given in Fig. 1. That of the triiodide conforms fairly well with results reported[8,13] for the triiodide ion in water or ethanol. All three spectra are nearly identical except that the molar absorbancy index increases slightly as the mole ratio of iodine to monoiodide in the polyiodide increases. These results are consistent with the interpretation that the triiodide is the only polyiodide stable in dilute solutions and that its slight dissociation is suppressed in the solutions of the higher polyiodides by the iodine formed when the polyiodide dissociates to triiodide and iodine. In fact a solution with an excess of iodine greater than that to be found in a solution of the enneaiodide gave a spectrum identical with that of the enneaiodide except that the iodine peak at about 500 mμ was higher. For comparison the spectra of iodine and tetramethylammonium iodide in ethylene chloride are given in Fig. 2.

To verify the fact that the polyiodide existing in solution is the triiodide the method of continuous variation[14] was applied to mixtures of tetramethylammonium iodide and iodine varying in concentration from 1:9 to 9:1. Measurements were made at four wave lengths, and the difference between the absorbancy of the solution and the calculated absorbancy, assuming simple mixing of the monoiodide and the iodine, was plotted against the mole fraction. The results are given in Fig. 3. The peak for each wave length appears at a mole fraction of 0.5 which verifies the 1:1 compound, the triiodide, as the absorbing molecule. One must conclude from these results that the existence of the higher polyiodides in dilute solutions in appreciable concentrations is doubtful.

The equilibrium constant for the dissociation of the triiodide in ethylene chloride at 25° was calculated by the method previously outlined.[15] The dissociation was suppressed by excess iodine as shown in the spectrum of the enneaiodide in Fig. 1. For a solution of concentration 2×10^{-5} M the degree of dissociation was found to be 0.068 ± 0.020 which corresponds to a pK value of 7.0 ± 0.2. This value can be compared with some of the reported values for the dissociation of triiodide ion in water: 2.90[16] at 16°, 2.87[17] at 25° and 2.68[13] at 39°. In alcohol a higher pK of 4.52 at 14° has been reported.[18] The still higher value in ethylene chloride is the result that would be expected in this relatively non-polar solvent.

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(13) A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1842 (1951).

(14) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

(15) A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, THIS JOURNAL, **73**, 514 (1951).

(16) P. Job, *Compt. rend.*, **182**, 632 (1926).

(17) V. K. LaMer and M. H. Lewinsohn, *J. Phys. Chem.*, **38**, 171 (1934).

(18) P. Job, *Compt. rend.*, **182**, 1621 (1926).

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The Thermal Decomposition of Deuterated Barium Butyrate

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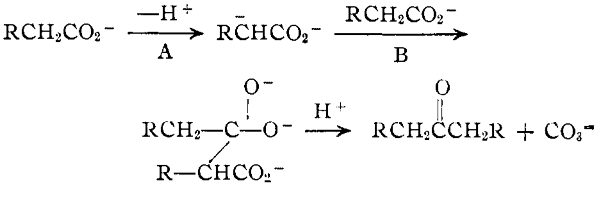
The thermal decomposition of a mixture of deuterated and undeuterated barium butyrate has been effected. It is observed that deuterium exchange between the deuterated and undeuterated species is rapid with respect to the decomposition.

Although the thermal decomposition of barium salts of carboxylic acids has been known for many years, little is known about the details of the reaction. Among the few known facts are: (1) aliphatic acids lacking an α-hydrogen do not react,[1] (2) benzoic acid, however, does react,[2] (3) in the reaction of barium formate with barium acetate, the carbonyl group in the acetaldehyde formed is derived from the formate,[3] (4) there is no C^{13} isotope effect in the reaction,[4] and (5) cyclopentanone reacts with carbon dioxide and sodium acetate to give adipic acid.[1]

Two significantly different mechanisms have been proposed for this reaction. The first, that of Neunhoeffer and Paschke,[1] involves the initial formation of a β-ketoacid anion, followed by decarboxylation



The second, that of Bell and Reed,[3] suggests that in the reaction of barium acetate with barium formate, a methyl radical is first formed, which then reacts with the formate anion to give acetaldehyde or with acetate anion to give acetone.

