action bulb they decompose at the same rate as aluminum borohydride.

The initial decomposition rate for 1000 seconds at 159° was found to be unaffected by the nature of the flask surface (either clean or coated with solid products in various stages of decomposition). Furthermore, this rate was the same in the presence of added hydrogen. Half-lives were about 6500 seconds at 159° and 450 seconds at 189°.

The borohydride pressure as a function of time may be expressed by the equation

$$P_{Al(BH_4)_3} = P_{0Al(BH_4)_3} [ae^{-k_i t} + (1 - a)e^{-k_f t}] \quad (1)$$

where

$P_{Al(BH_4)_3}$ = pressure of aluminum borohydride at time t
$P_{0Al(BH_4)_3}$ = initial pressure of aluminum borohydride
a = constant $1 > a > 0$
k_i, k_f are constants

In Table I the experimental results are summarized in terms of the constants of equation (1). The runs at 159° and 85 mm. initial pressure were performed in a reaction vessel packed with glass beads so that the area–volume ratio was increased by a factor of about twelve, and it is seen that the rate is unaffected.

TABLE I

Temp., °C.	Initial Al(BH₄)₃ pressure (mm.)	a	k_i(sec.$^{-1}$)	k_f(sec.$^{-1}$)
159	110.0	0.127	1.68×10^{-3}	8.51×10^{-5}
	85.0	.146	....	8.25×10^{-5}
	57.5	.125	1.4×10^{-3}	7.88×10^{-5}
189	85.0	.406	4.48×10^{-3}	6.33×10^{-4}

In the hope of determining the number of hydrogen atoms split off in the initial stage of the reaction plots of pressure of hydrogen evolved divided by pressure of borohydride decomposed *versus* time at 159 and 189° were made. These plots were very steep near the origin and it was only possible to conclude that not more than three hydrogen atoms are lost in the initial process.

The differential equations for successive first order reactions with reversible steps have been solved by Rakowski.[5] For such systems expressions similar in form to equation (1) are obtained. However, one would expect that the reverse of the reactions in which hydrogen is split off should be second order and should show a dependence on the hydrogen pressure, yet such an effect is not observed.

It is to be concluded, therefore, that while equation (1) adequately describes the aluminum borohydride concentration as a function of time, the mechanism of the reaction may be determined only when the nature and concentrations of the intermediate species become known.

(5) Rakowski, Z. physik. Chem., **57**, 321 (1907).

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Condensation of Lactones with Benzene

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Eijkman[1] studied the reaction of benzene and its homologs with a few aliphatic lactones in the

(1) (a) J. F. Eijkman, Chem. Weekblad, **1**, 421 (1904); (b) J. F. Eijkman, ibid., **2**, 229 (1905); **4**, 191, 727 (1907).

presence of aluminum chloride. For example, γ-valerolactone with benzene gave γ-phenylvaleric acid in unspecified yield.[1a] The ready availability of several simple, aliphatic lactones suggested an examination of this reaction as a means for the synthesis of certain aryl-aliphatic acids.

It was found that the AlCl₃ catalyzed condensation of benzene with the appropriate lactone yielded γ-phenylbutyric acid, γ-phenylvaleric acid and δ-phenylvaleric acid in yields of 44, 61 and 51%, respectively. Significantly, no isomerization of the side chain took place and the phenyl radical was attached at the position of the alcohol function in the parent hydroxy acid. A competing reaction was the further alkylation of the initially formed product to yield polyfunctional acids. This could probably be minimized by a suitable choice of reaction conditions.

Lactide did not condense with benzene in the presence of aluminum chloride even upon heating at 70–80°. In the case of β-propiolactone the principal reaction seemed to be destruction of the lactone by the aluminum chloride and the expected β-phenylpropionic acid was not isolated in quantities sufficient to permit conclusive identification.

Experimental

The condensations were carried out in flasks equipped for reflux and mechanical stirring. The temperature during the early stages of the reaction was held below 45° by varying the rate of addition of the last component and by external cooling with water when necessary.

γ-Phenylbutyric Acid.—To a stirred solution of 43 g. (0.5 mole) of γ-butyrolactone (Cliffs Dow Chemical Co., Marquette, Michigan) in 100 g. of benzene, 93 g. (0.7 mole) of powdered aluminum chloride was added in small portions. After 4 hours 100 ml. of benzene was added and the mixture was allowed to stand overnight at room temperature. Subsequent to heating in a water-bath for an hour, the mixture was hydrolyzed with ice and hydrochloric acid. Distillation of the benzene layer gave 36 g. (44%) of white crystals of b.p. 120–125° (1 mm.). Crystallization from methanol and water yielded material whose melting point, 48–49°, was undepressed when mixed with authentic γ-phenylbutyric acid. Approximately 30 g. of higher boiling material was not examined further.

