A comparison of the coefficients of equations 1 and 4[13] confirms the view that the present mechanism is a reasonable one, compatible with the experimental data. Subsequent to the empirical evaluation of the coefficients of equation 1, a measurement of the maximum quantum yield of the fluorescence of pheophytin a[14] demonstrated that the factor, $k_3/2(k_2 + k_3)$, should be about 0.44 rather than 0.50. The introduction of this value would necessitate minor changes in the other coefficients. It is doubtful whether these differences would be significant.

[13] See reference 2, pp. 93–97.

[14] L. Forster and R. Livingston, *J. Chem. Phys.*, **20**, 1315 (1952).

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

Some Photochemical Oxidation–Reduction Reactions Sensitized by Chlorophyll a and by Pheophytin a[1]

BY ROBERT LIVINGSTON AND RUDOLPH PARISER

RECEIVED DECEMBER 3, 1955

The efficiency of the chlorophyll-photosensitized (and the pheophytin-photosensitized) reduction of azo dyes is strongly dependent upon the nature of the reducing agent. Of 23 reducing agents which were tested, only the following five reduced methyl red with a quantum yield greater than 0.005: phenylhydrazine, hydrazobenzene, semicarbazide hydrochloride, *t*-hexyl mercaptan and phenylhydroxylamine. The available, admittedly incomplete, data are consistent with the equation $\varphi = {}^1/_2[[AH_2]/(K' + [AH_2])]\ [[DD']/(K + [DD'])]$ where $[AH_2]$ and $[DD']$ represent, respectively, the concentrations of the reducing agent and of the dye.

Chlorophyll-sensitized photochemical autoöxidations of a wide variety of reducing agents occur with good to fair efficiency.[2] Since O_2, but not allylthiourea,[3] is known to accelerate greatly the "triplet"-to-ground transition of chlorophyll molecules in solution,[4] it appears probable that the primary act in the autoöxidations is an interaction between an O_2 molecule and a chlorophyll molecule, in a long-lived excited state, leading to the formation of a labile, reactive moloxide. This view is supported by the results of a recent quantitative study of the chlorophyll-sensitized autoöxidation of allylthiourea in solvents of widely varying viscosity.[5] At first glance, it might appear probable that azo dye molecules would play a role in oxidation–reduction reactions similar to that of O_2 in autoöxidations. However, it is difficult to reconcile this postulate with some of the available data.

Semi-quantitative Screening Experiments

A series of screening experiments were performed to determine which reducing agents are effective in the chlorophyll-sensitized photochemical reduction of methyl red. Methanolic solutions were prepared which contained 5×10^{-6} *m* chlorophyll a, 10^{-4} *m* methyl red and a reducing agent at 10^{-1} *m*. The solutions were contained in closed Pyrex tubes and were freed from oxygen by boiling off about 20% of the solvent under vacuum. About eight vessels were exposed at a time to equal intensities[6] of red light. The extent of the reaction was determined by comparing visually the solution in the reaction vessel to a series of solutions containing known, graded concentrations of methyl red in similar vessels. When, after suitable illumination, no bleaching was detectable by this method, the solution was transferred to a Beckman cell for spectrophotometric analysis. Two check experiments were performed with each reducing agent. A sample, identical with that which was illuminated, was kept in the dark during the period of illumination. If any bleaching was observed in the illuminated vessel, the dark vessel was analyzed for methyl red to determine whether thermal reaction had occurred. To discover whether a direct photochemical reaction occurred, a third solution, containing no chlorophyll but otherwise similar to the other two, was exposed to the same actinic light.

The standard reaction mixture contained phenylhydrazine as the reducing agent. The average quantum yield, corresponding to a 90% reduction of the methyl red in such a solution, was taken as 0.15.[7] In these screening experiments, the average yield for other solutions was calculated as 0.15 of the ratio of the times required for 90% completion of the reaction of the standard to that of the experimental solution.

The purification of the solvent and pigments have been described elsewhere.[7] The reducing agents were either of reagent grade or were carefully purified[6] before use.

Of the 23 reducing agents which were investigated, only 5 reduced methyl red with a quantum yield greater than 0.005. The effective reagents and their quantum yields are as follows: phenylhydrazine, 0.15; hydrazobenzene, 0.15, semicarbazide hydrochloride, 0.07; *t*-hexyl mercaptan + 0.05 *m* HCl, 0.02; and phenylhydroxylamine, 0.02. The following substances did not exhibit any detectable reaction: *t*-hexyl mercaptan in neutral solution, acetanilide, acetoacetanilide, methyl acetanilide, aniline, dimethylaniline, phthalimide, piperidine, pyridine, urea (alone or with 0.05 *m* HCl), allythiourea, urethan, hydroxylamine (alone or with 0.05 *m* or 0.10 *m* HCl), benzidine, benzoin, hydroquinone, oxalic acid and oxalacetic ester. In addition, negative results were obtained with the following pairs of oxidizing and reducing agents: azobenzene–ascorbic acid, nitrobenzene–piperidine, nitrobenzene–hydroxylamine hydrochloride, nitrobenzene–hydroquinone and azo turkey red ($C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_6{\cdot}CH_3$)-piperidine.

