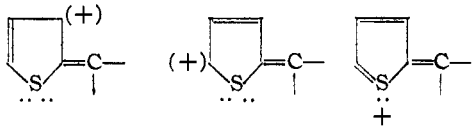
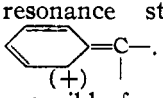
The thiophene compound of this series (compound 8) shows the greatest displacement of the maximum and thus it appears that the thiophene ring is a ready source of electrons. The electron deficiency on the thiophene ring distributes itself over three atoms as indicated in the following structures:



It may be of significance that the last of the resonance structures shown contains a continuous conjugated system absent in the corresponding resonance structure with a benzene ring:  . This difference may be in part responsible for the great "basicity"[18] of the 2-thienyl group as compared to the phenyl group. In the ultraviolet range compound 8 exhibits a secondary maximum at 255 mμ which probably corresponds to the independent absorption of the thiophene nucleus[19] in the DNPH structure of type V.

(18) Brooker, *et al.*, THIS JOURNAL, **67**, 1875 (1945).

Summary

The absorption spectra of *p*-phenyl-, benzyl-, phenoxy-, phenylmercapto-, phenylthionyl- and phenylsulfonylacetophenone 2,4-dinitrophenylhydrazones and of 2-thienyl methyl ketone 2,4-dinitrophenylhydrazone were examined in the ultraviolet and visible range and compared with the spectrum of the unsubstituted acetophenone derivative. Evidence with regard to the expansion of the valence shell of the sulfur atom is presented.

(19) Sease and Zechmeister, *ibid.*, **69**, 270 (1947), report the 231 mμ band for thiophene in hexane.

PITTSBURGH, PENNSYLVANIA

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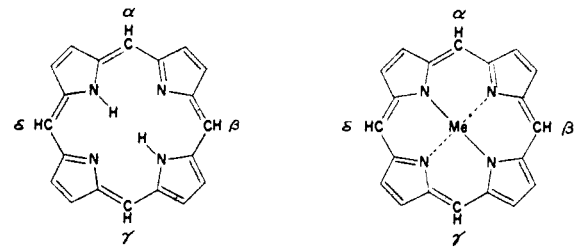
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Exchange and Replacement Reactions of $\alpha,\beta,\gamma,\delta$-Tetraphenyl-metalloporphins[1]

BY J. W. BARNES[2] AND G. D. DOROUGH

It has been known for many years that the two imino hydrogens of free base porphin compounds are replaceable by a great variety of metal ions to produce metallo-derivatives designated as metalloporphins (Fig. 1). It is apparent from even the most cursory examination of the properties of these metal compounds that they may be divided into two large categories with a minimum of overlapping. In one category are the metalloporphins derived from small divalent metal ions such as copper(II), nickel(II), zinc(II), and many others. These metalloporphins not only possess spectra which are similar in shape and extinction coefficient (see Fig. 2), but also exhibit on the whole a considerable reluctance to part with the bonded metal. Copper, for example, is so tightly bonded in the porphin ring that it is removed only by methods so drastic as to cause decomposition of the porphin structure. Although there is no definite relationship between bond type and rate of isotopic exchange,[3] it is not surprising that even after long contact times such metalloporphins have been found not to exchange with the corresponding metal ion in solution. Copper,[4] iron,[4] magnesium[5] and tin,[6] have been among the metalloporphins upon which exchange experiments have been conducted.



(a) Porphin free base. (b) Metalloporphin.

Fig. 1.

The second group of metalloporphins is derived from the large divalent metals such as lead and mercury, and the alkali metals. These metalloporphins show no great affinity for the bonded metal; the action of water or dilute acetic acid is quite sufficient to convert the metalloporphin rapidly and completely to the free base. For one porphin, at least, $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, the spectra of the lead, mercury, and alkali metal derivatives are somewhat similar, being characterized by broad absorption in the red region, and as a group differ markedly from the characteristic spectra shown by the metalloporphins derived

(1) Second in a series of papers on "Fundamental Properties of Porphyrin Systems."

