# Studies in Decarboxylation. Part VIII.[1] The Gas-phase Pyrolysis of βγ-Acetylenic Acids

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Some βγ-acetylenic acids are shown to undergo flash vacuum pyrolysis to give quantitative yields of an allene and carbon dioxide. At higher pressures the decarboxylation is obscured in some cases by competing reactions. Acetylenic acids decarboxylate faster than their olefinic counterparts, and the reaction is shown to involve a concerted 1,5-hydrogen shift. The participation of acetylenic bonds in electrocyclic reactions is discussed.

THE decarboxylation of βγ-unsaturated acids in the gas phase has been examined by a series of mechanistic probes, and has been firmly established as an electrocyclic process.[2] The reaction is well behaved kinetically and has all the characteristics of a unimolecular reaction and we have therefore chosen it to enquire into the variation of structure which can be accommodated by a concerted process. The first such variation we have examined involves the substitution of the olefinic by an acetylenic bond, and we report our findings below. This class of compounds is not at all well known, and for synthetic reasons we have confined our attention largely to the normal acids in this paper.

## EXPERIMENTAL

*Preparation of Acids*.—But-3-ynoic acid, m.p. 83–83.5° (lit.,[3] 83–83.5°) was made by Heilbron's method.[3] The higher homologues were prepared by the same route, the appropriate acetylene being made *in situ* before reaction with ethylene oxide; pent-3-ynoic acid had m.p. 103.5—104.5° (lit.,[4] 103—104.5°); hex-3-ynoic acid m.p. 63—64° (lit.,[5] 61—63°); *hept-3-ynoic acid* b.p. 140—141° at 22 mmHg (Found: C, 66.6; H, 8.0. $C_7H_{10}O_2$ requires C, 66.6; H, 8.0%).

2,2-Dimethylbut-3-ynoic acid was made from ethyl 2,2-dimethylbut-3-enoate.[6] The olefinic ester was brominated with a 5% solution of bromine in $CCl_4$ at room temperature, and the product immediately treated with excess of lithium ethoxide in ethanol (2.5 h at 25°). We were not successful in attempts to dehydrobrominate the vinyl ester, but the corresponding acid (KOH hydrolysis) yielded to butyllithium in hexane (3 mol) at −30°. The resulting acetylenic acid (overall yield *ca.* 30%) had the expected i.r. and n.m.r. spectra, b.p. 55—56° at 2 mmHg, $n_D^{23}$ 1.4292 (Found: *M*, 112.051 735. Calc. for $C_6H_8O_2$: *M*, 112.052 426). Pent-3-enoic acid, b.p. 89—90° at 10 mmHg was made by the method of Lane *et al.*[7]

*Stoicheiometry*.—The stoicheiometry of the reaction was measured under three sets of conditions. In evacuated sealed tubes, with typically 15 cmHg pressure at 480 K, the acids gave the following products:—but-3-ynoic acid: allene (20%), $CO_2$ (80%), and polymer; hex-3-ynoic acid: penta-1,2-diene (13%), $CO_2$ (35%), lactone (40%), and polymer; hept-3-ynoic acid gave only lactone. The stoicheiometry was also measured in the flow apparatus previously described.[8] It was found necessary to replace the stainless steel connection tube between the flow tube and the vapour phase chromatograph by an all glass system. At 693 K but-3-ynoic and pent-3-ynoic acids gave quantitative yields

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of allenes and carbon dioxide. At the same temperature, hex-3-ynoic acid gave penta-1,2-diene (45%) and lactone (30%). At 420 K, hept-3-ynoic acid passed through the apparatus unchanged as a single peak. By 520 K this peak had spread to two further components of similar retention time, and by 640 K there were at least six volatile components which appeared to be hydrocarbons, but which were not identified, and a seventh peak which was lactone. Hept-3-ynoic acid was successfully decarboxylated by flash vacuum pyrolysis. Quantitative yields of carbon dioxide and hexa-1,2-diene were obtained by exposure (1.5 s) to 700 K. Under similar conditions, 2,2-dimethylbut-3-ynoic and hex-3-ynoic acids gave quantitative yields of 3-methylbut-1,2-diene and penta-1,2-diene respectively.

*Kinetics.*—Kinetic runs were carried out with but-3-ynoic and pent-3-ynoic acids in the flow reactor modified as described above. The results are given in Table 1. With 2,2-dimethylbut-3-ynoic acid a small but constant (*ca.* 2—3%) proportion of lactone was produced at all temperatures. We believe this to have been formed in the act of volatilization in the flow tube. If this is so, the first-order kinetics should not be affected; however, the activation parameters quoted for this acid in Table 1 should be treated with caution.

Pent-3-enoic acid, examined in the temperature range 680—720 K, had $\Delta H^{\ddagger}$ 167.8 ± 6.5 kJ mol$^{-1}$ and $\Delta S^{\ddagger}$ −41.8 ± 10.5 J K$^{-1}$ mol$^{-1}$; $10^3 k_{630}$ 1.05 s$^{-1}$.

*Deuterium Labelling.*—The carboxy hydrogen of the above four acids was exchanged for deuterium.[9] Table 2 shows the results of flow tube pyrolysis.

