

Cleavage with Sodium Sulfide.—The reaction mixture from 0.1 mole of the quaternary salt and 0.05 mole of sodium sulfide was acidified with concentrated hydrochloric acid and extracted with ether. Benzyl sulfide was obtained by evaporation of the ether; yield 8 g. (75%); a portion recrystallized from ether melted at 49–50°. Dimethylaniline was isolated from the acidified reaction mixture as described above; yield 8.2 g. (68%); b. p. 190–193°.

Cleavage with Potassium Thiocyanate.—Benzyl dimethylphenylammonium thiocyanate (II) precipitated immediately in nearly quantitative yields when the reaction mixture was prepared as described above. After crystallization from a mixture of alcohol and ether it melted at 104°.

Anal. Calcd. for $C_{16}H_{18}N_2S$: N, 10.37. Found: N, 10.26.

The reaction mixture after refluxing for one hour was acidified with hydrochloric acid and extracted with ether. Removal of the ether gave benzyl thiocyanate; yield 9 g. (60%). A portion recrystallized from ethyl alcohol melted at 43°. Dimethylaniline was obtained from the acid solution as described above; yield 8.2 g. (68%).

Cleavage with Sodium Bisulfite.—Sulfur dioxide was evolved when this reaction mixture was boiled. After cooling and addition of sodium hydroxide sodium- α -toluenesulfonate crystallized. This was identified by conversion to α -toluenesulfonyl chloride, m. p. 93°. Dimethylaniline was separated from the alkaline solution and from the sodium α -toluenesulfonate by extraction with ether and distillation; yield 2.9 g. (24%).

When the reaction was run with 0.20 mole of sodium bisulfite the yield of sodium α -toluenesulfonate was 12.3 g. (63%); the yield of dimethylaniline was 4.9 g. (40%).

Cleavage with Sodium Sulfite.—From the reaction¹⁰ of 0.03 mole of the quaternary salt and 0.04 mole of sodium

sulfite, heated in 50 cc. of water at 80° for five hours there was obtained 63% of dimethylaniline. The excess sulfite was removed from the aqueous solution with barium hydroxide. After removal of excess barium with carbon dioxide and evaporation of the solution to the point of crystallization there was obtained 82% of sodium α -toluenesulfonate.

When the reaction was carried out as described in the general procedure above there was obtained 7 g. (58%) of dimethylaniline.

Cleavage with Sodium Thiosulfate.—A solution containing 0.05 mole of sodium thiosulfate and 0.10 mole of the ammonium salt was boiled under reflux for one hour. After cooling the mixture was extracted with ether. A heavy ether-insoluble oil originally present crystallized during the extraction. From the ether there was obtained 6.0 g. (99%) of dimethylaniline. The crystalline material was found to be benzyl dimethylphenylammonium S-benzyl thiosulfate; yield 19.5 g. (94%); m. p., after crystallization from alcohol and ether, 104°.

Anal. Calcd. for $C_{22}H_{26}O_2NS_2$: C, 63.7; H, 6.03; N, 3.38; S, 15.42. Found: C, 63.61; H, 6.10; N, 3.31; S, 15.42.

A sample prepared from sodium S-benzyl thiosulfate⁸ and the quaternary salt melted at 104° and gave no depression in melting point when mixed with the above product.

Summary

Benzyl dimethylphenylammonium chloride is readily cleaved by aqueous solutions of sodium hydrosulfide, sodium sulfide, sodium thiosulfate, potassium thiocyanate, sodium bisulfite and sodium sulfite. In each case dimethylaniline is liberated and the benzyl group becomes attached to the sulfur atom of the reagent.

URBANA, ILLINOIS

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(10) This experiment was carried out by Mr. R. W. McCready.

An Investigation into the Causes of Gel Formation by Some Organic Salts in Methanol Solution

BY HERBERT HENSTOCK

The salting out of substances from aqueous solutions by means of both like and unlike ions is usually used as a method of precipitating them in more or less crystalline condition; comparatively few are thrown out in a gelatinous state. The use of organic substances as precipitants is necessarily confined to those which readily mix with water; the most frequent being alcohol, by the employment of which the first of a series of aqueous gels was produced with calcium acetate as the only solid,¹ and similar ones with sodium benzoate,²

and with potassium ethyl sulfate.³ In these communications it was also shown that, although these salts are only slightly soluble in ethanol, they exhibit marked solubility in methanol,⁴ from which they can be thrown out of solution as perfectly clear gels by organic liquids, many of these being immiscible with water. Since this work was published it has been found that a number of other salts of organic acids (see List I) readily form transparent gels in methanol solution with various organic liquids as dispersion media or pre-

(1) Henstock, *Trans. Faraday Soc.*, **29**, 1101 (1933).