(2) Monsanto Research Fellow, 1948. Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

(3) A. C. Wahl, editor, "Radioactivity Applied to Chemistry," Chapter 3, John Wiley and Sons, Inc., New York, N. Y. in preparation.

(4) Ruben, Kamen, Allen and Nahinsky, THIS JOURNAL, **64**, 2297 (1942). The iron in this case was trivalent.

(5) Ruben, Kamen and Frankel, *J. Phys. Chem.*, **46**, 710 (1942).

(6) Prof. R. B. Duffield, private communication.

from the small divalent metals (compare Figs. 2, 3 and 4).

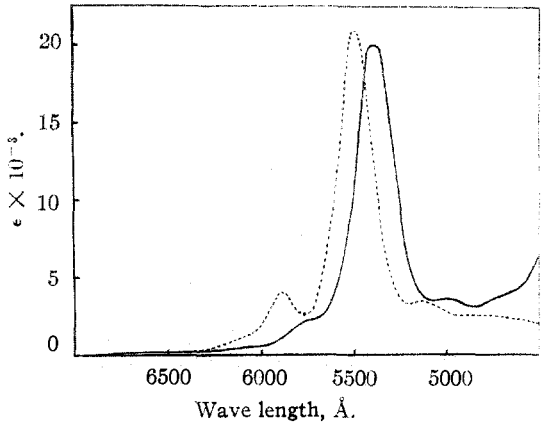


Fig. 2.—Absorption spectra in benzene: dotted curve, zinc salt of tetraphenylporphin: solid curve, copper salt of tetraphenylporphin.

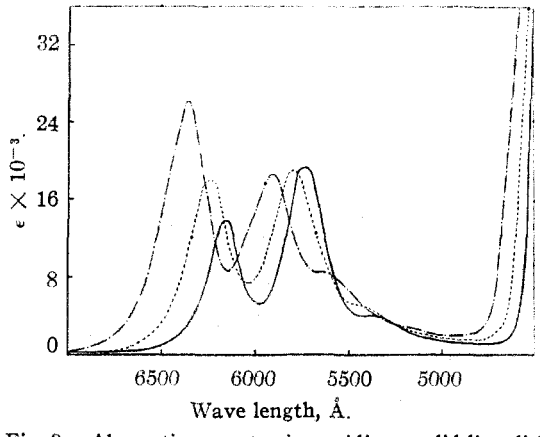


Fig. 3.—Absorption spectra in pyridine: solid line, lithium salt of tetraphenylporphin; dotted line, sodium salt of tetraphenylporphin; dashed and dotted line, potassium salt of tetraphenylporphin.

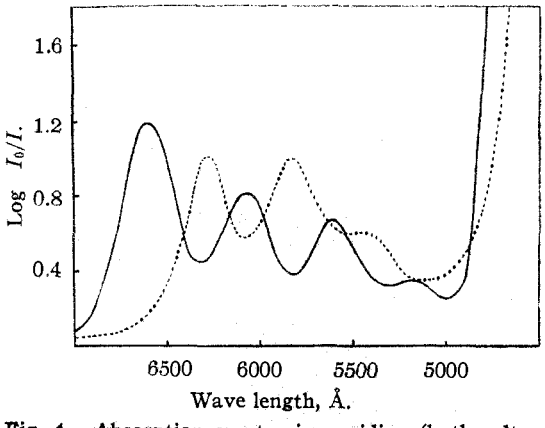


Fig. 4.—Absorption spectra in pyridine (both salts at same concentration): solid line, lead salt of tetraphenylporphin; dotted line, mercury salt of tetraphenylporphin.

In view of the contrast in properties of the lead, mercury, and alkali metalloporphins with those derived from copper, nickel, etc., a study of exchange and replacement[7] reactions in the former group seemed of interest. Accordingly, the exchange reaction, sodium ion–disodium* tetraphenylporphin was investigated in detail, and numerous replacement reactions of the type mercuric ion–lead tetraphenylporphin, sodium ion–dipotassium tetraphenylporphin, *et cetera*, were studied. The replacement reactions differ from isotopic exchange reactions, of course, in that there can be an appreciable free energy change in going from a less stable to a more stable configuration.