It was hoped that some evidence concerning this reaction could be derived from a study of the thermal decomposition of a mixture of deuterated and undeuterated barium butyrate. If the ionic mechanism is correct, one would expect an isotope effect if step A (above) is rate controlling since it is known that the breaking of a carbon–deuterium bond is usually considerably slower than the

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(1) O. Neunhoeffer and P. Paschke, *Ber.*, **72**, 919 (1939).

(2) E. Péligot, *Ann.*, **12**, 39 (1834). Other products of this reaction are: benzene, biphenyl (G. Chancel, *ibid.*, **72**, 279 (1849); **80**, 285 (1851), anthraquinone (A. Kekule and A. Franchimont, *Ber.*, **5**, 909 (1872)), anthracene and 9-phenylfluorene (A. Behr, *ibid.*, **5**, 970 (1872)). Considering the variety of products formed, it is not unlikely that the mechanism of this reaction is different from that of the aliphatic acids.

(3) J. Bell and R. I. Reed, *Nature*, **165**, (1950).

(4) A. A. Bothner-By, L. Friedman and J. Bigeleisen, Brookhaven Conf. Rept., Chem. Conf. No. 4, 39 (Jan., 1950); *C. A.*, **45**, 3807 (1951).

breaking of a carbon-hydrogen bond.[5] On the other hand, if step B were rate controlling, one would expect an exchange of deuterium between deuterated and undeuterated butyrate anions.

The deuterated butyric acid was prepared by equilibrating ethylmalonic acid with deuterium oxide, followed by decarboxylation. The undeuterated acid was also prepared from ethylmalonic acid. The acids were converted to the barium salts and mixed to give the material used in the decomposition runs. The deuterium content was determined by converting the acid to methyl butyrate (II) followed by determination of the cracking pattern in a mass spectrograph.[6] The mass numbers 87, 88 and 89 were used for the deuterium analysis since the parent peaks are of low intensity and are obscured by mercury isotope peaks. No isotope effect would be expected since the fragments used are derived by the loss of a methyl, presumably from the ester group.[7] The details of the decomposition runs may be found in the experimental section, and a summary of the data obtained may be found in Table I.

TABLE I

SUMMARY OF DECARBOXYLATION DATA

Run No.	1	2	3	4	5
Initial					
mole % undeuterated[a]	63.4	63.4	63.4	46.0	46.0
mole % monodeuterated	9.5	9.5	9.5	14.0	14.0
mole % dideuterated	27.0	27.0	27.0	40.0	40.0
Total % deuterium[b]	31.8	31.8	31.8	47.0	47.0
Final					
mole % undeuterated	48.8	50.6	54.0	31.1	33.1
mole % monodeuterated	41.5	40.3	38.2	47.0	47.0
mole % dideuterated	9.8	9.1	7.9	21.9	20.0
total % deuterium	30.6	29.3	27.0	45.4	43.5
Yield of ketone, %	26.6	36.8	49.7	23.4	36.5
Yield of barium carbonate,[c] %	29.1	38.5	51.6	24.0	38.5
Time, hr.	4	6	8	4	6
Temperature, °C.	365 ± 5	365 ± 5	365 ± 5	365 ± 5	365 ± 5

[a] All values ±0.5 mole %. [b] Per cent. of maximum deuterium in α-position. [c] The yield of barium carbonate is probably more nearly correct than that of the ketone. The closeness of the values indicates the absence of any considerable side reaction.

As a result of these experiments, it was found that deuterium exchange between the deuterated and undeuterated anions was rapid compared to the decomposition reaction,[8] thereby showing that the anion I was present during the reaction.

$$C_2H_5\overset{-}{C}HC\overset{-}{O}_2$$

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This cannot be considered conclusive evidence for the ionic mechanism since the exchange may be a fast side reaction. The reaction nevertheless is shown to fulfill a necessary requirement for that mechanism.

It is hoped that future experiments will make feasible a definite decision between the above and other possible mechanisms for the reaction. The small isotope effect noted may be due to any of a number of factors and will not be further considered at this time.