(2) Henstock, *ibid.*, **30**, 560 (1934).

(3) Henstock, *ibid.*, **31**, 1 (1935).

(4) Henstock, *J. Chem. Soc.*, 1341 (1934).

precipitants, and to a less degree with one or two of these liquids other salts (see List II) also form gels, which are opaque. Many salts of these and other metals come out of solution as colloidal precipitates with suitable dispersion media, and there are a correspondingly large number, which show no tendency to colloid formation.

LIST I

Salt	Dispersion medium
Lithium acetate	Acetone
Potassium propionate	Acetone, benzene
Potassium <i>n</i> -butyrate	Acetone, benzene
Sodium <i>n</i> -butyrate	Aniline, toluene
Calcium lactate	Benzene, acetone, ether, propanol
Potassium succinate	Benzene
Potassium methyl sulfate	Benzene, toluene, chloroform, bromobenzene, ethyl iodide, anisole, xylene, etc.

(These form transparent gels)

LIST II

Salt	Dispersion medium
Sodium formate	Benzene, propanol
Calcium <i>n</i> -butyrate	Ether
Calcium ethyl sulfate	Aniline
Sodium ethyl sulfate	Benzene
Sodium methyl sulfate	Benzene, toluene, anisole, etc.

(These form opaque gels)

It appears from this that these gels are formed by a variety of organic acids but the cations are confined to the alkali metals and calcium. It is not apparent why gels should be formed under the above conditions, especially when the very small amounts of solids contained in some of them are considered; *e. g.*, in the calcium acetate, methanol, benzene gel¹ the amount of anhydrous salt is less than 0.2% of the whole. The present communication describes an attempt to investigate these two points.

In scrutinizing the causes which might be connected with this property of gel formation, one is led to conclude that it is not dependent upon a large number of molecules of solvent taken up by the anions of a salt. As is well known, the sulfonates of the benzene series have this property to a high degree in aqueous solution and, therefore, should readily form gels, but it has been found that none are produced by the sodium, potassium or calcium salts of benzene and other aromatic sulfonic acids in either aqueous or methanol solutions. On the other hand, gel formation seems to depend on (1) a cation having a large volume, but

of an element of small atomic number, (2) an anion of fairly low molecular weight and low oxygen content, especially among carboxylic acids, (3) a fairly concentrated solution, (4) a dispersion medium or precipitant, in which the salt is insoluble, but which is miscible with the solvent in all proportions and (5) to a less extent on the crystalline or amorphous nature of the salt. Nevertheless, these do not go to the heart of the problem since none, except perhaps number (4), is applicable in all cases.

Gel formation must, therefore, be closely connected with some inherent property of the salts themselves, but only when in solution in a suitable solvent coupled with a suitable dispersion medium. The salt solutions are not, strictly speaking, sols capable of forming gels on standing, cooling or other appropriate treatment, until the dispersion medium is added to them; but when that has been done, the gels form so rapidly that detailed examination of the true sols is not practicable. The most important parts of these true sols are the methanol salt solutions, and these have been investigated, as being most likely to yield useful information.

Experimental

In order to enquire into the relationships between the conditions existing in these gel forming and non-gel forming salt solutions, the suggestions of Marc⁵ were improved into a method for estimating the relative quantities of adsorbed salts. He states that in general (1) "Colloids adsorb crystalloids with small amounts of colloids, and (2) crystalloids adsorb colloids with small amounts of crystalloids." If, then, the methanol salt solutions are treated with solid colloids, *i. e.*, adsorbents, these should adsorb more of those salts which are of a crystalline, non-gel forming nature, and less of those of a more colloidal gel forming type: in other words, the amounts adsorbed should indicate their colloidal nature.

The salts (see table) chosen for examination readily gelatinize with a number of dispersion media: and since three metals are involved, the salts of each one with each acid were examined under comparable conditions. The salt, which gives gels in the most dilute, but almost saturated, solutions is calcium acetate, 0.5 g. in 100 g. of methanol, and this was adopted as the standard for all the solutions.

