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A Diffusion-controlled Step in Chlorophyll-sensitized Photochemical Autoöxidations[1]

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The quantum yield of the chlorophyll-sensitized photochemical autoöxidation of allylthiourea was measured in methanol, acetone, isoamyl alcohol. benzyl alcohol and cyclohexanol as a function of the oxygen concentration. These data fit the following equation within the apparent limits of accuracy, with the exception of methanol containing oxygen at concentrations in excess of 10^{-3} *m*. In these solutions, the yield continues to rise slowly and linearly with the oxygen concentration, rather than approaching an asymptotic limit. $\varphi = A\ ([O_2]/(2 \times 10^{-6} + [O_2]))$. The value of A depends on the solvent: for methanol, $A = 0.78\ [R]/([R] + 0.100)$ and for acetone, $A = [R]/([R] + 0.0117)$, where [R] represents the molarity of allylthiourea. At $[R] = 0.051$, the values of A for methanol, isoamyl alcohol, benzyl alcohol and cyclohexanol are 0.255, 0.53, 0.655 and 0.80, respectively. These data are consistent with a mechanism which involves as intermediates the first excited singlet state, the lowest triplet state and an unstable, reactive moloxide of chlorophyll. The values of the rate constants of eight of the nine postulated reaction steps were estimated, previously, from other kinetic and spectroscopic measurements. These published values are compatible with the mechanism and data presented in this paper. The ninth step is determined only by the present measurements.

Introduction

Indirect evidence indicates that the primary act in chlorophyll-sensitized autoöxidations is an interaction between a molecule of oxygen and one of chlorophyll in its "triplet" state, resulting in the formation of a labile, reactive moleoxide. The quantum yield of such a reaction should depend upon the mean life of the triplet state and upon the rates of one or more diffusion-controlled bimolecular reactions. In an attempt to evaluate these quantities, we have studied the chlorophyll-sensitized autoöxidation of allylthiourea, in solvents having widely different viscosities and over a broad range of oxygen concentrations. The results appear to be consistent with a relatively simple mechanism, and the rate constants for the individual steps are in reasonable agreement with earlier published estimates. When direct flash-photolytic measurements of the mean life of the triplet state and of its rate of reaction with oxygen have been completed, it will be possible to test the reliability of the mechanism more directly.

Experimental Methods and Materials[2]

The measurements were made with a closed system, in which oxygen-containing gas was circulated continuously through the solution and through an oxygen meter. The reaction cell was made of 1.5 inch square Pyrex tubing and had a circular bottom, 1 inch in diameter of #20 porous glass plate, through which the gas entered the solution. The rate of flow was approximately 120 ml./minute. The gas appeared to be uniformly distributed throughout the solution as small bubbles of about 1 mm. average diameter. To prevent the solvent from being carried into the pump and oxygen meter, a condenser was placed directly above the cell. It was of the cold-finger type and was refrigerated with solid CO_2 and acetone. It efficiently condensed the vapors of the solvent which dripped back into the solution. After leaving the reaction vessel, the gas entered a small diaphragm pump, a Neptune Dyna pump which had been rebuilt to eliminate leakage. It then passed successively through a rotameter-type flow meter and a Beckman Oxygen Analyzer, Model E-2. A small open-tube mercury manometer was attached to the tube which led from the oxygen meter to the reaction vessel.

Actinic light of λ 436 mμ was isolated from the radiation of a GE AH-6 mercury arc by means of a $CuSO_4$ solution and Corning glass filters. A graphical integration, taking into account the frequency distribution of the intensity of the high pressure arc, the transmissivities of the filters and the extinction coefficients of the solution, indicated that the mean wave length of the absorbed light was 442 mμ. The light was rendered parallel by glass condensing lenses and, after being defined by a circular diaphragm, passed through the reaction vessel into a large-surface Moll thermopile. Both the reaction vessel and the thermopile were immersed in a water-filled thermostat. A glass plate was placed directly in front of the thermostat window at an angle of 45° to the light beam. The light reflected by this plate entered a barrier-type photocell, the output of which was used to monitor the light source. The monitoring was done manually, with the aid of a variac which preceded the AH-6 transformer. The thermopile-galvanometer combination was calibrated with a U. S. Bureau of Standards lamp in the usual way, and this calibration was checked every 3 months. The calibration showed a drift of about 4% a year.

