THE INCOMPATIBILITY OF SODIUM SALICYLATE AND SODIUM BICARBONATE MIXTURES.*

BY JOHN C. KRANTZ, JR.

INTRODUCTION.

It is surprising indeed to consider the number of substances incompatible with sodium bicarbonate in aqueous solution. Ricciardelli (1), in a summary of these cases, calls attention to the facts that borax in the presence of glycerin liberates carbon dioxide from this compound: its presence in solution with quinine salts causes the precipitation of the alkaloid; with magnesium oxide quantities of sodium hydroxide are formed and with diuretin a cleavage into theobromine and sodium salicylate results. Scoville (2) calls attention to the darkening of sodium salicylate in aqueous solution in the presence of sodium bicarbonate and suggests the cause of darkening to be oxidation. It was further recorded by Scoville that sodium hydroxide did not cause this darkening as readily as did sodium carbonate or sodium bicarbonate. Greenish and Beesley (3) studied the darkening of solution of sodium salicylate upon standing. The frequent observation of the rapid darkening of sodium bicarbonate and sodium salicylate in aqueous suggested the present investigation to the author.

EXPERIMENTAL.

Samples of chemically pure sodium salicylate and sodium bicarbonate were obtained that did not give a positive reaction for iron. As this combination often is prescribed on physicians' prescriptions—one dram each in two fluidounces of solution—this concentration was employed as the basis for study.

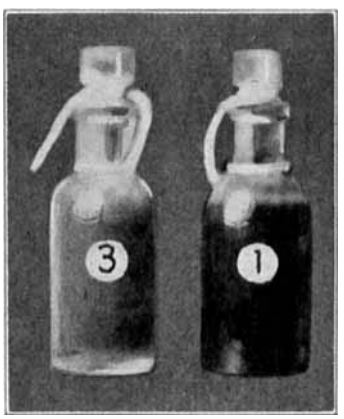

Fig. 1.—See tables.

Action of Bicarbonate, Carbonate and Hydroxide.—Using the foregoing concentrations as a basis, solutions were prepared containing the bicarbonate, carbonate and hydroxide of sodium, respectively, and sodium salicylate. The concentrations of the carbonate and hydroxide were molecularly equivalent to the foregoing concentration of sodium bicarbonate. These solutions were prepared in boiled distilled water and their hydrogen-ion concentrations measured electrometrically. The following table records the observations made upon these solutions stored in flint bottles.

TABLE I.

1.	Sodium salicylate + Sodium bicarbonate	7.97 p_H	Intensely black with ppt. in 6 days
2.	Sodium salicylate + Sodium carbonate	10.55 p_H	Brown in 10 days
3.	Sodium salicylate + Sodium hydroxide	12.86 p_H	Practically colorless after several months

Figure 1 shows Samples 1 and 3 after one month's standing.

Influence of p_H.—One might judge from the foregoing results that the darkening

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was a function of the hydrogen-ion concentration and that, if the hydroxyl-ion concentration of the solution were sufficiently increased, the darkening would not take place.

In order to ascertain the influence of hydrogen-ion concentration upon the darkening of the salicylate several solutions of sodium salicylate of the before mentioned concentration were prepared in solutions of sodium hydroxide of definite p_H. Table II records the observations upon these solutions.

TABLE II.

			After 3 months.
1.	Sodium salicylate in NaOH sol.	p_H 7.55	Very light yellow
2.	Sodium salicylate in NaOH sol.	p_H 8.02	Yellow
3.	Sodium salicylate in NaOH sol.	p_H 9.25	Yellow
4.	Sodium salicylate in NaOH sol.	p_H 10.97	Light brown
5.	Sodium salicylate in distilled water	p_H 6.63	Colorless indefinitely
6.	Sodium salicylate in distilled water	p_H 8.95	After one week
7.	Sodium salicylate in distilled water saturated with salicylic acid	p_H 4.41	Colorless indefinitely

Unlike the observations made from Table I the darkening increased with an increase of hydroxyl-ion concentration up to p_H 10.97 when the alkalinity was produced by free alkali, instead of alkali bicarbonate or carbonate.

Influence of the Positive Ion.—In order to study the influence of the positive ion upon the discoloration of the solution, the carbonates of lithium and ammonium and the bicarbonate of potassium were studied. Table III records these observations. Molecular equivalents of the other ions were employed.

TABLE III.

1.	Sodium salicylate + Sodium bicarbonate	7.97 p_H	Intense black in 6 days
2.	Sodium salicylate + Sodium carbonate	10.55 p_H	Brown in 10 days
3.	Sodium salicylate + Potassium bicarbonate	8.27 p_H	Intense black in 6 days
4.	Sodium salicylate + Lithium carbonate	10.63 p_H	Brown in 10 days
5.	Sodium salicylate + Ammonium carbonate	9 + colorimetric	Brownish black in 10 days

These results indicate that changing the alkali ion in combination with the ion of carbonic acid does not influence the rate or degree of darkening of sodium salicylate in aqueous solution.

Action of Bicarbonate upon Compounds Related to Sodium Salicylate.—Samples of solution of sodium bicarbonate and the sodium salts of meta and para hydroxy benzoic acids were prepared and their permanence studied. In order to determine whether it was necessary to have the hydroxyl and carboxyl groups in the same molecule and which was responsible for the darkening, solutions were prepared containing sodium benzoate, phenol and mixtures of sodium benzoate and phenol. Table IV records the observations made in this series of experiments.

