higher acidity of hydrogen peroxide than water (pK = 11.6 *vs.* 15.6) more than compensates for the difference in concentrations between H_2O_2 and H_2O in our experiment (about 100-fold), so that at pH 7 there is about 100-fold more OOH^- than OH^-. There are other concurrent reactions of hydrogen peroxide with the protein.[13] These will be reported in the full paper.

Acknowledgments. We are grateful to the Public Health Service (GM 15100) and the Research Corporation (Cottrell Fund) for partial support of this work and to Mr. Michael MacLean for able assistance at the outset.

---

(13) (a) H. Weiner, C. W. Blatt, and D. E. Koshland, Jr., *J. Biol. Chem.*, **241**, 2687 (1966); (b) Y. Hachimori, H. Horinishi, K. Kurihara, and K. Shibata, *Biochim. Biophys. Acta*, **93**, 346 (1964).

(14) National Science Foundation undergraduate research participant, summer 1969.

Morton J. Gibian, D. Lauriston Elliott, William R. Hardy[14]
Department of Chemistry, University of California
Riverside, California 92502

Received September 2, 1969

The Oxidation of Iron(II) Porphyrins by Organic Molecules

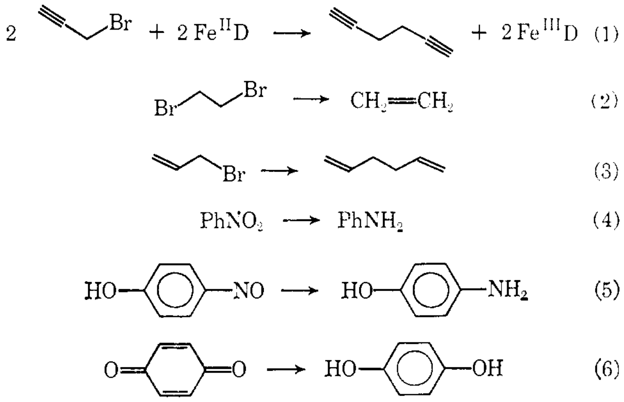
Sir:

A knowledge of the nature of bond types capable of effecting the oxidation of iron(II) to iron(III) porphyrins is a requisite for formulating mechanisms of hemoprotein function. Moreover, low-valent metalloporphyrins, by virtue of their unique coordination, should be highly efficient reagents for organic synthesis.

The unusually rapid rates of oxidation of iron(II) deuteroporphyrin and iron(II) protoporphyrin by alkyl halides and the stoichiometric conversion of DDT to DDD have been noted.[1] Most recently, a report of the oxidation of iron(II) porphyrins by olefins and acetylenes has appeared.[2]

We wish to outline the general nature of some rapid, quantitative room-temperature reactions of iron(II) deuteroporphyrin ($Fe^{II}D$) and its dimethyl ester with alkyl halides, quinones, and nitro and nitroso compounds and present a brief discussion of our findings. The selected illustrative cases (eq 1–6) are representative of a broad range of molecules possessing these reactive groupings. Typical reaction concentrations employed were $\sim 2 \times 10^{-3}$ M in $Fe^{II}D$ and $\sim 10^{-3}$ M substrate in 1:1 *n*-methylpyrrolidone–acetic acid. Calculated yields range from 97 to 100% in all cases. No other products are detectable.

It is to be emphasized that the reactive bond types reported herein were found by a very broad scan of a wide array of organic substances. In addition to peroxides, they represent the only reactive kinds of molecules encountered. The scan was conducted by injecting substrate (initial concentration 10^{-3} to 10^{-2} M) into a 10^{-4} M $Fe^{II}D$ solution under nitrogen and monitoring for the appearance of the iron(III) band at 630 mμ. The reactivity of bond types indicated by the scan were corroborated by scaling up to reaction conditions and establishing the stoichiometry.



In our system, the solvent is not so highly coordinating as to preclude any association that may be necessary for reaction. Consequently, these results *do not* accord with the reported[2] oxidative reactivity of olefins and acetylenes toward iron(II) porphyrins. Indeed we have examined some 30 olefins and acetylenes of widely differing linkage without observing oxidation by these substances. For example, the spectrum of a solution of 0.1 M methylcyclohexene and 10^{-4} M iron(II) deuteroporphyrin dimethyl ester was not altered in 8 hr.[3]

The typical coupling of halides (eq 1 and 3) is striking in contrast to the total reduction of these substances (to propylene) by "uncomplexed" metal ions like chromium(II).[4] Furthermore, the quick oxidation of $Fe^{II}D$ by quinones (eq 6), and in particular ubiquinone, is instructive. The reverse reduction of $Fe^{III}D$ by ubihydroquinone does not occur. However, this hydroquinone is a known physiological reductant of some cytochromes.[5] These results suggest that ubiquinone can function as a long-range "electron-transfer" agent at the cellular level and, further, that it is the nature of the axial ligands and the conformation of the protein about the porphyrin complex that control the redox capacities of hemoproteins toward this quinone–hydroquinone pair.

