

Chemiluminescent Decomposition Products of Citric Acid

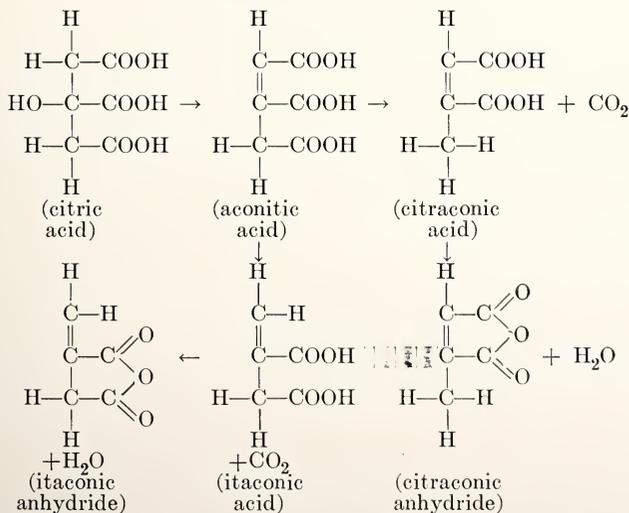
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Introduction

There are a number of compounds which are not chemiluminescent themselves, but which, upon fusion and at high temperatures, yield decomposition products which are chemiluminescent upon oxidation. Among these may be mentioned glucose, sucrose, levulose, lactose, tartaric acid, galactose, malic acid, lactic acid, dextrin, potato starch, gum arabic, allantoin, alloxan, uracil, creatine, and citric acid. The citric acid yielded decomposition products which far surpassed all the others in the brilliance of their chemiluminescence. The writers have therefore attempted the separation and isolation of the various decomposition products of citric acid and have studied their chemiluminescent properties.

Discussion

Citric acid breaks down at 105°-120° to form aconitic acid, which in turn breaks down to produce citraconic acid, citraconic anhydride, itaconic acid, and itaconic anhydride. Using a supply of C. P. citric acid and following the method described by Shriner, Ford, and Roll¹, the writers succeeded in isolating all of the above compounds with the exception of the aconitic acid. There remained in the distillation flask, after driving off the above products, a dark brown residue of unknown composition. The reaction may be represented thus:



¹ Shriner, Ford, and Roll. *Organic syntheses*. **2**, 23.

Melting points and boiling points of these products were determined as shown in Table I.

TABLE I.

Name	Melting Point	Boiling Point
Citraconic acid.....	68°-69°*
Citraconic anhydride.....	10°	83° at 7 mm pressure
Itaconic acid.....	157°
Itaconic anhydride.....	69°-72°	95°-100° at 1 cm pressure

*This one melting point seems to be quite out of line with the accepted values. However, we note a considerable discrepancy between authorities. Organic Syntheses records this melting point as 92°-93°; Kamm and the Handbook of Chemistry and Physics place it at 80°.

Of the above list of compounds which were isolated, citraconic anhydride was the only one which exhibited chemiluminescence. This luminescence was much brighter in dilute solution than in those of greater concentration, the optimum being at about 0.11 M. Either alcohol or acetone may be used as the solvent. The oxidizing agents used in this work were a combination of sodium hypochlorite and hydrogen peroxide in alkaline solution. This procedure has been described in a previous article².

The dark brown residue which remains in the distilling flask after the decomposition reaction is soluble both in alcohol and water, producing a brown solution. This is strongly luminescent when oxidized. It undoubtedly contains some complex condensation product which is responsible for this action. An attempt was made to remove the brown color from the solution by filtering it with animal charcoal. The color was adsorbed, but with it was removed the light giving substance also.

Summary

1. When citric acid is fused and heated to a high temperature, decomposition products result which are strongly chemiluminescent when properly oxidized.
2. Several of these decomposition products were isolated and tested for chemiluminescence.
3. Citraconic anhydride was found to be luminescent, optimum results being obtained from a 0.11 M solution.
4. Other light-giving substances of unknown composition are present in the dark brown residue from the citric acid decomposition.

² Cottman, Moffett, and Moffett, 1938. Proc. Indiana Acad. Sci., 47, 124-129.