The chlorophyll-sensitized oxidation of phenylhydrazine (alone or with 0.05 *m* HCl) by azobenzene is a moderately efficient reaction, having a yield of about 0.01. The yield of the oxidation by azo turkey red of phenylhydrazine and of phenylhydrazine + 0.05 *m* HCl are 0.02 and 0.06, respectively.

Effect of Dye Concentration upon Quantum Yield.—The effect of the changing concentration of azo dye, DD′, upon the quantum yield was determined for four different systems. In each

---

[1] This paper is based upon part of a Doctoral Dissertation submitted in 1950 by Rudolph Pariser to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was made possible by the support of the Office of Naval Research to which the authors are indebted.

[2] E. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, New York, N. Y., 1945, Table 18, I:B.

[3] H. Gaffron, *Ber.*, **60**, 755 (1927); *Biochem. Zeit.*, **264**, 251 (1933).

[4] R. Livingston, THIS JOURNAL, **77**, 2179 (1955).

[5] K. Owens, Doctoral Dissertation, University of Minnesota, 1955.

[6] R. Pariser, Doctoral Dissertation, University of Minnesota, 1950.

[7] R. Livingston and R. Pariser, THIS JOURNAL, **70**, 1510 (1948).

TABLE I

EFFECT OF AZO DYE CONCENTRATION UPON QUANTUM YIELD

Sensitizer	Reductant	Oxidant	Max. φ (obsd.)	K	No. of independent exp.
Chlorophyll a $5 \times 10^{-6}\ m$	Phenylhydrazine	Methyl red	0.5	2.0×10^{-5}	Ref. 7
Chlorophyll a $0.6 - 1.5 \times 10^{-5}\ m$	Ascorbic acid $7.5 \times 10^{-2}\ m$	Butter yellow $0.2–2.7 \times 10^{-4}\ m$	.24	3.1×10^{-4}	8
Pheophytin a	Ascorbic acid	Butter yellow	..[a]	5×10^{-5}[a]	Ref. 8
Pheophytin a 1.7×10^{-5}	Ascorbic acid $7.5 \times 10^{-2}\ m$	Methyl red $0.7–2.2 \times 10^{-4}\ m$	.16	5×10^{-4}[b]	3
Pheophytin a 1.6×10^{-5}	Phenylhydrazine $1.5 \times 10^{-1}\ m$	Methyl red $0.5–1.4 \times 10^{-4}\ m$	.35	2×10^{-5}	1
Allom. Chph. a 1.2×10^{-5}	Ascorbic acid $7.5 \times 10^{-2}\ m$	Butter yellow $0.3–1.1 \times 10^{-4}\ m$	.20	1.5×10^{-4}	2

[a] Not strictly comparable to the other cases, since this reaction appears to be more complex and the factor to which this K pertains represents the "initial reaction" only. [b] These data are relatively discordant, and conceivably φ is independent of [DD′]; *i.e.*, $K \leqslant 5 \times 10^{-4}$.

case, an equation of the following form appears to fit the data, which were obtained with solutions containing relatively high concentrations of the reducing agent.

$$\varphi = \frac{1}{2}\frac{[\mathrm{DD'}]}{K + [\mathrm{DD'}]}$$

where φ is the experimentally determined ratio of the number of moles of dye reduced to the number of einsteins absorbed.

The apparatus, experimental procedures and (with one exception) the purification of the materials have been described elsewhere.[8] The allomerized chlorophyll a was a sample which had been prepared by Dr. W. F. Watson in this Laboratory and was repurified chromatographically before use. All experiments were performed in unbuffered methanolic solutions at approximately 27°. In no case was an appreciable dark reaction observed. An induction period, which is prominent in the system pheophytin–butter yellow–ascorbic acid,[8] was not detected in the present experiments.

