the ratio of bromide ion to ethyl radical, ether solutions of anhydrous magnesium bromide prepared by fusion of magnesium bromide with ammonium bromide, or of diethylmagnesium from diethylmercury and magnesium, were added in the desired amounts. The solutions were analyzed by titration with standard sulfuric acid followed by titration with standard silver nitrate.

The precipitation with dioxane was carried out in Babcock milk-testing bottles with a volume of about 40 cc. All glassware was dried at 150° and swept out with nitrogen before use. To 20 cc. of absolute ether and 2 cc. of purified dioxane[6] was added 10 cc. of the Grignard solution. The flasks were tightly stoppered with dried No. 00 rubber stoppers that fitted well down into the neck, and fastened to a shaking machine. After shaking for the desired length of time at room temperature, the flasks were centrifuged, the stoppers removed, and a 20-cc. aliquot taken for analysis. In all cases only traces of halogen were present in the solution. For all analyses duplicate determinations checked within 0.1 to 1.0%.

Summary

1. The rapid change in composition after precipitation of the halogen compounds in a Grignard reagent by dioxane makes the method useless for determining the composition of the original Grignard solution.

2. In most cases greatly improved yields of solutions of dialkylmagnesium can be obtained from ordinary Grignard reagents by shaking for four to ten hours before removing the precipitate formed on the addition of dioxane.

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[6] Dioxane is hygroscopic and it, as well as the ether, was kept over clean sodium.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Behavior of Inulin in Liquid Ammonia[1]

BY F. W. BERGSTROM AND A. E. GILMORE

Haworth[2a] and Irvine[2b] have shown by chemical methods that the molecular weight of inulin in water is about 5000, while Berner[3] has found values in water lying between 4600 and 5100 by cryoscopic means. In marked contrast are the results of a number of workers who have repeatedly obtained low results for the molecular weight of inulin in solvents such as liquid ammonia, acetamide, formamide and water. Thus, Schmid and co-workers[4,5] as a result of cryoscopic determinations in liquid ammonia conclude that inulin dissolves as a difructose anhydride, in agreement with the earlier work of Pringsheim, Reilly and Donovan[6] with solutions in acetamide. Pringsheim[6] and Reilly,[7] however, report that inulin has a molecular weight of around 1200 in water. Bergmann,[8] in an attempt to explain the low values given by these cryoscopic measurements, advanced the theory that inulin and certain of its derivatives were depolymerized when dissolved in liquid ammonia, formamide or acetamide. Berner,[3,9] on the other hand, has contended that the low results obtained by other investigators were due to the use of specimens of inulin which may have contained alcohol or other impurities.

The present investigation has as its purpose an examination of solutions of inulin in liquid ammonia to determine whether any reaction occurs between solute and solvent, and whether the physical properties of these solutions are best to be explained by assuming a solute of high or of low molecular weight.[10]

Behavior of Inulin in Liquid Ammonia.—If inulin is stirred into liquid ammonia contained in an open Dewar vessel, it dissolves readily, forming a water clear solution. If added faster than it will dissolve, it forms a clear very sticky gummy mass, which slowly passes into solution when broken up and agitated with the solvent. If this gummy mass is allowed to stand overnight in liquid ammonia, it changes to a non-adhesive translucent gel, which breaks up easily underneath the solvent, but does not again dissolve. If ammonia is allowed to evaporate rapidly from a freshly prepared solution of inulin, a thick sirup is formed, which hardens to a brittle crystal clear glass when all of the solvent has disappeared. Specimens of this glass

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[1] Original manuscript received April 27, 1936.

[2] (a) Haworth, *J. Chem. Soc.*, 2384 (1932); (b) Irvine, THIS JOURNAL, **55**, 1988–1994 (1933).

[3] Berner, *Ber.*, **66**, 397–400 (1933).

[4] Schmid and Becker, *ibid.*, **58**, 1968–1971 (1925).

[5] Schmid and Haschek, *Monatsh.*, **59**, 328–334 (1932).

[6] Pringsheim, Reilly and Donovan, *Ber.*, **62**, 2378–2381 (1929).

[7] Reilly, *Proc. Roy. Soc. Dublin*, **19**, 409–414 (1930).

[8] Bergmann, *Ann.*, **449**, 302–312 (1926).

[9] Berner, *Ber.*, **63**, 1356–1362 (1930).

[10] Taft, *J. Phys. Chem.*, **34**, 2792–2800 (1930), finds that inulin disperses well in liquid ammonia at its boiling point.

were exposed to the laboratory atmosphere for two weeks without visible change.

Solutions of inulin at room temperature or at −33° invariably are unstable, and a white flocculent precipitate begins to separate, usually within about half an hour of the beginning of the experiment. The following description is typical.

