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Studies in Decarboxylation. Part 14.¹ The Gas-phase Decarboxylation of But-3-enoic Acid and the Intermediacy of Isocrotonic (*cis*-But-2-enoic) Acid in its Isomerisation to Crotonic (*trans*-But-2-enoic) Acid

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At 593 K the complex system (A) is shown to be rapidly set up starting from any of the pure acids. Of particular
crotonic acid \rightleftharpoons isocrotonic acid \rightleftharpoons but-3-enoic acid \longrightarrow propene + CO₂ (A)

interest is the intermediacy of isocrotonic acid (the thermodynamically least stable of the three) in the interconversion of crotonic and but-3-enoic acids. A mechanism involving the enolic form of a carboxylic acid is proposed to account for this feature. The interconversion of crotonic and isocrotonic acids is much more rapid than that of their ethyl esters and a basis is proposed for the difference. Activation parameters relating to the decarboxylation of but-3-enoic acid are isolated by the flow technique.

It has been known for many years that $\alpha\beta$ - and $\beta\gamma$ -unsaturated acids are readily interconverted. Generally the *trans*- $\alpha\beta$ -form is favoured over either the *cis*- $\alpha\beta$ - or the $\beta\gamma$ -forms, and the interconversion may be achieved thermally or by acid or base catalysis. The latter was systematically examined by Kon and Linstead, but evidence for the uncatalysed thermal interconversion is based on a series of unrelated observations. The pertinent references are given in Beilstein,² more recent work (*e.g.* ref. 3) not altering the picture.

In our previous studies of the decarboxylation of $\beta\gamma$ -unsaturated acids,⁴ we avoided kinetic complication by the use of α -*gem*-dimethylated acids, which are structurally incapable of isomerisation. In this paper we report our studies on the decarboxylation of the parent acid, but-3-enoic acid. We also give what we believe to be the first full analysis of the thermal interconversion of the C₄-unsaturated acids, a system showing some unexpected and novel features.

RESULTS AND DISCUSSION

Definition of the System.—The overall reaction for the pyrolysis of but-3-enoic acid to completion is (1), the



precise 2 : 1 stoichiometry being convenient for measurement by pressure change in a static reactor. Figure 1 is a typical pressure-time curve for the reaction and shows a region of fast reaction up to 2 h followed by a region of much slower reaction. If the two regions are treated

separately, each shows a good fit with a first-order rate expression (calculation of P_∞ for each region is described in the Experimental section); the derived plots are also shown in Figure 1. While the rate constants so derived

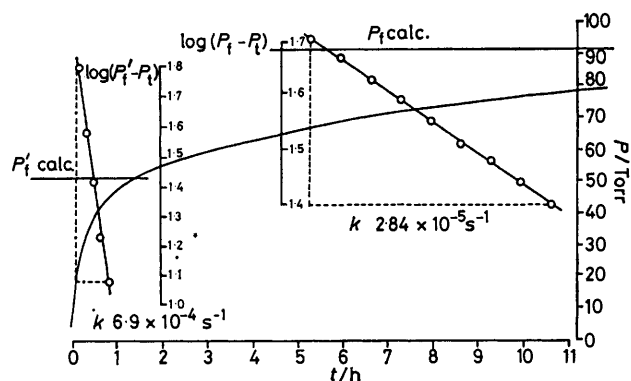


FIGURE 1 Pressure-time curve and derivatives for the decarboxylation of but-3-enoic acid at 593 K

have no simple significance, they do constitute a convenient measure of reproducibility. Table 1 shows that the first part of the but-3-enoic acid decomposition is reproducible and is largely unaffected by initial pressure or by additives. We have therefore done the bulk of our work on the pure acid.

