temperature. The spectral behavior of alpha with changing temperature is therefore indicative of a tetrahydroporphine structure.

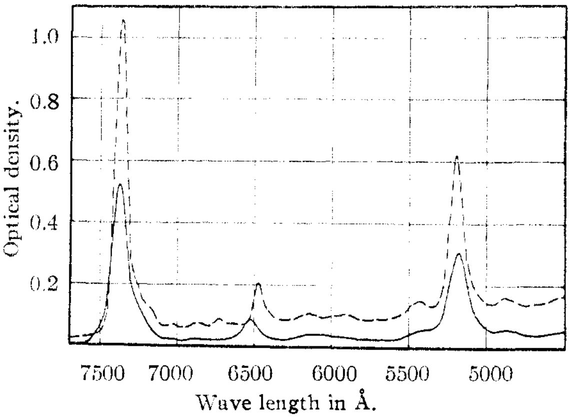

Fig. 4.—Spectra of alpha free base at different temperatures: solid line, room temperature; dotted line, liquid nitrogen temperature. (Uncorrected for contraction of solvent. The factor is 0.76. Notice that the peak at 6500 Å., which is due to a small amount of chlorin impurity, shifts with temperature. The solvent for this experiment was an ether, isopentane, alcohol mixture in the ratio of 5:5:2.)

To summarize, alpha has a spectrum like that of a known tetrahydroporphin, is at a reduction level more reduced than a chlorin, can be oxidized to the chlorin by a reagent which attacks saturated pyrrole rings in reduced porphyrins, and possesses chemical and physical properties either recorded for or to be expected of tetrahydroporphines. Alpha therefore appears to be a tetraphenyltetrahydroporphine.

A complete identification of alpha would require some type of quantitative analysis which would show that it possessed two more hydrogens than tetraphenylchlorin, and some sort of information which would permit one to place the extra hydrogens on either adjacent or opposite pyrroles. We have no information which could be considered to meet the latter requirement, other than the somewhat tenuous evidence that bacteriochlorophyll is reduced on opposite pyrroles, and that alpha is spectrally similar to bacteriochlorophyll. (The spectral characteristics of a tetrahydroporphine with adjacently reduced pyrroles are unknown.) The former requirement might be met by the usual analysis for the percentage of the elements, although the C and H values of tetraphenyltetrahydroporphin do not differ very much from those of the corresponding chlorin. (For tetraphenylchlorin: C, 85.68; H, 5.24. For tetraphenyltetrahydroporphin: C, 85.41; H, 5.54.) However, since alpha is obtainable in only very low yields from a starting product which itself is not too readily available, we were not able to procure enough alpha for a conventional microanalysis. Several attempts were made to follow the reaction of 1,2-naphthoquinone and alpha quantitatively on a 15–30 microgram scale, the assumption being that if a 1:1 ratio of alpha reacted to naphthoquinone used could be demonstrated, this would be strong evidence that alpha was a tetrahydroporphine. The experiments were not successful due to difficulties involved with oxygen removal and quinone volatility.

The identification of beta has proven to be very elusive. Like alpha, beta may be photoöxidized to tetraphenylchlorin with 1,2-naphthoquinone, which would suggest that beta might also be a tetrahydroporphine (*e.g.*, a tetrahydroporphine with adjacent pyrroles reduced is a possibility). However, the other properties of beta such as its spectrum, its ability to form readily acid salts and metallo-derivatives, and the behavior of its spectrum when the temperature is changed are similar to the properties of a chlorin. One possibility is that the catalytic hydrogenation has effected a reduction of a benzene ring to a cyclohexadiene ring to give a compound which would have the properties of a chlorin and yet be more reduced than a chlorin. The absorption spectra of the free base and the zinc derivative of beta are given in Fig. 5. The molar extinction coefficient of the free base was calculated from a quinone oxidation experiment on the assumption that one mole of chlorin is formed for each mole of beta oxidized. The value was 29,000 at 5910 Å. in benzene solution at room temperature.

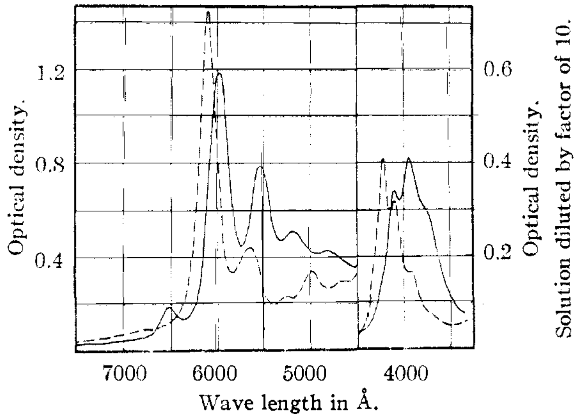

Fig. 5.—Absorption spectra in benzene: dotted line, zinc-derivative of beta; solid line, beta free base. The small peak at about 6500 Å. is due to chlorin impurity.

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The Diffusion Coefficient of Cupric Glycinate

BY ROBERT B. DEAN[1] AND HENN SOONPÄÄ[2]

RECEIVED AUGUST 5, 1952

Cupric glycinate is one of the few non-ionic water-soluble colored molecules. Since it showed promise as a colorimetric standard for calibrating diffusion cells we have determined the diffusion coefficient, D, in sintered glass diffusion cells[3] using KCl as a standard.[4] The membrane surfaces were stirred by magnetic stirrers encased in polythene. The denser solution was on top to facilitate stirring of the more remote parts of the cells.