Inulin[11] (1.95 g.) was placed in a straight glass reaction tube sealed at one end, and provided with a small stopcock, sealed on as a side tube a few cm. below the open upper end. After tightly stoppering, the tube was evacuated with a mercury vapor pump, cooled to −78° (solid carbon dioxide–alcohol) and partially filled with liquid ammonia (about 27 cc.), distilled through the stopcock from a supply tank of the solvent dried over sodium. With a pressure slightly in excess of atmospheric within the tube, the stopper was removed cautiously and, while a vigorous stream of ammonia was maintained through the stopcock and out of the open end to prevent entry of air, the inulin was stirred up with the solvent (a stiff wire used) until it had dissolved. The end of the tube above the stopcock was sealed off and annealed (a relief valve on the ammonia line having been opened to establish atmospheric pressure within) and the stopcock closed. The solution became slightly cloudy within a short time, and after four and one-half hours contained a considerable amount of white flocculent precipitate. The tube was now removed from the cooling bath, and warmed to room temperature. After standing overnight, the entire contents had solidified, the solid behaving somewhat as a thixotropic gel, since it could be broken up by vigorous shaking of the tube, yielding a milky liquid which again solidified on standing.

The process by which the solid is formed does not strictly resemble gelatinization. Its rate of formation is slowed down rather than accelerated by low temperature. However, there is no apparent increase in viscosity as the process proceeds. The inulin separates as an exceedingly voluminous precipitate, which nearly fills the liquid. On standing, the particles of precipitate form a semi-solid sponge, which holds most of the liquid. The precipitate settles somewhat before solidifying, causing the solid to be more compact at the bottom. This precipitated inulin cannot be dissolved by adding more ammonia, but if it is removed from the tube, it quickly dries, and is then as soluble as the original inulin. Apparently solvation plays a leading role in its precipitation. This behavior is more characteristic of a colloid than of a substance of the molecular magnitude of a difructose anhydride.

Dialysis of Sucrose and Inulin.—If inulin dissolves in liquid ammonia as a difructose anhydride, as claimed by others,[4,5] it should dialyze through a membrane as readily as does cane sugar, a substance of the same molecular magnitude. The following experiments indicate that this is not the case.

The Pyrex cell shown in Fig. 1 consists of an outer compartment 4 × 52 cm. and an inner compartment, JH, held in position by means of the rubber slip joint at C. The membrane H was a short length (10 cm.) of Visking cellophane sausage casing, tied tightly at the lower end with a string, and fastened by means of a cord to the lower end of the inner cell.[12]

A weighed quantity of dried inulin was placed in tube B, which was rotated around the ground glass joint so that the closed end pointed downward. Dry ammonia gas was passed through E and A, and out of the hole J and stopcock D to displace air in the apparatus. (The rubber stopper at A was removed momentarily to displace air above J.) With D connected to a mercury bubbler[13] the outer cell was filled with ammonia by distillation through E. First, liquid ammonia for the cooling bath was run from a tank of the commercial liquid into the Dewar vessel through G. Tube F, which likewise passes through the stopper, leads to the waste. Ammonia readily condensed in the outer compartment, but it usually was advisable to condense the pure liquid in an external apparatus, and force it into H through tube A. With liquid levels in the two compartments the same, B was rotated to the position shown in Fig. 1, to introduce the specimen. This soon dissolved, when ammonia gas was passed into the outer cell through E for stirring. Dialysis was allowed to continue for about twenty-four hours, the Dewar being kept filled with liquid ammonia during this time. At the end of the experiment, the membrane and supporting tube were withdrawn, and the solvent inside allowed to boil off. The membrane was then cut open and the dialysate removed from its inner surface.

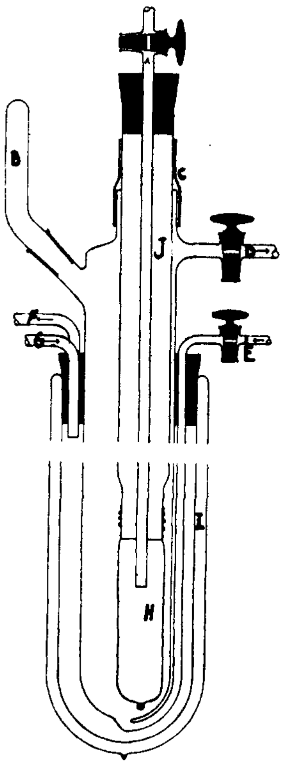

Fig. 1.

Sucrose was found to pass readily through the cellophane membrane, and was always found on the inside in rather large quantity. Inulin dissolved in the outer compartment to give a water clear solution, from which it slowly precipitated. In none of the experiments carried out was there any indication that inulin passed through the membrane. This may be regarded as further evidence that inulin forms colloidal solutions in liquid ammonia.