Results and Discussion

In Table I are summarized the results of all the replacement reactions which we investigated. If it is assumed that replacement occurs when the reaction leads to the formation of a more stable metalloporphin, then all of the replacements involving the lead, mercury, and alkali metalloporphins are consistent with two simple rules which define orders of stability. The first rule states that the over-all stability of the metalloporphins is in the order

Small divalent > large divalent > alkali

Replacement thus occurs when the replacing metal lies in a group to the left of the metal bound in the porphin. The second rule states that in each of the two less stable groups, the metalloporphin with the smallest metal is the most stable; thus in the alkali group potassium is replaceable by sodium which in turn is replaceable by lithium, and in the large divalent group, lead is replaceable by mercury.

No deviations to these stability rules were found, either in the sense of a reaction proceeding when a less stable metalloporphin would be formed, or a reaction not proceeding when a more stable metalloporphin would be formed. There easily could be apparent exceptions of the latter type since other factors such as rates, solvent complexing of the reactants, etc., are certainly involved. This is illustrated by experiments 11, 8, and 12 which show that copper rapidly replaces mercury, mercury rapidly replaces lead, yet copper replaces lead with some difficulty. Replacements in accordance with the stability rules do require, however, that both the replacing metal ion and the metalloporphin dissolve in the solvent media, for sodium iodide which is insoluble in toluene has no effect on a toluene solution of dipotassium tetraphenylporphin (experiment 6). In none of the replacement reactions studied was there any evidence of a measurable equilibrium; the reactions either went to completion or did not proceed at all.

(7) It had been observed for the related phthalocyanine salts that cupric and some other ions readily replace the lithium in a lithium phthalocyanine: Barrett, Frye and Linstead, *J. Chem. Soc.*, 1157 (1938).

TABLE I

REPLACEMENT REACTIONS OF METALLO-TETRAPHENYLPORPHINS

Expt.	Replacing ion[a]	Metalloporphin[b]	Solvent[c] and temperature[d]	Result
1	Lithium	Disodium	r. t.	Spectrum of product agreed point for point with that of dilithium porphin. Reaction very rapid
2	Lithium	Mercury	r. t.	No reaction
3	Lithium	Lead	r. t.	No reaction
4	Sodium	Dilithium	r. t.	No detectable reaction
5	Sodium	Dipotassium	r. t.	Spectrum of product agreed point for point with that of the disodium porphin. Reaction very rapid
6	Sodium	Dipotassium	Toluene at r. t.	No detectable reaction
7	Potassium	Disodium	r. t.	No detectable reaction
8	Mercury	Lead	r. t.	Conversion to mercury salt in one minute
9	Mercury	Dilithium	r. t	Rapid conversion to mercury salt
10	Lead	Mercury	r. t.	No reaction
11	Copper	Lead	B. p. of pyr.	Very slow reaction at r. t. Quant. conversion to copper salt in one-half min. at b. p. of pyr.
12	Copper	Mercury	r. t.	Rapid conversion to copper salt
13	Zinc	Lead	B. p. of pyr.	No perceptible reaction at r. t. Quant. conversion to zinc salt in five minutes at b. p. of pyr.
14	Zinc	Mercury	r. t.	Conversion to zinc salt in one minute
15	Zinc	Dilithium	r. t.	Quant. conversion to zinc salt
16	Copper(II)	Silver(II) Tin(II) Cobalt(II) Zinc, magnesium	B. p. of pyr.	No detectable reaction in ten minutes
17	Copper(II)	Zinc	B. p. of pyr.	Detectable replacement in one hr., nearly complete in forty-eight hrs.
18	Zinc	Silver(II) Tin(II) Cobalt(II) Copper(II) Magnesium	B. p. of pyr.	No detectable reaction in ten minutes

[a] The alkali metals were added as iodides in about a 100-fold excess. The other metals were added as acetates in about a 1000-fold excess. [b] The concentration of the metalloporphin was about 10^{-5} M. [c] The solvent is pyridine unless otherwise specified. [d] "r. t." is room temperature, "b. p. of pyr." is the temperature of pyridine at its boiling point.

