The Kinetics of the Decarboxylation of *tert*-Butylpropionic Acid and its Sodium Salt in Water

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In order to determine to what extent the rates of decarboxylation of α,β -acetylenic acids are influenced by various structural effects, a kinetic study has been made of the decomposition of *tert*-butylpropionic acid and its sodium salt in water at six temperatures. The data obtained have been used to calculate values of the activation energy, frequency factor, free energy of activation, heat of activation and the entropy of activation. The rates of decomposition of *tert*-butylpropionic acid and its salt are approximately equal to those of tetrolic acid and its salt, but the activation energies for the former are of the same magnitude as those found for propiolic acid and its sodium salt. It has been concluded that the low rates of decomposition of tetrolic acid and its salt compared to those of propiolic acid and its salt are due to the occurrence of hyperconjugation in the former.

In previous work¹ on the decarboxylation of some α,β -acetylenic acids and their salts, it was established that the decompositions reactions of tetrolic acid ($\text{CH}_3\text{—C}\equiv\text{C—COOH}$) and its sodium salt are much slower than those of propiolic acid ($\text{HC}\equiv\text{C—COOH}$) and its salt. It seemed that this could be attributed to hyperconjugation in tetrolic acid. To determine the validity of this assumption, the decarboxylation of *tert*-butylpropionic acid and its sodium salt in aqueous solution has been studied. The reactions involved are the following:

EXPERIMENTAL

Pinacone hydrate and pinacolin. Pinacone hydrate was first synthesized according to the method given in the Organic Syntheses². The product was then transformed into pinacolin by a method also given in Organic Syntheses².

*Chlorination of pinacolin with phosphorus pentachloride*³. 140 g of pinacolin was slowly added to 300 g of phosphorus pentachloride in a flask immersed in a mixture of

ice and water. The reaction mixture was then allowed to stand 4 hours at room temperature, after which it was gradually added to a mixture of water and ice. The precipitate formed was separated by filtration, washed with water and dried by suction. The liquid reaction product in the filtrate was separated from the water in a separating funnel and dried with calcium chloride. The yield of the solid product was 92 g, that of the liquid product 84 g.

*Tert.-butylacetylene*⁴. The chlorinated products of the preceding synthesis were heated six hours with 500 g of potassium hydroxide and 40 ml of ethanol in a graphite bath at 150–270° C. The liquid distilling from the mixture below 50° C was collected, washed with water, dried over potassium hydroxide and subjected to fractional distillation in a Widmer column. The yield of *tert.-butylacetylene* boiling at 37.5–38.5° was 55 g.

*Sodium tert.-butylacetylde*⁵. 23.8 g of the *tert.-butylacetylene* was dissolved in 150 ml of anhydrous ether in a flask fitted with an efficient reflux condenser to which a calcium chloride tube was attached. 6.5 g of thin sodium wire were added. The reaction was allowed to continue 24 hours at room temperature, the flask being shaken at intervals. The mixture was then boiled 18 hours until a sample no longer gave a precipitate on adding ammoniacal silver nitrate solution.

*Tert.-butylpropionic acid*⁵. Carbon dioxide gas dried by passing it through concentrated sulphuric acid was led into the flask containing the ether solution of *tert.-butylacetylde* during 26 hours at room temperature with intermittent shaking, after which the mixture was boiled for six hours. During this time the grey precipitate of sodium *tert.-butylacetylde* turned white and a sample no longer gave off *tert.-butylacetylene* when water was added to it. The contents of the flask were carefully added to ice-water and the solution was extracted with ether after acidification with sulphuric acid. The combined ether solutions were dried with anhydrous sodium sulphate, and the ether removed by distillation. The rest of the *tert.-butylacetylene* was treated in a similar manner. The products were combined and distilled by fractionation. The yield of product boiling at 112.5–113.0° at 14 mm Hg was 42.7 g. Its melting point was 47.9–48.0°. Analysis by titration: 30.0 mg of the acid consumed 11.65 ml of 0.0202 *N* barium hydroxide, which corresponds to an equivalent weight of 127.48 (calc. 126.15). The odour of the acid resembled those of propionic and tetrolic acids and the acid was very hygroscopic.

Tetrolic acid. The tetrolic acid was the same as that used in the previous work¹.

Methods. The apparatus and the methods used in the measurement of the rates of decomposition were the same as in the earlier investigation¹.

RESULTS

The rates of decomposition of *tert.-butylpropionic acid* and its sodium salt were measured in aqueous solution at six temperatures. The rate of decomposition of sodium tetrolate was measured in aqueous solution at three temperatures to extend the temperature range of the earlier measurements¹. Similarly as in the earlier work, the initial concentrations of the acids were 0.01 *M*, those of the salts 0.02 *M*.

The reactions studied were all of the first order. The specific rates of the salts showed a good constancy over the range 20–70 % reaction, as seen from the example in Table 1. The rate constants were computed from the equations employed earlier¹.

Table 1. The decarboxylation of sodium *tert.-butylpropionate* in aqueous solution at 130.19° C.

Time in sec.	7 260	10 620	13 200	15 660	21 060	26 400	35 640
% reaction	22.8	31.4	38.0	42.8	52.8	61.0	72.0
10 ⁵ <i>k</i> sec. ⁻¹	3.565	3.549	3.621	3.567	3.565	3.567	3.572

The plots of $\log k$ against $1/T$ gave excellent straight lines for both sodium *tert.*-butylpropiolate and sodium tetrolate, the relative maximum deviations of the experimental points from the line calculated by the method of least squares being approximately 1 %.