(1) Borden Co., Chemical Division, Bainbridge, N. Y.

(2) Based on material in the thesis of Henn Soonpää filed in the University of Oregon Library; M.S., 1953.

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Cupric (di) glycinate was prepared from glycine and a small excess of freshly precipitated and washed basic cupric carbonate. It was purified by repeated crystallization from water and obtained as the monohydrate. The solutions were analyzed on a Beckman spectrophotometer. The composition of the crystals was determined by iodometric titration for copper. At 25° the solubility was 0.0364 *M* and the molar extinction coefficient at 6300 Å. was 46. The molar conductivity was 2.8×10^{-6} mho $cm.^{-1}$ indicating very slight dissociation into ions.

Values of *D* obtained at 0.00917 *M* and 0.0274 *M* were not significantly different and the pooled results gave a normal cumulative probability distribution. The mean value of *D* at 25.0 was $0.723 \pm 0.004 \times 10^{-5}$ $cm.^2$ $sec.^{-1}$. The indicated error is the 95% confidence range for the mean.[5] The molar volume was found from density measurements to be 100.4 $cm.^3$ and independent of concentration. *D* calculated from the Einstein–Sutherland equation assuming a sphere is 0.717×10^{-5}. If approximate corrections for departures from a spherical shape are applied *D* is calculated to be 0.67×10^{-7}.[6]

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The Distribution of the Subgroup VII Elements between Pyridine and 4 *N* NaOH[1]

BY W. GOISHI[2] AND W. F. LIBBY

RECEIVED JULY 28, 1952

In the course of studies directed toward the development of a new method for isolating technetium activities from meson irradiated silver samples, extraction from basic media with pyridine was attempted. It appeared reasonable to try this in view of the fact that permanganate has been found to be extractable under these conditions.[3] A preliminary experiment with carrier-free $NH_4Tc^{99}O_4$ indeed showed that pyridine extracted pertechnetate almost quantitatively from 4 *N* NaOH. The following is a report of the results of the distribution measurements which were made. The distribution of +7 rhenium and of +7 manganese between the same liquids was also studied.

Experimental

Perrhenate.—Measured volumes of 4 *N* NaOH containing known amounts of NH_4ReO_4 were equilibrated with measured volumes of pyridine saturated with 4 *N* NaOH. The layers were analyzed by acidifying to about 4 *N* with HCl, heating almost to boiling, precipitating Re_2S_7 by passing in hydrogen sulfide,[4] dissolving the collected precipitate in a 1:1 mixture of 6 *N* NaOH and 30% H_2O_2, and gravimetrically determining the amount of rhenium by conversion to the tetraphenylarsonium derivative.[5] In each case the sulfide precipitation was repeated on the filtrate from the first sulfide precipitation after first diluting with 4 *N* HCl, until no more sulfide was precipitated.

Technetium.—Carrier-free $NH_4Tc^{99}O_4$ solutions were extracted with pyridine exactly as in the perrhenate extractions. Measured volumes of standardized NH_4ReO_4 solution were added to the separated layers and the sulfide precipitated[6] and determined as the tetraphenylarsonium derivative as before. The tetraphenylarsonium perrhenate precipitates carrying the pertechnetate[7] were measured with a Geiger counter for their Tc^{99} content.

Manganese.—A small measured volume of a freshly prepared dilute solution of $KMnO_4$ was poured into a centrifuge bottle containing some pyridine. After shaking for a few seconds 4 *N* NaOH was poured into the bottle, the mixture again shaken for a few seconds and then immediately centrifuged to hasten the separation of the layers. Speed was essential to minimize the decomposition of the permanganate to form the green manganate. The alkaline layer was siphoned off and a measured portion of it was reextracted with a measured volume of pyridine. A measured volume of the first pyridine extract was diluted with pyridine until a color match was obtained visually between the diluted solution and the second pyridine solution with the two solutions in long test-tubes filled to the same depth.

The results obtained are summarized in Table I.

TABLE I

DISTRIBUTION BETWEEN PYRIDINE AND 4 *N* NaOH

Element, M	Distribution coefficient, $\frac{[M]_{Py}}{[M]_{aq}}$	$[M]_{Py}$, (mg. of M/ml.)
Re	255	3.8
	195	7.4
	130	12.8
	30	13.5
Tc	778	3.8×10^{-5}
Mn	8000	5

It is clear from Table I that all the subgroup VII elements in their heptavalent states are extractable into pyridine from strongly alkaline aqueous solution.

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[1] This research was supported in part by the Office of Scientific Research of the Air Research and Development Command of the U. S. Air Force.

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Polarographic Behavior of Organic Compounds. XIII. Chloroacetic Acids and their Ethyl Esters. *p*H-Independence of Carbon–Halogen Bond Fission. Wave Splitting Due to Buffer Interaction

BY PHILIP J. ELVING* AND CHING-SIANG TANG

RECEIVED NOVEMBER 20, 1951

In view of the S-shaped relation between *p*H and $E_{1/2}$ for the polarographic reduction of acids of various types[1,2] including those involving carbon–halogen bond fission, the related system of acid–

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