Although beyond the stated objectives of this paper, we investigated briefly replacement reactions in the small divalent group. No detectible replacements were observed among various combinations of small divalent metals within ten minutes, a period of time considerably longer than that required for replacements involving the less stable metalloporphins (see experiments 16 and 18). Such replacements are possible, however, copper ion finally replacing nearly all the zinc in zinc tetraphenylporphin after forty-eight hours of refluxing at the boiling point of pyridine (Experiment 17).

In the sodium ion–disodium porphin exchange study, it was found that in a pyridine solution of sodium iodide and disodium* tetraphenylporphin at concentrations of about 10^{-5} M and in the presence of about 10^{-8} M sodium methylate, complete equilibration of the activity occurred at room temperature in less than six minutes. The six minutes correspond to the time required to evaporate off the pyridine solvent under vacuum and replace it with toluene, a solvent in which sodium iodide is insoluble. The exchange is presumed stopped at this point. (See replacement experiment 6.) The equilibration of activity was determined by centrifuging off the sodium iodide, and counting it and the toluene fraction (see experimental section for details).

An interpretation of the results of these exchange and replacement studies involves partly a concept of the nature of the metal to nitrogen bonding in the various metalloporphins, and partly a consideration of steric factors. The difference in behavior of copper and alkali metalloporphins, for example, is largely concerned with the fact that the alkali metals are bonded ionically, while the copper is bonded covalently. In a general way, reference to the properties associated with ionic and covalent bonding would suggest the pattern of results found for the two types of metalloporphins. Also concerned, however, are the vulnerable positions occupied in space by the alkali metals, for these metals, because of their large size and because there are two of them, lie in positions well outside the porphin ring, making them more susceptible to replacement and exchange than metals such as zinc and magnesium which have a large ionic contribution to their bonding, but which occupy positions securely in the center of the porphin structure.

The anomalous behavior of the lead and mercury metalloporphins may also be attributable to steric factors. Metalloporphins derived from metals of the same group in the periodic table show, as might be expected, a marked similarity in such properties as spectra, ease of hydrolysis, *et cetera*. Mercury, however, deviates somewhat from zinc and cadmium, and lead is in very great contrast to tin which forms one of the most stable of all metalloporphins. A reasonable explanation of the deviation of mercury and lead from other members of their groups might be that these metals are too large to fit easily into the center of the porphin ring which is only 2.4 Å. in diameter.[8] If lead and mercury were forced to lie outside the porphin ring, they would be held mostly by coulombic forces, due in part to difficulties concerned with the directional qualities of the s and p orbitals available for covalent bonding. These facts, then, would account for the ease with which these metals can be replaced, and the rough similarity of their spectra to the alkali metalloporphins. It would be interesting to test these assumptions by the determination of the dipole moments of the lead and mercury metalloporphins.

Acknowledgment.—The authors wish to acknowledge helpful discussions on the sodium exchange with Professor A. C. Wahl.

Experimental

PART 1. THE SODIUM ION-DISODIUM TETRAPHENYLPORPHIN EXCHANGE

General Procedure.—Pure disodium tetraphenylporphin (PNa_2) in solution is extremely unstable with respect to hydrolysis by water, and must be completely protected from atmospheric moisture. Because of the limited solubility of the porphin salt in some of the solvents employed, the amount of PNa_2 in an experiment was never greater than 10^{-6} mole. All of the experiments were carried out on a high vacuum line as the most feasible means of avoiding the hydrolysis of such small amounts of material. The method of studying the exchange as it finally evolved is as follows:

