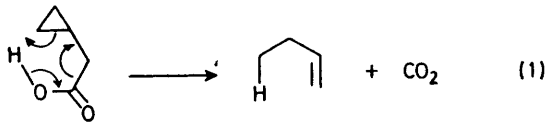
Studies in Decarboxylation. Part 13.[1] The Incursion of a Stepwise Mechanism in the Gas-phase Decarboxylation of Cyclopropylacetic Acids

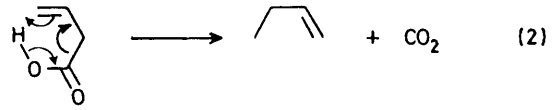
By **David B. Bigley,* Clive L. Fetter,** and (in part) **Michael J. Clarke,** University Chemical Laboratory, Canterbury, Kent CT2 7NH

The cyclopropylacetic acids (I)—(IV) have been decarboxylated in the temperature range 720—820 K. It is demonstrated that at 725 K, 2′,2′-dimethylcyclopropylacetic acid is decarboxylated by both concerted and stepwise mechanisms. The latter is favoured by higher temperature. Cyclopropylacetic acid is decarboxylated by the concerted mechanism at 725 K, but also exhibits the stepwise mechanism at higher temperature.

USING kinetic and isotopic techniques, we showed that eight cyclopropylacetic acids undergo gas-phase decarboxylation by the concerted mechanism (1); the



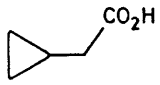
(1)



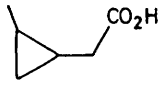
(2)

cyclopropane ring takes the place of the double bond in the well established mechanism for the decarboxylation of βγ-unsaturated acids (2).[2] For both classes of acid, dimethylation of the α-carbon atom accelerates the reaction, the effect being greater for the olefinic acid. A β-alkyl group greatly enhances the reactivity of the olefinic acids [3] while γ-alkyl groups decrease it.[4] Assuming these tendencies persist in the cyclopropylacetic acids, all the acids in Part 12 must be regarded as reactive.

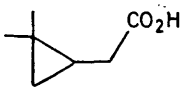
We report below on cyclopropylacetic acid itself (I) and on three of its γ-alkylated homologues (II)—(IV), acids which may be regarded as unreactive.



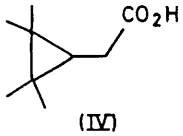
(I)



(II)



(III)



(IV)

EXPERIMENTAL

Acids (I)—(III) were prepared by a Simmons–Smith reaction on the ethyl ester of the corresponding unsaturated acids, as described in Part 12.[1] Cyclopropylacetic acid (I) had b.p. 78—78.5° at 1 mmHg; n_D^{21} 1.4350 (lit.,[5] 189—191° at 750 mmHg; n_D^{23} 1.4330).

trans-2′-*Methylcyclopropylacetic Acid* (II).—This was prepared from the ethyl ester of *trans*-pent-3-enoic acid.[6] It had b.p. 67—69° at 0.1 mmHg; n_D^{24} 1.4317 (Found: C, 63.3; H, 8.8. $C_6H_{10}O_2$ requires C, 63.1; H, 8.8%).

2′,2′-*Dimethylcyclopropylacetic Acid* (III).—This was prepared by the following sequence. The hydroxy-ester from a Reformatsky reaction between isobutyraldehyde and ethyl bromoacetate was dehydrated to the αβ-unsaturated ester with $POCl_3$ in pyridine. This was hydrolysed and isomerised (80% βγ, 20% αβ [6]) by 48 h reflux with 40% KOH in aqueous ethanol; the βγ-unsaturated acid was preferentially esterified by the method of Ecott and Linstead [7] and the resultant ester was then cyclopropanated and hydrolysed.[1] The acid had b.p. 75—77° at 0.15 mmHg; n_D^{23} 1.4279 (Found: C, 65.5; H, 9.4. $C_7H_{12}O_2$ requires C, 65.6; H, 9.4%).

