homogeneous when only 150 g. of the solvent was used. When 70% acetone was used as a solvent hydration did not take place rapidly enough to maintain miscibility, although more solvent was used than was required to keep the 2-hexanone in solution.

When hydration of 1-hexyne was carried out in 60% acetic acid it proceeded sufficiently rapidly so that the mixture remained practically homogeneous despite the fact that much less solvent was used than required to dissolve the acetylene.

In the cases of hydration with aqueous methanol or acetic acid it is possible that the organic solvent may react with the acetylene by addition.[14,15] The resulting ketal or ester would hydrolyze to ketone under the conditions of the experiments.

A number of experiments were performed with the object of determining the mechanical losses which resulted from washing, drying and distilling the products. These were found to amount to 10–15% of the material when half-mole quantities of the acetylenes were used. Consequently the actual extent of hydration was, in each case, considerably higher than indicated in Table III.

The application of this method to the hydration of other acetylenic compounds is being further studied in this Laboratory.

Summary

Catalytic hydration of three higher alkylacetylenes to ketones has been accomplished readily and with excellent yields by use of aqueous solvents.

NOTRE DAME, INDIANA RECEIVED NOVEMBER 29, 1937

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[14] Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

[15] Hennion and Nieuwland, *ibid.*, **56**, 1802 (1934).

NOTES

The Explosion of Chloroform with Alkali Metals

BY TENNEY L. DAVIS AND JOHN O. MCLEAN

The explosion which occurs when chloroform and sodium in contact with each other are subjected to shock seems to have been discussed for the first time in 1925 by Staudinger,[1] who described a safe technique for demonstrating it and reported only sodium chloride and carbon as the products. We have wished to account for the hydrogen which the chloroform contains and to identify other products in the hope that light might be thrown upon the mechanism of the reaction.

About 0.3 g. of sodium or of potassium or of the liquid alloy was sealed up in a small glass bulb, 6 to 8 mm. in diameter, which had a capillary stem 15 to 20 mm. in length. This was placed in the bottom of a narrow test-tube and held in place by a collar of glass (a section of glass tubing) which was sintered to the inner wall of the test-tube. The latter was then drawn down, chloroform (1 to 2 cc.) was introduced, and the explosive capsule was sealed. These capsules could be prepared in advance and could be kept safely as long as desired.

For studying the products of the explosion a steel bomb, such as is used for laboratory high pressure syntheses, was taken, about 25 cm. long and having a capacity of 380 cc. It was equipped with valves and copper tubes, by means of which the bomb was flushed out with nitrogen for at least fifteen minutes before each experiment, the pressure existing in the bomb after the explosion was determined, and the gaseous products were swept out with nitrogen. The inside of the bomb was fitted with a cylindrical block of steel by which the explosive capsule was gripped and by the crushing action of which it was fired. The details of the apparatus are shown in Fig. 1. The steel block and capsule being at the end of the bomb which is uppermost in the figure, the explosion was made to occur by inverting the bomb quickly or by dropping it on the floor. The explosion produced heat enough to make the bomb perceptibly warm to the touch.

When one of the capsules was dropped on the concrete pavement from a height of 2 meters, a loud explosion was produced, accompanied by a flash which was visible even in the sunlight, and a cloud of white smoke or mist which smelled distinctly of phosgene.

When the explosion occurred in the bomb in an atmosphere of nitrogen, the interior of the bomb was found to be covered with a deposit of soot. After the bomb had resumed room temperature, the pressure within it was determined by means of a manometer, and the gases were swept out by a stream of nitrogen and bubbled through water for the removal of hydrogen chloride, until a total of 1800 cc. of the mixed gases (mostly nitrogen) had been collected. Twenty-five cc. portions ($^{1}/_{72}$ of the whole)

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[1] Staudinger, *Z. Elektrochem.*, **31**, 549 (1925).

were taken for analysis, and the results were calculated in cc. of each gas present in the bomb after the explosion. The part absorbed by sodium hydroxide solution was taken to be phosgene, for the reasons that carbon dioxide appeared improbable and that the gases precipitated barium carbonate from baryta water producing chloride ions in the solution at the same time. The amount of phosgene was greater than can be ascribed to the air which was sealed up in the capsule, and probably indicates that we had not succeeded in displacing completely the air which was originally present in the bomb. The gases contained no material which reacted with bromine water. They were mixed with oxygen and fired with an electric spark, and the resulting contraction was calculated as hydrogen. The material absorbable by sodium hydroxide which resulted from the combustion, phosgene or carbon dioxide, was taken as equal to the partial volume of chloroform vapor which had been present in the gases. The average results from three analyses on each of three different experiments are reported in Table I.

TABLE I

GASES RESULTING FROM THE EXPLOSION

	I	II	III
Phosgene, cc.	58	43	65
Hydrogen, cc.	36	17	7
Chloroform vapor, cc.	34	43	22
Total gas produced, cc.	128	103	94
Observed increase of pressure, mm.	326	...	195
Calculated increase of pressure, mm.	255	...	161

Since the actual amounts of the gases in the 25-cc. samples which were analyzed varied between 0.1 and 0.8 cc., it is probable that the figures are 20 or 30% in error—and the agreement is considered satisfactory between the observed increases of pressure and those calculated to result from the production of the gases in a space of 380 cc. already filled with nitrogen at atmospheric pressure. If it is supposed that the gaseous organic compound is not chloroform, but is one which contains two carbon atoms, then the agreement is poorer. It seems probable, moreover, regardless of the stoichiometric relations between the amounts of the alkali metal and chloroform, that a certain portion of the chloroform would be blown by the force of the explosion out of the sphere of the reaction and would survive unchanged in the gas phase.