We assumed that the known² isomerisation of but-3-enoic acid to crotonic acid would occur in our reactor. However, since it would result in no pressure change, it

would not be directly detectable. The first part of the pressure-time curve of Figure 1 would derive from the decarboxylation of but-3-enoic acid; the second shallower part would represent the decarboxylation of the accumulated crotonic acid after depletion of the but-3-enoic acid. In order to test this theory we examined the

TABLE 1

First-order rate constants for the first region in the gas-phase pyrolysis of but-3-enoic acid

T/K	Additive	$10^3 k/s^{-1}$	$P_0(\text{total})/\text{mmHg}$
633.5	None	5.0	60
633.5	1 : 1 Cyclohexene	4.6	102
633.5	1 : 1 Cyclohexene	4.7	152
633.5	1 : 4 Cyclohexene	4.3	200
633.5	1 : 4 Cyclohexene	3.7	384
633.5	1 : 1 $m\text{-C}_6\text{H}_4\text{Cl}_2$	5.0	105
651.0	None	12	85
651.0	None	12	79
651.0	None	12	161
651.0	None	13	47

decarboxylation of authentic crotonic acid. Figure 2 shows the pressure-time curve for the decarboxylation of this acid. There is a point of inflection near 15% reaction after which the curve becomes identical with that for the second region of the but-3-enoic acid curve; each has the same rate constant (20–90% reaction). Table 2 summarises our examination of the decarboxylation of crotonic acid (crotonic acid, being a solid, was

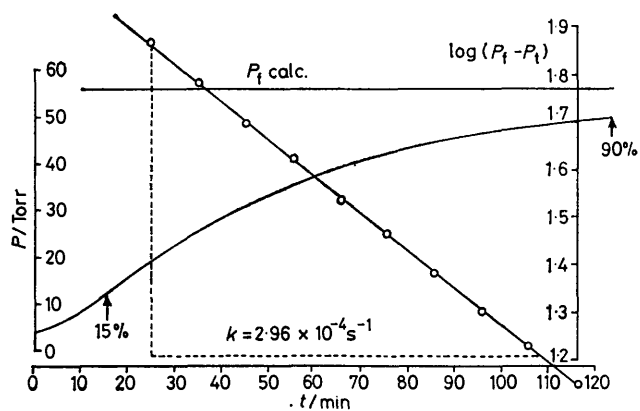


FIGURE 2 Pressure-time curve and derivative for the decarboxylation of crotonic acid in the presence of *m*-dichlorobenzene at 633.9 K

introduced into the reactor as a solution); the results were less reproducible than for the first part of the but-3-enoic acid decomposition but showed no systematic pressure dependence.

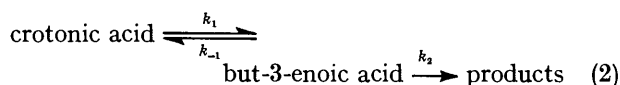
The pyrolysis of crotonic acid has been reported only once previously;⁵ propene, water, and carbon dioxide were recorded as 'important products', traces of propionaldehyde and carbon monoxide also being detected. No rate datum was obtained. We observed only propene and carbon dioxide; the earlier workers used packed unseasoned vessels and we assume that the other products resulted from heterogeneous reactions.

TABLE 2

First-order rate constants for the pyrolysis of crotonic acid

T/K	Solvent	Initial pressure (Torr)		$10^4 k/s^{-1}$
		Total	Acid	
633.5	<i>m</i> -C ₆ H ₄ Cl ₂	82	58	2.54
633.7	<i>m</i> -C ₆ H ₄ Cl ₂	86	61	2.18
633.7	<i>m</i> -C ₆ H ₄ Cl ₂	103	74	2.23
633.7	<i>m</i> -C ₆ H ₄ Cl ₂	125	89	2.44
633.8	<i>m</i> -C ₆ H ₄ Cl ₂	75	53	2.96
633.6	<i>m</i> -C ₆ H ₄ Cl ₂	70	50	3.21
633.7	Cyclohexene	155	51	3.33
633.7	Cyclohexene	221	72	3.32
633.9	Cyclohexene	75	25	2.85
633.8	Cyclohexene	184	60	2.52
633.9	Cyclohexene	192	62	2.14

As a result of the evidence described so far reaction (2) was envisaged, identical with that of Arnold *et al.*⁶



This apparently simple scheme is extremely difficult to analyse numerically;⁷ when modelled on an analogue computer, and starting with but-3-enoic acid, the correctly shaped pressure-time curve is easily obtained, but values of k_1 and k_{-1} are not reliable since they are strongly influenced by the last 15% of reaction. It therefore seemed simpler to test reaction (2) by sampling the reaction at various times for v.p.c. analysis; this could conveniently be done by the use of evacuated sealed tubes, since it had already been shown that the reaction was not sensitive to pressure. Isocrotonic acid, the least thermodynamically stable isomer of the series,² became evident as an important intermediate.

