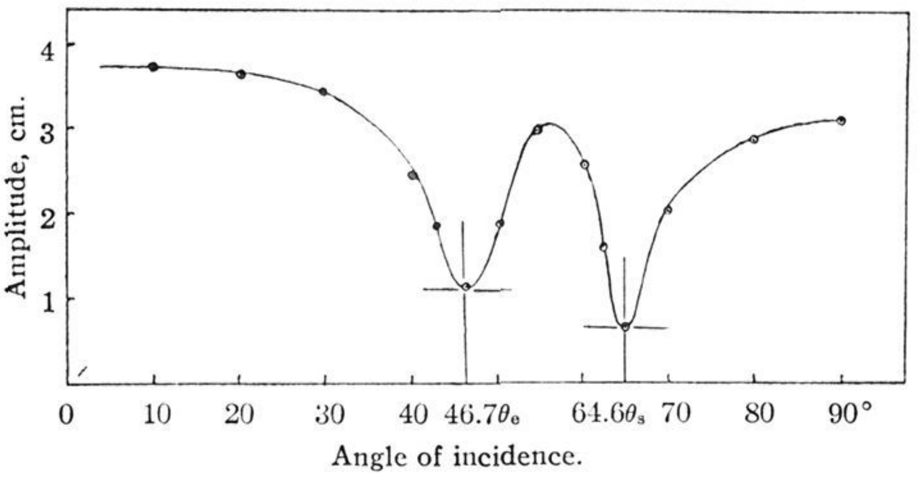

Fig. 4.—Showing the variation of amplitude with angle of incidence: $V_e = 1.55 \times 10^5/\sin \theta_e$; $V_s = 1.55 \times 10^5/\sin \theta_s$.

Density of the iron silicate gel, for which these results are given, was 1.180 at 23°. Figure 4 shows the variation of the amplitude of the transmitted rays; the two dips correspond to the values θ_e and θ_s in a particular case. Figure 5 is the oscillogram in which A is the instant of start of the ultrasonic pulse and B the amplitude of the transmitted waves.

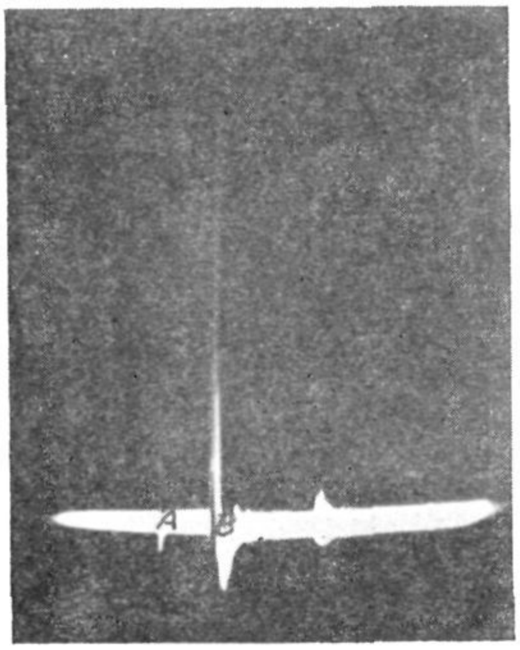

Fig. 5.—Showing the amplitude of the transmitted wave on the oscillograph.

Since there is so far no agreed mechanism of gel formation this work has been undertaken to study the problem from a physical standpoint. Details of this work on iron silicate gels and other gels of the Weimarn type will appear in forthcoming publications.

My thanks are due to Dr. R. N. Ghosh for help and guidance in undertaking this work.

DEPARTMENT OF PHYSICS
UNIVERSITY OF ALLAHABAD
ALLAHABAD, INDIA

RECEIVED MAY 22, 1950

An Apparent Reduction of Halogens by Zinc Halides in Methanol Solution[1]

BY FRANCIS J. SHELL AND HOWARD K. ZIMMERMAN, JR.

In the course of an investigation of the decomposition potentials of zinc halides in methanol solution (to be published at a later date), we have observed an interesting reaction of iodine in the presence of zinc halide in methanol and of bromine in methanol solution with zinc chloride or bromide, some qualitative aspects of which we wish to report here. If separate solutions of iodine and one of the zinc halides be prepared in dry methanol and then mixed, the mixing is followed by a rapid fading of the iodine color until the solution becomes colorless. The rate of fading varies directly as the halide/iodine ratio, the total period being of the order of a few minutes, and all of the halides seem to be about equally effective. Repetition of the experiments with solutions containing approximately 0.05% water shows an induction period of several hours followed by fading at a considerably reduced rate, the total elapsed period to a colorless solution being of the order of 24 hours or more. Tests with varying amounts of water show that water content apparently controls both length of the induction period and diminution of fading rate after reaction has started. Aeration and exposure to light seemingly have no effect upon the reaction. Replacement of the zinc halide by $AlBr_3$, aluminum isopropoxide, $ZnSO_4$, CdI_2, KI, NH_4Cl and HBr appeared to give no reaction, but use of $Zn(CH_3SO_3)_2$ produced a partial fading after about one month. Some of these latter systems may have contained small quantities of water which may account for their failure to react rapidly, but such was definitely not the case with NH_4Cl and HBr.

