the heats of reaction of the above reactions are not known, and the effect of temperature cannot be accurately predicted. The temperature coefficients of the inhibited reaction at present do not seem to be as much help in the solution of the mechanism of the inhibition as had been anticipated.

Summary

1. The velocity of the decomposition of malic acid by sulfuric acid has been measured in the presence of nine different solutes, all of which retarded the reaction velocity, at two concentrations and three different temperatures.

2. Solubility measurements of malic acid in aqueous sulfuric acid solutions of different concentrations point to the existence of a molecular addition compound between the two, which strengthens the assumption previously expressed by Whitford that the first step in the decomposition of malic acid by sulfuric acid consisted of molecular compound formation.

3. The logarithm of the velocity constant of the inhibited reaction in most cases is not an exact linear function of the concentration of the inhibitor.

4. The critical increment of the reaction is in most cases only slightly increased by the inhibitor.

5. Although all of the inhibitors used, except two, form molecular compounds with one of the reactants of this decomposition—sulfuric acid—the mechanism of the inhibition can be satisfactorily explained, for some solutes, at least, by the formation of addition compounds between the inhibitor and malic acid.

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THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF LITHIUM

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RECEIVED APRIL 1, 1930 PUBLISHED JULY 3, 1930

Due to the fact that lithium salts in general are freely soluble in a variety of solvents, few precipitation reactions for lithium are known. Of these none are suitable for the detection and quantitative estimation of very small quantities of this element. It has been found that a relatively sensitive reaction for lithium may be based upon the fact that lithium stearate, in contrast to the stearates of the other alkali metals, is relatively insoluble in certain organic solvents. Unfortunately this reaction cannot be applied in aqueous solutions due to hydrolytic effects, nor can it be used in dilute or concentrated solutions of ethyl alcohol by reason of the solubility of the lithium soap in this solvent. Amyl alcohol was found to be the most convenient medium to use. In the practical qualitative or quantitative application of this reaction, the lithium chloride is extracted from the mixture of alkali chlorides with amyl alcohol and a reagent is used which consists of a solution of ammonium stearate in this alcohol.

Preparation of the Reagent.—The ammonium stearate required for this reagent is conveniently and rapidly prepared by passing dry ammonia gas into a solution of stearic acid in ether according to McMaster's[1] method for preparing the ammonium salts of the higher fatty acids. In practice a 1.5 to 2.0% solution of pure stearic acid in ether should be used and a rapid current of ammonia gas passed in until no further precipitation takes place. During the process, which only takes ten to fifteen minutes with a liter of stearic acid solution, ether should be added from time to time to replace that lost by evaporation. Without this precaution the mixture becomes pasty and difficult to handle. After precipitation is complete, the mixture is poured upon a large glass tray or dish and when the ether has evaporated the material is ready for use. The reagent proper is made by dissolving the powdered ammonium stearate in warm amyl alcohol at the rate of 2 g. for each 100 cc. of the solvent. The amyl alcohol should not be heated above 50° since at higher temperatures the ammonium stearate is more or less rapidly decomposed. On cooling to room temperature the reagent is ready for use. This reagent is a nearly saturated solution of ammonium stearate in amyl alcohol. It should be freshly prepared since it was found that these ammonium stearate solutions evolve ammonia on standing and become useless for reagent purposes in the course of a few days. Amyl alcohol solutions of sodium or potassium stearate were found less satisfactory as reagents due to the lower solubility of these soaps in this solvent.

Experimental Part

General Technique.—The standard solution of lithium chloride used was checked by pipetting out 50-cc. portions and determining the lithium content of these by evaporating with sulfuric acid and weighing as the sulfate. In the experiments where lithium alone was present, measured portions of standard solution were acidified with dilute hydrochloric acid to prevent hydrolysis of the salt, and evaporation to dryness was conducted over a very low burner flame or over the steam-bath. The residual lithium chloride was then dissolved in a measured volume of warm amyl alcohol and, after allowing the solution to cool to room temperature, the reagent was added and the solutions mixed in the usual manner. It was found that agitation had little or no effect in promoting the separation of the lithium stearate, but it was essential to use the solutions at room temperature, due to the appreciable solubility of the soap in warm amyl alcohol. In those experiments where the lithium chloride was mixed with large proportions

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[1] McMaster, This Journal, **36**, 1918 (1914).

of sodium and potassium chlorides, the aqueous solution of the salts was evaporated in the same manner and the residue was extracted three or four times with portions of hot amyl alcohol. These extracts were then evaporated to the proper volume and the final solution obtained by pipetting or filtering it off from the small amounts of sodium or potassium chlorides that had separated during the concentration.

Qualitative Experiments.—The first experiments conducted qualitatively were with amounts of lithium approximating 0.001 g. In all of these cases precipitation was almost instantaneous and the precipitate was so large in amount and volume that the mixtures set to a semi-solid mass. The experiments shown in the table indicate the lower limits of sensitivity of the reaction with varying proportions of the amyl alcohol solution of lithium chloride and the reagent.