Through the stopcock opening in vessel A (see Fig. 5) are placed 15 ml. of pyridine solution containing approximately 10^{-6} mole of tetraphenylporphin and 0.5 ml. of approximately 0.02 *M* sodium methylate in anhydrous methanol. The free base is converted to PNa_2 by the reaction

$$PH_2 + 2NaOCH_3 = PNa_2 + 2CH_3OH$$

The reaction is accompanied by a color change from the pink of the free base to the brilliant green with red fluorescence of the PNa_2. The stopcock plug is replaced in A, the methanol and pyridine removed under vacuum, and the system pumped for twenty-four hours at 10^{-6} mm. with intermittent flaming of the fritted filter in A. Dry toluene is then distilled in from reservoir E, and the resulting toluene solution is filtered through the sintered disk in A into the "cow" B by the rotation of vessel A to an upright position. The change to toluene solution is to effect a separation of the PNa_2 from pyridine soluble but toluene insoluble sodium methylate. This toluene solution, containing about 10^{-6} mole of PNa_2 with a counting rate of up to 3000/c./m./10^{-7} mole, is distributed among four centrifuge tubes like the one shown at C in Fig. 5 by the appropriate rotation of the lower part of the cow B. The tubes are sealed off the line, and centrifuged one and one-half hours before using them in an exchange run. The reasons for the rather elaborate filtration and centrifugation are as follows: Since sodium methylate is insoluble in toluene, it should be removed by the sintered glass filter in vessel A. However, this filter was of a coarse porosity (Pyrex C), and some sodium methylate leaked through. Use of a filter of finer porosity failed because such a filter could never be outgassed and dried well enough to give consistent filtration without hydrolysis. Since the coarse filter does remove the bulk of the sodium methylate, it is left in the apparatus for this purpose, and the remainder is removed in the centrifugation. The centrifuge cones are constructed with a very fine capillary tip which held the trace of sodium methylate during the succeeding manipulations very well. Two blanks showed that with 60,000 counts/min. of sodium methylate in vessel A, only 10 ± 3 c./m. and 4 ± 1.5 c./m. were obtained in the toluene after centrifugation.

After centrifugation, the tube is sealed onto the apparatus shown in Fig. 6. A tube (F) containing inactive sodium iodide in pyridine is also present (see below for its preparation). After thorough evacuation of the apparatus, the break-off seal on the PNa_2 tube (C) is broken, the

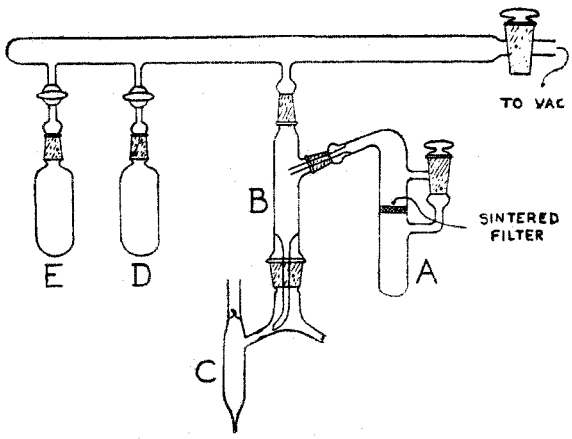


Fig. 5.—Preparation apparatus.

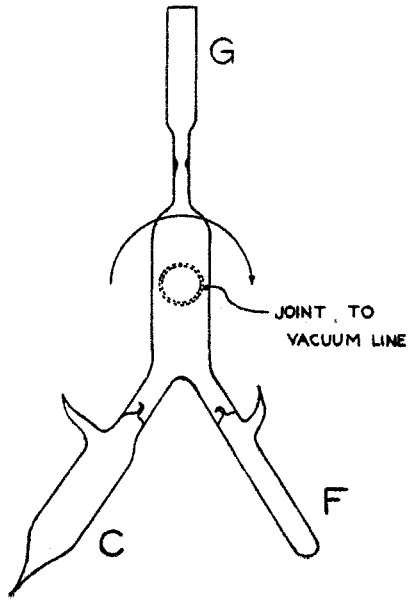


Fig. 6.—Mixing apparatus.