γ-Phenylvaleric Acid.—To a stirred suspension of 50 g. (0.38 mole) of aluminum chloride in 60 g. of benzene, there was added dropwise 30 g. (0.3 mole) of γ-valerolactone (Monsanto Chemical Co., St. Louis, Missouri). After being heated in a water-bath for 30 minutes, the mixture was hydrolyzed as before. Distillation of the benzene layer gave 32.5 g. (61%) of colorless liquid boiling at 123–126° (0.5 mm.).

That the substance was γ-phenylvaleric acid was confirmed by conversion to 4-methyl-1-tetralone[2] from which the known solid semicarbazone[2,3] was obtained in the usual manner. The heretofore undescribed p-bromophenacyl ester was also prepared. It crystallized from dilute methanol as white leaflets melting at 76°. Anal. Calcd. for C₁₉H₁₉O₃Br: Br, 21.3. Found: Br, 21.1.

In other experiments, the residue remaining after distillation of γ-phenylvaleric acid was esterified with ethanol. The resulting material had boiling point 165–169° (0.5 mm.), d^{25}_4 1.0212, n^{25}D 1.4914. Analysis indicated that it was probably diethyl γ,γ'-phenylenedivalerate. Anal. Calcd. for C₂₀H₃₀O₄: MR_D, 94.62; sapn. equiv., 167; C, 71.9; H, 9.04 Found: MR_D, 94.84; sapn. equiv., 169, 171; C, 72.2; H, 9.37.

δ-Phenylvaleric Acid.—Aluminum chloride (33.4 g., 0.25 mole) was added in portions to a stirred solution of 20 g. (0.20 mole) of δ-valerolactone (prepared in quantitative yield from δ-hydroxyvaleraldehyde[4] by oxidation with per-

(2) M. C. Kloetzel, THIS JOURNAL, **62**, 1708 (1940).
(3) F. Mayer and G. Stamm, Ber., **56**, 1424 (1923); J. von Braun and A. Stuckenschmidt, ibid., **56**, 1724 (1923).
(4) G. F. Woods, Jr., Org. Syntheses, **27**, 43 (1947).

acetic acid) in 150 ml. of benzene. After the mixture had stood overnight at room temperature it was heated at 100° for an hour and then hydrolyzed in the usual way. The benzene layer was distilled to yield 18 g. (51%) of solid boiling at 130–140° (2 mm.). Crystallization from petroleum ether (b.p. 35–45°) gave colorless crystals of m.p. 58–59°; this was unchanged by mixture with authentic δ-phenylvaleric acid.

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Exchange between the Tris-(5,6-dimethyl-1,10-phenanthroline) Complexes of Iron(II) and -(III)[1]

BY LOIS EIMER AND A. I. MEDALIA

Exchange reactions which proceed via transfer of an electron are of interest as a simple, symmetrical class of oxidation–reduction reactions. Uncertainties as to the states of complexing, which arise in studying simple ions, may be avoided by studying complexes of known structure, such as the phenanthroline complexes of iron(II) and -(III).

In undertaking such a study, an experimental survey was first made of seven commercially available phenanthrolines and analogs. It was established[2] that the most suitable compound for such a study, from the standpoint of the stability of both the ferrous and ferric forms in aqueous acid, is 5,6-dimethyl-1,10-phenanthroline, with which therefore all further work was conducted.

Experimental.—The 5,6-dimethyl-1,10-phenanthroline was used as obtained from the G. F. Smith Chemical Co. The red ferrous complex (designated as ferroin-5,6) was prepared by complexing of ferrous iron with 5–10% excess of the phenanthroline at pH 8.5–9.0; the blue ferric complex (ferriin-5,6), by oxidation of ferroin-5,6 with lead dioxide in 1 N sulfuric acid, followed by filtration through sintered glass to remove PbO_2 and $PbSO_4$. These compounds have been prepared with inactive iron; and with samples of radioactive iron of both low and high activity (Fe^{55}), which were obtained from Oak Ridge and then purified by extraction, fumed with sulfuric acid, and reduced with sulfur dioxide under the conditions suggested by Marti and Conde.[3] All water used was purified in a continuous quadruple Pyrex still.

Two methods of separation have been developed: (1) The ferroin-5,6 is precipitated as the perchlorate in 50% perchloric acid and is collected on a glass frit, the ferriin-5,6 remaining in solution. The precipitate is counted on the frit after drying 48 hours in a vacuum desiccator. (2) The ferroin-5,6 is extracted with a solution of camphorsulfonic acid (0.013 f) in chloroform, the ferriin-5,6 remaining in the aqueous phase.