TABLE I

SOLUBILITIES OF O_2 IN THE SOLVENTS

Solvent	*t*, °C.	*l*, Ostwald's absorption coefficient	Ref.
Methanol	20	0.2470	3
Acetone	0	.2570	3
	0	.2550	4
	20	.2749	3
	20	.2736	4
	35	.2900	4
Cyclohexanol	26	.193	5
Benzene	20	.2186	4
	20	.225	1
Isoamyl alcohol	20	.216	1
Benzyl alcohol	20	.101	1

The oxygen meter was a double scale, 0–5 and 0–25% instrument. It was calibrated with dry, CO_2-free air (assumed to contain 20.94% O_2) and with N_2 which had been freed from O_2 by a column containing Cu supported on kieselguhr.[3] Since the several parts of the circulating system were at different temperatures, it was necessary to determine the separate volumes of these parts in order to calculate the total quantity of oxygen in the system.

In calculating the concentration of oxygen in the solution, allowance was made for the (measured) pressure drop through the sintered glass disk. The preceding table lists

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(1) (a) This paper is based upon a Doctoral Dissertation submitted in 1955 by Kenneth E. Owens to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) The work was made possible by the support of the Office of Naval Research to which the authors are indebted.

(2) Detailed descriptions of the apparatus, experimental procedure and calculation methods are given in the Doctoral Dissertation of K. E. Owens, University of Minnesota, 1955.

(3) (a) F. Meyer and G. Ronge, *Z. angew. Chem.*, **52**, 637 (1939); (b) M. Pollack, P. Pringsheim and D. Terword, *J. Chem. Phys.*, **12**, 295 (1944).

the values of the solubility of O_2 in the solvents. Since reliable values for isoamyl alcohol and benzyl alcohol were not available in the literature, they were determined by a static method (ref. 2, Appendix III) which was checked against benzene.[4,5]

Materials.—The methods of purification of chlorophyll a and of methanol have been described elsewhere.[6] The chlorophyll a contained no detectable chlorophyll b and less than 1% of pheophytin a. The allylthiourea was twice recrystallized from ethanol and had a melting point of 72.4–72.6° (uncorrected). The other solvents were commercial products of good grade and were carefully dried and purified (1) before use.

Experimental Procedure.—In starting a run, appropriate volumes of separate solutions of chlorophyll and allylthiourea were added to the darkened vessel, and N_2 was passed through the vessel to mix the solution. The entire line was then flushed out with a N_2–O_2 mixture of the desired composition. The line was then closed off, and the gas circulated for several hours in the dark. Since no dark reactions were observed, the reading of the oxygen meter became practically constant after mixing was complete. However, it proved impossible to eliminate all drift when the O_2 concentration was low. The concentration increased steadily even after many hours of circulation, due, presumably, to gradual desorption of O_2 from the walls of the system or to slow leakage through ground glass joints, the rubber diaphragm of the pump, etc. This slow drift was usually less than 5% of the observed photochemical rates, and the measured rates were corrected for it. During the course of each run, the O_2 concentration was determined at approximately 15-minute intervals. To check for drifts, the measurements were continued for half an hour or more after the light was cut off.

The change in intensity which the light underwent as it passed through the cell was due chiefly to absorption by the pigment, but it was influenced by reflection from the windows and by scattering from the gas bubbles. The correction due to reflection and subsequent absorption of the reflected light increase the measured absorption by about 6%. Measurements made with the solvent in the cell, with and without the flow of gas, showed that about 10% of the light incident is so scattered that it does not reach the thermopile. The problem of determining the fraction of this scattered light which is absorbed is a complex one, involving the angular distribution of scattered light from each bubble, the position of the bubble in the cell and the attenuation of the light as it penetrates the absorbing solution. However, an approximate numerical solution of this problem was carried out (ref. 1, appendix I) and applied to all of the measurements. For most cases this correction was less than 5%.

