1155. *Studies in Decarboxylation. Part II.*[1] *Kinetic Evidence for the Mechanism of Thermal Decarboxylation of βγ-Unsaturated Acids*

By D. B. Bigley and J. C. Thurman

The rates of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid have been measured in the gas and liquid phases at five temperatures between 239 and 290·5°. The reaction is of the first order, and there is no difference in rate between gas- and liquid-phase decarboxylation. An Arrhenius plot gave $\Delta H^{\ddagger} = 37{\cdot}7$ kcal./mole and $\Delta S^{\ddagger} = -11{\cdot}7$ e.u. at 551°K. These results are interpreted in terms of a multicentre reaction. Comments are made on the decarboxylation of but-3-enoic acid.

In Part I[1] we predicted that the cyclic transition state involved in the decarboxylation of βγ-unsaturated acids should result in a negative value for the entropy of activation, $\Delta S^{\ddagger}$. Shortly before the appearance of that Paper Smith and Blau reported that the gas-phase pyrolysis of but-3-enoic acid (I; $R^1 = R^2 = R^3 = R^4 = H$) occurs with $\Delta S^{\ddagger} = -10{\cdot}2$ e.u. at 650°K.[2] We now comment on these authors' results in the light of our own work on the same acid, and bring forward further evidence concerning the general mechanism.

Results and Discussion

The double bond in βγ-unsaturated acids is well known to be thermally mobile, and an equilibrium with the αβ-unsaturated isomer is rapidly set up.[3] The position of this equilibrium depends on the degree of substitution of the three-carbon system involved: it appears that only when the γ-carbon atom bears two alkyl groups, and the α-carbon none, does the equilibrium favour the βγ-form of the acid. Even in this case, there is a substantial quantity of αβ-isomer present at equilibrium.[4] Assuming such equilibrium we were able to account for the scrambling of isotopic label in the decarboxylation of 2-methylbut-3-enoic acid labelled with deuterium in the carboxyl group (I; $R^1 = R^2 = R^3 = H$; $R^4 = Me$).[1] However we noted further that preliminary results indicated that tiglic acid decarboxylates more slowly than its βγ-unsaturated isomer; Smith and Blau observed a similar relationship between crotonic acid and but-3-enoic acid.[2]

$$R^1R^2C{:}CH{\cdot}CR^3R^4{\cdot}CO_2H$$
(I)

The above considerations prompted us to re-examine the decarboxylation of but-3-enoic acid, since Smith and Blau followed their reaction by observing the increase of pressure in a closed system, and did not examine the disappearance of the starting acid. From the published data one cannot rule out the possibility that decarboxylation occurs from a mixture of but-3-enoic and crotonic acids.

In our first experiment but-3-enoic acid was sealed in an evacuated tube and heated at 250° for 3 hr. It was calculated that approximately 60% of the material remained in the liquid phase. Examination of the acid by v.p.c. analysis showed crotonic acid to be present; the ratio of crotonic to but-3-enoic acid was 56 : 44. We next examined the vapour-phase isomerisation at 289°. But-3-enoic acid was sealed in an evacuated tube; it was calculated that all the acid would vaporise to give an initial pressure of *ca.* 45 cm. After 45 min., it was found that 13% of the acid had decarboxylated and that the residual acid was a mixture of crotonic and but-3-enoic acids in the ratio of 16 : 84. Finally we diluted the but-3-enoic acid with a six-molar excess of cyclohexene to give an initial pressure of *ca.* 45 cm. After 55 min. at 289° there was now less than 2% of crotonic acid in the residual acid.

The most reasonable explanation of these results is that while the decarboxylation of

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[1] Part I, D. B. Bigley, *J.*, 1964, 3897.

[2] G. G. Smith and S. E. Blau, *J. Phys. Chem.*, 1964, **68**, 1231.

[3] R. P. Linstead, *J.*, 1930, 1603.

[4] R. P. Linstead and J. T. W. Mann, *J.*, 1930, 2064.

but-3-enoic acid is a first-order process,[2] its isomerisation has an order greater than unity. There therefore appears to be no reason to doubt that the data of Smith and Blau do really apply to the decarboxylation of but-3-enoic acid, since they similarly diluted their acid with a 6 molar quantity of cyclohexene.

Although reactions involving cyclic transition states normally have negative values for $\Delta S^{\ddagger}$, there are exceptional cases. Thus Clark has shown that the liquid-phase decarboxylation of benzylmalonic acid has $\Delta S^{\ddagger} = -2{\cdot}6$ e.u.,[5] whilst hexylmalonic acid, which must presumably involve a similar mechanism, has $\Delta S^{\ddagger} = +2{\cdot}8$ e.u.[6] A confirmatory test of multicentre reactions is that the reaction should proceed at equal rates in the gas and liquid phases.[7] In view of the above discussion, it is evident that but-3-enoic acid is not a suitable material for decarboxylation as a melt. From the point of view of isomerisation, a more suitable acid would appear to be pyroterebic acid (I: $R^1 = R^2 =$ Me; $R^3 = R^4 =$ H). However, this type of acid very readily forms a lactone,[8] which again should complicate the kinetics.

