their salts is made in Table I which gives the concentration of metal in the salt phase of the two-phase equilibrium between liquid metal and liquid salt. The metals chosen for the comparison are those whose cationic radii are approximately equal because it has been shown that for divalent systems the solubility depends on the cationic radius.[5]

TABLE I

Metal	Solubility in mole %	Cationic radius[a] in Å.
K	1[b]	1.33
Sr	20[c]	1.13
Ce	33	1.15[d]

[a] Radii from Pauling "The Nature of the Chemical Bond." [b] Estimated from the data of Mollwo, *Z. Physik*, **85**, 56 (1933), on the solubility of potassium in its solid halides and Rogener, *Ann. Phys. Leipzig*, [5] 29, 386 (1937), on the solubility of potassium in liquid potassium bromide. [c] Estimated from data on other alkaline earth systems, see ref. (5). [d] The radius of trivalent cerium is assumed to be the same as that for trivalent lanthanum.

From Table I it appears that the solubility of a molten metal in its chloride depends upon the charge of the cation of the pure salt. However, this dependence may be a dependence of the solubility upon some property related to the cationic charge. Thus, the significant property may be the ratio of number of cations to number of anions in the salt, which, for a given anion, is proportional to the cationic charge. Additional data would be required to select the property upon which the solubility truly depends.

Summary

The temperature–composition diagram has been determined for the liquid–solid equilibria in the cerium–cerium chloride system. The diagram is similar to those previously reported for some alkaline earth metal–halide systems.

BERKELEY, CALIFORNIA RECEIVED MAY 28, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Quantitative Determination of Amino Acids on Filter Paper Chromatograms by Direct Photometry[1]

BY LOUIS B. ROCKLAND AND MAX S. DUNN

The following types of procedures have been suggested for the determination of amino acids on filter paper chromatograms: (A) elution of the spots before or after staining with a chromogenic agent (such as ninhydrin) and analysis of the elutes,[2–8] (B) modified isotope dilution analysis of the spots with the aid of radioactive tracer amino acids,[9] (C) visual comparison of the color intensities of standard and test sample chromatograms stained with ninhydrin,[2] and (D) direct comparison of spot sizes or color intensities of ninhydrin-stained standard and test-sample chromatograms.[10–14] Amino acid test mixtures have been analyzed by Bull, *et al.*,[11] and Woiwod[3] and protein hydrolyzates by Polson, *et al.*,[2] Martin and Mittlemann,[4] Keston, *et al.*,[9] and Block.[13]

Alanine and glycine have been determined in silk fibroin in the present study by a rapid, direct photometric analysis of color intensities of filter paper chromatograms stained with ninhydrin.

Experimental

Filter paper chromatograms were prepared by the capillary ascent test-tube method of Rockland and Dunn.[15] Ten dilutions, 2×10^{-4} ml. each, of standard containing from 0.625 to 6.250 mg. per ml. of DL-alanine and of glycine were placed on eight replicate strips (10 × 18 × 140 mm.) of Whatman No. 1 filter paper with the aid of a 0.01 ml. total displacement Gilmont ultramicroburet.[16] Similarly, seven dilutions of an acid hydrolysate[17] containing from 3.010 to 12.040 mg. per ml. of silk fibroin (moisture- and ash-free basis) were placed on three replicate strips of the filter paper. The chromatograms were developed simultaneously for three hours at room temperature in 8-inch test tubes containing water saturated phenol, dried for 5 minutes at 100°, sprayed lightly eight times on each side with 0.25% ninhydrin solution in water saturated butanol and heated for five minutes at 100°. The alanine was resolved completely at the seven levels but glycine only at the two lowest levels.

In order to determine the concentrations of the amino acids, the filter paper strips were placed in a special sample holder containing an opening of a size just sufficient to enclose the entire area of the colored spot and the color intensities were read directly with the aid of a photoelectric colorimeter.[19] The alanine and glycine content of silk fibroin were estimated by interpolation from the standard curves drawn from plots of per cent. transmission against concentration of amino acid on coördinate paper.

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(1) Paper 61. For Paper 60, see Murphy and Dunn, *Proc. Soc. Exp. Biol. Med.*, **71**, 241 (1949). This work has been aided by a grant from the National Institutes of Health of the United States Public Health Service. The described chromatographic procedures were presented in a symposium before the Division of Chemical Education at the San Francisco, California, meeting of the American Chemical Society, March 30, 1949. The authors are indebted to Jeremiah C. Blatt for technical assistance.

(2) Polson, Mosley and Wyckoff, *Science*, **105**, 603 (1947).

(3) Woiwod, *Biochem. J.*, **42**, xxviii (1948).

(4) Martin and Mittlemann, *ibid.*, **43**, 23 (1948).

(5) Woiwod, *Nature*, **161**, 169 (1948).

(6) Naftalin, *ibid.*, **161**, 763 (1948).

(7) Awapara, *Archiv. Biochem.*, **19**, 172 (1948).

(8) Awapara, *J. Biol. Chem.*, **178**, 113 (1949).

(9) Keston, Udenfriend and Levy, THIS JOURNAL, **69**, 3151 (1947).

(10) Fischer, Parsons and Morrison, *Nature*, **161**, 764 (1948).

(11) Bull, Hahn and Baptist, THIS JOURNAL, **71**, 550 (1949).

(12) Block, *Science*, **108**, 608 (1948).

(13) Block, *Fed. Proc.*, **8**, 185 (1949).

(14) Fosdick and Blackwell, *Science*, **109**, 313 (1949).

(15) Rockland and Dunn, *ibid.*, **109**, 539 (1949).

(16) Emil Greiner Company, 161 6th Avenue, New York City.