The results of these experiments are summarized in Table I. Also included are the corresponding quantities for the system chlorophyll a–methyl red–phenylhydrazine[7] and for the initial reaction (*i.e.*, the reaction in the absence of *p*-dimethylaminoaniline) of the system pheophytin a–butter yellow–ascorbic acid.[8]

Two simple, mutually exclusive mechanisms consistent with the equation

$$\varphi \cong \frac{1}{2}\frac{[\mathrm{AH_2}]}{K' + [\mathrm{AH_2}]} \times \frac{[\mathrm{DD'}]}{K + [\mathrm{DD'}]} \qquad (1)$$

have been suggested for the chlorophyll a–methyl red–phenylhydrazine case.[7] When the concentration, $[\mathrm{AH_2}]$, of the reducing agent is large compared to K', the equation reduces to the form which was fitted to the data summarized in Table I.

$$\varphi \cong \frac{1}{2}\frac{[\mathrm{DD'}]}{K + [\mathrm{DD'}]} \qquad (2)$$

In the first of these, mechanism A, it is assumed that the reducing agent reacts with a sensitizer molecule in its metastable state, GH′

$$\mathrm{AH_2 + GH' \longrightarrow AH_2{\cdot}GH'}$$

to form an unstable, reactive complex, $\mathrm{AH_2{\cdot}GH'}$. This intermediate either decomposes

$$\mathrm{AH_2{\cdot}GH' \longrightarrow AH_2 + GH} \qquad v_{\mathrm{AI}} = k_{\mathrm{AI}}[\mathrm{AH_2{\cdot}GH'}]$$

or reacts with a dye molecule

$$\mathrm{DD' + AH_2{\cdot}GH' \longrightarrow GH + AH + DD'H}$$
$$v_{\mathrm{AII}} = k_{\mathrm{AII}}[\mathrm{DD'}][\mathrm{AH_2{\cdot}GH'}]$$

and starts the sequence of follow reactions which lead to the final products.

In the alternative mechanism, B, it is assumed that the dye reacts with the metastable form of the sensitizer

$$\mathrm{DD' + GH' \longrightarrow DD'{\cdot}GH'} \qquad v_{\mathrm{BII}} = k_{\mathrm{BII}}[\mathrm{DD'}][\mathrm{GH'}]$$

and that the complex so formed either decomposes or reacts with a molecule of the reducing agent to produce the same intermediates as does step AII.

In terms of mechanism A, $K = k_{\mathrm{AI}}/k_{\mathrm{AII}}$, but in terms of mechanism B, $K = (k_{\mathrm{BII}}\tau')^{-1}$, where τ' is the actual mean life of the metastable state of the sensitizer. If the reaction occurs by mechanism B, K should be independent of the nature of the reducing agent and should be inversely proportional to τ'. Mechanism A implies that K may be a function of the nature of the reducing agent and be not directly related to τ'. The data of Table I are consistent with mechanism A but not with mechanism B. Mechanism A was formerly rejected[7] on the grounds that the presence of reducing agents (such as allylthiourea and hydroquinone) do not effect the reversible bleaching of chlorophyll a in methanol[9] and therefore do not change the mean of life of the triplet state.[4] Unfortunately, neither phenylhydrazine nor ascorbic acid was used in either steady-state bleaching or flash illumination experiments. Since the effect of reducing agents is highly specific in these sensitized reactions, the evidence cited above does not exclude mechanism A.

Another plausible mechanism (C) which is consistent with equation 1 can be based upon the assumption that an equilibrium exists between an addition complex of the reducing agent and chlorophyll in its ground state and its components. If it be further assumed that only light absorbed by this complex is photochemically effective and that the extinction coefficient (for red light) of the complex does not differ appreciably from that of the un-

---

(8) R. Livingston and R. Pariser, THIS JOURNAL, **78**, 2944 (1956).

(9) Photosynthesis in Plants, Iowa State College Press, Ames, 1949, pp. 189–194.

complexed chlorophyll, the mechanism leads to equation 1. In terms of this mechanism, K' of equation 1 is the dissociation equilibrium constant of the complex and K has the same significance as in mechanism A.

A mechanism essentially similar to C was suggested by Watson[10] to explain certain observations on the quenching of the fluorescence of methanolic solutions of chlorophyll a or b by phenylhydrazine. The value of K' based upon the fluorescence quenching is 3×10^{-1} mole^{-1}, while that based upon the chlorophyll-sensitization of the methyl red oxidation of phenylhydrazine[6] is 1×10^{-2} mole^{-1}. While there are obvious plausible interpretations of this difference, the data hardly warrant further speculation.

Qualitatively, all of the data are in agreement with the assumption that the sensitized molecules in their triplet, rather than their ground state, are in the equilibrium[11]

$$GH' + AH_2 \rightleftarrows AH_2{\cdot}GH'$$

and that the reaction is due to collisions between this labile complex $AH_2{\cdot}GH'$ and a dye molecule. This mechanism leads to an equation consistent with the data obtained at higher, constant concentrations of the reducing agent. However, it does not fit the data of reference 6, particularly at low and variable phenylhydrazine concentrations, and for this reason probably should be rejected.

