

**354.** *Stereospecificity in Thermal Elimination Reactions.  
Part III.\* The Pyrolysis of (–)-Menthyl Benzoate.*

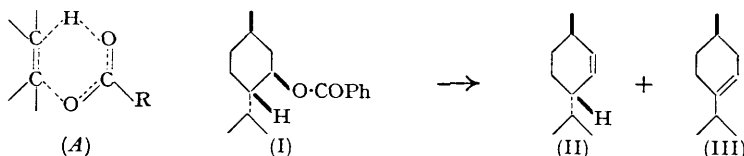
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The pyrolysis of (–)-menthyl benzoate to give a mixture of (+)-*p*-menth-2- and -3-ene and benzoic acid has been investigated by both static and dynamic methods. The reaction is homogeneous and unimolecular in mechanism. The rate-constant equation can be represented by the expression  $k = 10^{14}e^{-38,100/RT}$  sec.<sup>-1</sup>. The ratio of  $\Delta^2$ - to  $\Delta^3$ -olefin produced in the decomposition is approximately 1 : 2. The formation of the latter hydrocarbon by the unimolecular mechanism confirms the correlation previously proposed (Barton, *J.*, 1949, 2174) between the mechanism of ester pyrolysis and its stereospecificity.

THE thermal decomposition of esters to give olefins and carboxylic acids is a smooth reaction which is frequently of preparative value. It has been suggested (Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419) that such reactions are unimolecular, proceeding through a transition state of type (*A*). Granted this, then *cis*-stereospecificity for the reaction follows (Barton, *J.*, 1949, 2174; Barton and Rosenfelder, *J.*, 1949, 2459;

\* Part II, *J.*, 1952, 453.

Alexander and Mudrak, *J. Amer. Chem. Soc.*, 1950, **72**, 1810, 3194; 1951, **73**, 59; Arnold, Smith, and Dodson, *J. Org. Chem.*, 1950, **15**, 1256). It must be emphasized, however, that this conclusion is only justified theoretically if the mechanism can be *proved* to be both homogeneous and unimolecular.



The present investigation is concerned with the pyrolysis of a typical ester, (–)-menthyl benzoate (I), to give a mixture of (+)-*p*-menth-2-ene (II) and –3-ene (III) and benzoic acid. The formation of the latter hydrocarbon, together with the appropriate mechanistic study, provides the first demonstration of *cis*-elimination in a carboxylic ester pyrolysis of authenticated homogeneous and unimolecular character. A corresponding investigation on

FIG. 1.

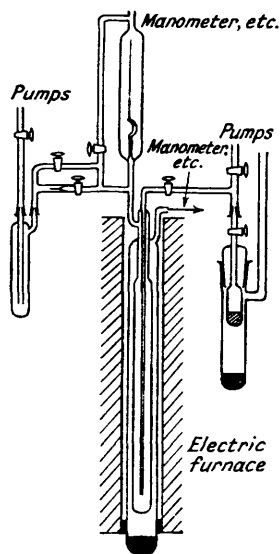
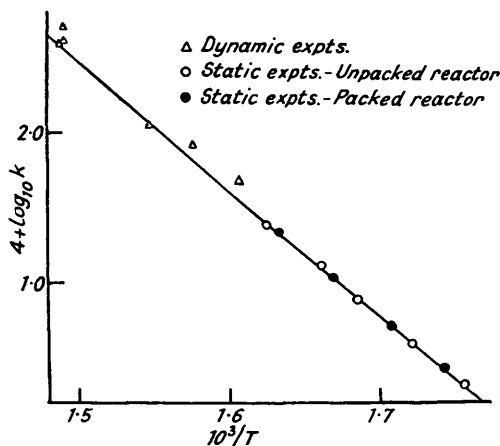


FIG. 2.



xanthate decomposition has been reported recently by O'Connor and Nace (*J. Amer. Chem. Soc.*, 1952, **74**, 5454).

In previous studies of the thermal decomposition of the related (–)-menthyl acetate (McNiven and Read, *J.*, 1952, 2067; Wibaut, Beyerman, and van Leeuwen, *Rec. Trav. chim.*, 1952, **71**, 1027, and references there cited) *cis*-elimination was adequately established by product analysis, but no kinetic or other criterion of reaction mechanism was applied.

#### EXPERIMENTAL

**Materials.**—(–)-Menthyl benzoate was prepared by benzylation of (–)-menthol in pyridine at room temperature. Recrystallisation from methanol gave the pure benzoate, m. p. 56°,  $[\alpha]_D -86.9^\circ$  (*c*, 8.8 in  $\text{CHCl}_3$ ).

**Apparatus.**—(i) *Static experiments.* The apparatus and technique were as described in Part II (*loc. cit.*). In order to overcome difficulties caused by the low vapour pressure of (–)-menthyl benzoate, the ordinary storage trap was replaced by a large cylindrical bulb fitted with a thermometer pocket and heated by external electrical windings. The benzoate was outgassed *in vacuo* at 140°. A reservoir temperature of 200° was sufficient to introduce 20 mm. of (–)-menthyl benzoate vapour.