(8) Estimated from the values given by Robertson, *J. Chem. Soc.*, 1195 (1936), for the closely related phthalocyanine.

TABLE II

Expt.	W_1	W_2	C_1	C_2	M_1	M_2	M_3	F_p	F_e	% Exchange
19	1.419	1.937	31 ± 4	806 ± 17	0.21×10^{-7}	0.39×10^{-7}	17.0×10^{-7}	0.075	0.086	99 ± 8
20	1.574	1.625	112 ± 5	908 ± 15	$.30 \times 10^{-7}$	$.44 \times 10^{-7}$	6.60×10^{-7}	.204	.223	97 ± 7

apparatus rotated 180°, and the toluene solution collected in cuvette G. The toluene is evaporated off, the break-off seal on the sodium iodide tube (F) broken, and the pyridine solution of sodium iodide allowed to run down into the cuvette (G) and dissolve the PNa_2. The apparatus is rocked gently to insure complete mixing. This solution constitutes the homogeneous exchange mixture.

After any desired time, the pyridine is removed and again replaced with toluene from E. The cuvette (G), which is constructed from 10 mm. square mandrel tubing with opposite sides polished optically flat, is sealed off the line, and the concentration of PNa_2 determined in the solution by measuring the optical density on a Beckman Spectrophotometer at 6150 Å. where the extinction coefficient has a value of 17,100 in toluene. (Since PH_2 has a very small extinction coefficient at 6150 Å., this value of the concentration of PNa_2 will be valid even if there has been considerable hydrolysis.)

A file mark is now cut on the tip of the cuvette tube, and the cuvette centrifuged. The cuvette is then cracked open by the application of a hot glass rod to the file mark, and about half of the contents rapidly pipetted into a weighed beaker and the aliquot weighed. Only half of the solution is removed in order not to disturb the sodium iodide precipitate. The toluene in the beaker is evaporated under a heat lamp, and the residue digested with concentrated nitric acid. The resulting sodium nitrate is transferred quantitatively to a microscope cover glass, and the counting rate determined.

The cuvette, which still contains roughly half of the PNa_2 solution and the sodium iodide, is weighed, and then allowed to stand a short while until the PNa_2 is completely hydrolyzed. The optical density of the solution is measured at 5150 Å. where PH_2 has a large absorption peak (ϵ is 19600), and the concentration of the total porphin present calculated. (This concentration will agree with the concentration of PNa_2 in the exchange mixture if there has been no hydrolysis. If the two values do not agree, the difference will represent the amount of hydrolysis, and twice the difference will represent the amount of sodium hydroxide liberated by such hydrolysis. Since sodium hydroxide is toluene insoluble, it will appear with the centrifuged precipitate of sodium iodide.) After obtaining the spectral data, the counting rate of the contents of the tube is determined in a manner analogous to the first toluene aliquot. The weight of toluene in the tube is determined by subtracting the weight of the empty tube from that of the tube and its contents.

Utilizing the density of toluene (0.8623) and the various measurements previously described, the following data are collected

W_1 = wt. of the toluene aliquot from the cuvette
W_2 = wt. of the toluene remainder in the cuvette
C_1 = count/min. of the toluene aliquot
C_2 = count/min. of the toluene remainder–sodium iodide
M_1 = moles of PNa_2/g. of toluene solution
M_2 = moles of PH_2 after hydrolysis of sample/g. of toluene solution
M_3 = moles of sodium iodide added

It is easily shown that F_p, the fraction of the total sodium present as PNa_2 is equal to

$$F_p = \frac{2M_1(W_1 + W_2)}{2M_1(W_1 + W_2) + 2(M_2 - M_1)(W_1 + W_2) + M_3}$$

and that F_e, the fraction of counts present in the PNa_2 is equal to

$$F_e = \frac{((W_2 + W_1)/W_1)C_1}{C_1 + C_2}$$

For complete exchange, F_p and F_e are equal. The percentage exchange is given by

$$\% = \frac{(C_1 + C_2) - F_e(C_1 + C_2)}{(C_1 + C_2) - F_p(C_1 + C_2)} \times 100 = \frac{1 - F_e}{1 - F_p} \times 100$$

In Table II are given the results of two exchange runs. The homogeneous exchange mixtures were allowed to stand the minimum time in these experiments (about six minutes).