## DISCUSSION

The four acids studied comprised the homologous series from but-3-ynoic to hept-3-ynoic acids and one tertiary acid. In evacuated sealed tubes, only but-3-ynoic acid had decarboxylation as its main reaction, and even here there was extensive loss of allene. The higher homologues showed an increasing propensity towards lactonisation with length of alkyl chain, a situation familiar in the βγ-olefinic acid series.[6]

Only but-3-ynoic and pent-3-ynoic acids behaved well in the flow reactor and will be discussed below. The two higher homologues were less reactive and, at temperatures sufficient for decarboxylation, showed lactonization and further decomposition.

All the acids gave quantitative yields (within experimental error) of the expected allene and carbon dioxide under the conditions of flash vacuum pyrolysis. This is perhaps a little surprising since the negative entropy of activation discussed later should prove very unfavourable at these high temperatures, and a reaction involving bond scission might be expected. However the products, and those of deuterium labelling, confirm the concerted pathway for the high temperature reaction. The absence of the decarboxylation reaction at lower temperature and higher pressure must result from competing intermolecular reactions.

Before interpreting the data of Table 1, it is necessary to establish that the reaction is of the first order. We have done this in other cases by heating varying pressures of substrate in evacuated sealed tubes, and demonstrating that for a given time the degree of reaction is independent of the starting pressure. We applied this test to but-3-ynoic acid and found that over an initial pressure range of 7—28 cmHg the extent of decomposition was indeed invariant. However, since none of the products was obtained in quantitative yield at 100% decomposition, it could be argued that this test is no longer totally rigorous.

TABLE 1

Flow tube pyrolysis of βγ-acetylenic acids

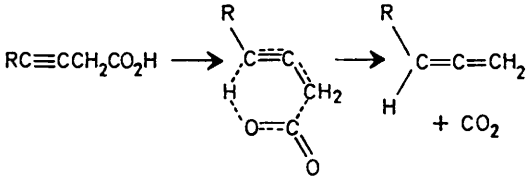
$$R^1C{\equiv}C{-}CR^2{}_2CO_2H \longrightarrow R^1CH{=}C{=}CR^2{}_2 + CO_2$$

| $R^1$ | $R^2$ | Temp. range (K) | $\Delta H^{\ddagger}$/ kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/ J K$^{-1}$ mol$^{-1}$ | $10^2 k$/s$^{-1}$ [a] |
|---|---|---|---|---|---|
| H | H | 613—648 | 153.6 ± 6.3 | −42.3 ± 8 | 630 K;<br>$1.4_9$, $1.4_4$ [b] |
| H | $CH_3$ | 580—630 | 147.7 ± 6.3 | −41.8 ± 8 | |
| $CH_3$ | H | 618—663 | 156.1 ± 6.3 | −41.8 ± 8 | 662.3 K;<br>$4.4_3$, $4.3_0$,[b]<br>$3.9_8$ [c] |

[a] ' Best ' rate constant at temperature of confidence elipse.[10] [b] Runs in the presence of 500 mol % of cyclohexene. [c] Runs in tube packed with helices (*s*/*v* × 13).

The expressions used to calculate rates of reaction from the flow apparatus assume ' plug-flow ' in the reactor and reactions of the first order,[10] and we [8] and others [10] have shown that good rate constants are obtained on this basis. As the flow approximates to plug-flow, the order of reaction cannot be established by altering the injection size, since this will simply alter the size of the plug and not the vapour pressure or ' concentration ' of the reactant. However if the reactant is diluted with an inert material, but the size of the injection kept constant, the size of the plug injected will be constant and the concentration of reactant in that plug will be decreased. Accordingly for a reaction of order greater than unity, the extent of reaction should decrease. The results of a five-fold dilution with cyclohexene are shown in Table 1 for the two acids investigated, and it is clear that the rate constant is unaffected. As a result of this argument and that of the previous paragraph, we believe the reactions to be of the first order.

The first two acids of Table 1 decompose by a homogeneous unimolecular mechanism to give quantitative yields of carbon dioxide and allenes. The activation parameters imply the concerted transition state shown in the Scheme. In the olefinic acids there is always migration of the double bond during decarboxylation;[11] a similar migration of one of the π-bonds of the present acetylenic acids gave allenes as the only detectable hydrocarbon



SCHEME R = H or Me

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[11] D. B. Bigley, *J. Chem. Soc.*, 1964, 1231.

products. The deuterioallenes recovered from decarboxylation were specifically labelled (Table 2) showing that the deuterium on the carboxy group becomes attached to the original $\gamma$-carbon atom.

