treatment of selected substrates with cobalt hydrocarbonyl at atmospheric pressure are compared in Table I with the products secured by reaction of the same substrates under hydroformylation conditions. The experiment at atmospheric pressure with cyclohexene is typical: Cobalt hydrocarbonyl (4.0 g., 0.023 mole) was collected in a liquid-nitrogen trap containing 7.0 g. (0.085 mole) of cyclohexene. On warming, the cobalt hydrocarbonyl dissolved in the olefin without noticeable decomposition. At about 15°, the solution began to darken, a small amount of gas was given off, and a noticeable amount of heat was evolved. Upon addition of 2,4-dinitrophenylhydrazine, the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde was obtained from the reaction mixture; it melted at 167.5–168.3°[4] after one recrystallization from ethanol. The yield of cyclohexanecarboxaldehyde, determined from the weight of hydrazone obtained, was 16 per cent., based on cobalt hydrocarbonyl added.

Further, it has now been found that bases suppress the hydroformylation reaction. Thus, the hydroformylation 'of a mixture of 2,3-dimethylbutene-1 and -2 at 135° and 230 atmospheres of synthesis gas was completely inhibited in the presence of triethylamine. The hydrogenation of benzhydrol, which proceeds readily under the usual hydroformylation conditions,[5] failed to occur when pyridine was used as a solvent.

These results strongly support the hypothesis that cobalt hydrocarbonyl catalyzes the variety of reactions that occur under hydroformylation conditions.

TABLE I

PRODUCTS SECURED FROM VARIOUS SUBSTRATES BY HYDROFORMYLATION AND BY REACTION WITH COBALT HYDROCARBONYL

Substrate	Products	
	Hydroformylation conditions	Cobalt hydrocarbonyl
Cyclohexene	Cyclohexanecarboxaldehyde[a]	Cyclohexanecarboxaldehyde[b]
Hexene-1 (excess)	Heptaldehyde[c]	C_7 aldehydes[d]
	2-Methylhexanal[c]	
	Hexene-2[d]	Hexene-2[d]
	Hexene-3[d]	Hexene-3[d]
	No hexene-1[d]	No hexene-1[d]
α-Methylstyrene	Isopropylbenzene[e]	Isopropylbenzene[f]
	3-Phenylbutyraldehyde[g]	C_{10} aldehyde[d,f]
Benzyl alcohol	Toluene[h]	Toluene[f]
	2-Phenylethanol[h]	
Benzhydrol	Diphenylmethane[h]	Diphenylmethane[d,i]
Triphenylcarbinol	Triphenylmethane[h]	Triphenylmethane[j]

[a] 35% yield. 2,4-Dinitrophenylhydrazone, m.p. 167.5–168.5°; see reference 4. [b] 16% yield. 2,4-Dinitrophenylhydrazone, m.p. 167.5–168.3°; a mixed melting point of the hydrazones from both sources gave no depression. [c] H. Adkins and G. Krsek, THIS JOURNAL, **71**, 3051 (1949). [d] Identified by infrared analysis. We wish to thank Dr. R. A. Friedel for the spectra determinations. [e] 69% yield; $n^{25}\text{D}$ 1.4910. [f] Identified by mass spectrometric analysis. [g] 9% yield. The aldehyde was reduced to the corresponding alcohol; the infrared spectrum of this alcohol was identical with that of an authentic sample. [h] See ref. 5. [i] Reaction run in acetone. Product isolated by chromatographic adsorption on alumina in 33% yield; benzophenone (12%) was present. [j] Reaction run in acetone. Product obtained in 95% yield, m.p. 92–93°, not depressed when mixed with an authentic sample.

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[4] G. Natta, P. Pino and E. Mantica, *Gazz. chim. ital.*, **80**, 680 (1950).

[5] I. Wender, H. Greenfield and M. Orchin, THIS JOURNAL, **73**, 2656 (1951).