To test for a possible reaction between inulin and ammonia, in which water is formed, inulin was placed on the inside of the membrane, and the dialysis carried out as described. After several hours, metallic sodium was introduced from B (H having been raised above the level of liquid in the outer compartment), in order to convert di-

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[11] The highest grade Dahlia Inulin from the Pfanstiehl Chemical Co., dried for three weeks *in vacuo* over phosphorus pentoxide, $[\alpha]^{20°}\mathrm{D}$ −40.5°. Berner[9] found −40.2°.

[12] The diaphragm must be examined with a lens for pinhole leaks or imperfections both before and after use. If a leak developed during a run, the run was discarded.

[13] *Cf.* J-K, Fig. 1, *J. Phys. Chem.*, **35**, 742 (1931).

alyzed water to hydrogen, which was collected in a gasometer. No significant amounts of hydrogen were ever obtained. Experiments which will be described later have shown that no water is formed by the action of liquid ammonia on inulin at room temperatures.

Tyndall Effect in Liquid Ammonia Solutions of Inulin

Qualitative information regarding the relative size of the dissolved particles of inulin and the disaccharides in liquid ammonia was obtained with the use of a Tyndallmeter, constructed in the following manner.

The light source, a photo flood lamp, was mounted at one end of a wooden box, 110 cm. long and 10 × 10 cm. in cross section. A mirror at the other end reflected the light upward and at right angles to the incident beam, so that it passed lengthwise through the sealed tube containing the ammonia solution under examination. A lens between the mirror and the source was so adjusted that the light was brought to a focus about 3 cm. above the base of the ammonia tube. The intensity of the light was measured by photographic means. Neither the camera nor the meter was moved during the course of the experiments. The films and prints were uniformly exposed and developed.

Filtered liquid ammonia solutions of the sugars were prepared in the following manner. A long soft glass tube was constricted at the middle, and two small stopcocks sealed on as side tubes close to the constriction and on either side. A sintered Jena filter plate of finest porosity was ground into the constriction with emery and a solution of camphor in turpentine, and cemented in place with strong sodium silicate solution. Sugar, after thorough drying, was placed in one end of the tube (which was likewise carefully dried) and both ends of the tube sealed in a current of ammonia. Ammonia was distilled in to dissolve the specimen, the solution being forced through the filter by inverting the tube and cooling the empty half. It was immediately placed on the Tyndallmeter and photographed. (The concentration of the solutions was about 0.5%.) Solutions of sucrose and lactose were almost optically clear, but usually gave very slight Tyndall cones in spite of many filtrations, presumably because of material not retained by the filter. Solutions of inulin on the other hand gave very pronounced Tyndall cones, suggesting again the presence of colloidal particles.

Summary

Inulin, in liquid ammonia solution, behaves as a gelating colloid, and not as a difructose anhydride, as claimed by some investigators: since (1) it slowly precipitates on standing, forming a translucent gel; (2) it exhibits the Tyndall effect; and (3) it will not diffuse through a cellophane membrane, while sucrose does so readily.

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[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 592]

Measurement of a Reaction Rate at Equilibrium by Means of a Radioactive Indicator. The Reaction between Arsenic Acid and Iodine

By J. Norton Wilson and Roscoe G. Dickinson

In the study of chemical kinetics and equilibrium, it is customary to correlate the specific rates k_f and k_r for a pair of forward and reverse reactions with the corresponding equilibrium constant K, in accordance with the equation

$$k_f/k_r = K$$

In making empirical tests of this relation, however, the specific rates k_f and k_r are in general measured with the system considerably displaced from equilibrium in order that accurate values may be obtained more easily. Hence it is of interest to appreciate that such methods do not eliminate the possibility that k_f and k_r might actually change as equilibrium is approached, but in such a way as to keep the ratio k_f/k_r approximately constant. The use of radioactive indicators, which have become an important chemical tool, permits the measurement of rates at equilibrium and thus makes it possible to place the kinetic theory of equilibrium on a sounder experimental foundation.

In the present paper are described some experiments involving reactions on which previous rate[1] and equilibrium[2] measurements have been made by customary methods; these reactions are the oxidation of arsenious acid by iodine, and its reverse

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+ \quad (1)$$

Experimental Procedure.—A radioactive arsenic with a half period of twenty-six hours is formed from ordinary arsenic by neutron capture.[3] To utilize this we exposed 15 to 20 g. of pure crystalline arsenic (Kahlbaum) for two to three days to a radon–beryllium source of neutrons whose initial strength was 200 to 300 millicuries; the exposure occurred in a large block of paraffin. The arsenic

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(1) J. R. Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905); W. C. Bray, *ibid.*, **9**, 578 (1905); H. A. Liebhafsky, *ibid.*, **35**, 1648 (1931).

(2) E. W. Washburn and E. K. Strachan, *ibid.*, **35**, 681 (1913).

(3) F. A. Paneth and J. W. J. Fay, *Nature*, **135**, 820 (1935).