2′,2′,3′,3′-*Tetramethylcyclopropylacetic Acid* (IV).—2′,2′,3′,3′-Tetramethylcyclopropanecarboxylic acid was prepared from 2,3-dimethylbut-2-ene and ethyl diazoacetate using anhydrous $CuSO_4$ as catalyst followed by hydrolysis of the resultant ester.[8] The acid had m.p. 118—119° and was subjected to the Arndt–Eistert procedure.[9] Hydrolysis of the resultant ester gave the desired acid (IV), contaminated with a little starting acid, m.p. 33—35°. Careful recrystallization (pentane) gave (IV) containing only 1% of the starting acid, m.p. 35—36°, but it did not prove possible to purify it further on the scale used (Found: M^+, 156.116 37. $C_9H_{16}O_2$ requires M^+, 156.115 02). All the acids (I)—(IV) had i.r. and n.m.r. spectra in accord with expectation.

Products and Stoicheiometry.—Products were isolated from evacuated break-seal tubes (15 min at 770 K) and the olefins separated by preparative g.l.c. Acids (I)—(III) gave 95—98% CO_2 under these conditions together with the following hydrocarbons: (I), but-1-ene, 86%, but-2-ene, 2%; (II), 3-methylbut-1-ene and pent-1-ene, 59%, 2-methylbut-2-ene, 31%; (III), 3,3-dimethylbut-1-ene, 2,3-dimethylbut-1-ene, 4-methylpent-1-ene, 77%, 2,3-dimethylbut-2-ene, 11%. In each case there was a small amount of more volatile hydrocarbon present, assumed to result from secondary decomposition; it is assumed that the minor olefins also arose from isomerisation since they were not apparent in the kinetic flow machine.

Acid (IV) required a higher temperature for decomposition. There appeared to be at least seven products of decomposition, the main ones being propene and 2-methylbut-2-ene.

Kinetics.—Kinetic runs were performed in our flow machine; the reactions were followed by disappearance of the acid and were shown to be first-order by the test described earlier.[10] Activation parameters are listed in

Table 1, $\Delta S^{\ddagger}$ being calculated at 760 K. The reactions also survived the normal tests for heterogeneity, *e.g.* acid (II) at 760 K, 10^3 k/s^{-1}: normal reactor 8.2; packed reactor, 10.2; 500 mole % of cyclohexene, 8.0. Table 2 shows the rate constants for the decomposition of acids (I)—(III), overall and dissected into the various reaction modes. The data for acid (IV) were not good enough for entry in Tables 1 and 2.

TABLE 1

Activation parameters for the gas-phase pyrolysis of some cyclopropylacetic acids (750—820 K)

Acid	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Gradient of confidence ellipse α/K *
(I)	$188._5 \pm 6$	-44 ± 7	807.8
(II)	192 ± 5	$-40._5 \pm 3$	698.7
(III)	195 ± 6	-38 ± 10	734.0

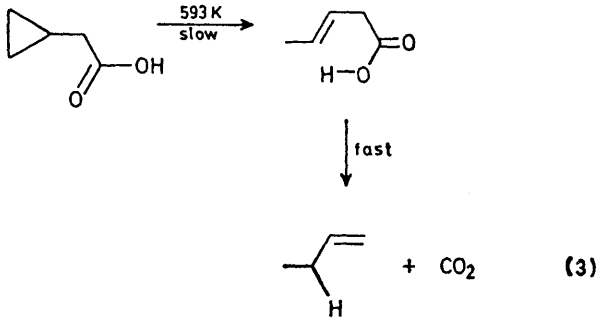
* J. C. Sheer, E. C. Kooyman, and F. L. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

Deuteriated acids were prepared by the reported method [11] and the product olefins isolated as described above.

Flash vacuum pyrolysis was carried out in a horizontal quartz tube, *ca.* 20 cm × 2.5 cm i.d., at 0.05 mmHg.