To obtain a further clue concerning the nature of the reaction, a solution of iodine and zinc chloride was allowed to fade completely. The resulting solution was then electrolyzed without stirring. At from 2 to 3 volts and about 1 milliamp., iodine was regenerated. Increasing the potential to 6 volts caused fading of the iodine color again, beginning at the bottom of the cell; under these conditions zinc simultaneously plated out on the cathode with evolution of gas. Fading of the iodine color under such conditions was never complete. When the potential was removed gas evolution continued, and in ten to fifteen minutes the iodine color had returned to full strength. Three hours later the solution was again nearly colorless and gas still was being evolved. On the basis of these observations it appears that the fading reaction probably involves reduction of the iodine to iodide. Electrolysis oxidizes the iodide first to iodine and then to hypoiodite or some higher oxidation state which, in presence of the zinc halide, is unstable and reverts to iodine and then to iodide with the passage of time.

The literature appears to be devoid of information which provide an explanation of the phenomena described here. Frey[2] refers to a reaction between zinc chloride and iodine which occurs in fibers and may be used for biological staining procedures, but no details of the reaction seem to be available. The remarkable specificity of the zinc halides in

---

[1] Based upon research performed under contract No. W36-039-sc-38184 for the U. S. Army Signal Corps.

[2] A. Frey, *Jahrb. wiss. Bot.*, **67**, 597-634 (1927).

promoting the present reaction will be made the subject of further study.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KENTUCKY
LEXINGTON, KENTUCKY RECEIVED SEPTEMBER 20, 1950

The Synthesis of Hydroxylysine from the Cyanohydrin of γ-Acetamido-γ,γ-dicarbethoxybutyraldehyde[1]

BY OSCAR TOUSTER

Bergström and Lindstedt[2] and Sheehan and Bolhofer[3] have recently presented degradative evidence which establishes the structure of natural hydroxylysine as α,ϵ-diamino-δ-hydroxycaproic acid. The latter workers also synthesized this amino acid by two routes.[4] The first method was based upon the reduction and hydrolysis of methyl α,ϵ-diphthalimido-δ-keto-DL-caproate, which was originally prepared in several steps from glutamic acid.[3] The second synthesis involved the catalytic hydrogenation of the cyanohydrin of γ-acetamido-γ,γ-dicarbethoxybutyraldehyde[5] in acetic anhydride, followed by hydrolysis and decarboxylation of the reduction product. We have independently synthesized hydroxylysine from this cyanohydrin by a similar procedure, except that crystalline cyanohydrin was employed in our work and the amino acid was isolated in a different manner. The yield of crystalline hydroxylysine was 40%, based on the cyanohydrin. This initial product and material obtained from it by recrystallization in 60% yield gave similar amounts of formaldehyde on reaction with periodate. The identity of the amino acid was established by elementary analyses of its monohydrochloride, monopicrate and dipicrate, by its reaction with periodate to form formaldehyde and ammonia, by its behavior in a new modified ninhydrin test and by paper chromatography.

Experimental

Nine grams of the cyanohydrin of γ-acetamido-γ,γ-dicarbethoxybutyraldehyde[6] was dissolved in 135 ml. of a 3:1 mixture of ethyl acetate and acetic anhydride and hydrogenated for 6 hours at three atmospheres pressure and room temperature, using 0.6 g. of Adams platinum oxide as catalyst. After removal of the catalyst by filtration and removal of solvents by distillation *in vacuo*, the colorless product was dissolved in 70 ml. of concd. HCl and the solution refluxed for 15 hours. The acid was then removed under reduced pressure and an aqueous solution of the residue decolorized with charcoal. Evaporation to dryness yielded 7.2 g. of crude dihydrochloride as a yellow oil which partially crystallized on drying over phosphorus pentoxide.

