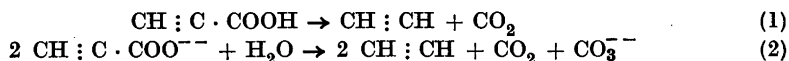


A Kinetic Study on the Decomposition of Propiolic Acid in Aqueous Solution

EERO TOMMILA and EERO HALONEN

Institute of Chemistry, University of Helsinki, Helsinki, Finland

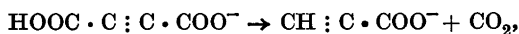
It has long been known¹ that propiolic (propargylic) acid and its alkali salts decompose in water according to the following equations:



The purpose of the present work was to investigate the kinetics of these reactions, on which there is no information in the literature. The work is a continuation of a previous investigation, which concerned the thermal decomposition of acetylenedicarboxylic acid in aqueous solution².

EXPERIMENTAL

Preparation and properties of propiolic acid. — Propiolic acid was prepared by decomposing the potassium hydrogen salt of acetylenedicarboxylic acid³



obtained by the method given in Organic Syntheses⁴ starting from fumaric acid. 50 g of the salt in 700 ml of water was kept on a boiling water bath and the evolution of the gas watched. After about 1 ½ hours, when the gas began to contain large amounts of acetylene, the flask was taken off the water bath. After cooling, the solution was acidified with sulphuric acid, saturated with ammonium sulphate and extracted about 20 times with ether. The ethereal solutions obtained from four such decompositions were united and dried with calcium chloride. The ether was distilled off and the residue fractionated at reduced pressure. At the third distillation a large (32 g) constant-boiling (b.p. 64.5°/15 mm) fraction was obtained. From this fraction the physical constants of the acid were determined, and it was also used in the kinetic investigations.

The sodium salt of propiolic acid was prepared by adding propiolic acid in slight excess⁵ to a 5 per cent sodium ethylate solution. The separation of the sodium salt was

brought about by adding dry ether. The sodium salt, as colourless needles, was filtered off by suction and dried in a desiccator containing sulphuric acid and solid paraffin. This method of preparation was used, since the salt is decomposed by water and thus a product prepared in aqueous solution contains sodium carbonate. Sodium propiolate turns gradually reddish.

The physical properties of the purest propiolic acid obtained were: m.p. 17.6° (18°⁶); b.p. 64.5°/15 mm (62–63°/15.5 mm⁶); d_4^{25} 1.1308 (d_4^{25} 1.1325⁶, d_{25}^{25} 1.301^{3a}); refractive index n_D^{20} 1.43316, n_D^{25} 1.43100; molar refraction $[R]$ 16.034 (calc. 15.588); surface tension (by double capillary method) γ^{25} 36.28 dyn/cm; parachor $[P]$ 152.0 (calc. 158.4). To test the purity of the fraction for which the above data were obtained, a weighed amount of the acid was titrated with 0.0194 *N* Ba(OH)₂. Mean of four determinations: $M = 70.20$ (70.05 calculated from the formula). The acid is very hygroscopic. Propiolic acid is readily soluble in benzene, toluene, light petroleum, hexane, and carbon tetrachloride, and rather soluble in *n*-octane and carbon disulphide.

Method. The kinetic experiments on propiolic acid were carried out in Pyrex glass ampoules. A series of identical samples was quickly pipetted into the ampoules, which were sealed and placed in a thermostat. At appropriate times ampoules were taken from the bath, cooled quickly with cold water, opened, and, after removing the carbon dioxide and acetylene formed by the reaction (1) by suction, the contents were titrated with a 0.01 *N* baryta solution, cresol red being used as indicator. The rate constants were calculated by the first order formula in the form

$$k = \frac{2.303}{t} \log \frac{100}{100-p} \quad (3)$$

where p is the percentage change, obtained from the volumes of the standard base used at the times t and zero.

In the first experiments the initial concentration of the acid was 0.1 mole/l. However, this concentration is obviously too great, for as the reaction proceeded, the rate constants tended to decrease, which may, at least in part, be accounted for by a side reaction, since, especially at higher temperatures, the solution gradually became brownish. Therefore the later experiments were carried out with 10 ml samples of a 0.01 *M* solution. In these cases the above formula always gave a good constancy for k . The following run at 90.50° C. may serve as an illustration:

t mins.	570	690	840	1033	1258	1930	2190
p	20.5	24.2	28.5	33.8	40.2	54.0 ¹	58.6
$10^6 k$ sec. ⁻¹	6.69	6.70	6.67	6.65	6.71	6.70	6.71

The experiments with the sodium salt were conducted by the following method. Into a 100 ml round-bottomed flask with a ground neck 100 ml of water saturated with acetylene was measured by pipette and the flask placed in a thermostat. After temperature equilibration, 0.4602 g or 0.05 moles of sodium propiolate weighed in a micro decanter glass was introduced into the flask and finally the micro decanter was dropped into the water. The gas formed in the reaction (2) was passed through an absorption apparatus containing 50 per cent potassium hydroxide solution, saturated with acetylene, for the absorption of the carbon dioxide. The gas leaving the absorption apparatus was acetylene. It was collected in a gas burette in a pneumatic trough. Water saturated with

