2. A rough classification has been made of the types of vibration involved in the stronger bands.
3. It has been pointed out that the great intensity of the bands involving the Si–O linkage confirms the large ionic character predicted from electronegativity difference.
4. Comparatively weak C–H vibration bands of the group Si–CH_3 indicate a dipole moment of the methyl group considerably smaller than in compounds where carbon replaces the silicon.

MIDLAND, MICHIGAN RECEIVED SEPTEMBER 20, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Polarographic Studies on Extracted Chlorophylls[1]

BY PIERRE VAN RYSSELBERGHE, JOHN M. MCGEE, ARMIN H. GROPP AND RALPH W. LANE

Complete and final elucidation of the mechanism of photosynthesis will require the accumulation of as much information as possible concerning oxidation–reduction reactions involving the chlorophylls. The present situation of the problem is admirably presented in Rabinowitch's[2] recent book. The investigations reported in the present paper were started before the publication of this book, but it seems to us that they are partial answers to certain questions posed by Rabinowitch. At an early date in our study of the polarographic reduction of carbon dioxide[3,4,5] we felt that results of significance would probably be obtained if extracted chlorophylls could be submitted to polarographic reduction. A comparison between the reduction potential of carbon dioxide and possible reduction potentials of the chlorophylls was considered as very desirable information. Two highly interesting phenomena were observed in our work: a reduction at a high cathodic potential which we have been able to ascribe to the double bond in the phytol chain, and another one at a very low cathodic potential which we have tentatively ascribed to the vinyl group. In mixtures of the chlorophylls with carbon dioxide a merging of the high potential reduction of chlorophyll with that of carbon dioxide was observed, a fact which may have some direct or indirect bearing on the establishment of possible mechanisms of photosynthesis.

Experimental

Chlorophyll was extracted in exact accordance with Zscheile and Comar's[6] latest method from several kinds of green leaves: lilac, Virginia creeper, grass, spinach and pine needles (this last source is unsatisfactory). Chlorophyll a was also extracted from *Vaucheria sp.* which does not contain any chlorophyll b.[7] A few extractions were carried out on smaller amounts of green material by the method of Strain and Manning.[8] The a and b components of the chlorophyll mixtures were separated in chromatographic columns packed with powdered sucrose. The final fractions were kept either in highly purified ethyl ether or, more frequently and with more satisfactory results, in highly purified dioxane. Whenever possible polarograms were taken immediately after extraction and separation. In a number of cases the polarograms were repeated at intervals of a few days in order to follow possible effects of aging of the chlorophylls or of their solvents. The chlorophyll solutions were kept in the dark in an ice box, the solutions in dioxane being then actually congealed. A Heyrovsky polarograph of the Sargent Company with photographic recording was used. Carefully recrystallized tetramethylammonium bromide was used as supporting electrolyte. Blanks were recorded with samples of 10 ml. of 0.1 molar solution. After passage of a stream of nitrogen to remove any dissolved oxygen a few drops of ether solution of chlorophyll were added. Stirring and further removal of oxygen were accomplished by a stream of nitrogen. In all cases enough chlorophyll was transferred to the aqueous solution to obtain good reduction waves. When a dioxane solution of the chlorophyll was used known volumes of up to 2 ml. were added to the 10 ml. of supporting electrolyte solution, the mixture was stirred with nitrogen and enough of the chlorophyll of the original dioxane solution stayed in solution in the resulting water–dioxane solvents to give suitable waves at sensitivities 50 and 100 of the Sargent polarograph. In all cases it had been previously established that the purified ether or dioxane alone had no disturbing effect on the polarograms. In a few cases the chlorophylls (several a + b mixtures, some samples of a from *Vaucheria*, as well as a commercial preparation obtained from the American Chlorophyll Co., Inc.) were saponified by a slight modification of the method of Willstätter and Stoll[9] using as alkali lithium or tetramethylammonium hydroxide in order to obtain chlorophyllins with positive ions having as high a polarographic reduction potential as possible.

