

be suggested that the binding of oxygen at one site of hemoglobin causes a structural change which juxtaposes aromatic amino acid donor moieties with a heme at another site. Stabilization of the low-spin state may occur at this second site by means analogous to those responsible for the effects of phen reported above. The consequence is that oxygen will be bound more strongly and K_2 will be greater than K_1 .

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- (18) Abbreviations: Fe(deut)Cl = deuteroporphyrin (IX) dimethyl ester iron(III) chloride; Im = imidazole; Fe(deut)Im₂⁺Cl⁻ = deuteroporphyrin (IX) dimethyl ester bis(imidazole)iron(III) chloride.
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E. H. Abbott,* P. A. Rafson

Department of Chemistry, Hunter College of the City University of New York
New York, New York, 10021

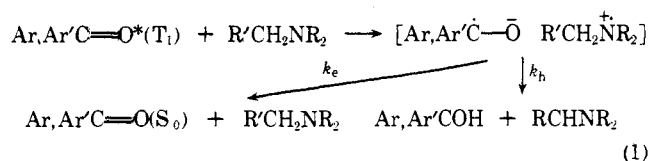
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Photoreduction by Hydrazinium Ions, Quenching by Hydrazines

Sir:

We wish to report that hydrazines, which are reducing agents in thermal processes, quench photoexcited ketones in water efficiently, with little photoreduction; however, certain monoprotonated hydrazinium ions, normally less effective thermal reducing agents, are good photoreducing agents.

Photoreduction of aromatic ketones by amines proceeds via rapid initial formation of a charge transfer complex, CTC, characterized by rate constant k_{ir} , followed either by regeneration of the ground state reactants, k_e , or by H transfer and formation of radicals, k_h , eq 1.¹ Formation of

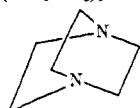


the CTC facilitates the subsequent hydrogen transfer, so that ketones which are not photoreduced by alcohols are photoreduced by amines, particularly tertiary amines.^{1b,2} Values of k_{ir} increase regularly with increasing electron availability in the amine.^{3,4} With very favorable ionization potentials or negative values of σ^+ , values of k_{ir} approach diffusion control,^{4,5} but the quantum yields for photoreduction may become very small.⁴ In such cases the charge transfer complexes are relatively stable and lead to quenching, as the hydrogen transfer requires excessive activation energy. Low electron availability, caused by electron withdrawing substituents, decreases k_{ir} , and may also decrease quantum yield,⁴ as insufficient development of positive charge in the CTC fails to facilitate adequately transfer of a proton from α -C.

Preliminary studies of photoreduction in water of 4-benzoylbenzoate anion by some hydrazines, amines, and their protonated forms are summarized in Table I.

Hydrazine is an efficient quencher at pH 12, $k_{ir} = 5.3 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, but it is not a good photoreducing agent, $\varphi \sim 0.01$. At pH 7, where it is 91% monoprotonated, reducing efficiency is increased manifold, $\varphi = 0.29$. From 0.005 to 0.10 M hydrazine at pH 7, φ rises from 0.14 to 0.31, and a linear plot of $1/\varphi$ vs. $1/c$ may be constructed, slope = 0.022 M, intercept = 3.1, limiting quantum yield 0.32, and $k_d/k_{ir} = 0.007 \text{ M}$. Methylhydrazine shows, on protonation, a similar increase in quantum yield for photoreduction of the carbonyl compound. However, tetramethylhydrazine shows little more increase in quantum yield than would result from the change in reduction product, from hydrol at pH 12 to pinacol at pH 7.⁵ The quantum yield at pH 7 remains low, ~ 0.026 , despite the presence of ample α -CH which normally leads to photoreduction by amines. Tetramethylhydrazine is only 17% protonated at pH 7, and the unprotonated base may be quenching most of the excited ketone. Yet hydrazine and methylhydrazine appeared to show efficient photoreduction when only partly monoprotonated at pH 9. The monoprotonated forms of the polyalk-

Table I. Photoreduction of 0.003 M 4-Benzoylbenzoate by 0.04 M Amine Compound in Water. Effect of pH on Quantum Yield

Compound	pK _a	pH	>NH ^d (%)	φ^e	$10^{-6}k_{ir},^f$ M ⁻¹ sec ⁻¹
H ₂ NNH ₂	8.07 ^a	12	0	0.011	0.53
H ₂ NNH ₂		9	9	0.16	
H ₂ NNH ₂		7	91	0.29	
CH ₃ NHNH ₂	7.87 ^a	12	0	0.011	
CH ₃ NHNH ₂		9	7	0.12	
CH ₃ NHNH ₂		7	88	0.21	
(CH ₃) ₂ NN(CH ₃) ₂	6.3 ^b	12	0	0.011	
(CH ₃) ₂ NN(CH ₃) ₂		7	17	0.026	
(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂	9.1 ^{b,c}	12	1	0.73	2.04
(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂		7	99	1.30	
(CH ₃ CH ₂) ₃ N	10.75 ^c	12	5	0.70	2.09
(CH ₃ CH ₂) ₃ N		7	100	0.35	
	8.8 ^{b,c}	12	0	0	1.69
		7	98	~0.003	

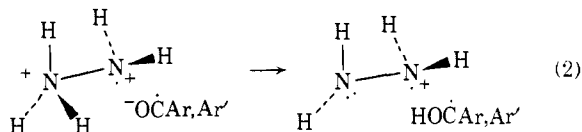
^a Reference 6. ^b Determined by titration. ^c Reference 7. ^d Percent of monoprotonated form at the indicated pH, calculated from pK_a. ^e The quantum yield for photoreduction by triethylamine at pH 12 was determined by ferrioxalate actinometry at 334 nm, ref 5. This solution was used as a secondary actinometer, irradiated simultaneously with the other solutions on a rotating wheel. Solutions were degassed by the freeze-thaw method and irradiated under argon. ^f Determined by quenching of phosphorescence of 0.008 M ketone by 0.0002 M amino compound in water pH 12, excitation at 350 nm, emission at 450 nm, $\tau_0 = 4.34 \times 10^{-6}$ sec.

ylated hydrazines will be examined at lower pH, but systems are needed in which the ketone remains soluble in acid medium.