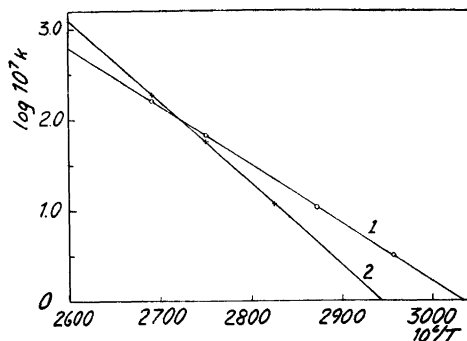


Fig. 1. Plot of $\log k$ vs. $1/T$. 1. Propionic acid. 2. Its sodium salt.

sodium chloride and acetylene was used in the trough. At appropriate times the volume of the acetylene was measured and reduced to NPT. The percentage change was obtained from this gas volume and from the calculated volume corresponding to the completed reaction. The rate constants were calculated by the formula (3). To save space only the series in Table 1 will be given in detail.

Table 1. Decomposition of sodium propionate in water. Initial concentration 0.05 mole/l. Temperature of thermostat 80.79°C . Volume of acetylene corresponding to the reaction when completed 112.07 ml. Barometric pressure b , temperature of the gas t .

Time mins.	b mm	$t^\circ\text{C}$.	V ml	V_0 ml	p %	$10^6 k$ sec. $^{-1}$
1 725	752.0	24.8	14.8	13.0	11.6	1.19
2 820	753.0	24.8	24.2	21.3	19.0	1.24
3 840	758.8	24.2	31.0	27.6	24.6	1.23
4 665	768.3	22.4	36.2	32.7	29.2	1.23
5 685	769.5	23.8	41.8	37.8	33.7	1.21
6 675	770.6	23.0	44.6	40.6	36.2	1.12
7 275	770.5	23.0	46.8	42.5	38.0	1.09
10 995	770.4	21.0	66.0	60.6	54.1	1.18
12 480	760.1	28.8	70.8	63.6	56.7	1.12
					Mean	1.18

The water thermostats used could be held constant within about 0.02°C . To prevent evaporation of the water, its surface was covered with a layer of liquid paraffin. The thermometers were checked against a normal thermometer calibrated by the U.S.A. National Bureau of Standards.

RESULTS AND DISCUSSION

The results of the kinetic determinations are collected in Table 2. The linear relation between $\log k$ and $1/T$ to be expected from the Arrhenius equation $k = Ae^{-E/RT}$ was well obeyed (Fig. 1). The activation energy E and

the frequency factor A were calculated by the method of least squares. The values of the entropy of activation ΔS^* , obtained by the formula

$$A = e \frac{kT}{h} e^{\Delta S^*/R}$$

are given for the temperature 90° C.

Table 2. Values of the kinetic quantities.

Reactant	$10^7 k \text{ sec.}^{-1}$					$E \text{ cal}$	A	ΔS^* E.U.
	65.00°	75.00°	80.79°	90.50°	98.38°			
CH : C · COOH	3.17	10.8		66.9	160	29 400	$2.98 \cdot 10^{12}$	-3.8
CH : C · COONa			11.8	58.5	186	41 000	$2.58 \cdot 10^{19}$	+27.8

A comparison of the values of the rate constants with those obtained for the decomposition of acetylenedicarboxylic acid and its sodium hydrogen salt² shows that the decomposition of propiolic acid and its sodium salt is much slower than these reactions, *e.g.*, the values of 10^7k for the four reactions for the temperature 75° C., calculated by the Arrhenius equation, are: 3 290, 2 510, 11.0, and 4.56 sec.^{-1} , respectively. Thus we can understand that propiolic acid can be profitably prepared by heating the sodium or potassium hydrogen salt of acetylenedicarboxylic acid in aqueous solution.

Although the values of k for the decomposition of propiolic acid and its sodium salt do not differ greatly, the activation energy and the frequency factor are very different in these two cases. The activation energy for the decomposition of the ion has the very high value of 41 000 calories, *i.e.* nearly 12 000 calories higher than that for the decomposition of the acid. It is very striking, too, that for the ion the frequency factor is 10^7 times greater than for the acid. These great differences unquestionably compel us to assume a different reaction mechanism in the two cases. The mechanisms proposed by Hall⁷ for the decarboxylation of malonic acid and its acid ion, and assumed also for the decomposition of acetylenedicarboxylic acid and its acid ion², are obviously applicable in the present case, and, in fact, the evidence for them is now much greater than in those previous reactions.