The saponifications were carried out at 20° using methyl alcohol solutions of the respective bases. The required amount of each base was calculated and a slight excess taken to ensure complete conversion of the chlorophylls to chlorophyllin salts. The saponification proceeded rapidly as indicated by the complete solubility of the green product in water and the absence of any green ether-soluble residue.

After saponification the methanol was removed under reduced pressure at 20° and the chlorophyllin was extracted repeatedly with petroleum ether (b. p. 35–50°) to remove the phytyl alcohol released by the reaction. This phytol was transferred to ether or dioxane solutions for polarographic examination, while the lithium and tetramethyl-

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(1) Presented in part under the title "Polarographic Studies on Carbon Dioxide and Chlorophyll" by Pierre Van Rysselberghe and John M. McGee at the Pacific Northwest Regional Meeting of the American Chemical Society in Seattle, Wash., October 20, 1945.

(2) E. I. Rabinowitch, "Photosynthesis and Related Processes," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945.

(3) P. Van Rysselberghe and G. J. Alkire, THIS JOURNAL, **66**, 1801 (1944).

(4) P. Van Rysselberghe, *ibid.*, **68**, 2047 (1946).

(5) P. Van Rysselberghe, G. J. Alkire and J. M. McGee, *ibid.*, **68**, 2050 (1946).

(6) F. P. Zscheile and C. L. Comar, *Botanical Gazette*, **102**, 463 (1941).

(7) E. I. Rabinowitch, ref. 2, p. 405.

(8) H. H. Strain and W. M. Manning, *J. Biol. Chem.*, **144**, 625 (1942).

(9) R. Willstätter and A. Stoll, "Investigations on Chlorophyll," English translation by F. M. Schertz and A. R. Merz, Science Press Co., New York, N. Y., 1928; see pp. 288–290.

ammonium chlorophyllin salts were each dissolved in water and then added to the tetramethylammonium bromide solution for polarographic examination.

Results

1. High Cathodic Potential Reduction of Chlorophylls.—All samples of chlorophylls examined in the polarograph (a + b mixtures, pure a and pure b) showed a characteristic wave of the type shown on Fig. 1. The half-wave potential $E_{1/2}$ was found to be practically independent of concentration. The values obtained with ether and dioxane are nearly identical. The half-wave slope $E'_{1/2}$ (equal to $\Delta E/i_d$ along the tangent at the half-wave[4]) is somewhat larger with dioxane than with ether. The height of the wave increases with the concentration of chlorophyll. With some dioxane extracts all the chlorophyll stayed in solution after addition to the aqueous supporting electrolyte and we were able to verify the proportionality of diffusion current with concentration. The results are summarized in Tables I and II. The half-wave potentials are referred to the saturated calomel electrode. In most cases the galvanometer light was turned on at potentials of 1.40 to 1.60 volts cathodic. With a few solutions complete polarograms were recorded from zero potential up. In the majority of cases the only feature noted below the reduction near 2 volts was a steady rise of current increasing in magnitude with the age of the preparation but a similar rise was observed with pure ether or pure dioxane mixed with 0.1 N tetramethylammonium bromide solution. We believe this rise to be due to the gradual accumulation of various peroxides of ether or of dioxane which reduce over an extended range of potentials. A long, practically flat segment of the curve always preceded the reduction wave of the chlorophyll. In a number of preparations studied at high galvanometer sensitivities in the low potential range the curious effect described under 4 below was noted.

