH < (CH_3)_2CHOH$) being counteracted by decreasing solubility of 1 in this same series. (In all cases, a suspension, i.e., a saturated solution, is being irradiated.) Our proposed mechanism accommodates the observed second-order transient decay if a disporportionation of the monoreduced form is a primary route to product.

The oxidation of 2 and 3 is accomplished by consuming air or oxidizing acids. We note that oxygen speeds the fading of the blue color and that acids which function as oxidants in organic transformations (e.g., H_2SO_4 and HNO_3) permit fading of blue color even in deaerated solution while a nonoxidizing acid (HCl) does not. Consistent with this ease of oxidation is the reduction potential of 1 (Figure 3) and the immediate chemical reaction of 3 with benzoquinone. That this interaction involves rapid electron transfer is established by the absence of blue color and the detection of hydroquinone when 1 is excited (under conditions expected to give rise to 3) in the presence of benzoquinone. Note that this experiment constitutes redox photosensitization induced by visible light. The relative concentrations of 1 and benzoquinone demand a photocatalytic turnover of at least 500 in this photosensitization. The production of weak anodic photocurrents in a potentiostatted cell containing the photolysis mixture obtained by irradiating 1 is consistent with photoreduction followed by Nernstian electrochemical reoxidation. This process has previously been reported in an electrochemical cell in which the quinone/hydroquinone equilibrium was tipped by photoreduction.[15]

The excited-state behavior of 1 is not unusual for a heterocyclic quinone, both fluorescence and phosphorescence being observable. Although comparable excited state lifetimes etc. are observed in its isomer 4, the absence of color development in the photoreduction of 4 suggests the dependence of such redox equilibria on structural effects. Generalizing our results to other heterocyclic quinones may be difficult, therefore.

Ultimately, repeated cycling in the reaction sequence causes quinone disappearance. Although the products could not be effectively purified and characterized, the reaction mixture becomes increasingly richer in oxygen as the quinone disappears. This disappearance is most rapid in water and may reflect photochemical production of OH· (or H_2O_2) which is known to attack simple quinones, giving rise to hydroxylated derivatives.[16] Alternatively, this degradation product may be formed by inefficient oxidative dimerization or by slow sulfonation.

Conclusion

We find that 1, a yellow compound, is reduced upon visible-light photoexcitation in alcoholic solvents to form an intensely blue direduced, diprotonated salt. This normal quinone photoreaction is novel in that the photoproduct is easily reoxidized by mild oxidants in near quantitative yield. Since the quantum yield for the photoreduction is high and the reoxidation is relatively slow, this system represents a new, recyclable photochromic system on an hour time scale. In the presence of reactive oxidants, the reoxidation is accomplished rapidly. Because of its absorption characteristics, 1 can therefore function as an effective redox photocatalyst. Because of its efficient reversibility, a single molecule of 1 can reduce many molecules of the related redox couple. (A catalytic turnover of ≥500 is observed when 1 functions as a redox photocatalyst for the reduction of *p*-benzoquinone.)

Experimental Section

Materials. Distilled technical grade solvents (CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$) were employed. Distilled water was redistilled from $KMnO_4$. Inert electrolytes (analytical reagent-grade $LiClO_4$ and Na_2SO_4) were pumped under high vacuum overnight to remove volatile impurities. 1 and 2 were sublimed under high vacuum before chemical and spectroscopic analysis was conducted. 3 was purified by elution through a short column of silica gel.

Analysis. Infrared (IR) spectra were obtained on a Perkin-Elmer Acculab 7 instrument. Mass spectra were obtained on a Du Pont 21-471 spectrometer. Fluorescence spectra were measured on a Spex fluorimeter and UV and visible absorption spectra were obtained on a Cary 14 spectrophotometer. Transient emission/absorption spectra were obtained at the Center for Fast Kinetics Research at The University of Texas at Austin.