Summary of the Experimental Results

The quantum yield of the autoöxidation can be represented by the following function of the oxygen concentration, when the other variables are held constant

$$\varphi = A\,\frac{[O_2]}{2 \times 10^{-6} + [O_2]} \qquad (1)$$

The value of A depends upon both the concentration of the allylthiourea and the nature of the solvent. Figure 1 represents the data for a methanolic solution, at 20°, containing 0.0511 m allylthiourea. In this and in all subsequent experiments, except when otherwise indicated, the concentration of chlorophyll was 3×10^{-6} m. Experimental values are represented by circles. Where these are superimposed upon horizontal lines, their length represents the range of concentrations covered by the experiment and the quantum yield is an average value. The solid line curves are plots of equation 1, with A equal to 0.254. At the highest oxygen concentrations, the experimental yields exhibit a positive departure from the values predicted by equation 1. This departure does not occur when the solvent is acetone, isoamyl alcohol or cyclohexanol. The data, corresponding to experiments made in benzyl alcohol, are not sufficiently precise or extensive to determine whether the yield increases with the oxygen concentration for values greater than 5×10^{-4} m.

It is apparent that the experimental points on the upper plot, which has an expanded scale, fall below the curve (equation 1) at concentrations less than 5×10^{-6} m. This deviation characterizes all of our measurements. The departure increases with the limiting quantum yield and with the viscosity of the solvent; being greatest for the reaction in cyclohexanol. For each of the following solvents, the deviation becomes noticeable at the concentrations indicated: methanol, 5×10^{-6} m, isoamyl alcohol, 2×10^{-5} m, benzyl alcohol, 2×10^{-5} m, cyclohexanol, 5×10^{-5} m, and acetone, 1×10^{-5} m.

While this effect could be the result of a complex reaction mechanism, it appears more probable that it is due to a systematic experimental error The S-shaped experimental curves are not compatible with any simple reaction mechanism and have not been observed for analogous reactions. A qualitatively similar deviation would be expected if the apparatus were unable to maintain equilibrium between the gas and liquid phases at low oxygen concentrations. The depletion of oxygen in the bulk of the solution should be greatest when the reaction is fast (*i.e.*, A is large) and when the viscosity of the solvent is high, as was observed. For these reasons, we have concluded that the data at low oxygen concentrations are in error and have not attempted to fit the empirical equation to the experimental data in this region.

Equation 1 represents all of the data (except for the reaction in methanol at $[O_2] > 10^{-3}$ m) within the apparent precision of the measurements. This is illustrated by Fig. 2, where $\varphi(2 + 10^{-6}m + [O_2])/[O_2]$ is plotted as a function of $[O_2]$. If the data fitted equation 1 exactly, all of the points would fall on horizontal straight lines, whose ordinates would be equal to A. The data taken at low concentrations, where the negative deviation is marked, have been largely omitted from this plot.

Plots I to V refer, successively starting from the bottom, to solutions in methanol, isoamyl alcohol, benzyl alcohol, cyclohexanol and acetone. The cyclohexanol solutions were at 25°; the others, at 20°. In all cases the concentration of allylthiourea was 0.051 m. In none of these systems was there an appreciable dark reaction. Except for the case of benzyl alcohol, there was no detectable uptake of oxygen when a solution free from allylthiourea was illuminated. A solution of chlorophyll a in benzyl alcohol exhibits a photochemical absorption of oxygen with a quantum yield of about 0.17. If 0.051 m allylthiourea is added to such a solution, the yield (for the disappearance of O_2) is about 0.7.

The variation of the quantum yield with the concentration of allylthiourea was studied only with methanolic solutions at 20° and at an oxygen con-

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[4] C. Kretschmer, J. Nowaskowaska and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

[5] (a) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), **17**, 125 (1931–1932); (b) G. Cauquil, *J. Chem. Phys.*, **24**, 53 (1927).

