



Fig. 1—Ultracentrifugal flotation patterns of a rabbit lipoprotein fraction before and after dialysis: A, original isolated lipoprotein; C, a portion of the original after dialysis for one week at 0–4° against a large volume of saline solution (density, 1.063) which contained 0.05% of material extracted from bovine serum; D, a second portion of the original after an identical dialysis against saline alone. The degradative changes are partially complete in D. Continued dialysis leads to extensive degradation as illustrated in B, whereas, the stabilized portion continues to be unchanged. (B refers to a different original fraction than that in A, C, and D, but the result shown is typical of all fractions.) Runs were made with a Spinco Ultracentrifuge using the double cell technique. Conditions: 22–26°; speed, 52,640 rpm.; medium density, 1.063; inclined slit angle, 45°; exposures, from left to right, at 8 min. intervals; acceleration time, 7 min.; first exposure, 4 min. after reaching maximum speed. The menisci are on the left of each pattern, thus the lipoprotein components are moving from right to left against the centrifugal field.

At one stage there would appear a complex of lower lipid content, of reduced size and changed character, for example, S_f 5–9 lipoprotein. This concept emphasizes that the pathogenesis of the atheromatous lesion is the result, not of the presence of "abnormal" lipoproteins, but of the errant breakdown of lipoproteins in general.

The stabilizing material is obtained as follows. The serum from fresh bovine blood is lyophilized and then extracted several times with glacial acetic acid. The combined extract is diluted with five parts of ether. Concentrated hydrochloric acid is added until no further precipitate forms. The tannish precipitate is filtered, washed with ether, dried, extracted with water, and finally lyophilized. Approximately 12 g. of white solid material is obtained from 4 l. of serum and as little as 0.05% added to saline will completely stabilize lipoproteins in our dialysis experiments. Heparin, as well as a number of other substances tested, does not possess stabilizing ability. This is of interest in view of the profound *in vivo* effect of heparin upon the lipoprotein picture and poses the question as to what relation our stabilizing factor may have to the "clearing factor" of Anfinsen,⁴ to the "active principle" of Graham,⁵ or to the "cofactor" of Snellman.⁶

Work is continuing toward the further isolation

(4) C. B. Anfinsen, E. Boyle and R. K. Brown, *Science*, **115**, 583 (1952).

(5) D. M. Graham, T. P. Lyon, J. W. Gofman, H. B. Jones, A. Yankley, J. Simonton and S. White, *Circulation*, **4**, 666 (1951).

(6) O. Snellman, B. Sylvén and C. Julén, *Biochim. Biophys. Acta*, **7**, 98 (1951).

and identification of the factor. Also the bearing these findings may have upon experimental atherosclerosis in the rabbit is being investigated.

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CHLOROPHYLL PHOTOSENSITIZED POLYMERIZATION AND FREE RADICAL INTERMEDIATES IN PHOTOSYNTHESIS

Sir:

We are interested in the question whether and what free radical intermediates occur in the process of photosynthesis and chlorophyll photosensitized reactions. We are also interested in efficient methods of photosensitized polymerization and their reaction kinetics. With these aims in view, photochemical experiments were carried out in the presence of a vinyl monomer (methyl methacrylate) and (a) chlorophyll in various solvents, (b) isolated chloroplast suspensions and (c) photosynthesizing algae. In the latter case some evidence suggesting free radical intermediates has been obtained but further investigation, including tracer experiments with $C^{14}O_2$, is in progress. Results with isolated chloroplast suspensions have been negative so far. Some more detail is cited of results observed with chlorophyll. The now generally adopted standard method developed by Zscheile and Comar was used for its preparation from spinach leaves. After we assured ourselves that pure chlorophyll a and chlorophyll b lead to similar results, we used a purified mixture of the two (although even crude spinach extracts were active). The solutions were deoxygenated by passing a stream of nitrogen through the mixture before irradiation. Ultra-violet and most of the visible light were filtered off so that practically only red light passed through the reaction mixture. The final concentration of chlorophyll was approximately 0.2 g./l. ($\sim 2 \times 10^{-4} M$). While in preliminary tests a number of monomers were applied, most experiments were carried out with methyl methacrylate.

This is a brief summary of results: in pure methyl methacrylate as well as in solutions of 10% methyl methacrylate in ethyl alcohol (polymer insoluble) and in pyridine, polymerization was observed in the absence of oxygen. The rate increased with time due to catalysis by dead polymer. Quantum yields in the initial stages were considerably below unity. Average molecular weights were of the order of magnitude of 10^5 . No polymerization was obtained when acetone or benzene were used as solvents (in the absence of other substances). Ferrous sulfate and ferrocyanides were found to inhibit polymerization. On the other hand, the rate of polymerization could be enormously increased in the presence of some organic reducing substances such as ascorbic acid and thiourea in pyridine and alcohol solutions and also in pure methacrylate. When all blank tests were taken into account, it was found that the quantum yield of monomer consumption in the system methyl methacrylate-chlorophyll ($\sim 2 \times 10^{-4} M$)-ascorbic

acid ($10^{-2} M$) or thiourea ($10^{-2} M$)—red light was over one hundred. No polymerization occurred in the presence of oxygen.