1. Quinone 1 was prepared by the method of Badger and Pettit.[8] 1: mp >300 °C; IR (KBr pellet) 1710, 1610, 1480, 1460, 1390, 1320, 1050 nm^{-1}; mass spectrum; *m/e* 76, 312 (P^+); UV (1 M aqueous H_2SO_4) λ_{max} 343, 360, 380 nm.

2 and 3. A suspension of 100 mg of quinone 1 in freshly distilled ethanol (250 mL) is made 1 M in H_2SO_4. The mixture is vibrated in an ultrasonic bath for 10 min. The resulting suspension is irradiated in a water-cooled jacket with a 200-W GE sunlamp. The solution becomes green in about 2 min and after 10–15 min of irradiation, intense blue color is evident. The irradiation is continued for 6 h. The mixture is placed on a silica gel column which is developed under nitrogen with freshly distilled ethyl acetate. Three fractions are collected (in order of elution): 2, 1, 3 (much slower moving).

2: mp >300 °C; IR (KBr pellet) 3400, 1710, 1650, 1630, 1620, 1480, 1380, 1330, 1210, 1110 cm^{-1}; mass spectrum, *m/e* 76, 314 (P^+); UV (1 M aqueous H_2SO_4) λ_{max} 400, 430 nm.

3: mp >300 °C; IR (KBr pellet) 3400 (br), 1610, 1480, 1460, 1380, 1210, 1060 (br) cm^{-1}; UV (1 M aqueous H_2SO_4) λ_{max} 630 nm. Anal. ($C_{14}H_{12}N_4O_2 \cdot H_2SO_4$): C, H, N, S.

4 was prepared by the method of Eistert et al.;[10] mass spectrum, *m/e* 313, 314 (P^+).

Quantum Yields. Quantum yields for the disappearance of 1 and the appearance of 3 were obtained in a double-baffle merry-go-round apparatus with RPR 3500-Å lamps. Dilute solutions (10^{-5} M) of 1 in 1 M, H_2SO_4 were irradiated simultaneously with a potassium ferrioxalate actinometer solution.[9] The disap-

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pearance of 1 was monitored by absorption spectroscopy as was the appearance of 3. Typically, a conversion of about 10% of starting material was used in the quantum-yield determinations.

General Photolysis Method. A suspension of 10 mg of 1 or 4 in 25 mL of aqueous or alcoholic 1 M acid was vibrated in an ultrasonic bath for 10 min. The resulting suspension was transferred to Pyrex test tubes sealed with serum caps. Such suspensions were either irradiated directly or were deoxygenated by a 30-min purge with dry argon. The process of the reaction was monitored by absorption spectroscopy after withdrawing an appropriate aliquot and diluting. Light source for the irradiation was either a circular array of 350-nm phosphor-coated low-pressure mercury arcs, natural sunlight, or a water-cooled 200-W GE Sunlamp.

Stability of 2 and 3. The photolysis mixtures obtained from 1 by the above procedure were wrapped in foil and stored in the dark in a desk drawer or in the refrigerator. The intense blue color of a 50:50 mixture of 1–photoproducts had completely disappeared overnight. If air was bubbled slowly through the resulting yellow suspension for 2 h, quinone 1 was the sole recoverable product after chromatography on silica gel (EtOAc eluant).

After five cycles (irradiation–fading) in water essentially the same results were obtained, except that poorer (>80%) mass balance in the recovery of 1 was obtained. A yellow-colored side product(s) eluting more slowly from the column gave elemental analysis with oxygen contents 50–200% higher that that required for 1.

Electrochemistry of 1. Cyclic voltammograms were obtained in a previously described three-compartment cell employing a silver wire quasi-reference electrode[17] or with a saturated calomel electrode separated from the electrolysis cell by a glass frit. The experiments were conducted with a PAR (Princeton Applied Research Corp.) Model 173 potentiostat and Model 175 universal programmer. An X-Y recorder (Houston Instruments) was used to record current-potential curves. The curves obtained for 1 and 3 are shown in Figures 2 and 3.