The extraction method can be used at lower concentrations than the precipitation method; however, a lower limit is set by the reduction of ferriin-5,6 by impurities in the chloroform. Of several methods which were investigated for purification of the chloroform, the following gave the best results: analytical reagent grade chloroform was washed at 0° with several portions each of water, concentrated sulfuric acid, 0.1 f sodium bicarbonate, and water, in succession; then dried with potassium carbonate, and distilled over calcium hydride in a nitrogen atmosphere. The product was collected in a chilled receiver and stored under nitrogen at 5°. Ethylene dichloride showed some promise as an alternative solvent but its use was not fully investigated.

Ferriin-5,6 remaining in the aqueous phase after extraction has been reduced by passage of sulfur dioxide for 30 seconds; after addition of carrier (inactive ferroin-5,6, 5 × $10^{-4} f$) the ferroin-5,6 was precipitated by addition of Na_2CdI_4 (0.02 f) at 0° and filtered through S&S #756 paper placed on a glass frit. The paper was dried at 110°, mounted and placed under an end-window G-M tube filled with 71.5 cm. of argon and 2.5 cm. of ethyl acetate, for counting.

Several methods have been investigated[2] for recovery of active iron from the chloroform extracts of ferroin-5,6. Satisfactory results were obtained by a procedure involving the following steps: evaporation of the extract in a silica dish, ignition at 500°, solution in boiling 0.6 f HCl, reduction with hydroxylamine hydrochloride, and re-formation of ferroin-5,6 in acetate buffer followed by addition of carrier, precipitation, filtration and counting as above.

Exchange Experiments with 4.2 × $10^{-4} f$ Solutions.—Mixtures were prepared at 0° of 2 cc. each of active and inactive ferroin-5,6 and ferriin-5,6 as shown in Table I. About five seconds were required for mixing. Six cc. of 70% perchloric acid at 0° was added and the mixture was shaken for one minute and then filtered. Filtration required approximately one minute. The precipitate was counted and in some cases the filtrate was treated with sulfur dioxide and the ferroin-5,6 thus formed was also precipitated as the perchlorate, filtered and counted. Results are given in Table I.

TABLE I

EXCHANGE OF 4.2 × $10^{-4} f$ SOLUTIONS IN 1 N SULFURIC ACID AT 0°

Total count on initially active species: 420 c./min.

Initially active species	c./min. ferroin-5,6 fraction	c./min. ferriin-5,6 fraction
Ferriin-5,6	198	...
Ferriin-5,6	204	...
Ferroin-5,6	185	183
Ferroin-5,6	194	249

Total activity of the ferroin-5,6 was determined by perchlorate precipitation; and of the ferriin-5,6 by reduction with sulfur dioxide followed by perchlorate precipitation. Completeness of precipitation of ferroin-5,6 and completeness of recovery of the ferriin-5,6 in the filtrate were checked spectrophotometrically.

It appears from the results in Table I that complete exchange took place in the experiments.

Exchange Experiments with 2.2 × $10^{-5} f$ Solutions.—Four cc. of a solution of camphorsulfonic acid (0.013 f) in chloroform was placed in a 30-cc. separatory funnel and chilled to 0°. To this were added simultaneously 2 cc. each of ferroin-5,6 and ferriin-5,6 at 0°, each 4.4 × $10^{-5} f$ before mixing. The separatory funnel was immediately stoppered and shaken for ten seconds; the chloroform was then drained off, and both phases were worked up as described above. Results are given in Table II.

TABLE II

EXCHANGE OF 2.2 × $10^{-5} f$ SOLUTIONS IN 1 N SULFURIC ACID AT 0°

Initially active species	c./min. in ferroin fraction	c./min. in ferriin fraction	Sum of fractions	Total on original ferroin solution	% of activity recovered
Ferroin-5,6	4350	4000	8350	8190	102
Ferroin-5,6	..	3820	..	8190	...
Ferriin-5,6	3980	3910	7890	8190	97
Ferriin-5,6	3780	3780	7560	8190	93
Blank (Ferriin-alone)	950	6720	7670	8190	94
Ferroin-5,6	4380	3400	7780	7750	100
Ferroin-5,6	4200	3890	8090	7750	104
Ferriin-5,6	3900	3880	7780	7750	100
Ferriin-5,6	3990	3720	7710	7750	100
Blank (Ferriin-alone)	620	6520	7140	7750	92

Reasonably good recovery was obtained in all experiments (between 92 and 104%). Reduction of ferriin-5,6 by the

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.
(2) L. Eimer and A. I. Medalia, BNL-1022.
(3) F. B. Marti and F. L. Conde, Anal. Chim. Acta, 3, 547 (1949).