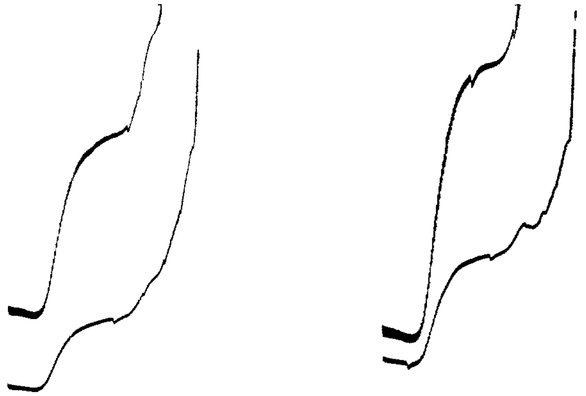


Fig. 1.—Reduction waves of phytol chain in chlorophylls: 1 ml. of dioxane solution of the chlorophylls added to 10 ml. of 0.1 molar tetramethylammonium bromide. Camera opened at 1.60 volts applied cathodic potential. Upper curves at sensitivity 20, lower curves at sensitivity 50 of Sargent Polarograph. Chlorophyll a on left, chlorophyll b on right half of figure. Diffusion currents: 3.0 microamperes for chlorophyll a, 5.1 microamperes for chlorophyll b. Approximate concentrations of dioxane extracts: 3.3 millimoles per liter for chlorophyll a, 5.6 millimoles per liter for chlorophyll b.

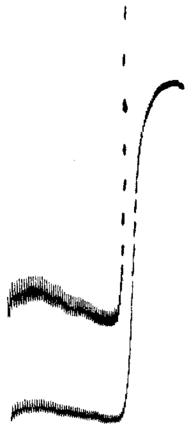


Fig. 2.—Reduction wave of pure phytol obtained from chlorophyll a of *Vaucheria:* 1 ml. of dioxane solution of phytol (containing approximately 0.02 g. of phytol) added to 10 ml. of 0.1 molar tetramethylammonium bromide. Upper curve at sensitivity 100, lower curve at sensitivity 200 of Sargent Polarograph. Camera opened at 1.40 volts applied cathodic potential: diffusion current 65.5 microamperes; approximate concentration of dioxane extract: 72 millimoles per liter.

2. Reduction of Phytol.—Samples of phytol obtained by the procedure described above were submitted to polarographic reduction in the same manner as the chlorophyll samples, both

TABLE I

HALF-WAVE POTENTIALS AND HALF-WAVE SLOPES OF THE "PHYTOL WAVE" IN CHLOROPHYLLS, PHYTOL, ETC., IN PRESENCE OF DIOXANE

Compound	$E_{1/2}$, volts[a]	$E'_{1/2}$, volt	Freundlich z
Chlorophyll a	1.88	0.175	3.9
Chlorophyll b	1.88	.171	3.7
Phytol	1.86	.147	2.8
Allyl alcohol	1.60	.143	2.6
Geraniol	1.68	.156	3.1

[a] These half-wave potentials are averages of values obtained by means of a Wolff potentiometer connected to the two electrodes of the polarographic cell. The values derived from readings on the drum of the polarograph are somewhat higher. The Ri correction was found negligible in all cases.

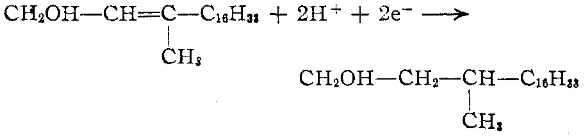
TABLE II

HALF-WAVE POTENTIALS AND HALF-WAVE SLOPES OF THE "PHYTOL WAVE" IN CHLOROPHYLLS, PHYTOL, ETC., IN PRESENCE OF ETHYL ETHER

Compound	$E_{1/2}$, volts	$E'_{1/2}$, volt	Freundlich z
Chlorophylls a + b	1.93	0.158	3.2
Phytol	1.92	.162	3.4
Allyl alcohol	1.71	.177	3.9
Geraniol	1.80	.164	3.4

ether and dioxane being again used as solvents. It was found that practically the same reduction wave as that of the original chlorophyll was now exhibited by the phytol. Figure 2 gives a typical phytol wave and the data are summarized in Tables I and II.