Figures 3–5 show isomer distributions obtained

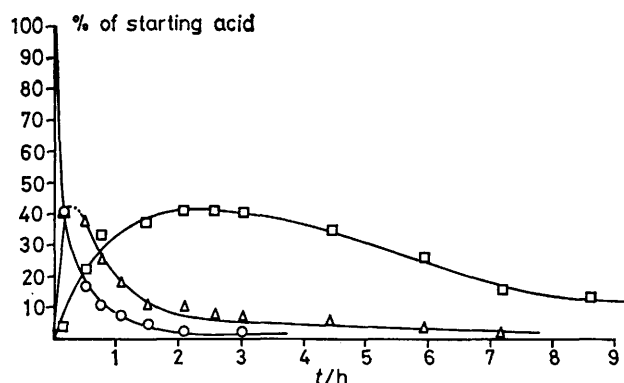
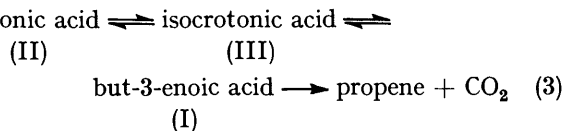


FIGURE 3 Isomer distribution during the pyrolysis of but-3-enoic acid at 593 K: ○, but-3-enoic acid; △, isocrotonic acid; □, crotonic acid

starting from each pure acid. The early steps of *series* reactions are characterised by steep initial slopes; using this criterion, inspection of Figures 3–5 leads to reac-



tion (3). The following points are noteworthy. (i) Direct decarboxylation from the conjugated acids (II) and (III) is not included as a route. Arnold *et al.* reported that 4,4-dimethylpent-2-enoic acid, which is structurally incapable of giving a $\beta\gamma$ -isomer, is recovered

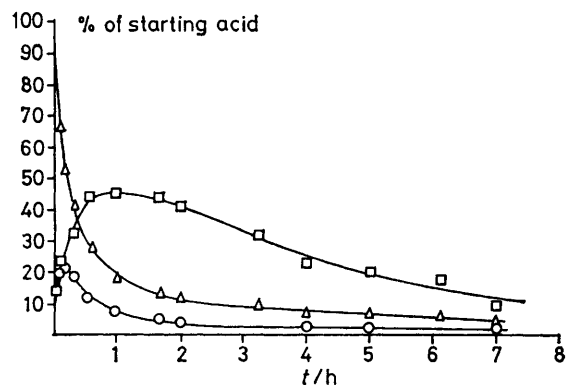


FIGURE 4 Isomer distribution during the pyrolysis of isocrotonic acid at 593 K: \circ , but-3-enoic acid; Δ , isocrotonic acid; \square , crotonic acid

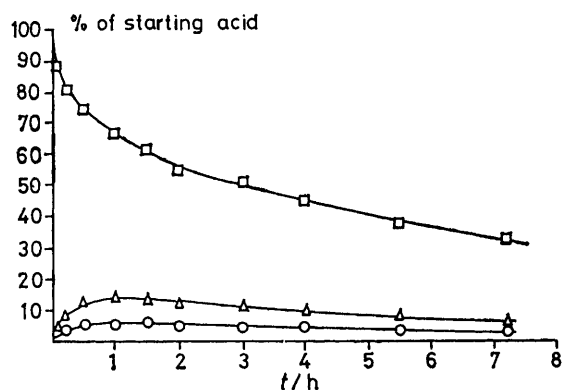


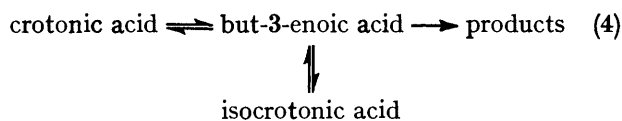
FIGURE 5 Isomer distribution during the pyrolysis of crotonic acid at 593 K: \circ , but-3-enoic acid; Δ , isocrotonic acid; \square , crotonic acid

unchanged after 5 h heating' at 573 K.⁶ We can confirm this statement for the recovered acid, but have found a slow decarboxylation at 664 K (k $6.7 \times 10^{-5} \text{ s}^{-1}$) which must be direct from the $\alpha\beta$ -isomer. We hope to report on this reaction more fully at a later date, but note for the present that it is two orders of magnitude slower than the reactions under discussion and will be neglected as a significant route.