The methanol was purchased as pure, and was further purified as already described.⁴ The salts were twice recrystallized from methanol or other solvent and dried at suitable temperatures to render them anhydrous. Solutions of each salt of the above strength were made in methanol and the solid content of each was determined exactly by evaporating a weighed quantity to dryness, heating

(5) Marc, *Kolloid Z.*, **13**, 281 (1913).

the residue for thirty minutes at 110° (85° for the ethyl and methyl sulfates) and weighing it as the total solid content. Aliquot portions of each solution were then shaken separately, in stoppered bottles, for one minute, at intervals of ten minutes, during one hour, with one-fourth their weight of each of the four adsorbents, kieselguhr, kaolin, animal charcoal and lampblack, and, after filtration through well dried filter paper, their solid content was found as detailed above for the untreated solutions. The four adsorbents each contained something soluble in methanol; they were, therefore, previously washed with successive portions of the solvent, until nothing more went into solution, and finally dried at 100°. Thus the quantities of salts adsorbed were found by subtracting the weight found after each experiment from the total solid content. The results given in the table are the mean values of several closely agreeing experiments and are expressed as % quantities of salts adsorbed from the total salt present in each solution.

TABLE OF % OF SALTS ADSORBED BY

	Kieselguhr	Kaolin	Animal charcoal	Lamp-black
Acetates				
Ca	31.0	11.4	26.1	24.7
Na	49.7	18.2	38.2	45.2
K	58.5	18.4	39.6	72.1
Benzoates				
Na	14.0	6.0	18.0	28.0
Ca	26.4	19.1	35.3	38.2
K	39.2	34.1	49.3	46.8
Ethyl sulfates				
K	0	6.4	0	3.7
Ca	4.1	15.2	0.9	8.5
Na	5.4	16.3	14.5	9.1
Methyl sulfates				
K	0	15.0	2.6	5.2
Na	6.1	33.3	10.2	12.9
Ca	13.4	40.3	11.5	28.8
Propionates				
K	7.2	11.5	8.1	7.0
Ca	15.0	25.0	15.4	12.7
Na	19.3	25.8	17.2	18.2
<i>n</i> -Butyrates				
K	6.3	9.0	5.4	16.0
Ca	12.2	15.8	10.5	28.0
Na	13.9	18.5	14.8	33.3
Succinates				
K	7.0	30.0	32.0	32.0
Na	26.3	58.0	68.4	63.0
Ca	Insol. in methanol			

The salts are arranged in the order of their respective gel forming capacities; those readily forming transparent permanent gels with a number of dispersion media are at the top of each series; those forming opaque gels with one or two dispersion media, and then only with difficulty, are next; those forming no gels are below. The least adsorption is shown by the first and the greatest by the last in

each series, and by these values they have arranged themselves in the same order as that of their gel forming powers. The salts forming no gels, but yielding colloidal solutions, were placed above those giving a crystalline precipitate or no precipitation at all.

Discussion of Results

These results show that more adsorption occurs upon the four colloidal adsorbents with those salts that do not form gels and, according to Marc. should be of a more crystalloid nature, the solutions of which are nearer to true solutions; whereas less adsorption takes place with the gel forming salts, the solutions of which should be more colloidal; and this corresponds with the actual facts observed on adding dispersion media to them. But a true solution is one in which the salt is dispersed into single molecules, which become completely ionized: judging from the very low values found for the electrical conductivity of these salt solutions,¹⁻³ it seems probable that these salts are not highly dissociated in methanol solution. On the other hand, a colloidal solution is one in which the dispersion is not carried quite so far.

It is now suggested that the conditions existing in these gel-forming salt solutions are of the second kind, where the dispersion into single molecules is not complete; but small numbers are bunched into aggregates, together with solvent molecules, although not having a sufficient number in each aggregate to constitute a colloidal condition; *i. e.*, they lie between true and colloidal solutions. When the dispersion media are added, the aggregates act as nuclei for the building of the gel micellae. During the formation of one or two of the gels, these nuclei were actually observed as soon as they began to expand into little globules, which, on still further expansion, appeared like small frog spawn floating about throughout the liquid; later these touched one another, coalesced and finally merged into one homogeneous, transparent jelly. The aggregates in the gel-forming salt solutions will consist of a larger number of molecules than will those in the non-gel forming ones, otherwise for each adsorbent the quantities of salts adsorbed should be equal in each series, which is not the case.