3. Behavior of Lithium and Tetramethylammonium Chlorophyllins.—The water-soluble chlorophyllins obtained in the saponification of the chlorophylls did not show more than a negligible residue of what we shall now call the "phytol wave." This fact was verified on mixtures of a and b chlorophyllins and on tetramethylammonium chlorophyllin derived from the chlorophyll a of *Vaucheria*. We conclude from the foregoing facts that this reduction wave of the chlorophylls is due to the phytol side-chain in the chlorophyll molecule and is probably a hydrogenation reaction (see Discussion below) of the double bond between carbons 2 and 3



$$CH_2OH{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}C_{16}H_{33} + 2H^+ + 2e^- \longrightarrow CH_2OH{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C_{16}H_{33}$$

Primary saturated alcohols do not reduce at any of the potentials accessible by means of the polarographic method. On the other hand, allyl alcohol $CH_2{=}CH{-}CH_2OH$, which like phytyl alcohol has a double bond between carbons 2 and 3, shows a similar reduction wave.[10] We have determined the half-wave reduction potential of allyl alcohol and the half-wave slope. In the same manner we have examined the behavior of geraniol $CH_2OHCH{=}CCH_3C_6H_{11}$, which also showed a reduction wave similar to that of phytol. On the other hand *n*-propyl alcohol, the probable reduction product of allyl alcohol, gave no reduction wave. Our experimental results on allyl alcohol and geraniol are given in Tables I and II.

4. Low Cathodic Potential Reduction of Chlorophylls.—In several preparations of chlorophyll (a + b mixtures, pure a and pure b) which were examined in the polarograph from small anodic potentials into the range of small cathodic potentials (using 0.1 molar potassium nitrate solution as supporting electrolyte) we observed a reduction wave of smaller magnitude (with a maximum current less than half and usually about one-tenth of that of phytol reduction), followed by an abrupt termination of the current. By using some of the highest galvanometer sensitivities available we were able to obtain a number of very satisfactory recordings of these peaks, such as those given in Fig. 3. We were able to observe that certain compounds containing the vinyl group exhibit a similar low-potential reduction with a more or less sharp peak: vinyl acetate, acetaldehyde (which contains a small amount of vinyl alcohol as a tautomeric form) and ethyl ether which, when not completely purified, contains vinyl alcohol as a common impurity. The low potential of this "vinyl reduction" makes the disappearance of the effect through accidental reduction during the extraction process of the chlorophylls quite plausible. This is the probable explanation of the following facts: 1. With many of our preparations this reduction wave was entirely absent. 2. When present the height of the wave was only a fraction of that of the phytol wave. 3. When observed with a fresh preparation the wave would usually disappear after a few days of aging of the chlorophyll solution. It is interesting to note that the vinyl group is known to be the most easily reduced group of the whole chlorophyll molecule.[11] It seems likely that the termination of the current is connected with the change of sign of the charge on the mercury drops at the electrocapillary maximum and with the resulting change in the orientation of the chlorophyll molecules.

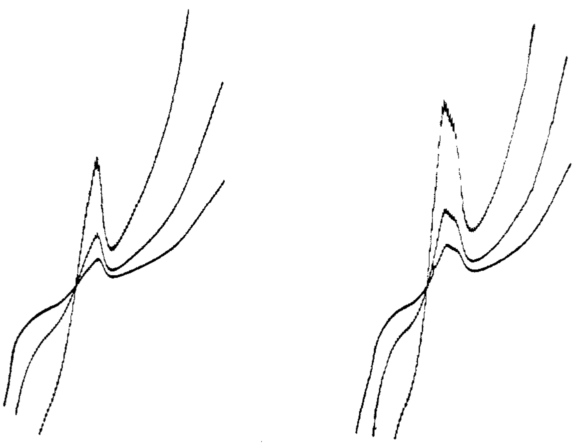


Fig. 3.—Reduction peak of the vinyl group of the chlorophylls: 1 ml. of dioxane solution of chlorophyll added to 10 ml. of 0.1 molar potassium nitrate. Point of intersection of curves corresponds to zero potential between electrodes. Sensitivities 10, 5, and 2 of Sargent Polarograph. Chlorophyll a on left, chlorophyll b on right half of figure. Currents at peaks: 0.29 microampere for chlorophyll a, 0.42 microampere for chlorophyll b. Vinyl group concentrations about one tenth of those indicated under Fig. 1 for the chlorophylls.