In these experiments no hydrogen chloride was produced; in later experiments in which larger amounts of chloroform and relatively smaller amounts of alkali metal were used it was produced in considerable amount.

For a study of the non-gaseous products extra large capsules, containing 2 g. of potassium and 15 g. of chloroform, were used. Several failed to explode in the bomb designed for smaller capsules, but two of them exploded successfully. The gases contained large amounts of hydrogen chloride, evident by its odor and by test with ammonia. The sooty material in the bomb was brought together and extracted with ether. The red ether extract on evaporation yielded 0.5 cc. of a green oil and 0.5 g. of a reddish solid. The oil had a sp. gr. of 1.100 and commenced to boil at 105°, but decomposed on distillation and yielded no identifiable products. The solid in the molecular still yielded a carbonaceous residue and 0.3 g. of crystalline sublimate, and the latter, recrystallized several times from alcohol in which it was sparingly soluble, yielded pure hexachlorobenzene, colorless needles, m. p. 223°, identified by mixed melting point with a known sample.

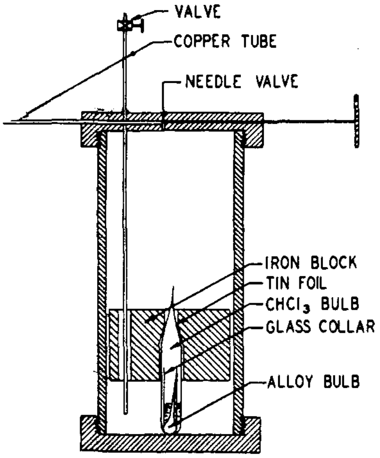

Fig. 1.—Steel bomb with capsule enclosed. The moving parts are in the position which they would occupy at the moment preceding the explosion.

Hydrogen chloride and hexachlorobenzene are known to be produced by the pyrolysis of chloroform.[2] It may be supposed that in our experiments while one portion of the chloroform enters into the explosive reaction, another portion is cracked or pyrolyzed by the energy thus liberated. This cracking however cannot be the sole source of hydrogen chloride or of hydrogen, for the hydrogen which was contained in the chloroform which was concerned in the first explosive reaction would remain to be accounted for. This hydrogen may perhaps be liberated in accordance with one or the other of the following equations, according to the amount of sodium which is available for reaction.

$$CHCl_3 + 3Na \longrightarrow 3NaCl + C + 0.5H_2 \quad (1)$$

$$CHCl_3 + 2Na \longrightarrow 2NaCl + C + HCl \quad (2)$$

These equations, however, fail to account for the hexachlorobenzene which we have found. While this substance may actually arise from a pyrolysis, it may on the other hand be explained, and the other facts accounted for, by supposing that the primary explosive reaction is in accordance with the equation

$$CHCl_3 + Na \longrightarrow NaCl + HCl + {>}CCl \quad (3)$$

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[2] Besson, *Compt. rend.*, **116**, 103 (1893); Conduché, *ibid.*, **158**, 1182 (1914).

Whether the hexachlorobenzene is formed by the explosion or by a pyrolysis, the $>$CCl radical seems an obvious intermediate between it and chloroform.

CONTRIBUTION NO. 165 FROM THE
RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
RECEIVED DECEMBER 3, 1937

The Fluorescence of Double Salts of Calcium Phosphate

BY JULIAN GLASSER AND GORTON R. FONDA

Ox teeth are known to consist of 1% of organic matter combined with calcium phosphate in an apatite structure. Their fluorescence under ultraviolet radiation is destroyed by burning out their organic content at 600° or higher, but is increased by firing at an optimum temperature of 400°. After solution in acid and precipitation in alkali, the fluorescence is fully restored by refiring at 400°.

A similar product can be made synthetically by coprecipitating a calcium salt with a mixture of sodium phosphate and tartrate and firing at 400°. An optimum fluorescence bluish-white in color is obtained when the solution of sodium phosphate contains 11 molar per cent. of sodium tartrate. The 400° treatment is effective only when carried out in the presence of oxygen. It burns off most of the tartrate but leaves an oxidized residue at a concentration of about 2% by weight combined with the phosphate. The fluorescence under 3650 Å. is double that of teeth and is about 4% of the theoretical, on the basis of complete quantum conversion. The product again has the apatite structure but with an apparently slight contraction of the lattice. Its fluorescence is retained after solution in acid and reprecipitation with alkali. It is destroyed by firing at temperatures above 400°.

A fluorescent product also results by firing at 400° the coprecipitate of calcium phosphate contaminated with some other organic radical, such as succinate or lactate. In fact it appears that the contaminant may even be the calcium salt of an inorganic acid radical, such as borate or chromate. The fluorescence of solids is generally associated with the presence of a small amount of metallic impurity as activator. In this case, however, it appears that the activator may be a foreign acid radical. The possibility of such a type of fluorescence is being studied further.

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RECEIVED JANUARY 22, 1938

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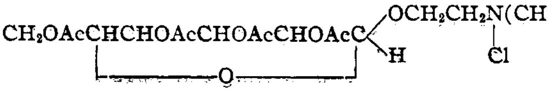
beta-Tetraacetylcholine-*d*-glucoside[1,2]

BY ERNEST L. JACKSON

Schroeter and Strassberger[3] prepared 2-chloroethyl-*d*-glucoside by the reaction of glucose with ethylene chlorohydrin containing hydrogen chloride, condensed their impure 2-chloroethylglucoside with trimethylamine, and from the products prepared a phosphomolybdate of cholineglucoside. The chloride of cholineglucoside, showing $[\alpha]^{15}D$ + 49.5° in water, was obtained in crystalline condition from the phosphomolybdate.