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

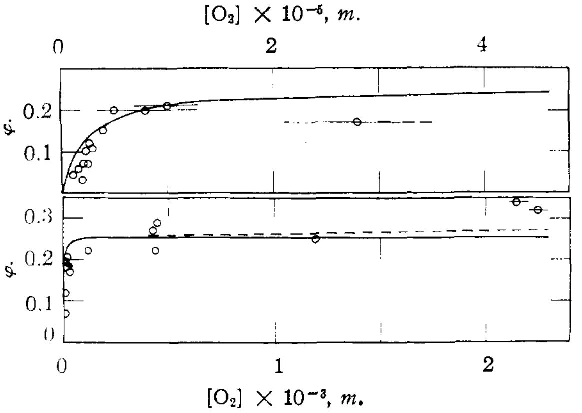

Fig. 1.—Quantum yield as a function of oxygen concentration in methanol at 20°.

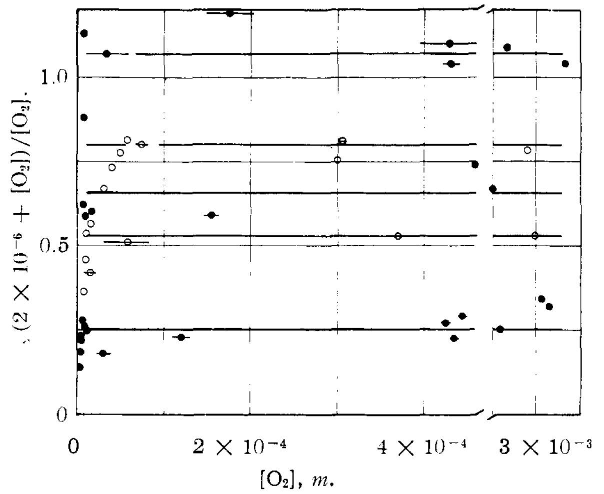

Fig. 2.—The effect of oxygen concentration upon the quantum yield, at [R] = 0.051 *m*. The dots correspond to the first, third and fifth lines; the circles, to the second and fourth lines.

Series	Solvent	Temp., °C.
I	Methanol	20°
II	Isoamyl alc.	20°
III	Benzyl alcohol	20°
IV	Cyclohexanol	25°
V	Acetone	20°

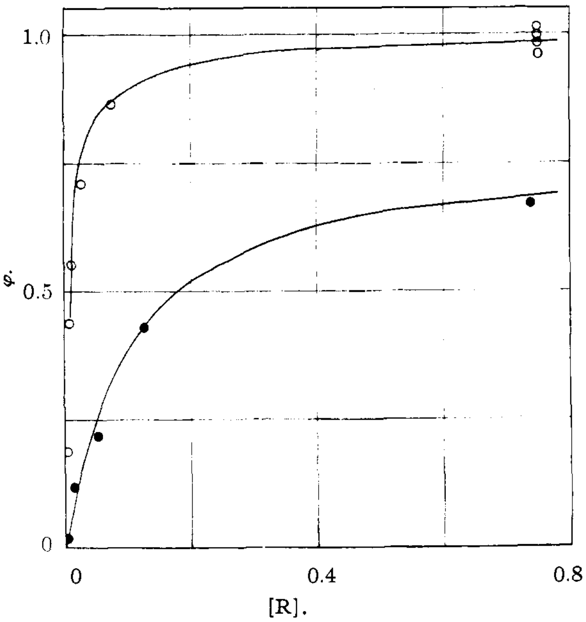

Fig. 3.—Quantum yield as a function of allylthiourea concentration: lower curve, methanol, 20°, $[O_2] = 4 \times 10^{-4}$ *m;* upper curve, "acetone," 18°, saturated with air (ref. 7).