(ii) The initial near-zero slope of the pressure-time curve for the decarboxylation of crotonic acid (II) (Figure 2) is due to the time required for the build-up of (II) and (III) before decarboxylation (and therefore pressure increase) can commence.

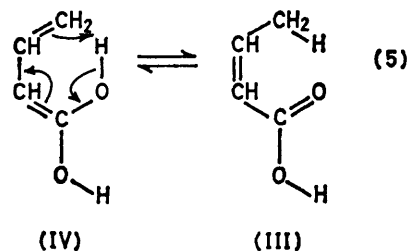
(iii) Direct interconversion of but-3-enoic acid (I) and crotonic acid (II), if it exists at all, must be slow or the sharp maximum of isocrotonic acid (III) would not be observed in Figure 3.

(iv) The alternative reaction (4) is improbable since, starting with pure isocrotonic acid, it requires that the

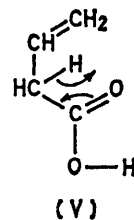


appearance of crotonic acid should have an initial zero slope (*cf.* Figure 4). In fact the pressure-time curve for the pyrolysis of isocrotonic acid at 649 K shows two regions. The first 35% of reaction is too fast to be followed in our static reactor; from Figure 3 and reaction (3) it is seen that isocrotonic acid rapidly distributes itself between crotonic and but-3-enoic acids; the latter decarboxylates almost instantaneously at this temperature. The last 60% of the curve is identical to that of Figure 2 and has the same rate constant ($4.4 \times 10^{-4} \text{ s}^{-1}$ versus $4.5 \times 10^{-4} \text{ s}^{-1}$ for crotonic acid at 649 K). Starting from any of the pure acids, therefore, the same equilibrium mixture is obtained, resulting in the same pressure-time curve in the later stages of reaction.

Mechanistic Inferences.—The most interesting feature of reaction (3) is the intermediacy of isocrotonic acid (III) in the isomerisation of but-3-enoic to crotonic acid; Figure 3 shows that after *ca.* 15 min it constitutes as much as 50% of the remaining acid mixture. The 1,5-hydrogen shift shown in reaction (5), starting from the enol (IV) of but-3-enoic acid, accounts for the sole production of isocrotonic acid, and of course for the reverse process.



The conversion of but-3-enoic acid into its enol (IV) presents an interesting problem. The overall rate of reaction is not pressure dependent, and the enolisation must therefore be unimolecular. A concerted 1,3-hydrogen shift [represented in (V)] is thermally forbidden; it seems possible, therefore, that the hydrogen

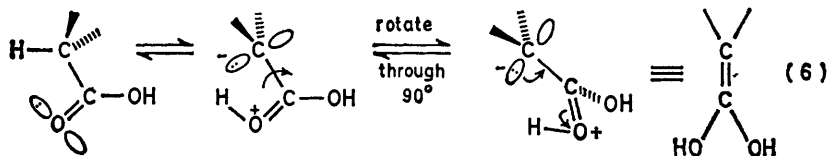


atom is transferred into the oxygen lone pair as a proton in an acid:base reaction to give a zwitterion [reaction (6)]. The lone pair of the resultant carbanion is orthogonal to the π -system of the protonated carbonyl group and the latter must rotate through 90° before the double bond can form. The reverse of reaction (6) (de-

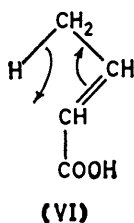
enolisation) may be expected to be aided by the flexibility associated with double bonds attached to two electronegative elements.⁸ On the other hand the selection rules for concerted transfer of a hydrogen atom on to each of the carbonyl oxygen lone pairs may be different; there would then be no need for zwitterion formation.

behaviour must therefore have a different origin. We suggest that the enolisation reaction (6) and 1,5-hydrogen shift (5) may be simultaneous, or nearly so, for the acids, as represented in (VIII; R = H). Clearly such a process is not available to the esters (VIII; R = CH₃).