By the reaction of trimethylamine with pure crystalline beta-tetraacetyl-2-chloroethyl-*d*-glucoside[4] in benzene solution the writer has prepared the crystalline chloride of tetraacetylcholine-*d*-glucoside (I) which has a melting point of 230° and a specific rotation[5] of −25.6° in water and −13.5° in chloroform.



$$CH_2OAcCHCHOAcCHOAcCHOAcC\begin{matrix}OCH_2CH_2\underset{\displaystyle Cl}{N}(CH_3)_3\\ H\end{matrix}$$

(I)

This compound must be a beta-pyranoside, since the parent tetraacetyl-2-chloroethylglucoside was prepared from ethylene chlorohydrin, acetobromoglucose and silver carbonate, a reaction which in the case of other alcohols is known generally to produce beta-pyranosides. Although the chloride of beta-cholineglucoside has not been prepared in crystalline condition, its rotation as determined by an indirect method is near −27° in water. The dextrorotation of Schroeter and Strassberger's product indicates it to be an alpha form which was separated from the mixture of glycosides expected to result from their method of preparation.

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] The pharmacological properties of this compound are under investigation by Dr. M. I. Smith of this Institute.

[3] G. Schroeter and L. Strassberger, *Biochem. Z.*, **232**, 454 (1931).

[4] Walter Schoeller and Hans-Georg Allardt, German Patent 527,036 (1926); *Chem. Zentr.*, **102**, II, 1452 (1931).

[5] Except where otherwise stated, all rotations in this article are specific rotations at 20° for sodium light.

Experimental

beta-Tetraacetyl-2-chloroethyl-*d*-glucoside.—A solution of 91 g. of acetobromoglucose (0.22 mole) and 268 g. of pure ethylene chlorohydrin (3.33 moles) in 625 cc. of dry benzene was shaken at 8–10° with 92 g. of dry silver carbonate until the test for bromine was negative. After filtration and thorough extraction with water, the solution was dried over anhydrous sodium sulfate and then concentrated *in vacuo* to dryness. The product was recrystallized as long, prismatic needles from absolute ethanol, a second crop being obtained from ether–petroleum ether; yield, 63 g. or 69% on the acetobromoglucose. The pure compound melts at 118.5–119.5° (uncorr.) and rotates −13.7° in chloroform (*c*, 3.9).

Anal. Calcd. for $C_{16}H_{23}O_{10}Cl$: C, 46.76; H, 5.64; Cl, 8.64; CH_3CO, 41.91. Found: C, 46.72; H, 5.74; Cl, 8.64; CH_3CO, 41.94.

beta-Tetraacetyl-*d*-glucosido-ethyltrimethylammonium Chloride (beta-Tetraacetyl-(choline Chloride)-*d*-glucoside).—A solution of the trimethylamine from 7 g. of trimethylamine hydrochloride, and 10 g. of pure beta-tetraacetyl-2-chloroethylglucoside in 110 cc. of dry benzene was sealed at 0°, and kept at 62–64° for eighty-seven hours; then, due to excessive coloration, the temperature was changed to 50–52° for fifteen days. After the flask had been opened at 10°, the crystals were filtered off, washed with 15 cc. of benzene and dried at 25° *in vacuo* over calcium chloride; yield, 6.8 g. or 60%. The reaction was incomplete, as shown by the separation of 2.9 g. of crystals (total yield, 85%) from the filtrate kept sealed at room temperature for several months. When the reaction was carried out at 50–52° for fifteen days, although there was less coloration, the yield was only 4.7 g. or 41%. After the solution of the product in two parts of absolute ethanol had been decolorized with activated carbon, the tetraacetate crystallized readily as white prismatic needles upon the addition of dry ether. The pure compound melted at 230° (uncorr.) and rotated −25.6° in water (*c*, 1.1) and −13.5° in chloroform (*c*, 1.1). It is hygroscopic, is readily soluble in cold water, chloroform and ethanol, and slightly soluble in benzene and ether. From its solution in cold water the chlorine is removed quantitatively by silver nitrate.

Anal. Calcd. for $C_{19}H_{32}O_{10}NCl$: C, 48.54; H, 6.87; N, 2.98; Cl, 7.55; CH_3CO, 36.63. Found (dried at 25° *in vacuo* over phosphorus pentoxide): C, 48.41, 48.30; H, 7.01, 6.85; N, 2.95, 3.00; Cl, 7.46, 7.46; CH_3CO, 36.66, 36.56.

For the chloride of beta-cholineglucoside a specific rotation of −26.5° in water was calculated from the rotation of the solution obtained by the deacetylation of the tetraacetate. To a solution of 0.2641 g. of pure tetraacetate in 8 cc. of water at 0–5° was added 6 cc. of *N* sodium hydroxide solution. After twenty hours at 0–5° the solution, neutralized to phenolphthalein with hydrochloric acid (calcd. 2.25 cc. of *N* sodium hydroxide; found 2.25 cc.) and diluted with water to 25 cc. at 20°, rotated 0.36° to the left in a 2-dm. tube.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

RECEIVED JANUARY 29, 1938

Changes That Occur in the Proteins of Soybean Meal as a Result of Storage

BY D. BREESE JONES AND CHAS. E. F. GERSDORFF

It has been observed from time to time when extracting proteins from ground seeds that the amount of nitrogen which can be extracted with neutral salt solutions decreases with the aging of the meal. These observations suggested that other changes may occur which could well affect not only the chemical properties of the proteins but also their nutritional value. If so, it is obvious that this presents a problem of far-reaching importance. Large quantities of grains and other seeds, both whole and ground, undergo periods of storage and shelf aging before they reach the consumer.