(ii) *Dynamic experiments.* The apparatus used was essentially as described in Part II (*loc. cit.*) except that the reactor was modified to the improved type illustrated in Fig. I. This

had the advantage of enlarging greatly the volume of the reactor at constant temperature. The technique for carrying out the experiments was as before except that (i) no capillary leak was needed for controlling the input of (–)-menthyl benzoate vapour, (ii) *p*-dichlorobenzene was used as reflux liquid for heating the storage trap, and (iii) the total products of reaction were collected in one trap only (at –80°).

The products were analysed as follows. The products were washed out of the trap quantitatively with chloroform and the solution made up to 25 ml. A 10-ml. portion of this solution was cautiously evaporated, carbon dioxide-free distilled water added, and the dissolved benzoic acid titrated in the usual way. A number of control experiments showed that no benzoic acid was lost in this procedure and that the accuracy of the determinations was  $\pm 2\%$ . The residual chloroform solution was then analysed for (+)-*p*-menth-2- and -3-ene as in Part II (*loc. cit.*).

The following experiments were carried out to test the adequacy of the analytical technique. (i) The benzoate (300 mg.) was heated in a sealed and evacuated tube at 200° for 1 hour. No detectable amount of benzoic acid was produced. (ii) The menthene mixture (160 mg.), obtained as a by-product (see Part II, *loc. cit.*) in the preparation of (–)-menthyl chloride, in chloroform (2 ml.), was treated with an equal weight of benzoic acid overnight at room temperature. No reduction in specific rotation was observed. (iii) (–)-Menthyl benzoate (59.1 mg.) in chloroform (10 ml.) was treated with hydrogen chloride as for the analysis of the menthene mixture (see Part II, *loc. cit.*). There was no detectable change in rotation.

## RESULTS

*Static Experiments.*—The kinetics of the decomposition were studied in both empty and packed reactors, the latter having an approximately six-fold increase in surface area : volume ratio. Contrary to experience in the pyrolysis of (–)-menthyl chloride (Part II, *loc. cit.*) reproducible results were soon attained (after about 10 runs) and it is clear that the ester decompositions are far less prone to exhibit heterogeneity than are those of chlorinated hydrocarbons. The reaction showed first-order kinetics to better than 50% decomposition, with no indication of induction periods. Within the limited pressure range accessible, the first-order rate constant was independent of initial pressure (see Table 1; these results refer to the packed

TABLE 1.

At 587.1° K		At 598.6° K		At 587.1° K		At 598.6° K	
<i>p</i> <sub>0</sub> , mm.	10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>	<i>p</i> <sub>0</sub> , mm.	10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>	<i>p</i> <sub>0</sub> , mm.	10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>	<i>p</i> <sub>0</sub> , mm.	10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>
2.7	0.63	3.0	1.17	21.2	0.54	21.4	1.09
10.9	0.58	11.0	1.10			27.1	1.10
15.1	0.54	14.8	1.06				

reactor). The rate-constant results over the temperature range 568.9° to 614.6° K are summarised in Table 2. The best straight line drawn through the points on the corresponding Arrhenius

TABLE 2.

Temp., K	No. of runs	Mean 10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>	Mean error (%) of the mean <i>k</i> *	Temp., K	No. of runs	Mean 10 <sup>3</sup> <i>k</i> , sec. <sup>-1</sup>	Mean error (%) of the mean <i>k</i> *
<i>Unpacked reactor.</i>				<i>Packed reactor.</i>			
568.9°	6	0.209	1.3	573.5°	5	0.274	0.6
580.6	6	0.392	1.3	585.1	9	0.524	1.3
593.1	9	0.774	0.8	598.6	7	1.10	0.9
601.5	6	1.30	0.7	611.6	7	2.22	0.4
614.6	6	2.49	1.2				

\* Given by  $100 \times \sqrt{\frac{\sum(x - \bar{x})^2}{n(n-1)}} / \bar{x}$ , where the symbols have the usual significance.

plot (Fig. 2) by visual inspection indicated an approximate rate constant equation of  $k = 10^{11}e^{-38,100/RT}$  sec.<sup>-1</sup>. Because of the experimental difficulties associated with pyrolytic work on compounds of very low vapour pressure, we do not attach error limits to this equation. The homogeneity of the reaction is clearly demonstrated. The addition of propylene or of nitric oxide, even in major amounts, had no significant effect (see Table 3; the figures refer to the packed reactor) on the rate of decomposition; in every run the kinetics remained of the first order.

*Dynamic Experiments.*—(i) *Stoichiometry.* A necessary condition for establishing the simple stoichiometry mentioned above is that the products of decomposition (the menthenes and the benzoic acid) should be stable under the reaction conditions chosen. The stability

1718 *Stereospecificity in Thermal Elimination Reactions. Part III.*

of the mixed menthenes follows from the work recorded in Part II (*loc. cit.*). The stability of benzoic acid was shown (a) by introducing 20 mm. of the acid into the reactor for static experiments at 615° K and noting that there was no change in pressure during a period corresponding to several half-lives of the ester, and (b) by passing benzoic acid vapour (at 13.9 mm.; contact time 116 sec.) through the reactor for dynamic experiments at 671° K and noting 99% recovery of acid by weight (confirmed by direct titration). The stability of benzoic acid under the conditions chosen also follows from Moser's work (*Helv. Chim. Acta*, 1931, 14, 971).