DISCUSSION

Cyclopropylacetic acid (I) is the most reactive of the four acids of this paper. It is nevertheless less reactive than any of its homologues of Part 12 [1] [acids (I)—(VIII) of the previous Part have relative rates 1.3—31.5 times faster]. The average entropy of activation of all the acyclic cyclopropylacetic acids of the previous Part was −42.6 J K^{-1} mol^{-1}, very close to that given for cyclopropylacetic acid in Table 1. The lower reactivity of the latter derives from its higher enthalpy of activation. In this temperature range, therefore, cyclopropylacetic acid appears to undergo decarboxylation by the concerted mechanism (1) and not by the stepwise mechanism (3) earlier preferred.[12] Confirmation of this

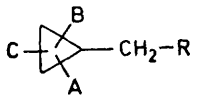
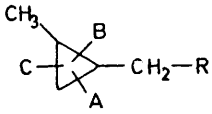
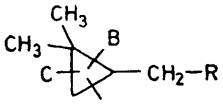


conclusion would come from the observation of a kinetic deuterium isotope effect for the reaction, as the rate-determining stage of the stepwise mechanism (3) should not be affected by the use of carboxy-deuteriated acid. At 760 K, carboxy-deuteriated (I) had $k = 4.3_5 \times 10^{-3}$ s^{-1} compared with 8.6×10^{-3} s^{-1} for the proton acid; therefore $k_H/k_D \simeq 2$ (maximum k_H/k_D at 760 K $\simeq 2.5$ [13,14]), which is incompatible with mechanism (3).

Table 2 shows a comparison of the rate constants measured for the decarboxylation of three cyclopropylacetic acids with those for the rearrangement of similarly methylated cyclopropanes. Substituting a β-carboxy-group into one of the methyl groups should slow the reaction a little (the powerful $-I$ CF_3 group decreases the rate ten-fold in the same position at 725 K [15]). The values calculated for the hydrocarbons therefore represent expected maxima for the acids reacting *via* the

TABLE 2

Comparison of rate constants (725 K) for decarboxylation of cyclopropylacetic acids with the rearrangement of similarly substituted alkylcyclopropanes

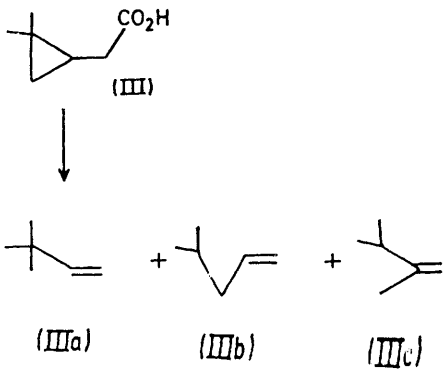
		10^5k/ s^{-1}	10^5k_A/ s^{-1}	10^5k_B/ s^{-1}	10^5k_C/ s^{-1}
	R = H [a]	11	5	5	0.5
	R = CO_2H	200	100	100	<4
	R = H [a]	9	0.6	8	0.6
	R = CO_2H	170	113	57	<4
	R = H [b]	11		7.5	3.0
	R = CO_2H	140	82	48	10

[a] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1968, **72**, 1866. [b] H. E. O'Neal and D. Henfling, *Internat. J. Chem. Kinetics*, 1972, **4**, 117.

stepwise mechanism. The comparisons for acids (I) and (II) show that the decarboxylation reaction is too fast to be accounted for by the stepwise mechanism involving the rearrangement of the cyclopropane as the first step.

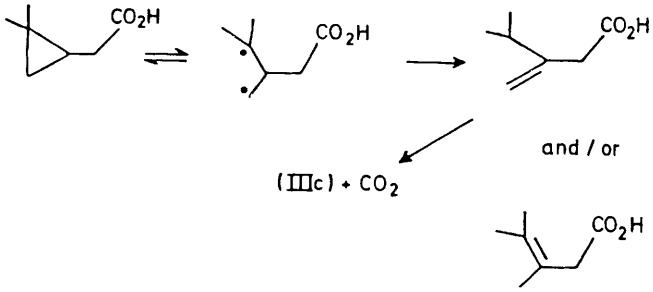
trans-2′-Methylcyclopropylacetic acid (II) reacts a little more slowly than the parent acid (I). This is consistent with the concerted mechanism; on the other hand, alkylation increases the rate of cyclopropane ring opening. The Arrhenius parameters confirm the cyclic mechanism.