Studies have been started to investigate the nature and extent of changes which occur in the proteins of seeds (both whole and ground) when stored under different conditions. Results thus far obtained show that marked changes in the chemical properties of the proteins of ground soybeans occur very soon after grinding. Some of these changes suggest a decrease in the biological value of the proteins.

Two portions of freshly ground soybeans were solvent-extracted. One portion was made practically fat-free, and the other to contain about 11% fat. Samples of both lots of the meal were stored in sealed jars and in bags, in constant temperature rooms at 76 and 30F°. The samples were analyzed at intervals of one, three, and six months, and the results compared with those obtained at the start on the freshly ground meal.

Table I shows percentage decreases in the amount of nitrogen extracted by 10% sodium chloride solution, in true protein content, as determined by the Stutzer method, and in digestibility of the protein *in vitro*. Analyses were made at the end of one, three, and six months' storage periods. At the end of one month significant decreases in values had occurred in all the samples. On further storage the values continued to decrease. By the end of six months the digestibility of the protein of the low-fat meal stored in bags at 76° had dropped nearly 19% below that of the meal when freshly ground. The greatest changes occurred at 76°, although at 30° the changes were surprisingly high. Greater changes occurred in the meals stored in bags than in those stored in sealed jars. Of

TABLE I

PERCENTAGE DECREASES IN VALUES FOR TRUE PROTEIN, SOLUBILITY AND DIGESTIBILITY OF PROTEIN, AFTER STORAGE OF SOYBEAN MEAL UNDER DIFFERENT CONDITIONS FOR ONE, THREE, AND SIX MONTHS

Storage conditions		True Protein, %			Extractability, %			Digestibility, %		
		1 mo.	3 mos.	6 mos.	1 mo.	3 mos.	6 mos.	1 mo.	3 mos.	6 mos.
STORED IN JARS										
High-fat meal	30°F.	0.31	2.88	4.35	1.18	3.08	4.53	0.92	5.61	7.26
High-fat meal	76°F.	2.15	4.83	7.16	2.92	5.91	8.71	4.53	9.49	12.05
Low-fat meal	30°F.	3.01	4.21	5.44	1.51	5.04	7.53	3.80	10.41	12.97
Low-fat meal	76°F.	3.95	6.36	8.71	3.82	8.47	10.72	5.57	15.30	17.25
STORED IN BAGS[a]										
High-fat meal	30°F.	..	..	5.85	..	..	8.92	..	...	10.43
High-fat meal	76°F.	..	..	8.75	..	..	13.11	..	...	14.48
Low-fat meal	30°F.	..	..	6.76	..	..	8.94	..	...	15.13
Low-fat meal	76°F.	..	..	9.97	..	..	12.39	..	...	18.94

[a] Analyses of meals stored in bags were made only after six months' storage.

interest is the consistently greater changes that occurred in the low-fat samples than in the high-fat samples. The total nitrogen and free ammonia content of all the samples remained constant throughout the storage periods. The high-fat samples showed a slight increase in free fatty acids, particularly in the samples stored at 76°.

Storage of soybean meal apparently results in partial denaturation of the proteins as indicated by their decreased solubility in salt solution. A proteolysis is also indicated by the drop in true protein values. The nature of the marked decrease in digestibility *in vitro* is being studied.

The chemical studies outlined above are being supplemented by feeding experiments to determine the effects of storage on the biological value of the proteins. Storage studies on the samples will be continued for two years or more. Final results and details of the work will be published later. Similar studies on the proteins of other seeds of importance as foodstuffs will be made both on the meals and on the whole grains.

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RECEIVED FEBRUARY 7, 1938

The Standard Electromotive Force of the Lead Electrode

BY JAMES J. LINGANE

There is considerable uncertainty in the literature regarding the standard e. m. f. of the lead electrode. The value 0.122 v., given in the "International Critical Tables,"[1] was calculated by Lewis and Randall,[2] from Gerke's measurements[3] of the cell $Pb/PbCl_2$, $AgCl(s)/Ag$, and an activity coefficient of saturated lead chloride computed from the data of Brönsted.[4]

Carmody[5] later studied this cell more carefully, extending the measurements to very small concentrations of lead chloride, and he obtained the value 0.1263 v. for E^0_{Pb} at 25°. Using the accurate activity coefficients of lead chloride obtained from his measurements, Carmody recalculated E^0_{Pb} from Gerke's data and obtained the value 0.1264 v., which agrees very well with his own value.

However, Randall and Cann,[6] in an apparently equally careful study, later obtained the value 0.1203 v. for E^0_{Pb}, from their measurements of the cell $Pb/Pb(NO_3)_2/KNO_3/KCl$, $AgCl(s)/Ag$ with *flowing* liquid junctions. Carmody recently[7] has attributed this lower value of Randall and Cann to the fact that they flowed the cell solutions *directly* over the silver–silver chloride electrodes. He has shown[8] that flowing the electrolyte directly over silver–silver chloride electrodes causes their potential to become about 6 mv. positive to the same electrodes in equilibrium with the cell solution. When this correction of 6 mv. is applied to the data of Randall and Cann, the corrected value becomes 0.1263 v., in exact agreement with Carmody's value.

Since this correction is somewhat uncertain, and may depend on the method of preparing the silver–silver chloride electrodes, it is very desirable to obtain further evidence before it is accepted.

The standard e. m. f. of the lead electrode can

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(1) "International Critical Tables," Vol. VI, 1929, p. 332.

(2) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 424.

(3) R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).

(4) J. N. Brönsted, *Z. physik. Chem.*, **56**, 645 (1906).

