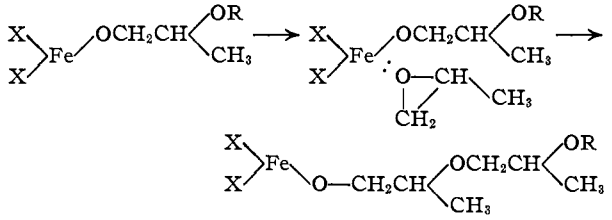
amorphous polymer evidently occurs during polymerization since monomer recovered from a polymerization experiment after two days at 80° had lost no optical activity.

We ascribe the difference in melting point between the crystalline polymers prepared by the two catalysts to the great difference in molecular weight, since the optical rotations, infrared spectra and X-ray spacings for the two materials were identical. The principal X-ray diffraction lines at 4.25 and 5.20 Å. and the density (1.03) are consistent with a model involving a compressed *trans* zig-zag chain.

These observations further support the accumulating evidence[4] that the configuration of the asymmetric centers along a polymer chain have a remarkable influence on the physical properties and that polymerization catalysts can exert a remarkable degree of steric control on the configuration of these asymmetric centers.

The fact that amorphous polypropylene oxide of random configuration and crystalline polymer with all centers of the same configuration are formed simultaneously suggests that two different catalyst sites are present. We believe that this high degree of steric selectivity may be accounted for by a mechanism of the following type.



If the iron atom of this alcoholate were at solid surface, the steric requirements for the intermediate coördination might be rigid enough to produce oriented polymer. A soluble catalyst of similar structure might be responsible for the amorphous polymer.

(4) C. E. Schildknecht, S. T. Gross and A. O. Zoss, *Ind. Eng. Chem.*, **41**, 1998 (1949); H. Staudinger, "Hochmolekulare organische Verbindungen," Springer, Berlin, 1932, p. 295; G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); C. W. Bunn and E. R. Howells, *ibid.*, **18**, 307 (1955).

CHARLES C. PRICE
DEPARTMENT OF CHEMISTRY MASEH OSGAN
UNIVERSITY OF PENNSYLVANIA ROBERT E. HUGHES
PHILADELPHIA 4, PA. CHARLES SHAMBELAN

RECEIVED DECEMBER 21, 1955

THERMO-OSMOSIS OF RARE GASES THROUGH A RUBBER MEMBRANE[1]

Sir:

Using an apparatus similar to the "membrane assembly B" of Denbigh and Raumann[2] we have observed the thermo-osmosis through a rubber membrane of carbon dioxide and of all the rare gases except radon, and have calculated from the experimental data the heats of transfer Q^* and the permeabilities p. The calculation of p was carried out by the method of Denbigh and Raumann.[3] Table I shows our results along with the few other comparable results that we have found in the literature.

TABLE I

Gas	Run	T, mean, °C.	Q^* 10^2 cal./mole	p (Pres. exp.), 10^{-8} cm.²/sec.-atm.	p (lit.) 10^{-8} cm.²/sec.-atm.
CO_2	1	33.0	− 9.8		
			−18.6[3]		
He	2	34.0	+11.2	33.7	33 (at 35°)[5]
	3	34.0	+11.4	53.4[4]	17 (at 25°)[6]
Ne	4	34.5	+ 9.0	8.6	
A	5	34.5	− 0.6		
	6–7			22.0	
	7	34.5	+ 0.3		
Kr	8	34.5	− 1.7	48.4[4]	
Xe	9	34.5	− 3.2	73.5[4]	33 (at 25°)

The principal difference between our method and that of Denbigh and Raumann is that we read the temperatures at the two sides of the rubber membrane directly from two thermocouples whose "hot" junctions were respectively flush with the two surfaces of porous bronze adjacent to the rubber membrane, whereas the authors mentioned used thermocouple junctions imbedded in the porous bronze and found the surface temperatures by extrapolation. Either method would seem to be subject to systematic errors. From the first of our runs to the last, we left the membrane assembly undisturbed save for the degassing and admission of gas involved in changing from one gas to the next. Because of this, the systematic errors were probably the same in all of our runs, and we therefore believe that our values of Q^* and p are rather better relatively than absolutely. Our value of p for helium agrees satisfactorily with that of Van Amerongen, and the differences between our values and those of Norton, for helium and xenon, we attribute to the differences of temperature.[7]

(1) This paper is based upon the dissertation submitted by R. J. B. to Stanford University in partial fulfillment of the requirement for the Ph.D.