For both (I) and (II), the near absence of product from scission at C (Table 2) is difficult to explain on the stepwise mechanism but is self-explanatory in terms of (1).



The overall rate for 2′,2′-dimethylcyclopropylacetic acid (III) is about ten times too fast for the mechanism to be stepwise as in (3). In this case there are three major olefinic products (IIIa—c). Compound (IIIa) can only result from the concerted mechanism (1). Attack of the carboxy-hydrogen atom on C(3′) will probably be easier than on the *gem*-dimethylated C(2′); 3,3-dimethylbut-1-ene is therefore the expected major product from the concerted mechanism. This product cannot arise by the stepwise mechanism (3).

On the other hand, 2,3-dimethylbut-1-ene (IIIc) cannot be derived from the concerted mechanism, but is easily explained by the fission at C (Table 2). It is satisfactory



in this connection that k_C is of the same magnitude for both olefin and acid, the only case in Table 2 where this is so.

4-Methylbut-1-ene (IIIb) could have come about from either mechanism. As noted above its production *via* the concerted mechanism should be less favourable than is the case for (IIIa); as with the parent hydrocarbon, the stepwise mechanism is more favourable for (IIIb) than (IIIc) as it involves a more stable diradical. Accordingly the observed intermediate value for k_B is equally consistent with either mechanism, and probably suggests that both are contributing.

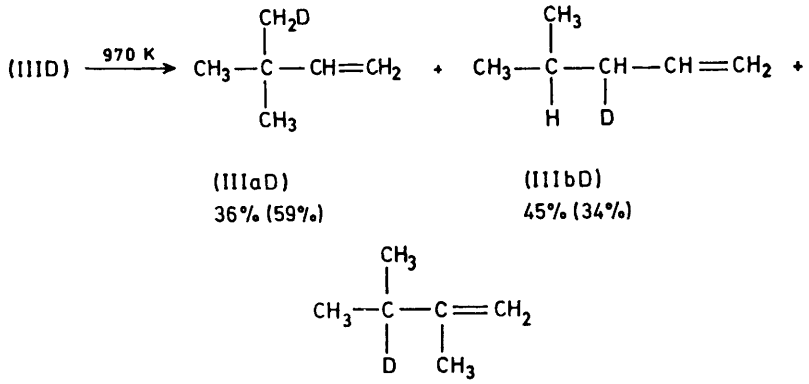
The $\Delta S^{\ddagger}$ value for acid (III) is 4.6 J K^{-1} mol^{-1} less than the average for the concerted mechanism.[1] This difference is probably within experimental error, but its sense is consistent with the incursion of the stepwise mechanism.

Carboxy-deuteriated (III) [(IIID)] was subjected to flash vacuum pyrolysis at 970 K. At this much higher temperature the stepwise mechanism (high E_a, positive $\Delta S^{\ddagger}$) should be favoured, while the concerted mechanism (low E_a, negative $\Delta S^{\ddagger}$) should be comparatively less important. The same three olefins constituted the main hydrocarbon fraction, and their respective proportions (g.l.c.) are shown in the Scheme. The position of the deuterium label was identified by noise-decoupled ^{13}C n.m.r. Each olefin appeared to be labelled only in the position shown, but up to 10% in other positions could have gone unremarked. The values in parentheses in the Scheme refer to the ratios of olefins obtained from protio (III) at 725 K.