TABLE 2

Flow pyrolysis of deuteriated $\beta\gamma$-acetylenic acid

$$R^1C{\equiv}C{-}CR_2^2CO_2D \longrightarrow R^1CD{=}C{=}CR_2^2 + CO_2$$

| $R^1$ | $R^2$ | Allene | $10^3k_{630}/s^{-1}$ | $k_H/k_D$ (630 K) |
|---|---|---|---|---|
| H | H | $HDC{=}C{=}CH_2$ | $5.0_8$ | $3.0_0$ |
| H | $CH_3$ | $HDC{=}C{=}C(CH_3)_2$ | | |
| $CH_3$ | H | $CH_3{-}CD{=}C{=}CH_2$ | $3.3_0$ | $2.9_7$ |

Our earlier work on the olefinic acids led to the conclusion that hyperconjugative-inductive interaction of methyl groups in the $\alpha$- and $\gamma$-positions are rather slight, with an $\alpha$-methyl group accelerating the reaction while a $\gamma$-methyl group decreases the rate.[6] Table 3 shows that alkylation of the $\alpha$- and $\gamma$-carbon atoms of acetylenic acids affects the rate of decomposition in the same sense, although the magnitude of the effects is smaller. It is noteworthy that the absolute rate of decarboxylation of the acetylenic acids is actually greater than their olefinic counterparts.

TABLE 3

Rates ($k$/s$^{-1}$) and relative rates for each row (in italics) of pyrolysis of some unsaturated acids at 500 K

| Acid | $\alpha\alpha$-Dimethyl | $\gamma$-Methyl |
|---|---|---|
| $CH_2{=}CHCH_2CO_2H$ [a]<br>$1.5_0 \times 10^{-6}$; *1.0* | $CH_2{=}CHC(CH_3)_2CO_2H$ [b]<br>$1.3_8 \times 10^{-5}$; *9.2* | $CH_3CH{=}CHCH_2CO_2H$ [c]<br>$2.0_1 \times 10^{-7}$; *0.13* |
| $CH_3CH{=}CHCH_2CO_2H$ [c]<br>$2.0_1 \times 10^{-7}$; *1.0* | $CH_3CH{=}CHC(CH_3)_2CO_2H$ [b]<br>$1.3_6 \times 10^{-6}$; *6.8* | |
| $HC{\equiv}C{-}CH_2CO_2H$ [c]<br>$5.8_0 \times 10^{-6}$; *1.0* | $HC{\equiv}CC(CH_3)_2CO_2H$ [c]<br>$2.4_4 \times 10^{-5}$; *4.2* | $CH_3C{\equiv}CCH_2CO_2H$ [c]<br>$3.3_6 \times 10^{-6}$; *0.58* |

[a] Ref. 12. [b] Ref. 6. [c] Present work.

Table 2 shows $k_H/k_D$ *ca.* 3.0 for two acetylenic acids. The decarboxylation reaction is essentially a 1,5-hydrogen shift, and the deuterium isotope effect is near maximum for the closely related decomposition of but-3-ynol.[13] In the same series, Viola *et al.* have shown that $k_{\text{but-3-ynol}}/k_{\text{but-3-enol}} = 2.8$ at 350°[14] (*cf.* $k_{\text{but-3-ynoic acid}}/k_{\text{but-3-enoic acid}} = 3.9$ at 500 K).

The acetylenic bond has been shown to participate in electrocyclic reactions by a number of authors. For example there are acetylenic analogues of the well known Claisen,[15] Cope,[16,17] and divinylcyclopropane [18,19,20] rearrangements and their thio-counterparts [21,22] and several isolated examples of other types. It is therefore well established that the linear acetylene function can readily replace the bent olefin bond in the cyclic transition state for these reactions. Most of the above studies have been qualitative, but where quantitative measurements have been made, the rates of reaction of the acetylenic compounds were found to be 2—6 times greater than their olefinic counterparts.

Viola *et al.* have suggested that the acetylenic group is accommodated in the transition state by use of its low frequency bending mode. We would support this suggestion. Dr. J. A. Creighton, of this laboratory, using the $C{-}C{\equiv}C$ bend for methylacetylene (336 cm$^{-1}$)[23] has shown that at the mean temperature of our reaction (625 K) all the lower vibrational levels will be significantly populated, with $v = 0$, 30%; $v = 1$, 27%; $v = 2$, 18.5%; and $v = 3$, 11.4%. Further, the amplitude of vibration for $v = 3$ will be of the order of 25° and should be readily accommodated in the cyclic transition state.

On the other hand Viola's explanation of the greater rate of reaction of the acetylenic compounds in terms of their greater nucleophilicity compared with olefins [14] seems less well founded, since there is at present no indication of the electronic nature of the hydrogen atom transferred in electrocyclic reactions. We prefer an explanation in terms of bond energies. Thus while $(C{=}C) - (C{-}C) = 264.4$, $(C{\equiv}C) - (C{=}C) = 225$ kJ mol$^{-1}$,[24] implying that one of the $\pi$-bonds of acetylene is more easily broken than that of ethylene. This argument is supported by the activation parameters of the present work. Thus while the $\Delta S^\ddagger$ values for pent-3-enoic and pent-3-ynoic acids are indistinguishable, $\Delta H^\ddagger$ is 167.8 for the former acid and 156.1 kJ mol$^{-1}$ for the latter.

Finally, we note that at 298 K $\Delta G_f^0$ (propyne) = 193.8 compared with $\Delta G_f^0$ (allene) = 202.4 kJ mol$^{-1}$,[25] showing that there can be no thermodynamic driving force for the enhanced rate of reaction of the acetylenic compounds.

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