(2) K. G. Denbigh and G. Raumann, *Proc. Roy. Soc.* (*London*), **A210**, 518 (1952).

(3) K. G. Denbigh and G. Raumann, *ibid.*, **A210**, 377 (1952).

(4) These permeabilities are based on fewer data than our others.

(5) G. J. van Amerongen, *J. Applied Phys.*, **17**, 972 (1946).

(6) F. T. Norton, *J. Chem. Phys.*, **22**, 1145 (1954).

(7) Details of our experimental work, together with an account of the theory, are given in the dissertation mentioned in Footnote (1), and will be published in a later paper. The dissertation itself will be available from University Microfilms, 313 N. First St., Ann Arbor, Mich.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY RICHARD J. BEARMAN
CALIFORNIA FREDERICK O. KOENIG

RECEIVED NOVEMBER 10, 1955

REDUCED UROPORPHYRIN III IN THE BIOSYNTHESIS OF HEME[1]

Sir:

The role of uroporphyrin and coproporphyrin in heme biosynthesis, although long a matter of speculation, is now becoming clearer. Rimington[2] has recently suggested that these tetrapyrroles actually are not in the main pathway of heme biosynthesis, but rather are oxidation products of heme precursors, or porphyrinogens. In addition,

(1) Aided by a grant from the Dazian Foundation.

(2) C. Rimington, *Endeavour*, XIV (55), 126 (1955).

Shemin, *et al.*,[3] have postulated how a reduced tetrapyrrole of the type III configuration might be formed by the coupling of two dipyrroles arising from porphobilinogen. Confirmatory evidence is noted in the work of Bogorad[4] and Granick,[5] who have found colorless intermediates between porphobilinogen and protoporphyrin which undergo autoxidation to uroporphyrin and coproporphyrin.

We have isolated uroporphyrin III from Turacus feathers according to Nicholas and Rimington.[6] The uroporphyrin was then reduced with sodium amalgam by a modification of Fischer's method.[7] This reduction results in the addition of hydrogen atoms to the four methene bridge carbon atoms and two of the pyrrole nitrogen atoms. The colorless non-fluorescent product reoxidized in air to uroporphyrin, which was identified by its absorption spectrum.

This reduced uroporphyrin III (RUP) in a lysed duck erythrocyte system[8] was found after incubation to increase the levels of free uroporphyrin, coproporphyrin, and protoporphyrin. Under similar conditions but with added Fe^{59}, RUP also significantly increased the radioactivity of the hemin,[9] indicating increased biosynthesis (Table I). Lowered Fe^{59} uptake found with the higher concentrations of RUP may be due to an inhibitor resulting either from a side reaction in the reduction process,[10] or from an impurity accompanying the uroporphyrin during its isolation.[6] Inhibition due to the RUP preparation was never seen below 0.30 μ mole. No increased labelling of the hemin with Fe^{59} was noted in samples incubated with uroporphyrins I or III or with reduced uroporphyrin I.

TABLE I

Fe^{59} INCORPORATION INTO HEME WITH ADDED RUP

Experiment	RUP added (μmole)	CPM (hemin)[9]
I	0	1680
	0.044	2580
	.088	4120
	.176	8720
II		1870
	.10	6000
	.20	7100
	.30	18000
	.40	7500
	.60	4730
	.80	1950
	1.00	1080

Experimental conditions: washed duck erythrocytes lysed with 1.5 vol. dist. H_2O,[8] made isotonic with sucrose, and 20 ml. used per sample. Incubation 9 hr. at room temp. with shaking; 1 μc Fe^{59} added per sample. Radioactivity of hemin in KOH solution determined with scintillation well counter.