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RECEIVED APRIL 14, 1953

SYNTHESIS OF A REVERSIBLY CONTRACTILE AMPHOTERIC POLYPEPTIDE

Sir:

K. H. Meyer[1] has suggested that the contraction and relaxation of muscle may be attributed to the electrostatic attraction and repulsion of the ionized ammonium and/or carboxyl groups in the molecule of myosin. Recently Kuhn, Katchalski and their collaborators[2–6] have synthesized such mechanochemical systems composed of vinyl-type polyanions. Such systems are, of course, very useful and instructive, but the polypeptide-type polyampholyte is more desirable. We have now synthesized a three-dimensional amphoteric polypeptide network, composed of L-glutamic acid, L-lysine and DL-cystine residues and realized its reversible contraction and extension.

A mixture of anhydro-α-N-carboxy-ε-N-carbobenzoxy-L-lysine (8 millimoles), anhydro-α-N-carboxy-γ-benzyl L-glutamate (8 millimoles) and bis-(anhydro-N-carboxy)-DL-cystine (0.4 millimole) was dissolved in dry chlorobenzene–pyridine mixture and polymerized. After being precipitated with petroleum ether, the polymer was obtained quantitatively as a white powder. *Anal.* Calcd. for $[(C_{12}H_{13}NO_3)_{20}(C_{14}H_{18}N_2O_3)_{20}(C_6H_8N_2O_2S_2)_1]_n$: N, 8.8. Found: N, 8.7.

The reduction of this polymer by phosphonium iodide gave the hydriodide of a linear polypeptide consisting of L-glutamic acid, L-lysine and DL-cysteine residues, the amino acid composition of which was approximately the same as that derived from the starting monomer mixture. *Anal.* Calcd. for $[(C_5H_7O_3N)_{20}(C_6H_{12}ON_2\cdot HI)_{20}(C_3H_5ONS)_2]_n$: I, 32.2; N, 10.9; amino-N, 3.54. Found: I, 32.1; N, 10.8; amino-N, 3.46. This polypeptide hydroiodide was soluble in water, methanol and ethanol, and gave positive biuret and nitroprusside reaction.

When the foil, made on the glass plate from its methanolic solution, was soaked in commercial (not purified) ether overnight, it became insoluble in water and colored yellowish brown, due to the liberation of iodine (this color vanished by soaking in very dilute alkali). This insoluble matter is considered to be a network polypeptide in which cysteine residues were converted into cystine ones.

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[1] K. H. Meyer, *Biochem. Z.*, **214**, 253 (1929); *Experientia*, **7**, 361 (1951).

[2] W. Kuhn, B. Hargitay, A. Katchalski and H. Eisenberg, *Nature* **165**, 514 (1950).

[3] A. Katchalski and H. Eisenberg, *ibid.*, **166**, 267 (1950).

[4] W. Kuhn, *Experientia*, **5**, 318 (1949).

[5] A. Katchalski, *ibid.*, **5**, 319 (1949).

[6] J. W. Breitenbach and H. Karlinger, *Monatsh. Chem.*, **80**, 311 (1949).

A piece of this foil, which was swelled (11%) in distilled water, showed strong dilation in dilute acid or alkali and then contracted to its initial length in pure water. This change was isotropic and the linear dilation in 0.01 *N* HCl and 0.01 *N* NaOH was 35 and 45%, respectively.

A piece of metal, attached to the one end of a strip made from the foil, was carried up and down reversibly following the *p*H change of its surrounding medium (Fig. 1).

Its elongation, observed in water and 0.01 *N* HCl, was proportional to the weight of load (observed range of it was up to about 2,000 times the dry weight of the strip per 1 cm. long).

Further studies are required for a quantitative theoretical treatment of these phenomena and the comparison with muscular contraction, though it is clearly demonstrated that this synthetic amphoteric polypeptide network can contract at its isoelectric region and dilate on both the acidic and alkaline sides.

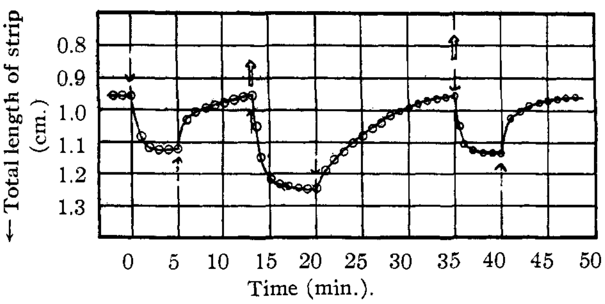

Fig. 1.—Reversible lifting and lowering of a load by a strip of amphoteric polypetide network: weight of dry strip (0.764 × 0.038 × *ca.* 0.003 cm.) 0.065 mg.; weight of load 5.07 mg.; medium 15 ml. 0.005*N* NaCl; ↓, acid (3 ml. 0.01*N* HCl) added; ↑, alkali (3 ml. 0.01*N* NaOH) added; ⇑, 6 ml. medium removed before addition of acid or alkali.