To summarize, the present more extensive data seem to be incompatible with the mechanism which Livingston and Pariser[7] postulated for the chlorophyll a–methyl red–phenylhydrazine system. Of the remaining possibilities, either of the following alternative mechanisms appears to be equally consistent with the available data.

Mechanism C	Mechanism A
$AH_2 + GH \rightleftarrows AH_2{\cdot}GH$	$h\nu + GH \longrightarrow GH^*$
$h\nu + GH \longrightarrow GH^*$	$GH^* \longrightarrow GH + h\nu_f$
$GH^* \longrightarrow GH + h\nu_f$	$GH^* \longrightarrow GH'$
$GH^* \longrightarrow GH' \longrightarrow GH$	$GH' \longrightarrow GH$
$h\nu + AH_2GH \longrightarrow AH_2{\cdot}GH'$	$AH_2 + GH' \longrightarrow AH_2{\cdot}GH'$

$$AH_2{\cdot}GH' \longrightarrow GH + AH_2$$

$$DD' + AH_2{\cdot}GH' \longrightarrow GH + AH + DD'H$$

$$2DD'H \longrightarrow DD'H_2 + DD'$$

$$2AH \longrightarrow \longrightarrow AH_2 + A$$

MINNEAPOLIS 14, MINN.

[10] W. F. Watson, *Trans. Faraday Soc.*, **48**, 526 (1952).

[11] *Cf.*, Th. Foerster, *Z. Elektrochem.*, **54**, 42 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

The Vapor Phase Dissociation of Some Carboxylic Acids. III.[1] Trifluoroacetic Acid and Trifluoroacetic Acid-*d*[2,3]

BY MODDIE D. TAYLOR AND MALCOLM B. TEMPLEMAN[4]

RECEIVED FEBRUARY 15, 1956

The vapor phase dissociation of trifluoroacetic acid and trifluoroacetic acid-*d* has been studied in the pressure range below one-tenth atmosphere, and over the temperature range of 30 to 150°. The data are summarized by the equation: $\log_{10} K(\text{mm.}) = -3071/T + 10.869$ for trifluoroacetic acid, and $\log_{10} K(\text{mm.}) = -3042/T + 10.815$ for trifluoroacetic acid-*d*. The heats of dissociation for the two acids are 14,060 and 13,920 cal., respectively, and their equilibrium constants at 100° are 435 and 461. These data suggest that the hydrogen bond is somewhat stronger than the deuterium bond. In agreement with the observation of Professor Nash, trifluoroacetic acid is found to be dissociated to about the same extent as formic acid; but, contrary to his observations, the former is found to be dissociated to a much greater extent than acetic acid. The results of this study bring the data obtained by the vapor phase dissociation technique in agreement with that obtained from studies in solution.

In recent years, much interest has been exhibited in the association of molecules through the mechanism of hydrogen bonding. Many studies have been performed in both the vapor phase and in solution in an effort to establish the relationship between the strength of the hydrogen bond and the structure of the molecule. Though this relationship has been essentially established for the carboxylic acids, the question as to whether the order obtained by studies in solution is the same as that obtained by studies in the vapor phase is not settled. Nash,[5] who made the most complete series of vapor phase studies, finds that although his constants obtained by vapor phase dissociation studies are not inconsistent with the order of hydrogen bond strength predicted by studies in solution, the heats of dissociation obtained appear to be invariant for the different carboxylic acids.[1,8] Heats of dissociation obtained by the present author, on the other hand, appear to give an order parallel to that indicated by studies in solution. One objective of this study was to determine whether the values for trifluoroacetic acid fall in line with the ones previously obtained in this series of studies for other acids.

Very few investigations have been performed to establish whether the hydrogen or deuterium bond is stronger. Studies made by Herman[6] are probably insufficiently precise to permit a conclusive decision. They suggest that the deuterium bond is slightly stronger than the hydrogen bond. Studies

[1] Paper II, M. D. Taylor and J. Bruton, THIS JOURNAL, **74**, 4151 (1952).

[2] This investigation was supported by a grant from The American Academy of Arts and Sciences.

[3] Presented before the Division of Physical and Inorganic Chemistry, 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

[4] Taken from a dissertation submitted by Malcolm B. Templeman in partial fulfillment of the requirements for the M.S. degree in Harvard University.

[5] R. E. Lundin, F. E. Harris and L. K. Nash, THIS JOURNAL, **74**, 1654 (1952).

[6] R. C. Herman, *J. Chem. Phys.*, **8**, 256 (1940); R. C. Herman and R. Hofstadter, *ibid.*, **6**, 531, 534 (1938).