(5) W. R. Carmody, THIS JOURNAL, **51**, 2905 (1929).

(6) M. Randall and J. Y. Cann, *ibid.*, **52**, 589 (1930).

(7) W. R. Carmody, *ibid.*, **54**, 210 (1932).

(8) W. R. Carmody, *ibid.*, **54**, 188 (1932).

be evaluated from the standard e. m. f. of the lead–lead sulfate electrode and the activity product, K, of lead sulfate by means of the relation

$$E^0_{\mathrm{Pb}} = E^0_{\mathrm{PbSO_4}} + (RT/2F) \ln K \qquad (1)$$

in which E^0_{Pb} is the standard e. m. f. of the lead electrode, Pb/Pb^{++} (a = 1), and $E^0_{\mathrm{PbSO_4}}$ is the standard e. m. f. of the lead–lead sulfate electrode, Pb/PbSO$_4$(s), SO$_4^=$ (a = 1).

According to Harned and Hamer[9] the standard potential of the *two-phase lead amalgam*–lead sulfate electrode is 0.3495 v. at 25°. This is in agreement with the value 0.3505 v. given by Shrawder, Cowperthwaite, and La Mer.[10] We will use the average value 0.3500 ± 0.0005 v. Since the potential of two-phase lead amalgam against solid lead is 0.0058 v.,[3,5,6] the standard e. m. f. of the *solid lead*–lead sulfate electrode becomes 0.3558 v.

Kolthoff and von Fischer[11] recently have completed a study in this Laboratory of the *solubility* of lead sulfate by the conductance method and by direct analysis of the saturated solutions. From their data the solubility of lead sulfate at 25° is 1.48 (±0.02) × 10^{-4} molar. This is in good agreement with the value 1.47 × 10^{-4} molar given by Crockford and Brawley,[12] and the value 1.48 × 10^{-4} molar taken from the data of Kolthoff and Rosenblum.[13]

The activity coefficient of lead sulfate in its saturated solution, computed from the Debye–Hückel limiting law, is 0.893. Using the extended Debye–Huckel equation, with the plausible value of 4 Å. for the ion-size parameter, the calculated activity coefficient is 0.897. From this value, and the value 1.48 (±0.02) × 10^{-4} molar for the solubility of lead sulfate, the activity product of lead sulfate at 25° is 1.76 (±0.04) × 10^{-8}.

By substituting these data into eq. (1), we find for the standard e. m. f. of the *solid* lead electrode

$$E^0_{\mathrm{Pb}} = 0.3558 + \frac{0.05915}{2} \log (1.76 \times 10^{-8}) = 0.1264 \text{ v.} \qquad (2)$$

This value, computed from independent data of different investigators, is in excellent agreement with the value 0.1263 v. found by Carmody, and with the corrected values of Gerke (0.1264 v.) and Randall and Cann (0.1263). It is evident, therefore, that the present accepted[1] value of E^0_{Pb} (0.122 v.) is too low, and that the most reliable value is very close to 0.1263 v.

SCHOOL OF CHEMISTRY OF THE
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RECEIVED DECEMBER 30, 1937

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[9] H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 33 (1935).

[10] J. Shrawder, Jr., I. A. Cowperthwaite, and V. K. La Mer, *ibid.*, **56**, 2348 (1934).

[11] Private communication, submitted to THIS JOURNAL.

[12] H. D. Crockford and D. J. Brawley, *ibid.*, **56**, 2600 (1934).

[13] I. M. Kolthoff and C. Rosenblum, *ibid.*, **55**, 2656 (1933).

The Diazotization of Picramide

BY WARREN C. LOTHROP

During further investigations of the coupling of 5-hydroxy-6-methylhydrindene[1] with diazotized amines it seemed of interest to use diazotized picramide. The diazonium solution obtained by the method recently described by de Milt and van Zandt,[2] however, gave no reaction and therefore their reported coupling with β-naphthol was repeated. The compound formed with this reagent had the properties ascribed to it by the authors: a relatively low melting point (147°), which, however, could be raised by repeated crystallization from acetic acid to 155°; remarkable solubility in common solvents, and, in addition, extreme solubility in cold dilute alkali. The latter seemed particularly significant since it was shown long ago[3] that azo compounds formed by the coupling of β-naphthol are usually insoluble in alkali.

The coupling of diazotized picramide with β-naphthol also has been reported by Schoutissen,[4] but the azo compound which this investigator obtained had properties very different from those given above. It melted at 260°, was insoluble in most common solvents, and dissolved in alkali only with decomposition.

It seemed possible that the product obtained by the newer method might in reality be the molecular addition compound previously prepared by Witt[5] and noted by Misslin.[6] This was found to be the case. A sample was prepared from equimolecular quantities of β-naphthol and picramide and analyzed: (calcd. for $C_{16}H_{12}O_7N_4$: N, 15.05. Found: N, 14.67). This bright red compound (m. p. 161–162°) when mixed with the disputed product (m. p. 155°) melted at 155–157°, and was indistinguishable from it in other respects.

These results explain the observed discrepancy and lead to the conclusion that the new method outlined by de Milt and van Zandt for the di-

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[1] Fieser and Lothrop, *ibid.*, **59**, 945 (1937).

[2] De Milt and van Zandt *ibid.*, **58**, 2044 (1936).

[3] Liebermann, *Ber.*, **16**, 2858 (1883).

[4] Schoutissen, THIS JOURNAL, **55**, 4533 (1933).

[5] Witt, *Ber.*, **41**, 3093 (1908).