"Photocurrent" measurements were obtained by monitoring current between a glassy carbon anode and a platinum cathode with a microammeter (Keithley Model 177 multimeter) while the potential was maintained at –0.75 eV with a PAR Model 173 potentiostat. The entire thermostatted electrochemical cell was inserted into the circular cavity of a Rayonet photochemical reactor equipped with 350-nm phosphor-coated low-pressure mercury lamps. The anodic current was monitored as a saturated solution of 1 in 0.1 M ethanolic H_2SO_4 containing 0.1 M $NaSO_4$ was irradiated. The blue color which developed upon irradiation was accompanied by an anodic current (0–0.3 mA). This color faded immediately upon the injection of 10 mL of a 0.01 M aqueous solution of benzoquinone.

Flash Photolysis. A N_2 laser (≤5 mJ/pulse) was used to excite a saturated solution of 1 in 0.1 M ethanolic H_2SO_4 after a 3-min nitrogen purge. Transients were observed in the range from 380–700 nm. Data analysis was conducted with a previously described system.[18]

Acknowledgment. We are grateful for financial support for this research by the U.S. Department of Energy and the Robert A. Welch Foundation. M. A. F acknowledges support as an Alfred P. Sloan Foundation Research Fellow (1980–82). The flash spectroscopic measurements were conducted with the assistance of Dr. M. A. J. Rodgers at the Center for Fast Kinetics Research, a facility sponsored by the National Institutes of Health and the University of Texas at Austin. We are especially grateful to Professor Roland Pettit for bringing this problem to our attention and for helpful comments during the course of the work.

Registry No. 1, 76447-82-0; 2, 76447-83-1; 3, 76447-85-3; 4, 25174-63-4; 5, 258-67-3.

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Neighboring-Group Participation in Organic Redox Reactions: Effect of Tertiary Amine and Pyridine Groups on the Kinetics and Mechanism of Thioether–Sulfoxide Interconversions

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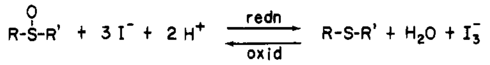
The effect of neighboring tertiary amine, quaternary ammonium, and pyridine substitution on both the oxidation of thioethers by aqueous I_2 and the reduction of sulfoxides by aqueous HI has been evaluated. The millionfold acceleration in the rates of the reactions of 5-methyl-1-thia-5-azacyclooctane and its sulfoxide is unique. The rates of the lower homologues and acyclic analogues are not accelerated and at a given acid concentration the rates of oxidation of amine sulfides follow the rate law $d[RSR']/dt = -k_{ox}[RSR'][I_2][I^-]^{-1}$. The rates of reduction of the amine sulfoxides follow the rate law $d[RSR']dt = k_{red}[RR'S–O][I^-]$. The pH profiles of the I_2 oxidation of 6-methyl-2-thia-6-azaheptane and 2-[2-(methylthio)ethyl]pyridine demonstrate neighboring-group participation and suggest N–S interacted intermediates.

Introduction

As part of our studies of intramolecular catalysis of organic oxidation and reduction reactions, the effect of neighboring tertiary amine, quaternary ammonium, and pyridine substitution on both the oxidation of thioethers by aqueous I_2 and the reduction of sulfoxides by HI (eq 1) has been evaluated. We previously had shown that in 5-methyl-1-thia-5-azacyclooctane, 1, the transannular tertiary amine group catalyzes both the oxidation of the



$$\text{R-}\overset{\overset{\text{O}}{|}}{\text{S}}\text{-R}' + 3\,\text{I}^- + 2\,\text{H}^+ \underset{\text{oxid}}{\overset{\text{redn}}{\rightleftarrows}} \text{R-S-R}' + \text{H}_2\text{O} + \text{I}_3^- \qquad (1)$$

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