Some pure liquids such as water or acetic acid are associated liquids and are known to contain aggregates of two or more molecules, and such liquids are not considered to be colloidal. The present suggestion extends this idea to solutes in

methanol,⁶ where the non-gel forming salts may possibly have two or more molecules in their aggregates and the gel-forming ones a larger number. A still greater number would be required to produce a colloidal solution or a gel, and this would be more easily attained by those solutions having aggregates ready formed as nuclei.

If the gel-producing solutions are visualized as consisting of a comparatively small number of ions, together with some single and some aggregates of molecules, each surrounded by solvent molecules, then a larger number of these latter would find steric possibilities of attachment round

(6) The conception of solutes forming aggregates of molecules is not new; it appears in widely differing textbooks. "Indeed, with most solutes and with most solvents, too, there is a certain degree of molecular association, as it is called." Jerome Alexander, "Colloid Chemistry," Lancaster Press, Lancaster, Pa., 1929, p. 32. Also in a paragraph on Solubility Product, "when a nearly saturated solution of sodium chloride is treated with alcohol, or with hydrogen chloride, the solvent combines with the added material, and less is available for the solution of the salt in question; the solute may form polymerized molecules in the solution." J. W. Mellor, "Modern Inorganic Chemistry," Longmans, Green, London, England, 1917, p. 320.

the large volumes of the atoms of the alkali metals and calcium than round the atoms of metals of smaller atomic volume, with the consequence that these three metals would produce larger aggregates of solute and solvent molecules, from which to form gel micellae with dispersion media.

This is being investigated further.

Summary

Gels are formed by some of the simpler organic acid salts of the alkali metals and of calcium, in methanol solution, on the addition of suitable organic liquids as dispersion media. The ultimate seat of gel formation will be the salt solutions, which have been investigated by means of adsorption experiments. The idea of molecular aggregation in varying degree is proposed as the reason for gelation, which is also partly due to the large atomic volume of the metals concerned.

EXMOUTH, DEVON, ENGLAND

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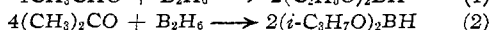
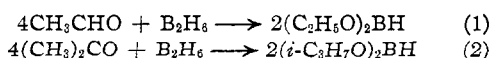
[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. XI. The Reaction of Diborane with Organic Compounds Containing a Carbonyl Group

BY HERBERT C. BROWN,¹ H. I. SCHLESINGER AND ANTON B. BURG

The investigation of the reaction of diborane with the carbonyl group in certain organic compounds was undertaken with two objectives in view. First, it was hoped that a knowledge of the mechanism of the reaction might shed light upon the electronic structure and modes of reaction of diborane; second, it seemed possible that results of significance to organic chemistry might be obtained.

Preliminary experiments showed that diborane (present in excess) reacts readily at room temperature with acetaldehyde and with acetone to yield the corresponding dialkoxy derivatives of borine



Attempts to isolate the mono-alkoxy derivatives have been unsuccessful. Conditions which would

(1) This paper is taken from a dissertation submitted by Herbert C. Brown to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was presented before the Organic Division at the Milwaukee Meeting of the American Chemical Society, September 6, 1938.

be expected to yield these compounds have resulted in the production of unstable white crystalline substances² which were not investigated further because their volatility was too low. In the presence of an excess of the aldehyde or ketone, the trialkyl boric ester is formed.

An attempt to apply this reaction to other compounds containing a carbonyl group disclosed the fact that these substances could be classified into three groups, depending upon their rate of reaction with diborane, as follows:

I. **Rapid**—reaction complete within fifteen minutes, either at room temperature or at $\sim 80^\circ$. Examples: acetaldehyde, trimethylacetaldehyde, acetone.

II. **Slow**—several hours required to obtain measurable changes at room temperature; no reaction observed at low temperatures. Examples: methyl formate, ethyl acetate.

(2) These crystalline substances appear to be polymers of the mono-alkoxyborines in which oxygen in one molecule occupies the fourth position in the coordination sphere of boron in another. Compare Burg and Schlesinger, *THIS JOURNAL*, **55**, 4020 (1933).