[6] Misslin, *Helv. Chim. Acta*, **3**, 636 (1920).

azotization of difficultly diazotizable amines is ineffective in the case of picramide.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY RECEIVED NOVEMBER 3, 1937
CAMBRIDGE, MASSACHUSETTS

The Preparation and Purification of Hydrous Lanthanum Hydroxide Sols

BY THERALD MOELLER AND FRANCIS C. KRAUSKOPF

Although hydrous lanthanum hydroxide sols have been prepared by several workers,[1–5] the methods used are laborious or yield unstable suspensions. While attempting to improve upon some of these methods, it was noted that lanthanum hydroxide freshly precipitated in the presence of lanthanum chloride is readily peptized by the latter when the temperature is raised to 50°. The following procedure based upon this fact has been found convenient: 3.5 g. of lanthanum chloride heptahydrate is dissolved in a small amount of carbon dioxide-free water and from three-tenths to nine-tenths of the equivalent amount of normal ammonium hydroxide added. This gives a slimy, gelatinous precipitate. Sufficient carbon dioxide-free water is added to make a total volume of 400 cc., and the suspension is warmed to 50°. Peptization begins immediately, and within a few minutes the entire precipitate is dispersed to an homogeneous sol. The sol is cooled to room temperature, diluted to 500 cc., and dialyzed in collodion bags[6] stoppered to exclude air.

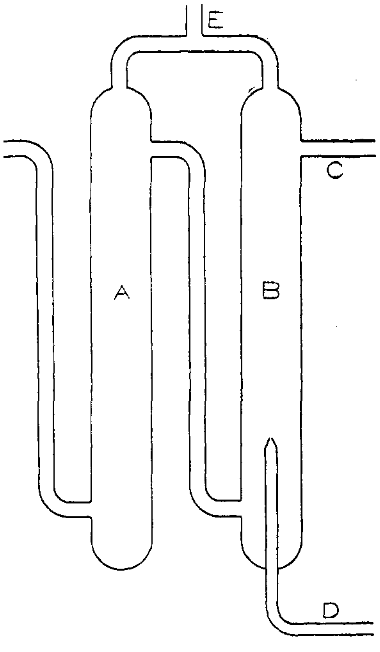

Fig. 1.—"Sweeping-out" apparatus.

In agreement with previous reports[7,8] concerning the relatively high basicity of lanthanum hydroxide and the ease with which its aqueous suspensions absorb carbon dioxide, it was found that dialysis against distilled water containing carbon dioxide converted the dispersed hydroxide into crystalline lanthanum carbonate. Accordingly, an apparatus was designed in which a continuous supply of carbon dioxide-free water was prepared by heating the water to 95° and sweeping out the residual gas with a current of nitrogen. The procedure is as follows: distilled water is heated by passing it through thirty feet (9.2 meters) of 10-mm. glass tubing immersed in an oil-bath maintained at 95 ± 1°. The hot water then enters the "sweeping-out" apparatus, the details of which are shown in Fig. 1. The two columns A and B are each 5 cm. in diameter and 40.5 cm. in height. The water enters at C and flows down column B countercurrent to a stream of nitrogen introduced at D. The exit gases are led off at E where a slight suction is maintained to ensure ready removal. From B the water flows into column A which serves to remove any entrained bubbles of gas not taken out in B. The exit water from A, after being cooled to any desired temperature in a countercurrent cooling system, flows into the dialyzer. The columns are supported in the oil-bath, and the nitrogen, after being passed over soda-lime, is preheated in a fifteen foot (4.6-meter) length of 8-mm. glass tubing before being passed into B. Pyrex glass is used throughout.

Sols dialyzed against water freed of its carbon dioxide in this apparatus are practically free from lanthanum carbonate. However, they readily absorb carbon dioxide from the air unless protected. Data for some of the dialyzed sols are given in Table I. It will be noted that all sols contain small amounts of chloride. Since attempts to remove the chloride completely by prolonged dialysis always have resulted in complete coagulation, it would appear that some lanthanum

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(1) Böhm and Niclassen, *Z. anorg. Chem.*, **132**, 1 (1923); *cf.* Müller, *ibid.*, **57**, 311 (1908).

(2) Freundlich and Schalek, *Z. physik. Chem.*, **108**, 153 (1924).

(3) Britton, *J. Chem. Soc.*, **127**, 2142 (1925).

(4) Sadolin, *Z. anorg. Chem.*, **160**, 133 (1927).

(5) McCutcheon and Smith, THIS JOURNAL, **29**, 1460 (1907).

(6) Madson and Krauskopf, *J. Phys. Chem.*, **35**, 3237 (1931).

(7) Vesterberg, *Z. anorg. allgem. Chem.*, **94**, 371 (1916).

(8) Euler and Nilsson, *Ber.*, **57**, 217 (1924).

TABLE I

DATA FOR LANTHANUM HYDROXIDE SOLS

Sol	NH_4OH, % of equiv.	Hours dialyzed[a]	La_2O_3, mg. per l.	Cl_1 mg. per l.	*p*H
6c	33.3	40	250	22.9	6.9
6d	33.3	45	500	17.2	7.0
6e	33.3	48	829	34.4	7.4
6f	33.3	51	755	37.0	
6g		84	438	10.5	7.3
6z	33.3	120	553	15.0	7.0
6h(1)	50.0	67	1158	103	7.8
6h(2)	67.0	67	1984	60.7	8.3
6h(3)	89.0	67	2312	48.7	7.9

[a] All sols dialyzed at 20 to 25°.

chloride is necessary for stability. When protected from carbon dioxide, the more dilute sols are reasonably stable, but slow sedimentation takes place in the more concentrated ones. The sols are bluish-white by both reflected and transmitted light, but on strong illumination, the light transmitted is rich in the orange, a qualitative verification of the Rayleigh equation. The particles are positively charged.