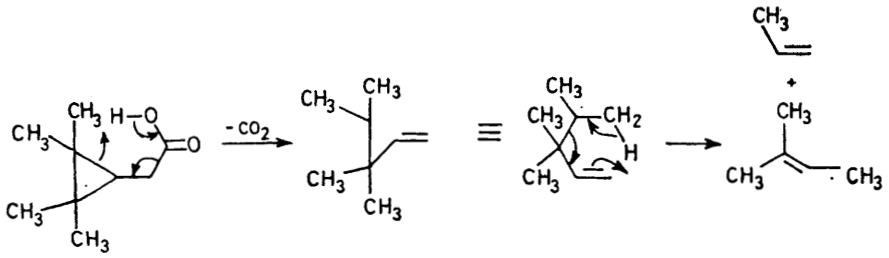
The position of the deuterium-label in (IIIaD) clearly derives from the concerted mechanism. The drop in its proportion is expected, but is probably magnified by the deuterium kinetic isotope effect. Compounds (IIIbD) and (IIIcD) both show the enhanced proportions and position of deuterium-label appropriate to the stepwise mechanism.

Acid (IV) was obtained in only small quantity at the end of a multi-stage synthesis. Its primary product olefins were not stable, propene and 2-methylbut-2-ene being the largest components of the product mixture. Assuming the concerted mechanism is predominant at 725 K, the expected 3,3,4-trimethylpentene may not be stable and deuterium-labelling experiments would not be possible. The disappearance of acid was first order and had $k \approx 9 \times 10^{-6}$ s^{-1} at 725 K, but there was insufficient material for a reliable estimation of Arrhenius parameters. Compound (IV) is therefore the least reactive of the acids (I)—(IV).

Conclusions of this Paper and the Previous Part.[1]—The gas-phase decarboxylation of cyclopropylacetic acids is a concerted process (1) similar to that of βγ-unsaturated acids (2). For both series α- and β-alkyl groups increase

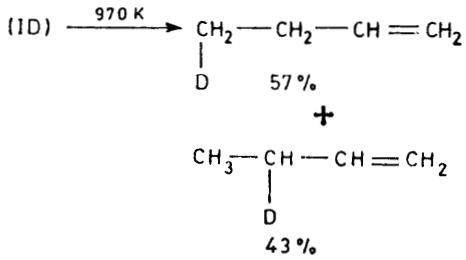


SCHEME



reactivity while γ-alkyl groups decrease it. With the least reactive cyclopropylacetic acids a stepwise mechanism (3) begins to contribute to the reaction, and this pathway may become dominant at high temperature.

Observations on Earlier Work.—Bigley and Thurman earlier incorrectly concluded that cyclopropylacetic acid decarboxylates *via* the stepwise mechanism (3) at 593 K.[12] They reported that the reaction carried out in evacuated break-seal tubes had k 1.1 × 10^{-6} s^{-1} at 593 K. The activation parameters of Table 1 (measured at 750—820 K) give k 1.6 × 10^{-6} s^{-1} at 593 K, in good agreement, and indicative of the concerted mechanism.



In order to test whether the stepwise mechanism is possible for (I) we carried out a flash vacuum pyrolysis of carboxy-deuteriated (ID) at 970 K [at this temperature (I) is calculated to have k 7 s^{-1} and methylcyclopropane 16 s^{-1}]. The collected [^{2}H]butene contained small quantities of other hydrocarbons and was examined by n.m.r. in CD_3OD [a control experiment showed that the impurities did not interfere with the protons on C(2)—C(4); CD_3OD obscures C(2)]. At 970 K the two mechanisms are about equally operative and at still higher temperature the stepwise mechanism might be expected to predominate.

There remains our earlier observation that pyrolysis of (ID) in a packed tube at 510 °C gave largely 3-deuteriobut-1-ene, which is clearly in error. The real temperature of the pyrolysis cannot have been much higher than reported as Pyrex softens above 550 °C. We conclude that the packed tube must therefore catalyse a surface reaction, either to open the ring of the cyclopropane or to effect simultaneous decarboxylation.

We thank the S.R.C. for a maintenance grant to one of us (C. L. F.).

[9/871 *Received*, 6*th June*, 1979]

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