We have not numerically analysed Figure 1 in terms



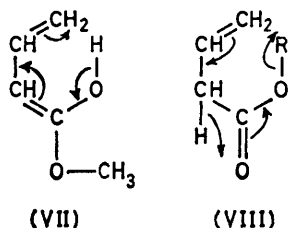
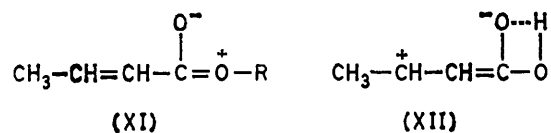
On either basis it is easily seen why crotonic acid cannot isomerise directly to but-3-enoic acid. The 1,3-hydrogen shift shown in (VI) is also thermally forbidden, and there are no strategically placed electronegative elements either to act as a base or to labilise the double bond. Instead crotonic acid must first isomerise to isocrotonic acid, this interconversion presumably taking place by the normal mechanism for *cis-trans*-isomerism.⁹



of reaction (3), but clearly the *cis-trans* isomerism of the crotonic acids cannot be slower than the slowest step, *i.e.* $2.8 \times 10^{-5} \text{ s}^{-1}$. By contrast, the *cis-trans* isomerism of ethyl isocrotonate to ethyl crotonate is a much slower process¹⁰ ($k \text{ ca. } 10^{-9} \text{ s}^{-1}$ at 593 K).

Nevertheless the activation energy for the latter process is *ca.* 21 kJ mol⁻¹ less than that for *cis-but-2-ene*,¹⁰ the difference having been attributed to 'some conjugative effect due to the highly electronegative oxygen atom so close to the double bond'. Detail was not given, but presumably either radical (IX) or polar (X) contributions to the transition state were referred to. On the other hand canonical extremes of type (XI) must be entertained, and the greater the contribution of (XI), the smaller must be that of (X). Species (XI) will be

The structural isomerism of the esters is much slower than that of the corresponding acids. Thus after 3 h at 673 K a sample of methyl but-3-enoate had 10% decomposed, but the remaining ester contained only *ca.* 1%

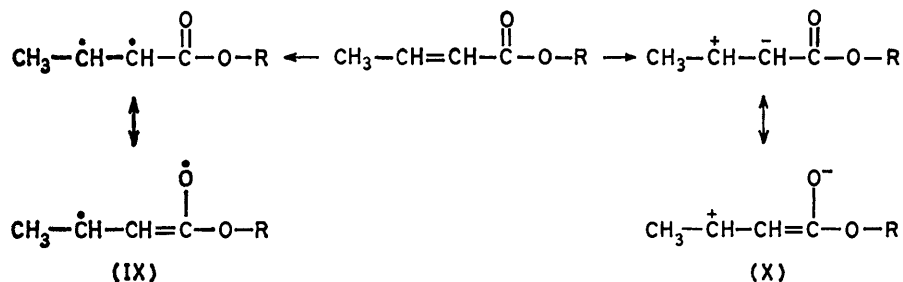


methyl crotonate and no detectable methyl isocrotonate. A structure (VII) can be drawn for the ester 1,5-shift analogous to that for the acid (IV), and the difference in

more important for esters (R = CH₃, electron donating) than for acids (R = H); it follows that (X) will contribute more in the transition state for acids than that for esters. Accordingly, *cis-trans* isomerism will be easier for acids than for esters. The hydrogen-bonded form of (X), *i.e.* (XII), may also be significant.

This discussion concerns the rate of attainment of equilibrium between *cis*- and *trans*-forms; the equilibrium ratio of isomers for the acids and esters is about the same.

Decarboxylation.—It is clear that the rate constants quoted earlier and those measured by Smith and Blau¹¹



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