It is felt that these systems might be of practical importance in the preparation of polymers and also help to elucidate some of the difficult problems in the photochemistry of chlorophyll, such as the nature of reversible bleaching.

A more detailed account of this work will be published when it is more complete.

The photosynthesis studies were aided by a contract between the Office of Naval Research, Department of the Navy, and the University of Chicago (NR 119-272).

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A NEW SUB-CHLORIDE OF BORON, B_4Cl_4

Sir:

In the spontaneous decomposition of tetrachlorodiborane (B_2Cl_4) at 0° , as well as in its preparation by the procedure of Wartik, Moore and Schlesinger (THIS JOURNAL, 71, 3265 (1949)), very small quantities of volatile, yellowish crystals are obtained by evaporation of the tetrachlorodiborane. Although the decomposition of tetrachlorodiborane is accelerated somewhat by rise in temperature or by exposure to ultraviolet radiation, no significant improvement in yield has been achieved thereby.

The formula, B_4Cl_4 , was established for the crystals by analysis of a 0.057 g. sample (24.2% B and 78.9% Cl) and by vapor density measurements, made at 65° and giving a molecular weight of 188 (average of two determinations at 17.9 and 30.1 mm., respectively). Vapor tensions are as follows:

t°	23.0	30.0	40.8	52.4	57.4	67.7
$p_{mm. obs.}$	1.60	3.15	7.05	13.0	17.7	34.3
$p_{mm. calcd.}$	1.94	3.16	6.42	13.2	17.8	31.2

The calculated values were obtained from the equation

$$\log_{10} p_{mm.} = -2719/T + 9.464$$

The very small quantities of the compound thus far accumulated have limited investigation of its chemical properties to exploratory experiments,

which have disclosed striking differences in the properties of the two sub-chlorides. Both inflame spontaneously in air, but the reaction of B_4Cl_4 is so much more vigorous that the inflammability of tetrachlorodiborane may be due to unavoidable traces of B_4Cl_4 . In the absence of air, the former decomposes moderately rapidly at 0° ; B_4Cl_4 , even at 70° , undergoes no appreciable decomposition.

Tetrachlorodiborane reacts very rapidly with hydrogen even considerably below 0° to give chiefly boron trichloride and diborane; B_4Cl_4 does not react with hydrogen or does so only very incompletely. Tetrachlorodiborane, with alkylating agents such as alkyls of boron, aluminum or zinc, produces non-volatile black solids presumably impure boron; B_4Cl_4 does not react with trimethyl boron at temperatures up to -10° , but with trimethyl aluminum produces colorless, volatile liquid and solid materials, which may be methyl derivatives of B_4Cl_4 since they give decomposition products similar to those of the latter. These products have not yet been obtained in quantities or purity adequate for identification.

Methanol converts tetrachlorodiborane to tetramethoxydiborane and generates hydrogen chloride, but no hydrogen; with B_4Cl_4 , methanol produces no hydrogen chloride but generates 6 gram equivalents of hydrogen per mole of B_4Cl_4 . With 6 moles of methanol per mole of B_4Cl_4 , the major other volatile product appears to be methyl chloride, though identification of the latter is still incomplete. A white solid is also observed. With excess methanol, the major products appear to be methyl chloride, the methanol-methyl borate azeotrope and the 6 gram equivalents of hydrogen.

The liberation of 6 gram equivalents of hydrogen per mole of B_4Cl_4 suggests that the latter contains 6 equivalent boron to boron bonds, as would be the case if the boron atoms were situated at the corners of a tetrahedron and were each associated with one chlorine atom. This supposition is in agreement with results of X-ray diffraction, communicated to us by Professor W. N. Lipscomb in advance of publication.

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BOOK REVIEWS

Thermodynamics of Alloys. By JOHN LUMSDEN, Research Department, Imperial Smelting Corporation, Ltd., Avonmouth. The Institute of Metals, 4 Grosvenor Gardens, London, S. W. 1, England. 1952. xv + 384 pp. 15 × 22.5 cm. Price, \$5.50.

This book will undoubtedly be welcomed by many metallurgical departments since it presents under one cover much material that has never before been set together in form suitable for the metallurgist or metallurgical chemist. The chemistry or science of metals is a field which has too long been neglected not only by authors and publishers but even by the American Chemical Society which has no division for this science. Any reasonably meritorious contri-

bution to this field must be gratefully received. The present work (not to be confused with an excellent recent book of identical title by Carl Wagner) cannot, in this reviewer's opinion, be classed as that of genius—and certainly cannot be classed as that of a hack rewrite.

The dust jacket claims that "The theory is developed from first principles with the mathematics kept as simple as possible. . . ." As pertaining to elementary chemical thermodynamics this optimistic viewpoint is not shared by your reviewer who notes that after many pages bristling with equations sufficient to thoroughly discourage the beginner, temperature is finally defined on p. 36 by the relation $(\partial\rho/\partial E)_V = 1/kT$; and later on p. 42 pressure is defined by the relation $(\partial E/\partial V)_S = -P$. In fact we are told that "Tem-