Obviously an exchange procedure as complicated as this was not evolved without considerable experimentation. Approximately 100 exchange runs were carried out under a great variety of experimental conditions before the data given in Table II were obtained. Many of these runs gave exactly the same results as Table II, but were experiments in which the sodium methylate or sodium iodide concentrations or both were relatively quite large. A few experiments were conducted in which the pyridine was sublimed from the frozen exchange mixture at −44°, rather than removing the pyridine in the liquid phase by evaporation. No difference was observed, indicating the exchange had taken place in solution, and was not "induced" by or a function of the separation procedure.

Miscellaneous Experimental Details.—The solubilities in toluene of sodium iodide and sodium methylate were determined by tracer experiments to be negligible. In 10 ml. of supernatant over a centrifuged precipitate of about 10^{-6} mole of sodium iodide containing 8000 c./m. there were only 2 counts/m. In 23.4 ml. of supernatant over a centrifuged precipitate of about 10^{-5} mole of sodium methylate containing 10,000 c./m. there were 14 c./m.

The toluene was dried in reservoir (E) with sodium-potassium alloy. The pyridine was dried in reservoir (D) by the addition of large amounts of sodium. The resulting liquid was jet black in color, and considerable amounts of the pyridine were decomposed, but the distillate was water white and very dry. Drying in the conventional manner over barium oxide failed completely to reduce the water content to the level required in our experiments.

The free base porphin was obtained by methods previously described.[9]

The active sodium^{22} was obtained by the reaction Mg^{24} (d, α) Na^{22} in the Washington University cyclotron. The three-year positron emitting Na^{22}, after allowing time for the short lived Na^{24} to decay, was extracted by conventional chemical procedures. It was converted to $Na^{22}Cl$ which was equilibrated with ordinary sodium methylate to obtain the active sodium methylate used in the experiments. Counting was done under a thin aluminum window Geiger tube designed by Professors A. C. Wahl and N. A. Bonner. Because of the long half-life (3 years), no correction for decay was necessary.

The inactive sodium iodide used was commercially obtainable C. P. sodium iodide. It was weighed into tubes equipped with break-off seals, the tubes attached to the vacuum line, and the salt dried by pumping for two or three days at 10^{-6} mm. at 200°. Pyridine was then distilled in from D, and the tubes sealed off the line. They were then attached to the apparatus shown in Fig. 6 as needed.

PART 2. THE REPLACEMENT REACTIONS

Since there are definite quantitative differences in the absorption spectra of any two metalloporphins, the progress of any replacement reaction can be followed by observing changes in the absorption spectrum of the reaction mixture. This was the method employed in all these experiments.

(9) Ball, Dorough and Calvin, THIS JOURNAL, 68, 2278 (1946).

Experiments 1, 4, 5, 6 and 7 were carried out as follows: On the vacuum line, the alkali metalloporphin desired was prepared from PH_2 and the corresponding alkali methylate in a manner analogous to the preparation of PNa_2 given in the preceding section. It was collected in pyridine solution in a cuvette which had a side tube containing the dried alkali iodide which was to be used in the attempted replacement. The cuvette was sealed off the line, and a quantitative curve was run on the Beckman from 7000 to 4500 Å. for the original alkali metalloporphin. The solution was then poured over into the side tube and allowed to mix with the alkali iodide. It was then poured back into the cuvette and the spectral curve run again.