The rate constants for the decarboxylation of *tert.*-butylpropionic acid were satisfactorily constant at the higher temperatures; at the lower temperatures the values tended to increase towards the end of the reaction. Also the plots of $\log k$ against $1/T$ deviated from the linear course at the lower temperatures, whereas the values for the four higher temperatures were situated close to the same straight line. For this reason, only the latter four values were employed in the calculation of the activation energy, and thus the value obtained is a maximum value. A similar deviation from the Arrhenius plot has not been observed for the decarboxylation reactions of other acetylenic acids that have been studied.

The values of the rate constants are collected in Table 2 and the values of derived kinetic quantities in Table 3. The values of E and A , the energy of activation and the frequency factor, have been computed by the method of least squares. The values of the free energy of activation ΔG^* , the heat of activation ΔH^* and the entropy of activation ΔS^* refer to 100° C.

Table 2. Decarboxylation rate constants.

Reactant	10 ⁷ <i>k</i> sec. ⁻¹						
	106.78°	115.03°	122.44°	130.19°	137.33°	144.32°	152.65°
(CH ₃) ₃ C—C≡C—COOH		34.6	69.6	142	270	501	1 010
(CH ₃) ₃ C—C≡C—COONa	26.7	68.5	160	357	747	1 510	
CH ₃ —C≡C—COONa	28.8				903	1 840	

Table 3. Values of derived kinetic quantities.

Reactant	<i>A</i> sec. ⁻¹	<i>E</i> cal.	ΔG^* cal.	ΔH^* cal.	ΔS^* E.U.
(CH ₃) ₃ C—C≡C—COOH	2.12 · 10 ¹¹	29 850	32 530	29 110	−9.1
(CH ₃) ₃ C—C≡C—COONa	8.03 · 10 ¹³	33 870	32 140	33 120	+2.7
CH ₃ —C≡C—COONa	3.51 · 10 ¹⁴	34 920	32 090	34 180	+5.6

DISCUSSION

For comparison, the rate constants at 90° C, the activation energies, frequency factors and entropies of activation at 100° C for the decomposition of propiolic, tetrollic and *tert.*-butylpropionic acids and their sodium salts are given in Table 4. It is seen that whereas sodium propiolate decomposes 25 times as rapidly as sodium tetrolate, sodium *tert.*-butylpropiolate decomposes at approximately the same rate as sodium tetrolate. The difference in the rates

Table 4. Kinetic data for the decarboxylation of propiolic, tetrolic and *tert.*-butylpropiolic acids and their salts in aqueous solution.

Reactant	$10^7 k_{90}^{\circ}$ *	E cal.	A sec. ⁻¹	ΔS^* E.U.
$\text{HC}\equiv\text{C}-\text{COONa}$	82.8	33 610	$1.38 \cdot 10^{15}$	+8.3
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COONa}$	3.41	34 920	$3.51 \cdot 10^{14}$	+5.6
$(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{COONa}$	3.36	33 870	$8.03 \cdot 10^{13}$	+2.7
$\text{HC}\equiv\text{C}-\text{COOH}$	67.2	29 850	$6.12 \cdot 10^{12}$	-2.5
$\text{CH}_3-\text{C}\equiv\text{C}-\text{COOH}$	2.09	31 190	$1.21 \cdot 10^{12}$	-5.7
$(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{COOH}$	2.30	29 850	$2.12 \cdot 10^{11}$	-9.1

* Calculated by the Arrhenius equation.

of the salts of propiolic and tetrolic acids is primarily due to a difference in the activation energies, while that between the rates of the salts of propiolic and *tert.*-butylpropiolic acids can be attributed to a difference in the value of the frequency factor. The relationships between the acids are approximately similar to those found for the salts. The difference in the rates of *tert.*-butylpropiolic and propiolic acid is determined primarily by the (+ *I*) inductive effect of the *tert.*-butyl group. If the rate of decomposition of sodium tetrolate were solely determined by the inductive effect of the methyl group, one would expect sodium tetrolate to decompose with approximately the same rate as sodium propiolate, and also the other kinetic quantities should have approximately the same values for these two salts, since the inductive effect of the methyl group is small compared to that of the *tert.*-butyl group. The fact that sodium tetrolate decomposes 25 times slower than sodium propiolate and at approximately the same rate as sodium *tert.*-butylpropiolate can readily be explained by the hyperconjugation in sodium tetrolate in the initial state (see below). As in methylacetylene, π_y - and π_z -hyperconjugation can be postulated in sodium tetrolate. This implies a lower energy of the compound

in the initial state. As the decomposing molecule enters the transition state, a partial negative charge develops at one end of the triple bond (transition state above). This charge, whose separation is opposed by the hyperconjugation, counteracts the hyperconjugative transfer of electrons and consequently hyperconjugation does not exist in the transition state. A similar explanation has been proposed by Ingold⁶ for the differences observed between the dipole moments of isocyanides and those of nitromethane and nitrobenzene, in which both conjugation and hyperconjugation are possible.

The difference, 1 310 cal., between the activation energies of sodium propiolate and sodium tetrolate is not as large as the energy of hyperconjugation for sodium tetrolate owing to solvation effects in aqueous solution.

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