For the decomposition of the free acid the frequency factor is $3 \cdot 10^{12}$, a value which is of a magnitude very usual in unimolecular reactions. The entropy of activation is slightly negative (-3.8 E.U.) and thus indicates that the transition state has a somewhat more rigid structure than the initial molecule; probably this is an indication of an incipient bond formation between

The net result is reaction (2). Evidence for the first stage of this mechanism lies in the unusually high values of E and A ; the later stages can be deduced on the ground of the reaction products. The decarboxylation must clearly be facilitated if the hydrogen atom is replaced by a substituent which is more strongly electron-attracting than hydrogen. The undissociated carboxyl is such a group, and thus $\text{HOOC} \cdot \text{C} : \text{C} \cdot \text{COO}^-$ should split off CO_2 more easily than does $\text{HC} : \text{C} \cdot \text{COO}^-$. This is in agreement with experiments. As was seen above, at 75° the former reaction is 550 times faster than the latter. For the latter the energy of activation is 41 000 cal, for the former 30 000 cal.² There are several reasons² for presuming that the reaction is $\text{HOOC} \cdot \text{C} : \text{C} \cdot \text{COO}^- \rightarrow \text{HOOC} \cdot \text{C} : \text{C}^- + \text{CO}_2$ and not $\text{HOOC} \cdot \text{C} : \text{C} \cdot \text{COO}^- \rightarrow \text{HC} : \text{C} \cdot \text{COO}^- + \text{CO}_2$.

The frequency factor is very large in both cases (for the acetylenedicarboxylate ion $A = 1.70 \cdot 10^{15}$), and accordingly the entropy of activation highly positive, 9 and 28 E.U., respectively. This indicates that in the transition state the bond which is to be broken must be greatly stretched, which is quite obvious if we think of the nature of the reaction. Especially in the case of the propiolate ion where energy of activation is so large the bond must be drastically stretched and the distribution of the charge far advanced before the critical state is reached. In addition, owing to the distribution of the charge, the transition state is less polar, and accordingly less solvated, than the reactant, the propiolate ion; this effect, too, will result in an increase of A and E .

According to the theory of absolute reaction rates, the specific rate of a chemical reaction can be expressed also by the equation

$$k = \frac{kT}{h} e^{-\Delta G^*/RT}$$

where $\Delta G^* = \Delta H^* - T\Delta S^*$ is the standard free energy of activation. $\Delta H^* = E - RT$ is the standard heat of activation. The values of ΔG^* for the two reactions considered here are close together and thus the velocities do not differ much. The entropies of activation are only slightly dependent on the temperature. For the decarboxylation of free propiolic acid the free energy of activation is nearly independent of the temperature, showing only a very small increase with temperature, whereas in the case of the propiolate ion it decreases rapidly with increasing temperature. The values for some temperatures are:

		HC : C · COOH						HC : C · COO ⁻			
<i>t</i>		25°	50°	75°	100°	<i>t</i>		25°	50°	75°	100°
ΔS^*	E.U.	-3.4	-3.6	-3.8	-3.9	ΔS^*	E.U.	+28.2	+28.1	+28.0	+27.9
ΔG^*	kcal	29.8	29.9	30.0	30.1	ΔG^*	kcal	32.0	31.3	30.6	29.9

At 94.5° C. ΔG^* is equal for both reactions; consequently, at this temperature they occur with equal velocities.

Propiolic acid is a strong organic acid, its dissociation constant being about $5 \cdot 10^{-3}$ (unpublished experiments), and its solutions contain, besides undissociated molecules, a remarkable concentration of ions. Thus *e.g.* at low temperatures, where the decomposition of the acid is faster than that of the ion, a greater initial concentration a or an addition of a strong acid should favour the reaction. This is really the case, as is shown by the following results at 75° C:

a_{Acid} moles/liter	0.01	0.1	0.01	0.01	0.1
a_{HCl} » »	0	0	0.01	0.02	0.1
$10^6 k$ sec. ⁻¹	1.08	1.30	1.27	1.41	1.53

However, in these cases k has a tendency to decrease as the reaction proceeds (see above). It is also possible that HCl molecules are added to the triple bond^{1a}. At any rate, these observations confirm the results presented and discussed above.

SUMMARY

The kinetic of the decomposition of propiolic acid and its sodium salt in water were investigated. The results are discussed.

REFERENCES

1. Bandrowski, A. *Ber.* **15** (1882) 2704; Baeyer, A. *Ber.* **18** (1885) 677.
2. Tommila, E., and Kivinen, A. *Suomen Kemistilehti B* **24** (1951) 46.
3. Perkin, W. H., and Simonsen, J. L. *J. Chem. Soc.* **91** (1907) 834; Ingold, E. H. *Ibid.* **127** (1925) 1202.
4. *Organic Syntheses*, Coll. Vol. II. 10, 177.
5. Strauss, F., and Voss, W. *Ber.* **59** (1926) 1681.
6. Strauss, F., Heyn, W., and Schwemer, E. *Ber.* **63** (1930) 1086.
7. Hall, G. A. *J. Am. Chem. Soc.* **71** (1949) 2691.

Received September 15, 1952.