TABLE I

SMALLEST AMOUNTS OF LITHIUM DETECTABLE WITH AMMONIUM STEARATE REAGENT

Lithium present, g.	Volume of lithium solution, cc.	Volume of reagent, cc.	Precipitation After 5 min.	Precipitation After 60 min.
0.00020	5	5	Slight	Marked
.00010	5	5	Very slight	Marked
.00010	5	10	Slight	Marked
.00010	5	2.5	None	None
.00005	5	10	None	None
.00010	2	5	Marked	Heavy
.00010	2	10	None	Slight
.00005	2	5	Slight	Marked
.000025	2	5	None	None
.00005	1	2.5	Marked	Heavy
.000025	1	2.5	Slight	Marked
.000015	1	2.5	None	None

It was found from these and other experiments that the optimum results were obtained when the volume of reagent was two and one-half times the volume of the amyl alcohol solution. In experiments on the detection of lithium in the presence of sodium and potassium, no difficulty was experienced in extracting 0.0001 g. of lithium from 1 g. of the mixed chlorides and detecting this amount by the method. With careful technique one part of lithium can be detected in admixture with twenty-five thousand parts of the mixed chlorides. Blank experiments made on the sodium and potassium chlorides used gave no evidence of a precipitate. Likewise rubidium and cesium cannot interfere in this method but it is essential that magnesium, the alkaline earths and heavy metals be carefully removed before applying this procedure, since these all interfere.

Quantitative Experiments.—Since the lithium stearate in the above reaction is precipitated in a very finely divided condition, resulting in a suspension the opacity of which increases as the amount of lithium increases, there was suggested a quantitative procedure for the estimation of small amounts of lithium. The method is most conveniently applied by using a series of turbidity standards prepared at the same time that samples are examined. A convenient series is one based upon the use of a 2.0-cc. volume of amyl alcohol solution and 5.0 cc. of reagent, the successive amounts of lithium in such a set being 0.00005, 0.000075, 0.00010, 0.00015, 0.00025 and 0.00040 g. Essential for the success of the process for quantitative purposes is the preparation of the sample and standards under like conditions, more particularly as regards the time and manner of adding the reagent. The latter should be added to the standards and to the samples at the same time and the tubes should be stoppered and shaken in a rack in order to insure the simultaneous mixing of solution and reagent. After shaking, the set of tubes must be allowed to stand for thirty minutes in order to secure complete precipitation. A further shaking of the tubes just before making the comparison promotes the uniformity of the suspensions. With the above series there is no difficulty in estimating the amount of lithium present to within 0.00002 g. when this falls in the lower end of the series or to within 0.00005 g. when it lies in the higher range. The suspensions may also be compared by means of a turbidometer but since samples must be compared with standards that contain approximately the same amount of lithium in order to obtain accurate results, this procedure is only to be recommended as a supplementary method to the comparison with a set of standards. Some typical results obtained in this manner are shown in Table II. The turbidities in these cases were compared by transmitted light in the ordinary plunger type of instrument. Different series of standards may, of course, be prepared, but in dealing with actual samples of rock material, for example, there can be no advantage in having standards ranging below 0.00005 g., due to the practical difficulty of removing minute amounts of interfering calcium and magnesium.

Application to the Usual Quantitative Procedure.—This process can be used to supplement the usual Gooch[2] method for the estimation of lithium in cases where the quantity of that element amounts to a few tenths of a milligram or less, since it is in this region that there is an element of uncertainty with this method due in part to the fact that the applied corrections may exceed the amount of lithium being determined and in part to the natural limitations of the balance. The turbidometric procedure given above enables these small amounts to be determined more accurately than can be done gravimetrically. The method of Gooch can be followed in the usual manner until there is obtained the final amyl alcohol solution containing all the lithium chloride and small amounts of other alkali chlorides. This extract may then be concentrated to a small volume and, after filtering off any separated sodium and potassium chlorides, the lithium

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[2] F. A. Gooch, *Proc. Am. Acad. Arts Sci.*, **22**, 177–194 (1886).

TABLE II

ESTIMATION OF SMALL AMOUNTS OF LITHIUM BY THE INSTRUMENTAL COMPARISON OF THE TURBIDITIES PRODUCED BY AMMONIUM STEARATE REAGENT

Lithium present in standards, g.	Observed depths of standards, mm.	Observed depths of samples, mm.	Lithium present in samples, g.	Lithium found in samples, g.	Errors, g.
0.00006	9.3	8.3	0.00009	0.00007	−0.00002
	12.3	10.0	.00009	.00007	− .00002
	10.6	8.5	.00009	.00007	− .00002
.00012	8.9	10.6	.00009	.00010	+ .00001
	11.1	12.5	.00009	.00011	+ .00002
	6.8	7.2	.00009	.00011	+ .00002
.00012	10.8	9.4	.00015	.00014	− .00001
	13.6	9.9	.00015	.00016	+ .00001
	14.0	10.9	.00015	.00015	.00000
.00019	9.6	8.4	.00025	.00022	− .00003
	9.2	7.6	.00025	.00023	− .00002
	9.8	8.3	.00025	.00023	− .00002
.00032	4.6	7.8	.00025	.00019	− .00006
	4.5	7.2	.00025	.00020	− .00005
	7.0	11.4	.00025	.00020	− .00005
.00032	5.2	4.0	.00038	.00042	+ .00004
	3.9	2.8	.00038	.00045	+ .00007
	4.3	3.1	.00038	.00044	+ .00006

may then be precipitated with the proper amount of ammonium stearate reagent and the resulting suspension compared with the series of standards in the manner previously described.

Summary

There has been described a method for the detection and estimation of small amounts of lithium based upon the reaction between ammonium stearate and lithium chloride in amyl alcohol solution.

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