centration of 4×10^{-4} *m*. These data fit the following equation

$$\varphi = 0.78 \frac{[R]}{0.100 + [R]} \qquad (2)$$

where [R] represents the molar concentration of allylthiourea. The lower curve of Fig. 3 is a plot of equation 2, and the experimental values are indicated by circles. The upper curve is a plot of

$$\varphi' = \frac{[R]}{0.0117 + [R]}$$

and the points represent Gaffron's data[7] which were obtained with acetone, saturated with air, containing 2% pyridine and 1% water at 18°. His chlorophyll concentration was 1.5×10^{-3} *m*. Other experiments show that the term (0.0117) in the denominator is, for the narrow range investigated, proportional to the chlorophyll concentration. Presumably, it would be very much smaller if concentrations in the range of 3×10^{-6} *m* were used.

In acetone, the sum of the quantum yields of autoöxidation and of fluorescence[8] reaches values well in excess of unity. A few experiments were performed in this solvent at various temperatures. They are summarized in Table I. In all of these experiments the concentrations of the reactants were high enough to ensure that the yield would have its maximum value. The empirical equation

$$\varphi = 0.99 + 2.2 \times 10^{16} \exp\left(\frac{12{,}800}{RT}\right) \qquad (3)$$

fits the data within their limit of precision, as is illustrated by the values listed in the last column of Table II.

TABLE II

EFFECT OF TEMPERATURE ON QUANTUM YIELD IN ACETONE SOLUTIONS

In all experiments: [R] = 0.51*m* and [Cph] = 3.0×10^{-6}*m*

t, °C.	$[O_2] \times 10^4$, *m*	φ (meas.)	φ (calcd.)
34.6	4.2–4.5	1.25	1.27
34.6	4.4–5.4	1.31	1.27
20.0	3.9–4.6	1.06	1.03
20.0	4.2–4.4	1.00	1.03
0.6	4.5–5.1	0.99	0.99

Equation 3 corresponds to two alternative reaction paths, only one of which is temperature dependent. While the available data do not permit an analysis of these paths, or mechanisms, the equation contains two noteworthy features. The maximum yield for the temperature-independent process is 0.99. Since the fluorescent yield for these solutions must be at least 0.10[9] the sum of the

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(7) H. Gaffron, *Ber.*, **60**, 755 (1927).

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

(9) Compare ref. 8, and R. Livingston and Chun-Lin Ke, THIS JOURNAL, **72**, 909 (1950).

measured yields is greater than unity. The most plausible explanation of this anomaly is that the measured yields (at least for acetone solutions) reported in this paper are too high by 10%. This criticism scarcely applies to Gaffron's[7] values, since, in his solutions, the chlorophyll was so concentrated that the loss of activation by fluorescence was greatly reduced by reabsorption and, to a lesser extent, by self-quenching.[10] The factor 2.2×10^{16} is presumably some combination of the frequency factors of rate constants. Its magnitude indicates that it contains the product of rate constants.

As a check on the accuracy of the method, four experiments were performed using Gaffron's solvent[7]: acetone containing 2% pyridine and 1% water. The temperature was 19.8°. The oxygen and allylthiourea concentrations were 2.5×10^{-3} *m* and 1.0×10^{-2} *m*, respectively. The chlorophyll concentrations and the corresponding mean yields were as follows: 1.54×10^{-5} *m*, 1.06, 3.4×10^{-6} *m*, 0.97; 3.2×10^{-6} *m*, 0.90; and 3.2×10^{-6} *m*, 0.85. The average of these yields is 0.95 ± 0.05, where the uncertainty is the average error of a single measurement. Gaffron's experiments were all made with much higher concentration of chlorophyll; however, his maximum yields fall in the range 0.98–1.03.