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BOOK REVIEWS

Rocks for Chemists—An Introduction to Petrology for Chemists and Students of Chemistry. By S. JAMES SHAND, Newberry Professor Emeritus of Geology in Columbia University, New York. Pitman Publishing Corporation, 2 West 45th Street, New York 36, N. Y. 1952. xii + 178 pp. 14.5 × 22 cm. Price $4.50.

Solution of the problems of the origin of rocks can come only as experimental work in physics and chemistry is combined with accurate geological field work. Interpretation of field data without the firm foundation of chemical principles properly understood and applied is valueless. One of the chief purposes of *Rocks for Chemists* is the creation of new interest on the part of chemists in the complex problems of the origin of rocks. Since the book is primarily for chemists, one might suppose that it would present important chemical aspects of the origin of all rocks. But this has not been done. More than three-quarters (105 pages) of the short book is devoted to eruptive rocks and their origin. Only 31 pages deal with metamorphic and sedimentary rocks.

A more appropriate title would have been *Eruptive Rocks for Physical Chemists*. Yet the book passes by much of the recent basic work on the physical chemistry of aqueous solutions of rock forming components. Hydrothermal solutions, derived from magmas, are considered in passing only, though these end products of differentiation effect profound changes on the parent and invaded rocks as well as giving rise to most concentrations of metallic ore minerals.

Elsewhere in the field of igneous rock petrology Dr. Shand has presented his own views to the exclusion of other widely held and strongly supported theories with which he does not agree. This is particularly true in his discussion of the origin of granite. Summary dismissal of the ideas of many geologists, who, on the basis of detailed field study, believe in the transformation of certain sedimentary rocks into granites by replacement through ionic diffusion, is hardly justified by the chemical data so far available. More study of ionic diffusion in silicate systems under conditions of high temperature and pressure is necessary.

Dr. Shand claims that sedimentary rocks do not offer as interesting problems as the eruptive rocks. This is the point of view of the igneous rock petrologist. A great number of geologists will disagree. In the pages on sedimentary rocks there is a superficial and even erroneous statement of the chemical aspect of sedimentary rock origin Such statements as "Most limestone begins as a simple accumulation of shells and shell fragments" and "Since no shells are so rich in magnesia as [$CaMg(CO_3)_2$], dolomite must be formed by exchange of bases between calcium carbonate and the magnesian salts held in solution by sea water" show a disregard for the complexities of carbonate rock origin, which is a field of research for intimate coöperation between chemists, biologists and geologists. With regard to the second statement quoted, some dolomites show clear evidence of having undergone base exchange in the presence of circulating ground water and, more locally, hydrothermal solutions. The use of the term *rock flour* with reference to shales is incorrect.

Chemists would be interested in the extremely complex problems in physical chemistry presented by the metamorphic rocks. In view of the carefully analytical studies recently published about these rocks and their origin, the 20 pages devoted to this topic are neither ample nor searching. Moreover, Dr. Shand, after showing that schists are complex equilibrium assemblages, and pointing out the unique place held by garnet because of the interchangeability of various bivalent and trivalent ions in the crystal lattice, says, in the last paragraph of the book, that "in the metamorphism of any rock which contains the components of garnet, that mineral will be formed in preference to others." In his concluding statement he suggests that, rather than indicating grades of intensities of metamorphism, assemblages of metamorphic minerals simply indicate an excess of certain components over the amount which may be incorporated in garnet. This speculation is not justified in view of much recent, careful field observation which clearly shows that metamorphic zones may be traced with great accuracy across lithologic boundaries.

Rocks for Chemists presents a partial statement of the status of petrology of igneous rocks in the light of selected chemical data. The book fails to present the equally important problems of sedimentary and metamorphic rocks. The narrowness of the views presented does injustice to the complicated variety of problems still unsolved and to many chemically minded geologists who, with the same facts and many others not presented, reach opposing conclusions.

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