5. Mixtures of the Chlorophylls with Carbon Dioxide.—In several of our mixtures of supporting electrolyte with ether or dioxane solutions of the chlorophylls variable amounts of carbon dioxide were dissolved after the recording of the phytol and vinyl waves and new polarograms were taken. In the case of the phytol wave the closeness of the reduction potential of carbon dioxide,[5] 2.1 volts, to that of the phytol chain (around 1.9 volts), causes a merging of the two waves as shown on Fig. 4. The half-wave slopes

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[10] I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **17**, 35 (1931). The statement concerning allyl alcohol in I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1941, p. 374, requires correction.

[11] E. I. Rabinowitch, ref. 2, p. 468.

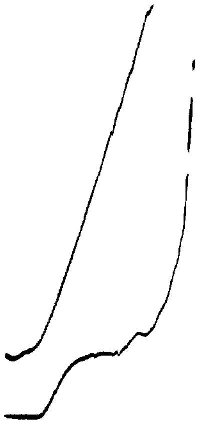

Fig. 4.—Effect of carbon dioxide on phytol wave of chlorophyll a. Lower curve: chlorophyll a alone. Upper curve: chlorophyll a and carbon dioxide. Sensitivity 50 of Sargent Polarograph. Camera opened at 1.60 volts applied cathodic potential. Diffusion current of lower curve: 3.4 microamperes. Approximate concentration of dioxane extract: 3.7 millimoles per liter.

of these two reductions are, however, quite different and this is usually noticeable on the combined waves. In the case of the vinyl wave the presence of carbon dioxide removes the peak, as shown on Fig. 5, probably on account of preferential adsorption of the carbon dioxide on the mercury cathode.

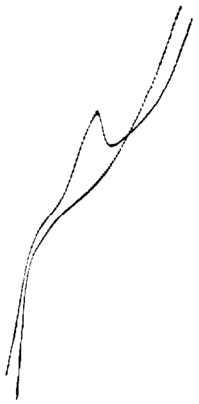

Fig. 5.—Effect of carbon dioxide on vinyl peak of chlorophyll a. Curve with peak: chlorophyll a in dioxane with 0.1 molar potassium nitrate. Other curve: same solution with carbon dioxide added. Sensitivity 2 of Sargent Polarograph. Curve with peak begins at 0.14 volt applied anodic potential and ends at 0.52 volt applied cathodic potential.

6. Effect of Acid and Base Additions on the Phytol Wave.—When hydrochloric acid is added to water–dioxane solutions of chlorophyll the phytol wave is reduced in height and finally disappears, the hydrogen ion wave of the excess acid appearing then at its usual potential (see Fig. 6). It was noted, however, that the half-wave slope of the hydrogen ion wave is greatly lowered ($\Delta E/i_d$ along the tangent at the half-wave is 0.075 volt instead of 0.22 volt as in pure aqueous solution) by either the dioxane or the chlorophyll. This interesting effect is being studied separately. The presence of free magnesium ion is noticeable in these acid solutions through the peculiar and irregular rise of current which this ion causes around 2.2 volts cathodic.[12]