TABLE IV.

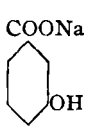
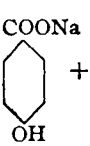
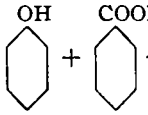
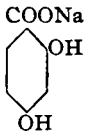
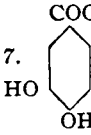
1.		+ $NaHCO_3$	No discoloration	2. 	+ $NaHCO_3$ No discoloration

TABLE IV (*Concluded*).

3. 	+ $NaHCO_3$	After four mos. slightly pink
4. 	+ $NaHCO_3$	After four mos. a light brown color
5. 	+ $NaHCO_3$	No discoloration
6. 	+ $NaHCO_3$	After three months a very light brown color
7. 	+ $NaHCO_3$	After three months a very light brown color, slightly darker than plain sodium gallate solution

These results indicate that in certain related compounds a darkening similar to that observed in sodium salicylate solutions does occur, but only to a far lesser degree than that with sodium salicylate. It is of special interest to note that neither the meta nor the para hydroxy benzoic acid reacts similarly to the ortho variety.

Influence of Oxidation and Reduction.—Several samples of sodium salicylate and sodium bicarbonate mixture were stored in containers in which the space above the liquid was evacuated, filled with hydrogen and carbon dioxide, respectively. The exclusion of the atmospheric air (presumably in part only) retarded the development of the black pigment, yet after a sufficient period of time had elapsed (3 weeks) these samples became black and showed a black amorphous deposit. Solution of hydrogen peroxide brings about incipient darkening within a period of fifteen minutes, whereas a small quantity of sodium hypophosphite will keep the solution colorless for a long period of time. This indicates that one of the principal factors involved in the darkening is oxidation.

Influence of Various Radiations.—Samples stored in colorless, purple, red and green pyrex tubes did not vary much in the rate of discoloration. Samples stored in plain and amber tubes exposed and not exposed to ultraviolet radiation did not vary appreciably in the rate of darkening. This would seem to imply that light is not an important factor in the reaction.

The Physical Properties of the Precipitate.—The deposit obtained is black and amorphous. It has a tendency to pass through ordinary filter paper, presumably in a colloidal state. The substance is insoluble in water and alcohol. Warm concentrated hydrochloric acid and five per cent sodium hydroxide, respectively, fail to exert a solvent influence upon it. In warm nitric acid the material dissolves to form a red solution with the liberation of the nitrogen dioxide.

CONCLUSIONS.

1. The nature of the incompatibility of sodium salicylate and sodium bicarbonate in aqueous solution has been studied.

2. The reaction has been shown to be accelerated by oxygen and considering the compounds investigated, it is peculiar to ortho hydroxy benzoic acid.

REFERENCES.

(1) Ricciardelli, *Boll. chim.-farm.*, 62 (1923), 577; through *Chem. Abstr.* (1924), 440.
(2) Scoville, "Art of Compounding," 408, Blakiston's Son & Co., Philadelphia.
(3) Greenish and Beesley, *Pharm. J.*, 94 (1915), 201.

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THE EFFECT OF HEAT ON TRAGACANTH AND ITS MUCILAGE.*

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The consistency of Mucilage of Tragacanth varies greatly when it is prepared under different conditions. The mucilage made without the application of heat is decidedly more fluid than the mucilage subjected to boiling for several minutes.

If the mucilage is boiled for 15 minutes, a very fluid preparation results. On the other hand, when the mucilage is boiled but two minutes, it remains viscous. Further, an increase in viscosity has been noted upon aging the mucilage prepared by bringing it to a boil, and then removing the source of heat.

These facts prompted the investigation presented in this paper.

Evers and MacLachlan (Year Book of Pharmacy (British) (1927), 504) generalized upon the above facts, but apparently did not investigate the range of viscosity changes produced in the Mucilage of Tragacanth when it is subjected to varying boiling periods.

The object of these experiments was twofold: (1) To secure a mucilage which will remain constant in viscosity. (2) Production of a mucilage of maximum viscosity.

The mucilage used in all the experiments conducted for this paper was prepared from the following formula:

Powdered Tragacanth	54 grains
Glycerin	2 ounces, avoir.
Water (60° C.), to make	8 ounces avoir.

The powdered tragacanth was mixed in a mortar with the glycerin and 6 fluid-ounces of water (60° C.) added slowly with constant stirring. The mucilage was transferred to a tared casserole and the mortar rinsed with a small amount of water, and the rinsing added to the mucilage in the casserole.

The following variations of time of boiling were established:

1. No application of heat
2. Mucilage brought to a boil (required four minutes for each experiment)
3. Mucilage boiled one minute
4. Boiled two minutes
5. Boiled three minutes
6. Boiled four minutes
7. Boiled five minutes
8. Boiled six minutes
9. Boiled seven minutes
10. Boiled eight minutes
11. Boiled nine minutes
12. Boiled ten minutes
13. Boiled twelve minutes
14. Boiled fifteen minutes

The following regulations were maintained throughout all the experiments: The casserole containing the mucilage was placed on a tripod, supported by an

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