(17) Prepared by Dr. M. N. Camien from the silk fibroin described by Dunn, *et al.*[18]

(18) Dunn, Camien, Rockland, Shankman and Goldberg, *J. Biol. Chem.*, **155**, 591 (1944).

(19) Lumetron, Model 402 EF, manufactured by the Photovolt Corporation, 95 Madison Avenue, New York City.

TABLE I

PERCENTAGES OF ALANINE AND GLYCINE IN SILK FIBROIN[a]

Amino acid			Alanine	Glycine
Analysis of filter paper chromatograms	Indirect photometric, Polson *et al.*[2]		37.6	39.9
	Direct	Visual Polson, *et al.*[2]	34.0	42.4
		Photometric, authors	34.9	43.4
Selective pptn., Bergmann and Niemann,[21]			26.4	43.8
Microbiological, Shankman, *et al.*[20]			..	43.6

[a] Corrected for moisture and ash.

The data obtained for glycine and alanine in silk fibroin are given in Table I. It may be noted that the value (43.4%) found for glycine in silk fibroin is in good agreement with the values (39.9 to 43.8%) reported by earlier workers who used microbiological,[20] selective precipitation[21] and analogous photometric-chromatographic[2] procedures. Although the value 34.9% found for alanine is in good agreement with the values, 34.0 and 37.6%, reported by Polson, *et al.*,[2] it is much higher than the value of 26.4%, obtained by Bergmann and Niemann.[21]

Summary

A method has been described for the quantitative determination of amino acids on filter paper chromatograms by direct photometry. It has been found by this method that silk fibroin contained 43.4 per cent. of glycine and 34.9 per cent. of alanine. These values are in good agreement with others given in the literature.

(20) Shankman, Camien and Dunn, *J. Biol. Chem.*, **168**, 51 (1947).

(21) Bergmann and Niemann, *ibid.*, **122**, 577 (1937-1938).

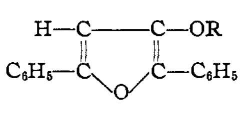
RECEIVED MAY 4, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

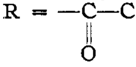
The Transetherification of 3-Alkoxy-2,5-diphenylfurans[1]

BY PHILIP S. BAILEY AND JOHN D. CHRISTIAN

The conversions of 3-methoxy- and 3-ethoxy-2,5-diphenylfurans (I), one into the other, in solutions of the opposite alcohol, triethylamine hydrochloride and a trace of hydrogen chloride was reported in an earlier paper.[2] In the present paper is described a further study of this reaction which might be termed a transetherification[1b] by comparison to the corresponding transesterification reaction which esters undergo. Both employ an acid catalyst and both involve the displacement of an alkoxy group directly attached to an unsaturated grouping.



I (a) R = CH_3
(b) R = C_2H_5
(c) R = C_3H_7-*n*
(d) R = C_4H_9-*n*
(e) R = C_4H_9-*i*
(f) R =



$-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$

Concerning the minimal conditions necessary for the reaction, it was found in the study that the hydrogen chloride was essential, whereas the amine hydrochloride was not. No conversion was observed in the absence of the hydrogen chloride even though the amine hydrochloride was present. Under the opposite conditions, conversion did occur, but in poorer yield than when both reagents were present. In all subsequent runs, therefore, both reagents were used.

The reaction using 3-methoxy-2,5-diphenylfuran was found to occur with ethanol, *n*-propyl alcohol, *n*-butyl alcohol and isobutyl alcohol. The yields varied from 68 to 55%. Isopropyl alcohol and *t*-butyl alcohol gave no reaction, and *s*-butyl alcohol, *n*-amyl alcohol and isoamyl alcohol gave principally non-crystalline products which are assumed to be of a different nature, since the corresponding alkoxyfurans should be crystalline by comparison to the others known.[3] Transetherifications of alkoxyfurans of higher molecular weight to alkoxyfurans of lower molecular weight were also carried out.

The alcoholysis reaction was extended also to 3-acetoxy-2,5-diphenylfuran, using methanol and *n*-propanol. Isopropyl alcohol, *n*-butyl alcohol and isobutyl alcohol reacted differently to yield oils plus a dimolecular oxidation product, 2,2′-bis-(2,5-diphenylfuranone-3).[4] The reaction failed with 3-(4-morpholinyl)-2,5-diphenylfuran (II) and, as reported earlier,[2] with 3-chloro-2,5-diphenylfuran. All of the above described transformations are listed in Table I.

From the viewpoint of synthesis of alkoxyfurans, the alcoholysis of 3-methoxy-(or 3-ethoxy-) and 3-acetoxy-2,5-diphenylfurans is of limited value. However, since only 3-methoxy- and 3-ethoxy-2,5-diphenylfurans can be made from 1,2-dibenzoyl-1,2-dibromoethane,[2,5,6] these transfor-

(1) (a) From the M. A. Thesis of J. D. Christian, January, 1949. (b) Since the paper was accepted for publication, similar transetherification reactions have been reported with different systems; see Croxall, Van Hook and Luckenbaugh, THIS JOURNAL, **71**, 2736 (1949), and Ogata and Okano, *ibid.*, **71**, 3211 (1949).

(2) Bailey and Kelly, THIS JOURNAL, **70**, 3442 (1948).

(3) Melting points: Me, 114-115°, Et, 94-95°, Pr, 86-87°, iso-Pr, 87-88°, Bu, 60-61°, iso-Bu, 71-72°.

(4) Previously reported by Lutz, McGinn and Bailey, THIS JOURNAL, **65**, 843 (1943); and Kohler and Woodward, *ibid.*, **58**, 1933 (1933).

(5) Bailey and Lutz, *ibid.*, **69**, 498 (1947).

(6) Conant and Lutz, *ibid.*, **47**, 881 (1925).