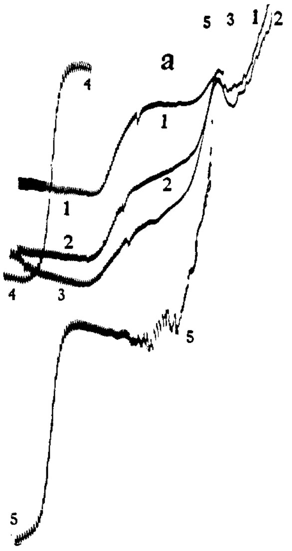

Fig. 6.—Effect of hydrochloric acid on phytol wave of chlorophyll a. Curve 1: 1 ml. of dioxane solution of chlorophyll a added to 10 ml. of 0.1 molar tetramethylammonium bromide. Curve 2: 0.5 ml. of 0.01 molar hydrochloric acid added. Curve 3: another 0.5 ml. acid added. Curve 4: 1 ml. acid added to previous solution, giving hydrogen ion wave. Curve 5: same as 4 with zero of galvanometer displaced. Curve 1 begins at 1.40 volts applied cathodic potential. Sensitivity 50 of Sargent Polarograph. Phytol diffusion currents for curves 1, 2, 3 are: 4.0, 3.0, 2.2 microamperes, respectively, corresponding to approximate concentrations of 4.4, 3.5, 2.5 millimoles per liter in terms of original dioxane extract. Hydrogen ion diffusion current for curves 4 and 5 is 9.6 microamperes.

When tetramethylammonium hydroxide is added to water–dioxane solutions of chlorophyll no effect is noted on either the half-wave potential or the height of the phytol wave. The half-wave slope is somewhat smaller when the hydroxyl ion concentration is large enough to be regarded as constant along the wave. This would be expected from the theory in the following discussion (see Fig. 7).

Discussion

Since the phytol side-chain of chlorophyll is rather easily replaced by a positive ion it seems natural to ascribe to this side-chain a positive character which in fact would be localized in the neighborhood of the ester linkage and hence close to the double bond. At all of the subsequent car-

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(12) I. M. Kolthoff and J. J. Lingane, ref. 10, p. 303.

bon atoms bending of the chain can occur and it is therefore possible for the chlorophyll molecule to attach itself to the negatively charged surface of the mercury drop at the carbons 2 and 3 of the phytol chain, the rest of the chain being bent away from the surface and somewhat parallel to the porphyrin ring. A detailed model of the chlorophyll molecule was constructed and showed that such a geometrical arrangement would be possible. The hydrogen ions and the electrons would then add themselves at the double bond through the direct contact with the mercury electrode. Rabinowitch's comparison of the chlorophyll molecule with a tadpole[13] may be useful in picturing its position and shape with respect to the surface of the mercury drop, but we believe that a more apt comparison is to regard the chlorophyll molecule as a plane kite with a tail which can be bent back over the plane.

The mathematical analysis of the phytol wave can be carried out by means of the theory recently developed.[4] The present case is Case II, subcase a of this theory: unbuffered solution of a non-acid substance with original solution neutral. The relationship between the potential and the concentration C_{R} of the chlorophyll, C_{X} of the reduction product and C_{OH^-} is of the form

$$E = E_0 + \frac{RT}{2F} \ln \frac{C_{\mathrm{X}}^{z} C_{\mathrm{OH}^{2}-}}{C^{x}} \qquad (1)$$

On account of the large size of the molecule of chlorophyll and the large distances between the phytol double bonds of neighboring adsorbed molecules it seems certain that only one molecule would be involved in the reduction with two hydrogen ions and two electrons. Therefore x is one, the Freundlich adsorption exponent z of the reduction product being obtainable from the slope at the half-wave and verifiable by means of the position of the point of inflection. Introducing the currents i and i_{d} (see our previous paper[4] for notations and details) we obtain

$$E = E_0' + \frac{RT}{2F} \ln \frac{i^{z+2}}{i_{\mathrm{d}} - i}$$

$$E = E_0' - \frac{RT}{2F} \ln \left(\frac{i_{\mathrm{d}}}{2}\right)^{z+1} + \frac{RT}{2F} \ln \frac{u^{z+2}}{1-u} \qquad (2)$$

The slope of the wave is given by

$$\frac{\mathrm{d}E}{\mathrm{d}u} = E' = \frac{RT}{2F}\left[\frac{z+2}{u} + \frac{1}{1-u}\right] \qquad (3)$$

At the half-wave $u = {}^1/_2$ and

$$E'_{1/2} = \frac{RT}{F}(z+3) = 0.0255\,(z+3) \qquad (4)$$

With dioxane the experimental value of $E'_{1/2}$ is 0.175 for chlorophyll a, 0.171 for chlorophyll b, and 0.147 for free phytol. We thus have $z = 3.9$ for chlorophyll a, 3.7 for chlorophyll b and 2.8 for phytol. The point of inflection of the wave should then be at a value of u such that[4]

$$\frac{z+2}{u^2} = \frac{1}{(1-u)^2} \qquad (5)$$

which gives us $u = 0.75$ for chlorophyll a, $u = 0.70$ for chlorophyll b and $u = 0.68$ for phytol. These values are in as good an agreement as could be expected with the graphically determined points of inflection of the waves.