We have now extended our investigations of the kinetics of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid (I: $R^1 =$ Ph; $R^2 =$ H; $R^3 = R^4 =$ Me).[1] This acid is incapable of the $\alpha\beta$–$\beta\gamma$ equilibrium and therefore should be a suitable subject for both gas- and liquid-phase decarboxylation. In addition, although its lactone is stable at *ca.* 350°, we have been unable to detect the accumulation of significant quantities of the lactone during decarboxylation. The olefin arising from the decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid was expected to be 2-methyl-4-phenylbut-2-ene, but in practice the product from a sealed-tube experiment was found not to have a clean infrared spectrum. This was attributed to subsequent isomerisation and possibly polymerisation reactions. In order to identify the first produced olefin, it was necessary to remove it from the presence of unchanged acid; in the present case the olefin was not volatile enough to be swept out by a stream of nitrogen from the apparatus we had previously used.[1] We overcame the problem of isomerisation by dropping a very dilute solution of the acid in light petroleum down a column packed with glass helices at 420°. The vapours were swept out by a stream of nitrogen; it was expected that the diluent light petroleum and nitrogen would prevent undue contact between the olefin and the unchanged acid. The olefin produced in this way had an infrared spectrum in accord with expectation for 2-methyl-4-phenylbut-2-ene and $\varepsilon_{\text{max.}}$ at 248 mμ $\simeq$ 350 (cf. allylbenzene $\varepsilon_{248} = 230$; β-methylstyrene, $\varepsilon_{248} = 14{,}000$).

The kinetics of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid were followed by the sealed-tube technique previously described.[1] The rate of decarboxylation in the gas phase was measured at five temperatures between 239 and 290·5°; the results are given in the Table. A plot of log $(p_\infty - p_t)$ against time gave a good straight line in all cases.

Kinetic data for the decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid

Temp. (°K)	State	10^6k (sec.$^{-1}$)	$\log_e k$ (mean)	$10^3/T$
563·5	Vapour	83·3	−9·42	1·775
563·5	Vapour	79·8		
551·0	Vapour	38·9	−10·17	1·815
551·0	Vapour	37·8		
551·0	30% Liquid *	36·5		
538·0	Vapour	15·4	−11·09	1·859
538·0	Vapour	15·3		
538·0	65% Liquid *	15·3		
528·0	Vapour	8·25	−11·71	1·894
528·0	Vapour †	8·33		
512·1	Vapour	2·97	−12·73	1·953
512·1	Vapour †	3·13		

* In admixture with tetralin. † Tubes packed with glass helices.

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[5] L. W. Clark, *J. Phys. Chem.*, 1963, **67**, 1481.

[6] L. W. Clark, *J. Phys. Chem.*, 1963, **67**, 2602.

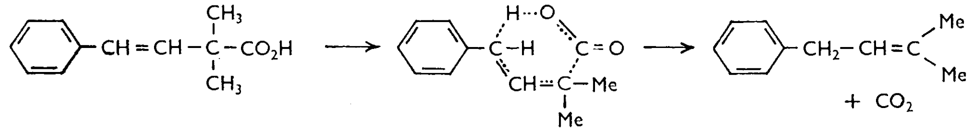
[7] J. Hine, " Physical Organic Chemistry," McGraw-Hill, New York, 1962, ch. 25.

[8] R. P. Linstead, *J.*, 1932, 115.

An Arrhenius plot using these rate constants also gave a good straight line. Values obtained were $\Delta H^{\ddagger} = 37{\cdot}7$ kcal./mole and $\Delta S^{\ddagger} = -11{\cdot}7$ e.u. at 278°. The homogeneity of the reaction was demonstrated by packing the total tube space with glass helices. It is seen from the Table that there is very little effect upon the rate constant.

To measure the rate of the liquid-phase decarboxylation it would have been ideal to confine the molten acid in a tube sufficiently small to leave no gas space. Since carbon dioxide is given off during reaction, such a procedure certainly would have resulted in breakage of tubes. We therefore had to use tubes large enough to accommodate the carbon dioxide produced during reaction, but where we could calculate that the bulk of the acid would remain in the liquid phase. Tetralin was added as a diluent to suppress vaporisation of the acid. In two such experiments at 265 and 278°, respectively, we obtained rate constants in good agreement with the gas-phase decarboxylation at the same temperature. We performed a second type of experiment in which increasing amounts of the acid, with no diluent, were enclosed in tubes of constant size. Of eight tubes, the smallest quantity of acid corresponded to a gas-phase decarboxylation at *ca.* 12 cm.; with the largest quantity of acid, it was calculated that 60% of the acid remained in the liquid-phase. These tubes were heated for $5\frac{1}{2}$ hr. at 269°. A plot of the amount of carbon dioxide produced from each tube against the original amount of acid in that tube was a straight line. If the rates of decarboxylation in the liquid and gas phases had not been identical one would have expected a curve to result.

