which, if one takes cellobiose octaacetate as being typical of a permutoid reaction, make k_1 and k_2 for acid hydrolysis the same and equal to 1.2 moles^{-1} min.^{-1} liters. This seems to be more nearly in accord with these previous authors who say that the rate of hydrolysis of the primary ester group is, at least equal to, and at most twice, that of a glycolic ester group in cellulose acetate.

Summary

The alkaline hydrolysis of sugar acetates in solution may be treated as that of a mixture of simple esters, each with its own characteristic velocity constant. Under these conditions, the primary acetate groups in glucose pentaacetate, triacetyl monoacetone glucose and sucrose octaacetate react at a slower rate than the secondary groups which have been shown to be glycolic in nature. In the case of sucrose octaacetate, the primary groups are made up to two types reacting at different rates.

In the case of cellobiose octaacetate, the hydrolysis can be carried out under permutoid conditions by precipitating the ester from chloroform solution in the presence of OH^- ions, when it behaves in a similar fashion to glucose pentaacetate. Under other heterogeneous conditions it behaves in a radically different manner.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Kinetic Studies on the Decarboxylation of Sodium Trifluoroacetate in Ethylene Glycol

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Sodium trifluoroacetate, like the salts of other halogenated acetic acids, undergoes thermal decomposition in the solid state, photochemical decomposition, hydrolysis and decarboxylation. This paper reports studies on the rate of the decarboxylation reaction, for comparison with the data on the decarboxylation of sodium trichloroacetate.[2]

Initial attempts to decarboxylate sodium trifluoroacetate or trifluoroacetic acid in solvents in which trichloroacetic acid and its salts decomposed were without success. Neither the salt nor the free acid decomposed in water, ethyl alcohol or pyridine at temperatures below the boiling points of the solvents, nor in aniline or *m*-cresol up to 138°. Decarboxylation of the sodium salt did occur at a conveniently measurable rate in ethylene glycol at temperatures near 180°, and the reaction was studied in this solvent. Since side reactions occurred if the solution was allowed to become basic, many of the experiments were carried out in the presence of boric acid. For comparison, a few experiments were made with sodium trichloroacetate.

Sodium trifluoroacetate from Columbia Organic Chemicals was dissolved in ethyl alcohol and thrown out by adding dioxane. The resulting solid was recrystallized four times from hot absolute alcohol and dried at 120–130° at 1 mm. pressure. Analysis gave 16.65% sodium (theoretical, 16.88%).

Sodium trichloroacetate was prepared according to the directions of Hall and Verhoek.[2b]

Ethylene glycol was dried over Drierite for several days, decanted, and distilled at a pressure of 2 mm. through an 18-inch column packed with multiple-turn quarter-inch helices. The first 10% of the constant boiling fraction was discarded and the remainder of the distillate collected and stored in nitrogen-filled glass-stoppered bottles.

The reacting solutions were prepared with precautions to exclude moisture, two 10-ml. samples removed, and the remainder sealed in a reaction flask and placed in the thermostat. The reaction flask had a capillary tube extending from the bottom up over the side of the thermostat, and ending with a stop-cock. The pressure of hot air and vapor in the flask forced a sample out when the stop-cock was opened. About 1 ml. of solution was discarded before each sample was taken, to remove any material which might have been in the capillary (volume 0.5 ml.) at a lower temperature than the bath. A sample of about 10 ml. was then collected, weighed, swept with nitrogen for ten minutes to remove carbon dioxide and titrated for the amount of base formed or boric acid left. The results were converted to volume concentrations using the measured densities of the solutions. The reaction was considered complete when two samples removed several hours apart showed the same titer. The difference between the initial and final values, compared to the weight of salt originally taken, gave the per cent. of the salt which underwent decarboxylation.

The products of the decarboxylation of trifluoroacetic acid would be expected to contain equimolar quantities of the two gases carbon dioxide and fluoroform. Analysis of the gas evolved on decomposing sodium trifluoroacetate dissolved in ethylene glycol showed only 24% carbon dioxide, however, due to retention of this gas by the basic solution formed. When boric acid was present in the solution, three separate experiments at 173° gave 51, 50 and 50% of the evolved gas absorbed in 30% potassium hydroxide, indicating that the over-all reaction was

$$CF_3COO^- + H^+ \longrightarrow CHF_3 + CO_2$$

A solution of boric acid and ethylene glycol heated alone produced no gas.