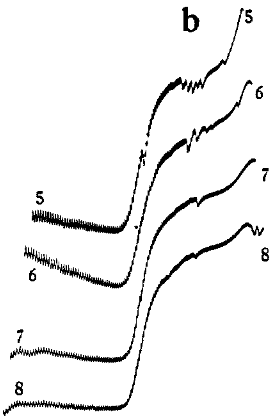

Fig. 7.—Effect of tetramethylammonium hydroxide on phytol wave of chlorophyll b. Curve 5: 1 ml. of dioxane solution of chlorophyll b added to 10 ml. of 0.1 molar tetramethylammonium bromide. Curve 6: 0.1 ml. of 0.1 molar tetramethylammonium hydroxide added. Curve 7: second 0.1 ml. added. Curve 8: third 0.1 ml. added. Zero of galvanometer displaced for each curve. Sensitivity 50 of Sargent Polarograph. Curve 5 begins at 1.40 volts applied cathodic potential. Diffusion current: 6 microamperes. Approximate concentration of dioxane extract: 6.6 millimoles per liter.

We shall not here present detailed considerations on free energy changes, but it seems interesting to note that if we refer the half-wave reduction potential of chlorophyll to that of a hydrogen electrode in a neutral solution we find, taking, $E_{1/2}$ obtained in ether, $1.93 - 0.25 - 0.42 = 1.26$ volts which corresponds to a free energy of

$$2 \times 23.1 \times 1.26 = 58.2 \text{ kcal.}$$

for the reduction reaction. The free energy of radiation absorbed per mole of chlorophyll at the major red maximum of absorption in ether[14] is 43.3 kcal. for chlorophyll a and 44.5 kcal. for chlorophyll b.

At the major blue maximum of absorption in ether we have 66.8 kcal. for chlorophyll a and 63.1 kcal. for chlorophyll b. A comparison of these data with the polarographic results leads to interesting speculations concerning the exact nature of the reactions resulting from these free energy intakes. If X is the free energy of formation of chlorophyll from its elements, $(X - 20)$ kcal. would be the free energy of the hydrogenated chlorophyll.[15] Free energy absorption would

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[13] E. I. Rabinowitch, ref. 2, p. 382.

[14] D. G. Harris and F. P. Zscheile, *Botanical Gazette*, **104**, 515 (1943).

[15] G. S. Parks and H. M. Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, see p. 210.

serve to decompose water. It is interesting to note that the free energy change of the reaction

$$\begin{array}{l} \text{Chl.} + 2H_2O = \text{Chl.}H_2 + H_2O_2 \\ X - 2 \times 57 \quad X - 20 - 31 \end{array}$$

is +63 kcal., while that of the reaction

$$\begin{array}{l} \text{Chl.} + H_2O = \text{Chl. } H_2 + {}^1/_2O_2 \\ X - 57 \qquad X - 20 \qquad 0 \end{array}$$

would be only +37 kcal.

Acknowledgments.—We are indebted to the General Research Council of the Oregon State System of Higher Education for the grant of a research assistantship to one of us (A. H. G.) and for continued support in the purchase of equipment and materials. We are also indebted to Dr. Leroy E. Detling of the Department of Biology, University of Oregon, for the location and identification of the *Vaucheria sp.* used in our work.

Summary

1. Polarograms obtained with solutions of the chlorophylls in ether and in dioxane added to aqueous solutions of tetramethylammonium bromide are described.