(3) D. Shemin, C. S. Russel and T. Abramsky, *J. Biol. Chem.*, **215**, 613 (1955).

(4) L. Bogorad, *Science*, **121**, 878 (1955).

(5) S. Granick, Absts. 128th Meeting, Am. Chem. Soc., p. 69C (Sept. 1955).

(6) R. E. H. Nicholas and C. Rimington, *Biochem. J.*, **50**, 194 (1951).

(7) H. Fischer, F. Rose and E. Bartholomaus, *Z. physiol. Chem.*, **84**, 262 (1913).

(8) D. Shemin and S. Kumin, *J. Biol. Chem.*, **198**, 827 (1952).

(9) Homogeneity of tbe hemin was indicated by constancy of specific activity on repeated recrystallizations.

(10) R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, New York, N. Y., 1949, p. 78.

In order to determine whether RUP is a direct intermediate in heme biosynthesis, an isotope dilution experiment was carried out using glycine-2-C^{14}, a known precursor of heme. Data in Table II show the markedly reduced glycine incorporation in the presence of RUP, a finding of particular importance in view of the small amount added. Since inhibition has never been noted at these substrate levels, the RUP appears to have diluted the labelled glycine and therefore to be in the main pathway of heme biosynthesis. Preliminary data indicate that reduced coproporphyrin III similarly serves as a heme precursor, but less effectively than RUP.

TABLE II

GLYCINE-2-C^{14} DILUTION BY RUP

RUP added	CPM (hemin)
None	82
0.15 μmole	50
.22 μmole	40
.29 μmole	37

27 μmole (1.3 μc.) glycine-2-C^{14} per sample. Experimental conditions: Table I. C^{14} activity determined with end window counter; values corrected to infinite thickness of hemin.

DEPARTMENTS OF BIOCHEMISTRY AND PEDIATRICS, UNIVERSITY OF OREGON MEDICAL SCHOOL, PORTLAND, OREGON
RICHARD A. NEVE
ROBERT F. LABBE
ROBERT A. ALDRICH

RECEIVED NOVEMBER 28, 1955

XYLULOSE 5-PHOSPHATE AND THE FORMATION OF SEDOHEPTULOSE 7-PHOSPHATE WITH LIVER TRANSKETOLASE

Sir:

Mitsuhashi and Lampen,[1] Hochster,[2] and Slein[3] have obtained evidence for a phosphate ester of D-xylulose as an intermediate in the metabolism of D-xylose in bacterial extracts. The first isolation of xylulose phosphate was that of Ashwell and Hickman,[4] who found this product to be formed when ribose 5-phosphate was incubated with spleen extracts and obtained evidence for a new enzyme which was responsible for its appearance.

The formation of xylulose phosphate now can be represented by the equation

Ribulose 5-phosphate (Ru-5-P) $\rightleftarrows$ xylulose 5-phosphate (Xu-5-P)

This enzyme occurs in extracts of *Lactobacillus pentosus*,[5] muscle,[6,7] spleen,[8] and spinach, and has been named phosphoketopentoepimerase (epimerase). Epimerase has been purified more than 100-fold from extracts of *L. pentosus* by a procedure involving manganous salt precipitation, ammonium sulfate fractionation, selective heat denaturation, and calcium phosphate gel adsorption. The

(1) S. Mitsuhashi and J. O. Lampen, *J. Biol. Chem.*, **204**, 1011 (1953).

(2) R. M. Hochster, *Canad. J. Microbiol.*, **1**, 346 (1955).

(3) M. W. Slein, THIS JOURNAL, **77**, 1663 (1955).

(4) G. Ashwell and J. Hickman, *ibid.*, **76**, 5889 (1954).

(5) P. K. Stumpf and B. L. Horecker, *J. Biol. Chem.*, in press.

(6) F. Dickens and D. H. Williamson, *Nature*, **176**, 400 (1955).

(7) P. A. Srere, J. Cooper, V. Klybas and E. Racker, *Arch. Biochem. Biophys.*, **59**, 535 (1955).

(8) G. Ashwell and J. Hickman, unpublished work.