An Interpretation of the Results

The following possibly oversimplified mechanism appears to be consistent with the available data on the chlorophyll-sensitized autoöxidation of allylthiourea

$$\begin{array}{ll}
h\nu + \mathrm{GH} \longrightarrow \mathrm{GH}^* & v_1 = I_{\mathrm{abs}} \\
\mathrm{GH}^* \longrightarrow \mathrm{GH} + h\nu_f & v_2 = k_2[\mathrm{GH}^*] \\
\mathrm{GH}^* \longrightarrow \mathrm{GH}' & v_3 = k_3[\mathrm{GH}^*] \\
\mathrm{O_2} + \mathrm{GH}^* \longrightarrow \mathrm{GH{\cdot}O_2} & v_4 = k_4[\mathrm{O_2}][\mathrm{GH}^*] \\
\mathrm{GH} + \mathrm{GH}' \longrightarrow 2\mathrm{GH} & v_5 = k_5[\mathrm{GH}][\mathrm{GH}'] \\
\mathrm{O_2} + \mathrm{GH}' \longrightarrow \mathrm{GH{\cdot}O_2} & v_6 = k_6[\mathrm{O_2}][\mathrm{GH}'] \\
\mathrm{GH{\cdot}O_2} \longrightarrow \mathrm{GH} + \mathrm{O_2} & v_7 = k_7[\mathrm{GH{\cdot}O_2}] \\
\mathrm{GH} + \mathrm{GH{\cdot}O_2} \longrightarrow 2\mathrm{GH} + \mathrm{O_2} & v_8 = k_8[\mathrm{GH}][\mathrm{GH{\cdot}O_2}] \\
\mathrm{R} + \mathrm{GH{\cdot}O_2} \longrightarrow \mathrm{GH} + \mathrm{RO_2} & v_9 = k_9[\mathrm{R}][\mathrm{GH{\cdot}O_2}]
\end{array}$$

The symbols have the following significance: R, allylthiourea; $\mathrm{RO_2}$, oxidized allylthiourea; $\mathrm{GH{\cdot}O_2}$, a reactive, unstable moloxide; GH, GH* and GH′, chlorophyll in its ground, excited singlet and metastable (triplet ?) states, respectively.

In terms of this mechanism, the quantum yield for the disappearance of oxygen is

$$\varphi = v_9/I_{\mathrm{abs}}$$

Introducing the usual steady-state assumption, we may write

$$\varphi = (P_4 + P_3P_6)P_9$$

where the quantities P_i are the probabilities that the intermediate in question reacts by step i rather than in any alternative way; *e.g.*, $P_4 = k_4[\mathrm{O_2}]/(k_2 + k_3 + k_4[\mathrm{O_2}])$. Introducing the values for the several probabilities and simplifying

$$\varphi = \frac{k_3}{k_2 + k_3 + k_4[\mathrm{O_2}]}\left(\frac{k_4}{k_3}[\mathrm{O_2}] + \frac{[\mathrm{O_2}]}{k_5[\mathrm{GH}]/k_6 + [\mathrm{O_2}]}\right)\frac{[\mathrm{R}]}{k_7/k_9 + k_8[\mathrm{GH}]/k_9 + [\mathrm{R}]} \quad (4)$$

In the experiments reported here, the variation of the chlorophyll concentration was small and constants B and C may be substituted for the denominator terms $k_5[\mathrm{GH}]/k_6$ and $k_7/k_9 + k_8[\mathrm{GH}]/k_9$, respectively. The effect of [R] upon φ was not determined for the solvents, isoamyl alcohol, benzyl alcohol and cyclohexanol, and these data appear to fit the simple relation

$$\varphi = A\,\frac{[\mathrm{O_2}]}{B + [\mathrm{O_2}]} \quad (5)$$

where

$$A = \frac{k_3}{k_2 + k_3} \times \frac{[\mathrm{R}]}{C + [\mathrm{R}]} \quad (6)$$

For methanolic solutions, the empirical values of $(k_2 + k_3)k_3^{-1}$, $k_4k_3^{-1}$, B and C are 1.30, 150 m^{-1}, 2×10^{-6} and 0.100, respectively. The first three of these quantities can be estimated independently,[11] from other published data. The limiting fluorescent yield, $\varphi_f = k_2(k_2 + k_3)^{-1}$, is 0.25.[8] However, at concentrations as high as 3×10^{-6} *m* and in the relatively large reaction vessel, an appreciable fraction of the fluorescent light is reabsorbed, which effectively diminishes φ_f. The value of $(k_2 + k_3)k_3^{-1}$ of 1.30 corresponds to $\varphi_f = 0.23$, and is in good agreement with the absolute measurements[8] of the fluorescent yield of chlorophyll a.