Amplified studies of each of these reactions will be reported later. Investigations of the parallel reactions with a variety of hemoproteins are under way.

Acknowledgment. We are grateful to the National Science Foundation for generous support.

---

(1) C. E. Castro, *J. Am. Chem. Soc.*, **86**, 2310 (1964).

(2) M. Tsutsui, R. A. Velapoldi, L. Hoffman, K. Suzuki, and A. Ferrari, *ibid.*, **91**, 3337 (1969).

(3) For comparison, at 0.01 times the substrate concentration, the reaction with benzoquinone is complete in less than 1 sec. A trace of peroxide impurity, however, will cause oxidation and degradation of the porphyrin. With no other substrates have we observed porphyrin degradation. Hence, we believe the results reported in ref 2 are due to peroxidic impurities in the unsaturated substrates employed.

(4) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **88**, 4447 (1966), and references therein.

(5) H. R. Mahler and E. H. Cordes, "Biological Chemistry," Harper and Row, New York, N. Y., 1966, pp 593–601.

Ruth S. Wade, R. Havlin, C. E. Castro
Department of Nematology and Biochemistry
University of California, Riverside, California 92502

Received October 10, 1969

Photosensitized Aquation of Some Chromium(III) Complexes

Sir:

We wish to report the observation that aquation of various Cr(III) complexes can be photosensitized by organic compounds known to have relatively stable

Table I. Photosensitization Experiments with Cr(III) Complexes

Complex	Sensitizer	Solvent[a]	Irradiating wave length, mμ	Result[b]
$[Cr(NH_3)_5(NCS)](ClO_4)_2$	Biacetyl	Water[c]	410	NH_3[d]
	Biacetyl	Water-acetone[e]	410	NH_3
	Acridine	Water-acetone[e]	410	NH_3, NCS^-
	Michler's ketone	Water-acetone[e]	410	NH_3, (NCS^-?)
$(NH_4)[Cr(NH_3)_2(NCS)_4]$	Biacetyl	Water-acetone[e]	410	NCS^-
	$Cr(urea)_6^{3+}$	Water	676	$\phi_{NCS} < 10^{-4}$
	Methylene blue	Water-acetone-dioxane	674	NCS^-
$K_3Cr(NCS)_6$	Biacetyl	Water-acetone[e]	410	NCS^-

[a] Nondeaerated solutions. [b] Sensitized aquation of indicated ligand observed. [c] 0.1 *N* sulfuric acid, and either in the presence or absence of dissolved oxygen. [d] Ratio of ammonia to thiocyanate ion produced greater than 100. [e] 0.05 *N* in sulfuric acid.

triplet excited states. Excitation energy transfer in low-temperature crystalline salts, such as $Cr(urea)_6Cr(CN)_6$, has been found,[1] as well as from benzil to $Cr(NCS)_6^{3-}$ in low-temperature, liquid solution,[2] as manifested by emission from the ^2E_g state of the Cr(III) acceptor. Our present finding of photosensitized ligand substitution seems not to have been reported before for a Cr(III) complex, although sensitized redox decomposition of cobalt(III) ammines,[3] and also the aquation of $Co(CN)_6^{3-}$,[4] are now known.

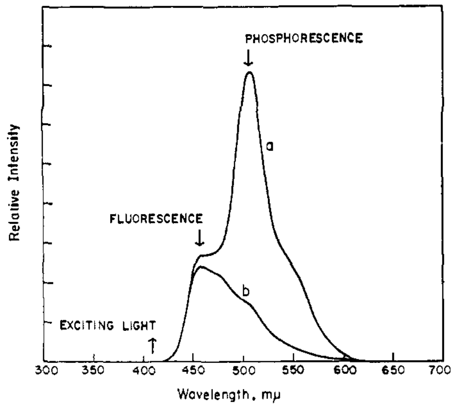


Figure 1. Emission spectra for 0.23 *M* biacetyl in deaerated 0.1 *N* H_2SO_4: (a) no added complex; (b) with 6.8×10^{-4} *M* $Cr(NH_3)_5(NCS)^{2+}$.

Some of our general results are summarized in Table I. The photolysis procedures and those for analysis for free thiocyanate ion and for ammonia were essentially as previously reported.[5] Concentrations were such that absorption was primarily by the sensitizer, and correction for direct photolysis was negligible except in the case of $Cr(urea)_6^{3+}$ as sensitizer. The results for this last system remain somewhat marginal even after numerous experiments,[6] but it appears that little if any sensitization occurs. The methylene blue sensitized production of thiocyanate from $Cr(NH_3)_2(NCS)_4^-$ (reineckate ion) led to $Cr(NH_3)_2(H_2O)(NCS)_3$ as a major product since, on making the irradiated system alkaline, an additional two- to threefold further release of thiocyanate occurred (see ref 7).