Three and five-tenths grams of the crude dihydrochloride was dissolved in 60 ml. of hot 95% ethanol and treated with 1.63 ml. of aniline in 5 ml. of 95% ethanol, followed by sufficient water (10 ml.) to prevent oiling out of monohydrochloride. The solution was allowed to stand at room temperature for a short time and then overnight in the refrigerator. The first crop of hydroxylysine monohydrochloride (0.61 g.) was collected by filtration and washed with ethanol. Cooling of the combined mother liquor and washings yielded a considerable amount (0.56 g.) of additional monohydrochloride. The total yield of amino acid, based on cyanohydrin, was 40%. A slightly smaller yield was obtained when pyridine was employed in place of aniline. Recrystallization from twenty volumes of 70% ethanol gave a product which decomposed at 215–220°.[7]

Anal.[8] Calcd. for $C_6H_{15}N_2O_3Cl$: C, 36.27; H, 7.61; N, 14.10. Found: C, 36.65; H, 7.58; N, 14.62; NH_2-N, 14.3.

An orange-yellow monopicrate was prepared by reaction of hydroxylysine with one equivalent of picric acid in aqueous solution. A small amount of light yellow dipicrate also formed. This was separated manually and the monopicrate was then recrystallized from water. It melted at 224–226°.

Anal. Calcd. for $C_{12}H_{17}N_5O_{10}$: C, 36.83; H, 4.38; N, 17.90. Found: C, 37.26; H, 4.25; N, 17.62.

The dipicrate was obtained by using slightly more than two equivalents of picric acid. It melted at 123–125°[9] after recrystallization from water.

Anal. Calcd. for $C_{18}H_{20}N_8O_{17}$: C, 34.85; H, 3.25; N, 18.06. Found: C, 34.97; H, 3.47; N, 17.76.

Synthetic and natural hydroxylysine monohydrochloride showed identical behavior in a new modified ninhydrin test which distinguishes hydroxylysine from other natural amino acids.[10] Using a periodate oxidation procedure in which natural hydroxylysine has been reported to yield ammonia and a 65% yield of formaldehyde as the dimedone condensation product,[11] ammonia and a 59% yield of formaldehyde–dimedone product were obtained from the synthetic preparation. The synthetic and natural amino acids had identical R_f values on paper chromatograms run in phenol–hydrochloric acid and phenol–ammonia systems.[12]

---

[1] Supported in part by The Rockefeller Foundation and Nutrition Foundation, Inc., through grants to the Division of Nutrition.

[2] Bergström and Lindstedt, *Arch. Biochem.*, **26**, 323 (1950).

[3] Sheehan and Bolhofer, THIS JOURNAL, **72**, 2469 (1950).

[4] Sheehan and Bolhofer, *ibid.*, **72**, 2472 (1950).

[5] Moe and Warner, *ibid.*, **70**, 3918 (1948).

[6] We are indebted to Dr. O. A. Moe, of General Mills, Inc., Minneapolis, Minn., for a sample of this compound.

[7] Melting points were taken with a Fisher–Johns microblock.

[8] Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[9] The different melting point behavior observed by Sheehan and Bolhofer[4] was probably due to difference in proportion of racemates or different technique for determining melting point, or both.

[10] An unpublished test of Dr. Francis P. Chinard of Johns Hopkins University. We are indebted to Dr. James Weisiger of the Hospital of the Rockefeller Institute for Medical Research for information regarding this test and for a sample of natural hydroxylysine.

[11] A. P. J. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 309 (1941).

[12] We are indebted to Dr. J. G. Heathcote, Cereals Research Station, St. Albans, Herts, England, for the paper chromatographic comparisons.

DEPARTMENT OF BIOCHEMISTRY
VANDERBILT UNIVERSITY SCHOOL OF MEDICINE
NASHVILLE, TENNESSEE RECEIVED JULY 5, 1950

The Solution Absorption Spectrum of Americium

BY B. J. STOVER,* J. G. CONWAY AND B. B. CUNNINGHAM

It has long been observed that the absorption spectra of the trivalent rare earth ions possess a unique sharpness, the structure of the peaks being discernible at room temperature and even in solutions. This phenomenon has also been observed in the case of the electronically analogous actinide elements.

The generally accepted explanation for the origin of the lines in the rare earth spectra is that they result from transitions within the 4f electron shell.

Trivalent europium, the analog of americium, has been shown by absorption spectra and magnetic susceptibility data to have a $4f^6$ electron configuration, a $7F_0$ ground state, and one or more low lying excited levels. Since americium ion probably has a $5f^6$ configuration, it also is expected to have a singlet ground state and one or more low lying excited levels. The following represents the first

---

* Department of Chemistry, University of Utah, Salt Lake City, Utah.