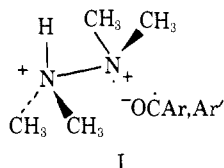
Tetramethylethylenediamine behaves like a normal photoreducing agent, similar to triethylamine, $\phi \sim 0.7$, and monoprotonation leads only to the increase in quantum yield due to the change in reduction product. The result with triethylamine is of interest since protonation, which might make the n electrons unavailable, appears to decrease quantum yield only moderately, to 0.35. The electrophilic excited ketone may react with the triethylammonium ion, displacing the proton, but less efficiently than it displaces the hydrogen bond of water. The bicyclic diamine DABCO is an effective quencher, $k_{ir} = 1.69 \times 10^8 M^{-1} \text{sec}^{-1}$, and a most inefficient reducing agent, both as the free base at pH 12 and in the monoprotonated form at pH 7.

The free hydrazines and DABCO readily form the charge transfer complexes, and these may be highly stabilized by interaction between the orbitals of the unpaired and the lone pair electrons in the cationic moiety.⁸ Spin inversion and quenching may occur before hydrogen transfer. It is possible but less likely that reversible hydrogen transfer accounts for quenching by the hydrazines. DABCO is a photoreducing agent for *p*-aminobenzophenone^{1b} and for benzophenone in hydrocarbon solvents where the CTC may not be excessively stable and thus not lead to quenching. It will be of interest to study photoreduction by hydrazines in nonpolar solvents.

In the monoprotonated hydrazines interaction begins at the nonprotonated n -electrons; the additional partial positive charge increases acidity and facilitates proton transfer from the protonated N, leading to reduction, eq 2. Interac-



tion with monoprotonated DABCO may occur similarly at the neutral N, but the geometry may lead to discharge of the proton to the solvent water, and quenching, as by the unprotonated base. Similarly protonated tetramethylhydrazine may lead largely to quenching if the CTC has I as its dominant conformer and the proton is transferred to water rather than to the ketyl radical anion. Transfer of proton to



water and quenching may be competitive with reduction in the reaction of eq 2 also. Transfer of an acidic proton from the γ -atom (oxygen) of a CTC in a noncyclic system in nonpolar solvent has been proposed in the benzophenone photosensitized decarboxylation of carboxylic acids⁹ and in the photosensitized fragmentation of 2-anilinoethanols.¹⁰ The importance of the basicity of the anionic part of the CTC has also been noted.⁴ The proper juxtaposition of groups which may separately transfer an electron and a proton may be an important property of biological redox systems.

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Salme Ojanpera, Abraham Parola, Saul G. Cohen*

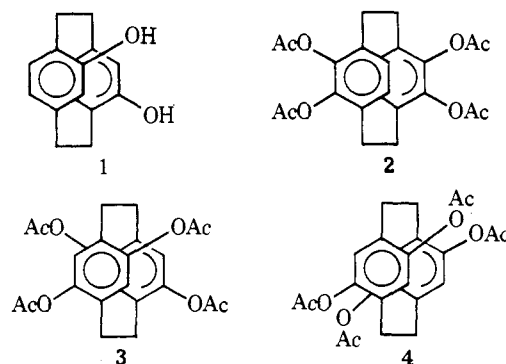
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154

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The [2.2]Paracyclophanyl Group as a Structural Unit in Host Compounds¹

Sir:

Former papers in this series demonstrated how the 1,1'-binaphthyl group incorporated into cyclic polyethers provided host compounds with chiral recognition in complexation of primary amines,^{2a} amino acids,^{2b} and amino esters.^{2c} This group also provided sites for attachment of arms terminated in functional groups that extended around, over, or under the central hole of the cycles.^{2b-e} The [2.2]paracyclophanyl group provides advantages as a shaping unit in host compounds. (1) The parent compound contains 16 potentially substitutable sites (eight aromatic and eight aliphatic) for its incorporation into large multiheteromacrocycles and for providing additional functionality. (2) The rigidity of the hydrocarbon system fixes the positions of attached chains relative to one another. (3) The symmetry properties of the system are highly manipulable.³ This paper describes the synthesis of a variety of host compounds containing this unit.



Diol **1**⁴ with pentaethylene glycol dichloride in 1-butanol-potassium hydroxide (reflux, 24 hr) gave 18% of **5**⁵ after chromatography on alumina, mp 73–74°. Tetraacetate **2**⁵ (mp 340° dec, 20%) was prepared by treating 3,6-bis(bromomethyl)catechol diacetate⁶ with sodium iodide in refluxing 2-butanone.⁷ Tetraacetates **3**⁵ (mp 263–264°, 25%)^{7b} and **4** (mp 283–284°, 5%)^{7b} were similarly obtained^{7a} from 2,5-bis(bromomethyl)hydroquinone diacetate⁶ (separated on silica gel, benzene-chloroform). These three tetraacetates were each reduced with lithium aluminum hydride (soxhlet extraction by tetrahydrofuran), and the corresponding tetrols were used directly in ring closures without characterization.⁸ Multiheteromacrocycles **6–10** were prepared from these tetrols and tetraethylene or pentaethylene