The first system of Table I was studied in more detail, using both oxygen-containing and deaerated systems. As illustrated in Figure 1, biacetyl phosphorescence is quenched by $Cr(NH_3)_5(NCS)^{2+}$ (as determined by means of an Aminco emission spectrophotometer). Figure 2 shows the quantum yields for the sensitized ammonia aquation (using ferrioxalate actinometry[8]), plotted as previously prescribed.[3] The limiting yield, given by the intercept, is 0.21, or comparable to that found in direct photolysis in the region of 410 mμ.[5]

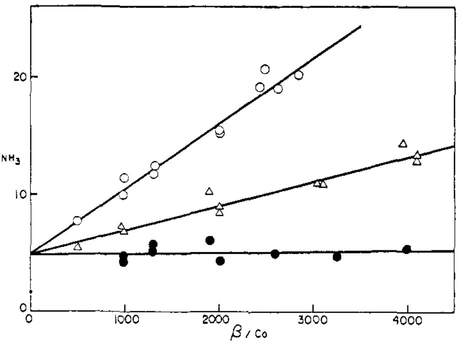


Figure 2. Data for the 410-mμ biacetyl-sensitized ammonia aquation of $Cr(NH_3)_5(NCS)^{2+}$, plotted according to eq 4 of ref 3; 0.23 *M* biacetyl in 0.1 *N* H_2SO_4: ●, deaerated; △, atmospheric dissolved oxygen; ○, oxygen saturated.

The phosphorescence quenching and sensitization results are reasonably consistent and indicate that the complex intercepts triplet state biacetyl, presumably as a sum of induced quenching and energy transfer processes (see ref 2), the latter producing excited state C* of the complex. We infer, from the observed >100:1

---

(1) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, **48**, 4056 (1968).

(2) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 3017 (1968).

(3) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968).

(4) G. Porter, *ibid.*, **91**, 3980 (1969).

(5) E. Zinato, R. Lindholm, and A. W. Adamson, *ibid.*, **91**, 1076 (1969) (with ammonia aquation determined by the procedure noted in connection with Table III).

(6) Several of the runs were made by Miss K. Eggers.

(7) E. Wegner and A. W. Adamson, *ibid.*, **88**, 394 (1966). The observation tends to rule out reaction through a redox cycle involving photoproduced leuco dye (G. K. Oster and G. Oster, *ibid.*, **81**, 5543 (1959); R. M. Danziger, K. H. Bar-Eli, and K. Weiss, *J. Phys. Chem.*, **71**, 2633 (1967)), since while such a sequence could release thiocyanate through Cr(II) production, the final product should then be $Cr(H_2O)_6^{3+}$.

(8) See J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964); C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

ratio of ammonia to thiocyanate aquation, that C* is the first excited quartet state rather than the doublet excited state. Direct photolysis gives a ratio of 22:1 on irradiation of the first ligand field band, and only 8:1 on irradiation in the region of the doublet band.[5]

In fact, pursuing an earlier suggestion,[5] it may be that the doublet state (^2E_g in O_h symmetry) undergoes only thiocyanate aquation, and the pure (nonvibrationally excited) first quartet excited state, only ammonia aquation. The ligand field excited quartet state produced in direct photolysis ($^4T_{2g}$ in O_h symmetry) is highly vibrationally excited and may more readily undergo intersystem crossing than does the pure state (see ref 9), thus accounting for the thiocyanate aquation component found in direct photolysis. In the sensitized reaction, however, energy transfer presumably occurs during the relatively long time scale of an encounter, and production of the pure excited state and hence only ammonia aquation might now be favored.

Acknowledgment. This study was supported in part by contract AT(11-1)-113 with the U. S. Atomic Energy Commission. F. D. C. is grateful for assistance from the National Science Foundation, through Grant No. 5725, and from the National Research Council of Italy.