2. A characteristic reduction wave near 1.9 volts *vs.* the saturated calomel electrode is exhibited by the chlorophylls and by the phytol separated from the chlorophylls by saponification. This wave is ascribed to the hydrogenation of the double bond in the phytol chain. Similar waves are exhibited by allyl alcohol and by geraniol.

3. Some chlorophyll preparations exhibit reduction current peaks at low cathodic potentials. These peaks are tentatively ascribed to the hydrogenation of the vinyl group.

4. The addition of carbon dioxide results in a merging of the phytol wave with that of carbon dioxide, while the vinyl peak is suppressed.

5. The effect of acids and bases on the phytol reduction is described.

EUGENE, OREGON RECEIVED JUNE 29, 1946

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXVI. The Conductance of Some Onium Type Salts in Ethylene Chloride at 25°[1]

BY ERNEST R. KLINE[2] AND CHARLES A. KRAUS

I. Introduction

Conductance measurements have been made with a series of onium type picrates and perchlorates in ethylene chloride in order to determine the effect produced on the dissociation constant by certain attainable structural variations in the cations. The structural variations accomplished in this investigation were: (a) in the number of the alkyl (or aryl) groups attached to the central atom; and (b) in the nature of the central atom to which they were attached. The effect of variation in the size of the substituent alkyl groups has already been studied in ethylene chloride.[3]

The salts prepared for this investigation were tetrabutylphosphonium picrate, tetrabutylarsonium picrate, tributylsulfonium picrate, tributylsulfonium perchlorate, diphenyliodonium picrate and diphenyliodonium perchlorate. The results obtained with these compounds, when combined with those of Mead[4] for tetrabutylammonium picrate, permit of evaluation of the two above mentioned constitutional factors on ionic equilibria.

II. Experimental

Solvent. Apparatus and Procedure.—The details appertaining to these have been fully described in earlier papers.[4]

Salts.—Tetra-*n*-butylphosphonium iodide was obtained by the interaction of *n*-butyl iodide and tri-*n*-butylphosphine. The salt was purified by precipitation from benzene solution by addition of petroleum ether; m. p., 98°.

Tetra-*n*-butylphosphonium picrate was prepared by the metathesis of an alcoholic solution of the iodide with the calculated amount of silver picrate in hot aqueous solution. After filtering, cooling in ice gave a crystalline product. The salt was recrystallized from a water–alcohol mixture; m. p., 55°.

Tri-*n*-butylarsine was prepared according to the method described by Davies and Jones[5] by the careful interaction of butylmagnesium bromide with arsenic tribromide in ethereal solution in the cold. Vigorous stirring was necessary during the addition. After treatment with ice and hydrochloric acid, the ether layer was separated, washed repeatedly with water and dried with calcium chloride. At this stage, some decolorizing carbon was added, the solution filtered and the ether removed by distillation. The residue was fractionated at low pressure and the tri-*n*-butylarsine which came over at 117–120° (at 8 mm.) was collected separately.

Tetra-*n*-butylarsonium iodide was obtained by the interaction of a slight excess of *n*-butyl iodide with the tri-*n*-butylarsine. The mixture was heated gently under reflux for several minutes. Amyl ether was then added and the mixture boiled to remove the excess butyl iodide. On cooling, the salt crystallized out. One portion was recrystallized by precipitation from ethanol with dry ether and another by precipitating from benzene with petroleum ether; m. p., 86°. Mannheim[6] reports that the

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[1] This paper comprises part of the subject matter of a thesis submitted by Ernest R. Kline in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1938.

[2] University Fellow at Brown University, 1926–1927; 1927–1928. Present address: Connecticut State College, Storrs, Conn.

[3] Tucker and Kraus, THIS JOURNAL, 69, 554 (1947).

[4] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936); compare, also, Tucker and Kraus, ref. 3.

[5] Davies and Jones, *J. Chem. Soc.*, 33 (1929).

[6] Mannheim, *Ann.*, **341**, 204, 222 (1905).