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RECEIVED DECEMBER 2, 1937

Preparation of Pellets of Radioactive Lead

BY JOHN E. RICCI AND MILTON BURTON[1]

In the lead mirror method of detecting free radicals,[2] the lead used must be as pure as possible; the presence of oxide is distinctly objectionable. In experiments in which the lead transported is measured by the use of a radioactive isotope (Ra D) it is found necessary to prepare lead pellets of minimum size and maximum purity so as to ensure maximum sensitivity of the method. Various methods of preparation, which might be expected to work but generally have proved unsatisfactory, are described in the literature. We have found that the one described below, based upon a reaction used by Stas,[3] gave pellets of desirable form and character.

Several hundred crushed radon tubes were triturated in a Pyrex mortar with concentrated aqua regia for a prolonged period of time, and the extract filtered, through paper, into a quartz beaker. The treatment with concentrated acids was repeated on the siliceous residue, and the two filtrates combined, giving a total volume of 60–70 cc. At this point a definite weight of pure lead nitrate was added, the quantity depending on the size of pellet and the degree of radioactivity desired; in the following procedure the amounts stated are for the preparation of a 0.1-g. pellet of lead.

The next step was the removal of nitric acid by repeated evaporation to dryness with hydrochloric acid, on a hot plate. The residue was then dissolved in 33 cc. of 5 *N* hydrochloric acid, and treated with hydrogen sulfide to precipitate the mercury (contained in the radon tubes as a result of the method of filling the latter), the mercuric sulfide being filtered off on paper and washed with hot dilute hydrochloric acid. The filtrate so obtained was again evaporated to dryness, repeatedly, this time with water, to remove hydrochloric acid, and the residue of lead chloride crystals was dissolved by warming in 30 cc. of water. The removal of the hydrochloric acid is necessary in order to precipitate the lead as oxalate from a neutral solution without too high a concentration of ammonium salts resulting from the neutralization of acid. To the cold aqueous solution, then, was added 4 cc. of saturated ammonium oxalate solution and 2–3 drops of dilute ammonium hydroxide. After stirring and thorough cooling the mixture was allowed to stand overnight. The precipitate was then filtered on a Neubauer porcelain microcrucible, with suction, washed with cold water, and dried partially with air. This was followed by thorough drying (and partial decomposition to oxide) at 250°.

For the reduction to the metallic state, the dry residue of oxalate + oxide was transferred into an ordinary porcelain crucible, and covered with 1–2 g. of dry potassium cyanide. The inclined, open crucible was heated slowly and carefully on a Bunsen flame, and finally heated very strongly for about ten minutes. On cooling, the potassium cyanide was washed away with water, and the lead pellet picked out and dried. If the lead thus finally obtained should prove to be powdery, or finely divided rather than in the form of one or a few pellets, the potassium cyanide treatment is repeated on the dry lead, until the metal is obtained in a satisfactory pellet or two.

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(1) Present address: University of California, Berkeley, California.

(2) *Cf.* Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

(3) Stas, *Bull. Acad. Belg.*, [2] **10**, 295 (1860); *Chem. News*, **4**, 307 (1861).

The Conductance of Dilute Solutions of Potassium Ferrocyanide

By Elijah Swift, Jr.

One of the most important problems in the study of the conductance of solutions is the selection of a reliable method for the extrapolation of the measured values to obtain the limiting conductance. This extrapolation has been made by the use of numerous empirical equations, such as the Jones and Dole equation,[1] which fit the data over a wide range, or by the use of the Onsager equation (or one of its modifications),[2] a limiting equation applicable only to dilute solutions. These two methods do not always yield concordant results, the disagreement being more marked in the case of the higher valence type salts.

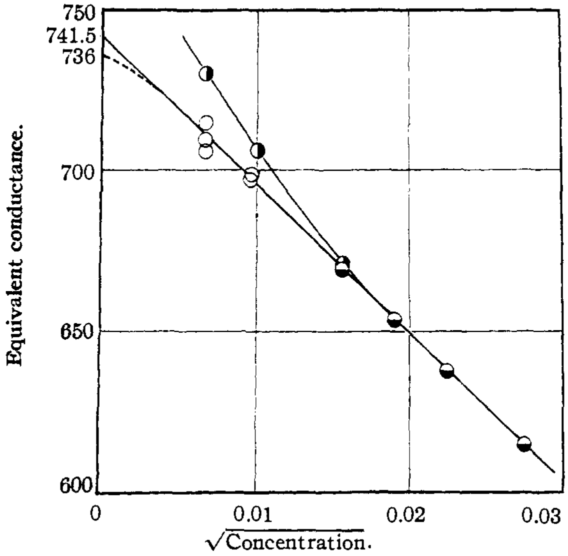

Fig. 1.—◒, Jones and Jelen, experimental points; ◑, calculated by Jones and Dole equation; ○, Swift, experimental points; - - - Davies' extrapolation.

Jones and Jelen[3] found in the case of potassium ferrocyanide that the Jones and Dole equation best fitting all their data up to saturation yields a value of 783 for the limiting conductance. If the equivalent conductance calculated by this equation is plotted against the square root of the concentration, the curve obtained has a positive curvature throughout. Because of this upward curvature, Jones and Jelen state that the value obtained by straight line extrapolation of their data (742) is probably too low. On the other hand, they believe that the extrapolation by means of the Jones and Dole equation gives too high a value.

Davies[4] has proposed a modification of the Onsager equation which makes allowance for the effect of partial association of the ions, and which requires a negative curvature at extreme dilution. (Figure 1.) Applying this equation to the data of Jones and Jelen, he obtained a value of 736 for the limiting conductance.