The results discussed above, together with the deuterium-labelling reported earlier,[1] enable the decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid to be described as



EXPERIMENTAL

But-3-enoic acid was prepared by the method of Reitz.[9] The isomerisations were carried out in evacuated sealed tubes of known volume. Products were analysed by vapour-phase chromatography (v.p.c.) (di-2-ethyl hexyl sebacate and sebacic acid column, 3 ft., 153°).

2,2-*Dimethyl*-4-*phenybut*-3-*enoic Acid*.—A mixture of phenylacetaldehyde (80 g.) and ethyl α-bromoisobutyrate (130 g.) in 50/50 dry ether–benzene (100 ml.) was added slowly to a stirred suspension of zinc dust (45 g.) in the same solvent (100 ml.). After addition of one quarter of the mixture the reaction had not started, and did not start during 1 hour's refluxing (cf. ref. 10). The reaction was easily started, however, by the addition of a very small quantity of methylmagnesium iodide. After completion of addition, the mixture was refluxed for a further 2 hr. The mixture was cooled, acidified with dilute hydrochloric acid, and the product was isolated with ether. Removal of the ether gave crude 2,2-dimethyl-3-hydroxy-4-phenylbutanoic acid as an oil, b. p. 90—120°/0·5 mm. (48·7 g.). This oil was dissolved in benzene (150 ml.) and was refluxed for 2 hr. over phosphoric oxide (140 g.). Water (1 l.) was added, and the unsaturated acid was isolated by ether extraction. The infrared spectrum of this product had bands corresponding to γ-lactone and ester. The oil was then refluxed with excess of 3N-sodium hydroxide for $1\frac{1}{2}$ hr., by which time the γ-lactone band had disappeared from the infrared spectrum of the oil. The aqueous layer was replaced by fresh 3N-sodium hydroxide, and refluxing was continued for a further 20 hr. After acidification of the homogeneous aqueous solution 2,2-dimethyl-4-phenylbut-3-enoic acid was isolated by ether extraction. Removal of the ether gave the acid, which spontaneously crystallised. It was recrystallised twice from aqueous ethanol and dried *in vacuo* to give needles, m. p. 111·5—112·5° (lit.,[11] m. p. 112—113°, prepared by the Perkin method), b. p. 295°.

[9] E. Reitz, *Org. Synth.*, Coll. Vol. III, 851.
[10] R. T. Arnold, O. C. Elmer and R. M. Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4359.
[11] E. N. Marvell and A. O. Geiszler, *J. Amer. Chem. Soc.*, 1952, **74**, 1259.

Identification of 2-*Methyl*-4-*phenylbut*-2-*ene*.—A solution of 2,2-dimethyl-4-phenylbut-3-enoic acid (70 mg.) in light petroeum (b. p. 40—60°, 50 ml.) was dropped during 30 min. through a 25 × 1 cm. glass tube packed with glass helices at 420°. A slow stream of nitrogen was passed throughout. The condensate from the bottom of the tube was washed with dilute sodium hydrogen carbonate, and was dried over calcium chloride. Removal of the light petroleum gave a colourless oil, b. p. 110° (bath)/40 mm. (30 mg.). The infrared spectrum of this oil had bands at 695s, 735s, 790m, 805m, 850m, 1604m, 1667w, and 3080s cm.$^{-1}$. There was no absorption in the region 900—1000 cm.$^{-1}$. The ultraviolet spectrum (ethyl alcohol) had two bands; $\varepsilon_{\text{max.}}$ at 218 mμ = 7000; $\varepsilon_{\text{max.}}$ at 248 mμ = $\simeq$ 350.

Kinetics.—The rates of decarboxylation of 2,2-dimethyl-4-phenylbut-3-enoic acid were measured using evacuated break-seal tubes as described previously.[1] Runs were performed in a molten-salt bath regulated to ±0·2°. Kinetic data treated by the least-squares method gave the expression:

$$\log_e k = (-18{,}958/T) + 24{\cdot}23$$

Activation parameters were calculated from the absolute rate expression [12]

$$k = (\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S^{\ddagger}/\boldsymbol{R})\exp(-\Delta H^{\ddagger}/\boldsymbol{R}T)$$

In comparisons of decarboxylation rates in the liquid and vapour phases, known weights of acid and tetralin were sealed in evacuated tubes of known volume. The vapour pressure of the acid at the temperature of each run was estimated from the boiling point of the acid together with published vapour-pressure curves for closely related compounds: [13] the proportion of acid in the liquid phase was estimated by assuming ideal gas behaviour for the vapours.

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LOUGHBOROUGH COLLEGE OF TECHNOLOGY,
LOUGHBOROUGH, LEICESTERSHIRE.

[*Received, April* 1*st*, 1965.]

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[12] K. J. Laidler, " Chemical Kinetics," McGraw-Hill, New York, 1950, p. 75.

[13] T. E. Jordan, " Vapour Pressure of Organic Compounds," Interscience, New York, 1954.