The quenching of the fluorescence of chlorophyll a by $\mathrm{O_2}$ has not been measured in methanol, but the Stern–Volmer constant, $K_{\mathrm{O_2}}$, is approximately 40 m^{-1} for ethanolic solution[12] and 39 m^{-1} for solutions in isopropyl alcohol.[13] The value for methanolic solution is probably close to 40 m^{-1}. There is some uncertainty in regard to the natural half-life of GH*,[11] but 1×10^{-8} sec. is probably correct within a two-fold uncertainty. The corresponding value of $k_2 + k_3$ is 3.0×10^8 sec.$^{-1}$, and $k_4 = K_{\mathrm{O_2}}{\cdot}(k_2 + k_3) = 1.1 \times 10^{10}$ m^{-1} sec.$^{-1}$. This leads to $k_4/k_3 = 1.1 \times 10^{10}/2.2 \times 10^8 = 50$ m^{-1}, which is to be compared to the approximate empirical value of 150 m^{-1}.

The evaluation of B rests upon even less certain ground. From an analysis of the reversible steady-state photobleaching of chlorophyll a in methanol, Knight and Livingston[14] concluded that $k_5/k_6 \sim 0.4$. If this value is accepted, $B = 0.4 \times 3 \times 10^{-6} = 1.2 \times 10^{-6}$ *m*, in fair agreement with the empirical value of 2×10^{-6} *m*. It should be emphasized that the empirical values of B are upper limits. If the falling off of the yield at low oxygen concentrations were due entirely to slow diffusion of $\mathrm{O_2}$ from the gas into the solution, the observed value of B might be much larger than the true value $k_5[\mathrm{GH}]k_6^{-1}$.

There appears to be no way, which does not depend upon the present kinetic measurements, of estimating k_9. The steady-state data for the reversible photobleaching have been interpreted[14] as indicating that $k_8 \cong 1.5 \times 10^{10}$ m^{-1} sec.$^{-1}$. The corresponding half life of $\mathrm{GHO_2}$ would be $\leqslant 2 \times 10^{-5}$ sec., depending on the value of k_7, and $k_9 \geqslant 5 \times 10^5$ m^{-1} sec.$^{-1}$.

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[10] W. Watson and R. Livingston, *J. Chem. Phys.*, **18**, 802 (1950).

[11] *Cf.* R. Livingston, *Rec. Chem. Prog.*, **16**, 13 (1955).

[12] R. Livingston and Chun-Lin Ke, THIS JOURNAL, **72**, 909 (1950).

[13] R. Bowman and W. Weinberger, unpublished work performed in this Laboratory, 1955.

[14] J. D. Knight and R. Livingston, *J. Phys. Colloid Chem.*, **54**, 703 (1950).

As is illustrated by Fig. 2 all of the data for the various solvents are roughly consistent with a single value, 2×10^{-6}, for B. However, the following values are in slightly better argeement with these data: acetone, 2×10^{-6}; methanol, 2×10^{-6}; isoamyl alcohol, 6×10^{-6}; benzyl alcohol, 3×10^{-6}; and cyclohexanol, 6×10^{-6}. In view of the uncertainty of the interpretation of the results which were obtained at low concentrations of oxygen, it is scarcely justifiable to use different values for the several solvents.

The other constant, which determines the effect of the concentration of O_2 upon the calculated yield, is k_4/k_3. The quenching constant, K_{O_2}, equals 26 and 6 for benzyl alcohol and cyclohexanol, respectively.[13] Using these values and assuming that K_{O_2} is inversely proportional to viscosity for the other solvents, k_4/k_3 can be calculated, if it be further assumed that k_3 does not vary[8] as the solvent is changed. Except for acetone and methanol the values are all less than 50, which is consistent with the fact that the yields in the other three alcohols fit the simple equation 1. The predicted high value of this constant for acetone would lead one to expect that φ would continue to increase with $[O_2]$ at relatively high concentrations. The present data, Fig. 2, are not compatible with this prediction. However, two measurements of Gaffron show a 20% increase of φ as $[O_2]$ is increased from 2×10^{-3} to $9.3 \times 10^{-3}\ m$.