The decarboxylation reaction was found to be of the first order throughout the course of each individual reaction, as shown by the fact that

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(2) (a) Verhoek, THIS JOURNAL, **56**, 571 (1934); (b) Hall and Verhoek, *ibid.*, **69**, 613 (1947); (c) Fairclough, *J. Chem. Soc.*, 1186 (1938).

straight lines were obtained when the logarithm of the concentration was plotted against the time. First-order constants calculated from the slopes of these lines are given in the table. The first-order nature of the reaction is also shown by the constancy of the velocity constants with change in initial concentration. There is nevertheless some indication in the data at 188.8° that the rate constant decreases with increasing concentration. Such a decrease has been established for the case of sodium trichloroacetate in ethyl alcohol,[2b] but the change in rate constant is there much greater than in the data presented here.

VELOCITY CONSTANTS IN THE DECARBOXYLATION OF SODIUM TRIFLUOROACETATE IN ETHYLENE GLYCOL

Temp., °C.	CF_3COONa m./l. × 10^2	H_3BO_3 m./l. × 10^2	% conversion	k min.$^{-1}$ × 10^5
170	4.719	6.468	90.1	1.79
	11.80	30.86	94.9	1.78
177.8	6.010	13.39	91.8	4.21
	8.872	25.07	92.2	4.38
	9.410	0.0	80.8	5.15
188.8	4.098	9.77	96.6	12.6
	7.050	14.23	92.9	13.3
	7.322	11.91	91.2	12.1
	14.44	25.44	96.9	11.0
	5.936	0.0	73.6	17.7
196.5	6.807	11.37	89.9	25.4

The first-order nature of the reaction is explained by a unimolecular decomposition of the trifluoroacetate ion as the rate-determining step, followed by the rapid addition of a proton to the trifluoromethide ion. Trifluoroacetic acid then belongs to the group of acids which decarboxylate as the anion by a first-order mechanism.[3]

In the experiments carried out in the absence of boric acid, a higher rate and a smaller percentage conversion is observed than when boric acid is present. The samples taken from the solutions without boric acid were found to contain fluoride ion, indicating a competing hydrolysis reaction due to the base formed, as has been observed by Swarts[4] for basic solutions in water. This hydrolysis reaction results in the consumption of base, and the concentration of base at a given time is less than it would have been if only decarboxylation occurred. In the boric acid solutions, acid hydrolysis of the CF_3-group might also explain the fact that 100% completion was not obtained. No test for fluoride ion could be made here, because the formation of fluoboric acid would make it meaningless. It is also possible that a thermal decomposition, similar to that found by Swarts[4] for the solid at 200–205°, might occur at these temperatures, forming base-neutralizing substances.

From the straight line obtained on a graph of log k against $1/T$, excluding the results in the absence of boric acid, the activation energy of decarboxylation was found to be 42,000 ± 500 calories per mole.

For comparison, the activation energy was determined for the decarboxylation of sodium trichloroacetate in ethylene glycol. For concentrations of sodium trichloroacetate close to 0.02 molar, first order velocity constants were obtained as follows: 55.5°, 1.49×10^{-4} min.$^{-1}$; 68.7°, 1.12×10^{-3} min.$^{-1}$; 76.7°, 2.84×10^{-3} min.$^{-1}$. From these an activation energy of 31,600 calories per mole is obtained. This is nearly the same as that obtained in ethyl alcohol at the same concentration: 31,800 calories per mole.[2b]

The difference in activation energy between salts of trifluoro- and trichloroacetic acid is to be expected from the strengthening of the carbon–carbon bond by the fluorine cluster.

Attempts were made to study the decarboxylation of the sodium salts of difluorochloroacetic acid and of fluorodichloroacetic acid. On heating these salts with ethylene glycol at 177.8°, the solutions rapidly became acidic, and showed the presence of appreciable amounts of fluoride and chloride ion. Below 100°, tests for acid and for halide ions were positive in the case of difluorochloroacetate; with the fluorodichloroacetate some decarboxylation occurred, but only about 23% of the expected base was produced. Both these acids therefore undergo hydrolysis more rapidly than decarboxylation, the difluorochloro compound suffering hydrolysis more readily than the fluorodichloro compound, in agreement with observations of Swarts.[5]

Summary

The decarboxylation of sodium trifluoroacetate in ethylene glycol is found to be a first-order reaction with an activation energy of 42,000 calories per mole. This compares with an activation energy of 31,600 calories per mole for the first-order decarboxylation of sodium trichloroacetate in the same solvent.

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(3) Schenkel and Schenkel-Rudin, *Helv. Chim. Acta*, **31**, 514 (1948).

(4) Swarts, *Bull. classe sci. acad. roy. Belg.*, 343 (1922).

(5) Swarts, *ibid.*, **1**, 42 (1906).