It was the purpose of this research to extend the measurements of Jones and Jelen to greater dilution in order to determine the direction of the limiting curvature and hence to evaluate the limiting conductance more exactly.

Measurements of the conductivity were made at 25° using the same technique as employed by Jones and Jelen and observing their precautions. Considerable difficulty was experienced at these low concentrations from a continuous change in the resistance of the solutions during measurement, which was perhaps due to an unknown reaction of the material in the cell. This uncertainty amounted to as much as 0.5% of the measured resistance and was corrected for by extrapolation of the measured values to obtain a hypothetical value at the time of dissolving the salt. With the best conductivity water available, which ranged from $0.2-0.6 \times 10^{-6}$ in specific conductance, the water correction amounted to 1–2% and so offered considerable opportunity for error. The results which are tabulated below are also shown in the figure. Measurements were made at concentrations below those given in the table, but the results were so discordant that they are not included.

Table I

c	$\sqrt{c}$	Λ
0.000093715	0.00968	697.9
.000091442	.00956	697.4
.000044078	.00664	706
.000044054	.00664	707
.000044083	.00664	710
.000044100	.00664	715
.000044097	.00664	714

The results for each of the two groups of concentrations gave on averaging: for c = 0.00009216, Λ = 697.7, and for c = 0.00004408, Λ = 710.4. The best straight line that could be drawn through these two points and Jones and

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[1] Grinnell Jones and M. Dole, This Journal, **52**, 2245 (1930).

[2] L. Onsager, *Trans. Faraday Soc.*, **23**, 341 (1927); T. Shedlovsky, This Journal, **54**, 1405 (1932).

[3] Grinnell Jones and F. C. Jelen, *ibid.*, **58**, 2561 (1936).

[4] C. W. Davies, *ibid.*, **59**, 1760 (1937).

Jelen's four lowest points, which cover the range 0.00025 to 0.00075 molar, was found by the method of least squares. The equation for this line is $\Lambda = 741.56 - 4621\sqrt{c}$, and there is no evidence of curvature from it within the experimental error up to 0.00075 molar.

Jones and Jelen stated that there was no experimental evidence or theoretical warrant for a change in the direction of curvature at the lowest concentrations. These measurements indicate that the curve straightens out in the most dilute solutions as is the case with lower valence type salts, and that the Jones and Dole equation gives too high a value of the limiting conductance due to the upward curvature it imposes on the extrapolated line. On the other hand, no evidence is found for the negative curvature postulated by Davies, although it is not necessarily excluded at still lower concentrations.

The author wishes to thank Professor Grinnell Jones for aid and advice during the course of this research.

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RECEIVED JANUARY 24, 1938

A Calcium Chloride Compound of *α-l*-Sorbose

BY ROY L. WHISTLER AND R. M. HIXON

Calcium chloride is known to form crystalline addition compounds with several sugars.[1-5] All of these compounds undergo mutarotation; the rotatory changes in most cases follow closely the changes exhibited by the pure sugar components. The preparation of a calcium chloride compound of *l*-sorbose was undertaken in the hope of obtaining a compound containing sorbose in either the alpha or beta stereoisomeric forms. Should such a compound be obtained its acetylation might yield a convenient method for preparing the corresponding sorbose acetate.

The compound produced showed a rapid but small upward mutarotation thus resembling the rotatory changes exhibited by pure sorbose.[6] The observed initial rotation was that calculated assuming the sugar component to be unaltered structurally and to possess the same specific rotation as pure sorbose. On acetylating the addition compound by the general procedures for acetylation, the keto sorbose pentaacetate was obtained. Hence, the property of sorbose to form preferentially an open chain pentaacetate is also exhibited by the calcium chloride addition compound. Acetylation using the special method[7] designed to give sorbose tetraacetate produced this tetraacetate in good yield. These facts indicate that the calcium chloride addition compound does not stabilize sorbose in a new form.

Experimental

Twenty grams of *l*-sorbose was dissolved in 25 cc. of warm water and 18 g. of calcium chloride slowly added with stirring. After effecting complete solution by stirring and heating on a hot-plate, the solution was placed in a desiccator over phosphorus pentoxide. In three weeks the solution had turned to a thick mush of crystals. These were stirred with absolute alcohol, filtered and washed free from sirup with absolute alcohol; yield 15 g. The crystals melted at 159° (corr.) and were stable in air. Recrystallization by dissolving in water and slow concentration of the sirup in a desiccator produced fine crystals melting at 159° (corr). Dissolved in water (*c*, 4.4) the rotation two minutes after solution was $[\alpha]^{26}_{D}$ −24.2°. In fifteen minutes the value became constant at $[\alpha]^{26}_{D}$ −23.9°.

Anal. Calcd. for $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$: Ca, 12.25; Cl, 21.72; α, 2.30. Found: Ca, 12.26; Cl, 21.77; α, 2.30.

The addition product can be prepared in a shorter time by adding three volumes of absolute alcohol to the prepared calcium chloride–sorbose sirup, described above, and then ether in small quantities until crystallization occurs.

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(1) Dale, THIS JOURNAL, **51**, 2788 (1929).

(2) Isbell, *Bur. Standards J. Research*, **5**, 741 (1930).

(3) Dale, THIS JOURNAL, **56**, 932 (1934).

(4) Austin and Walsh, *ibid.*, **56**, 934 (1934).

(5) Hann and Hudson, *ibid.*, **59**, 2075 (1937).

(6) Pigman and Isbell, *Bur. Standards J. Research*, **19**, 443 (1937).

(7) Arragon, *Compt. rend.*, **198**, 1508 (1934).