The quantity C can be calculated from the empirical values of A, equation 5, for the three solvents for which the dependence of φ upon the concentration of allylthiourea was not determined.

$$C = \left(\frac{k_3}{A(k_2 + k_3)} - 1\right)[\mathrm{R}]$$

Since φ_t and, therefore, $k_3/(k_2 + k_3)$ is practically independent of the solvent, and in all cases $[\mathrm{R}] = 0.051\ m$ and $[\mathrm{GH}] \cong 3 \times 10^{-6}\ m$, values of C for the alcoholic solvents may be calculated directly.

TABLE III

VALUES OF C FOR THE FOUR ALCOHOLS

Solvent	Methanol	Isoamyl alcohol	Benzyl alcohol	Cyclohexanol
A	0.255	0.53	0.655	0.80
C	.100	0.0230	0.0092	$\leqslant$0.001
η[15]	.59	4.0	6.4	57
$C\eta$	.059	0.092	0.059	$\leqslant$0.06 (at 25°)

As was stated before, the available information on the system in methanol indicates that $k_8 \cong 1.5 \times 10^{10}\ m^{-1}\ \mathrm{sec.}^{-1}$ and $k_9 << k_8$. It follows that step 8 is a diffusion controlled process and that the rate of step 9 is proportional to the number of collisions rather than to the number of encounters. The approximate constancy of $C\eta$, where η is the viscosity of the solvent, is consistent with the view that step 7 is relatively unimportant and that for the alcohols, k_9 is not greatly affected by the nature of the solvent. For cyclohexanol the approximate empirical values of 0.80 and 0.77 for A and $k_3/(k_2 + k_3)$, respectively, lead to a negative value for C. However, the uncertainty in the empirical values is such that $k_3/A(k_2 + k_3) = 1.02$ is certainly compatible with the experimental data. The corresponding value of C is 0.001, which is listed in Table III. In contrast to this, the value of C for acetone is surprisingly small, even at relatively high concentrations of chlorophyll. This suggests that k_9 is much greater for acetone than for the alcohols.

This mechanism could be tested critically by measuring the quantum yield for various concentrations of chlorophyll, when the oxygen and allylthiourea were, separately, kept at low constant concentrations. With the exception of Gaffron's[7] measurements in acetone, the present data are insufficient to determine the dependence of B and C upon [GH].

Concurrent with the sensitized autoöxidation, chlorophyll a undergoes a relatively inefficient irreversible change. The product is a green pigment, whose absorption spectrum closely resembles that of chlorophyll d.[16] Its red maximum is located at 698 mμ, and its blue maximum is split into two roughly equivalent peaks at 460 and 400 mμ. This pigment is formed only when a solution containing both allylthiourea and oxygen is illuminated. Its formation is most efficient in methanol and acetone, but even in these solvents the quantum yield for pigment formation is always less than 2% of the yield for oxygen uptake.

Because of its resemblance to chlorophyll d, a small sample of the pigment was isolated chromatographically from a reaction mixture and was sent to Mr. J. H. C. Smith of the Carnegie Institution laboratory at Stanford. He showed that it can be separated chromatographically from natural chlorophyll d, and that, unlike the natural product, the synthetic pigment does not give a phase test.

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[15] The values of η were taken from "Organic Solvents," J. Riddick and E. Toops, Interscience Publishers, New York, N. Y., 1955. Interpolations and extrapolations were based upon the assumption tbat $\eta = A\ \exp(B/T)$, where A and B are constants.

[16] E. Rabinowitch, "Photosynthesis," Vol. II, Interscience Publishers, New York, N. Y., 1951, p. 615.