Experimental

Deuterated Barium Butyrate.—Ethylmalonic acid (26 g., 0.2 mole, neut. equiv. calcd. 66.1, found 66.4) was added to 50 g. of deuterium oxide[9] (99.8% D_2O) and was allowed to equilibrate for a period of one month. The deuterium oxide was then removed under vacuum, and the residual acid decarboxylated by heating, giving a quantitative yield of deuterated butyric acid. One gram of the acid was treated with 10 ml. of methanol and a few drops of sulfuric acid under reflux for four hours.[10] The addition of 10 ml. of water followed by pentane extraction and distillation gave deuterated methyl butyrate (II) which had 67.0% II-αd_2 and 24.0% II-αd_1.[11]

The deuterated butyric acid was added to an equal volume of water and neutralized with a concentrated solution of barium hydroxide. Evaporation of the solution followed by drying under vacuum at 100° over phosphorus pentoxide gave the anhydrous barium butyrate. For the runs described, this barium butyrate was diluted with ordinary barium butyrate (also prepared from ethyl malonic acid), the product being thoroughly mixed and samples taken in a random fashion in order to obtain representative samples.[12]

Decarboxylation Runs.—About five grams of barium butyrate was weighed into a small cylindrical flask which was then connected to a small trap attached to a vacuum line. The pressure in the system was reduced to less than one micron, the trap was cooled in a Dry Ice-acetone-bath, and the flask was then placed in a preheated aluminum mortar wrapped with asbestos and nichrome wire. The temperature was maintained essentially constant during the reaction. At the end of the reaction, the di-*n*-propyl ketone formed was distilled into another trap and the system brought to atmospheric pressure. The ketone was transferred to a small vial and its weight determined. The mixture of barium carbonate and barium butyrate remaining in the flask was treated with hot water to dissolve the latter. The solution was filtered, and the collected barium carbonate dried and weighed. The aqueous solution was evaporated to dryness under vacuum, and the residue was treated with 10 ml. of methanol and 1 ml. of concentrated sulfuric acid under reflux for four hours. An equal volume of water was added, followed by pentane extraction and distillation giving the methyl butyrate. The results of five runs are summarized in Table I.

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(5) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(6) The cracking patterns were kindly obtained by Mr. M. Taylor of these laboratories using a Consolidated Engineering Corp. Model 21-103 mass spectrometer. The acid was converted to the ester to avoid adsorption in the mass spectrometer system. The peak intensities of the deuterated and undeuterated compounds were assumed to be the same for those peaks which should not show an isotope effect (H. W. Rollmann and H. L. McMurry, *ibid.*, **19**, 804 (1951)).

(7) In calculating the composition of the methyl butyrate (II), it was assumed that the ratio of the species having heavy carbon and/or oxygen to the normal species would be constant. This is not unreasonable since all of the butyric acid used was obtained from ethylmalonic acid. Furthermore, there were no peaks in the mass spectrum of undeuterated II, between the mass numbers 80 and 87. This indicated that the only important process leading to the peaks used in the analysis was the loss of a methyl. The observed mass spectrum of undeuterated II was essentially the same as that given in the A.P.I. Project 44, Catalog of Mass Spectral Data, Serial No. 392.

(8) An equilibrium constant may be calculated for the reaction of the butyrate ion (III): III-d_2 + III ⇌ 2III-d_1. Then $K = (\text{III-}d_1)^2/(\text{III})(\text{III-}d_2)$. The values of K thus obtained for the five runs are: 3.6, 3.5, 3.4, 3.2, 3.3. The constancy of these values indicated that equilibrium had been reached before the decarboxylation reaction had proceeded to the extent of 24%.

(9) Obtained from the Stuart Oxygen Co. on allocation from the Atomic Energy Commission.

(10) In a control experiment, this reaction was carried out for a 12-hour period. No significant difference in the deuterium content of the ester was noted. Even if a small amount of exchange occurred in the conversion to the ester, the conclusions would be unaltered since identical conditions were used in each case, and thus the error would be constant.

(11) All values ±0.5 mole %.

(12) Inhomogeneity of the barium butyrate–barium deuterobutyrate mixture would lead to a variation in initial deuterium content of the samples. It, however, would not affect the reaction itself, since the reaction temperature is above the melting point of the salt.