---

(9) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

A. W. Adamson, J. E. Martin, F. Diomedi Camessei
Department of Chemistry, University of Southern California
Los Angeles, California 90007

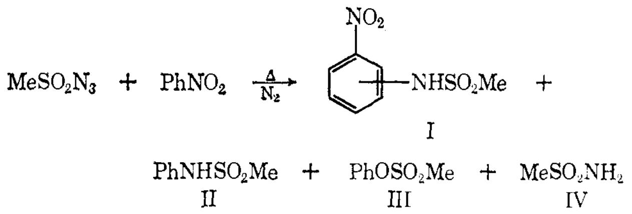
Received August 6, 1969

Aromatic Substitution by Sulfonyl Nitrenes. Singlet or Triplet Reactive Intermediates

Sir:

The reaction of methanesulfonyl nitrene, generated thermally from the azide, with benzene has been shown[1] to involve the addition of the singlet species to benzene (the same conclusion was reached for the reaction of carbethoxynitrene with benzene[2]) followed by ring opening of the aziridine intermediate and proton migration. The isomer ratios and reactivities in the reaction of $MeSO_2N$ with toluene, anisole, and chlorobenzene can be explained similarly, the rate-determining step being the addition step followed by a fast ring opening whose direction is determined by the nature of the substituent.[3] On this basis, it would be expected that an electron-attracting substituent would direct opening of the aziridine preferentially to that dipolar intermediate which would yield the *meta* isomer.

The proportion of this isomer did increase very markedly on going from toluene as substrate (2.4%) to benzonitrile (31.1%) and methyl benzoate (34.4%), but the *ortho* isomer still predominated: C_6H_5CN, *ortho*, 68.9; *meta*, 31.1; *para*, 0.0%; $C_6H_5CO_2Me$, *ortho*-, 64.3; *meta*, 34.4; *para*, 1.3%. The yields of anilides also dropped appreciably on going to C_6H_5CN (5.4%) and $C_6H_5CO_2Me$ (21.4%), but no product of addition to the substituent could be isolated. On going to nitrobenzene a dramatic change was observed. The results are summarized in Table I.



These results are entirely consistent with a rate-determining substitution by a highly electrophilic radical. The isomer ratio (degassed solvent) is similar to that observed in the homolytic *p*-nitrophenylation of nitrobenzene (*ortho*:*meta*:*para* 58:15:27).[4] The displacement of a nitro group by electrophilic radicals has been reported.[5] The effect of O_2 upon the yields of I and II is consistent with the interception of a triplet diradical by oxygen before it can react with nitrobenzene. The yield of III was not affected by O_2. In the presence of radicals, sulfonyl azides can undergo S–N bond cleavage.[8] The formation of III may then be rationalized as follows.

Table I. Reaction of $MeSO_2N_3$ with $PhNO_2$

Conditions	% products[a] I	II	III	IV
Degassed under N_2	5.3[b]	18.6	2.5	11.7
In air	2.8 (mainly *ortho*)	4.5	2.6	9.9
O_2 bubbled through	0.0	0.3	2.5	7.5

[a] In all cases much tar was formed. [b] *ortho*:*meta*:*para* 55.4:13.4:31.2.

$$MeSO_2N_3 + R\cdot \longrightarrow MeSO_2\cdot + RN_3$$

$$MeSO_2\cdot \xrightarrow{[O]} MeSO_3\cdot \xrightarrow{PhNO_2} MeSO_3Ph + [NO_2\cdot]$$

Oxygen abstraction by $MeSO_2\cdot$ either from nitrobenzene or possibly by disproportionation finds a parallel in the decomposition of $PhSO_2CHN_2$ in benzene when one of the products is $PhSO_3CH_2SO_2Ph$.[9]

Thus, the thermolysis of sulfonyl azides leads to singlet nitrenes which may add to surrounding aromatic molecules if the latter are sufficiently reactive to give aziridine intermediates. If the substrate is unreactive some of the singlet nitrenes may have time to drop to the triplet ground state[10] (alternatively, but less likely, the substituent could perhaps catalyze the singlet → triplet conversion), and the pattern of substitution then observed (with $PhCO_2Me$, PhCN, and $PhCF_3$) is consistent with an attack by a mixture of the two species, the singlet accounting for the marked increase in the proportion of *meta* isomer, but *ortho* still predominating because of the triplet contribution. With a sufficiently unreactive substrate ($PhNO_2$), complete conversion to

---

(1) R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).

(2) W. Lwowski and R. L. Johnson, *Tetrahedron Letters*, 891 (1967).

(3) R. A. Abramovitch, J. Roy, and V. Uma, *Can. J. Chem.*, 43, 3407 (1965).

(4) J. K. Hambling, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3782 (1960).

(5) For example, in the reaction of HO· with $PhNO_2$: H. Loebl, G. Stein, and J. Weiss, *J. Chem. Soc.*, 2704 (1950). Evolution of nitric oxide in the decomposition of sulfonyl azides in nitrobenzene had been observed[6,7] but not accounted for.

(6) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, 77, 70 (1955).

(7) J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, **28**, 902 (1963).

(8) D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, *J. Am. Chem. Soc.*, 91, 2273 (1969).

(9) R. A. Abramovitch and J. Roy, *Chem. Commun.*, 542 (1965).

(10) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 84, 3220 (1962).