Experiments 2, 3, 8, 10 through 14, and 16 through 18 were run in the open air by treating a dry pyridine solution of the metalloporphin with the appropriate inorganic salt. The reaction mixture was spectrally compared with solutions of the original metalloporphin and the metalloporphin that could have been formed to determine if replacement took place. The comparison was made on a Bausch and Lomb visual spectrophotometer. All metalloporphins were prepared by heating PH_2 with the acetate of the appropriate metal in either pyridine or glacial acetic acid. Benzene was then added, and the excess inorganic salt and the pyridine or acetic acid washed out by repeated extractions with water. The benzene solution was dried over anhydrous sodium sulfate, and the solution taken to dryness under vacuum. The metalloporphin was then taken up in dry pyridine for the replacement experiment.

Experiments 9 and 15 were conducted in the open air. The lithium salt was prepared by the addition of excess lithium methylate to a pyridine solution of free base. Such a solution is stable toward hydrolysis on a dry day for considerable periods of time if the lithium methylate is in appreciable excess. Dry zinc or mercuric acetate was then added, and complete replacement was observed as noted in Table I.

Summary

1. The metalloporphins derived from the smaller divalent metals are in general quite resistant to hydrolysis, show marked similarities in spectra, and undergo no known exchange reactions with isotopes of the same metal. Replacement reactions are possible, however; this has been demonstrated by the conversion of zinc tetraphenylporphin to copper tetraphenylporphin by prolonged heating with copper acetate.

2. The metalloporphins derived from the large divalent metals such as lead or mercury are less resistant to hydrolysis, differ in spectra from those of the smaller divalent metals, and undergo replacement reactions as follows: Lead or mercury in a metalloporphin is replaced quantitatively by a smaller divalent metal such as zinc or copper, and the larger lead ion in a metalloporphin is replaced by the smaller mercuric ion. Even with a large excess of inorganic metal ion, none of these replacements proceed in the reverse direction.

3. The porphin salts of the alkali metals are readily hydrolyzed by water, exhibit spectra in the case of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin somewhat similar to lead and mercury, and undergo replacement reactions as follows: The alkali metal ions in an alkali metalloporphin are rapidly and completely replaced by a small divalent, a large divalent, or a smaller alkali metal ion. Even with a large excess of inorganic metal ion, none of these replacements proceed in the reverse direction.

4. Complete equilibration of the activity in a pyridine solution of sodium iodide and disodium[22] tetraphenylporphin is observed at room temperature in less than six minutes.

ST. LOUIS, MISSOURI RECEIVED NOVEMBER 9, 1949

CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Quantitative Recovery of Carbon Dioxide in Lead Tetraacetate Oxidations of Sugars and Sugar Derivatives

BY SAMUEL ABRAHAM[1]

The selective cleavage of the weakened connecting bond of a 1,2 glycol can be accomplished with the use of either lead tetraacetate in glacial acetic acid[2a] or of periodate in aqueous solution[2b] The action of these two oxidizing agents on such glycols, by breaking the bond between the two hydroxyl-carrying carbon atoms and removing the hydroxyl hydrogens, produces the same carbonyl products.

Criegee,[2] in his original investigation, emphasized the use of dry organic solvents when lead tetraacetate is employed. However, Fischer[3] showed that the rate of hydrolysis of the oxidizing agent in water is much slower than the rate of oxidation of certain glycol compounds and that it is therefore possible to oxidize these substances with lead tetraacetate in the presence of water.

In the case of compounds which contain three adjacent hydroxyl groups, the reaction with two moles of periodate or two moles of lead tetraacetate will yield the corresponding aldehyde or ketone with the middle carbon splitting out as formic acid. Upon treatment with a third mole of lead tetraacetate in aqueous media, the formic acid formed is further oxidized to carbon dioxide.[4] No such reaction has been reported in the case of periodate oxidations.

Rate studies made on this oxidation by lead tetraacetate have shown that all the glycosides

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(2) (a) R. Criegee, *Ann.*, **481**, 275 (1939); *Ber.*, **64**, 260 (1931); *Agew. Chem.*, **50**, 153 (1937); (b) L. Malaprade, *Compt. rend.*, **186**, 382 (1927).

(3) E. Baer, J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607 (1939).

(4) J. M. Grosheintz, *ibid.*, **61**, 3379 (1939).