TABLE 3.

$p_0$ , mm., of ester	$p$ , mm., of addend	$100p/p_0$	$10^3k$ , sec. <sup>-1</sup>	$p_0$ , mm. of ester	$p$ , mm., of addend	$100p/p_0$	$10^3k$ , sec. <sup>-1</sup>
Propylene at 586.1° K.				Nitric oxide at 594.7° K.			
—	—	—	0.54 *	—	—	—	0.85 *
20.6	0.22	1.1	0.54	20.2	0.92	4.6	0.83
20.8	1.68	8.1	0.54	20.5	7.72	38	0.84
19.7	2.4	12	0.50	20.5	19.6	95	0.82
22.0	8.7	40	0.51	21.0	20.4	96	0.82
22.1	18.2	82	0.53				
21.3	29.6	139	0.51				

\* Mean of control determinations carried out just before the inhibitor experiments.

TABLE 4.\*

Temp., K	$p$ , mm.	Contact, time, sec.	Decomp., %	$10^3k$ , sec. <sup>-1</sup> Found	$10^3k$ , sec. <sup>-1</sup> Calc.	Loss, %	(+)- <i>p</i> -Menth-2-ene, %	[ $\alpha$ ] <sub>D</sub> of (+)- <i>p</i> -menth-3-ene, calc
672°	12.3	74	94.2	3.9	3.6	-1.0	—	—
671	15.0	70	94.4	4.1	3.5	0.0	—	—
671	15.0	70	79.3	2.3		+1.0	—	—
671	15.2	63	96.0	5.1		0.0	—	—
646	4.3	178	86.5	1.13	1.15	+1.2	—	—
634	4.6	169	75.6	0.84	0.66	-1.3	—	—
622	4.7	178	57.5	0.48	0.37	-0.9	—	—
647	—	—	96.2	—	—	—	35	+117°
647	—	—	96.2	—	—	—	33	+117
644	—	—	90.9	—	—	—	32	+117
628	—	—	82.5	—	—	—	36	+117

\* The last four runs (for menthene ratio) involved the passage of approx. 650 mg. of ester.

Convincing evidence for simple stoichiometry was obtained in dynamic experiments in the following way. The reaction products were dissolved in ethanol and made up to 25 ml. A 10-ml. portion of the solution was largely diluted with boiled-out distilled water and titrated for benzoic acid in the usual way. To a further 10-ml. portion there was added a known volume of *N*/20-aqueous potassium hydroxide approx. equivalent to 2.5 times the amount of benzoate pyrolysed, and the solution was refluxed overnight (soda-lime guard tube). The solution was then largely diluted with boiled-out distilled water and the excess of potassium hydroxide titrated in the usual way. The appropriate blank experiments were run at the same time. In this way the amounts of benzoic acid and of unchanged (-)-menthyl benzoate were determined. In two experiments at 631° and 643° K (11.4 and 17.6 mm. pressure respectively), involving the passage of 319 and 488 mg. of ester, balances of 100 and 102% respectively were obtained.

(ii) *Kinetics.* After the first few dynamic runs, the rate of decomposition became reproducible. The rate constants were calculated, first-order kinetics being assumed, by the equation already given (*J.*, 1949, 148). The results are summarised in Table 4 (see also Fig. 2). It will be seen that the rates observed were somewhat higher than those deduced from the rate-constant equation for static runs (see above). The latter are, of course, more reliable.

(iii) *Menthene ratio.* The percentage of (+)-*p*-menth-2- and hence of -3-ene is indicated in Table 4 for suitable runs. The calculated specific rotation for (+)-*p*-menth-3-ene is somewhat higher than that ( $[\alpha]_D + 109^\circ$ ) accepted in Part II (*loc. cit.*).

## DISCUSSION

The thermal decomposition of (-)-menthyl benzoate follows first-order kinetics, the rate constants being invariant with pressure. The reaction is homogeneous, exhibits no induction periods even at the lowest temperatures at which rates were measured, and is totally unaffected by addition of propylene or nitric oxide even in major amounts. These facts are adequate to exclude radical or radical-chain mechanisms and to establish beyond doubt that the decomposition is a true homogeneous unimolecular reaction.

The analysis of the menthene ratio (see Results section) shows that approximately twice as much  $\Delta^3$ - as  $\Delta^2$ -menthene is formed. The ratio is rather less than that found for pyrolysis of (–)-menthyl chloride (Part II, *loc. cit.*). The formation of the (+)-*p*-menth-3-ene provides a further unambiguous demonstration of the correctness of our general thesis as to the relationship between *cis*-elimination and unimolecularity of mechanism in thermal elimination reactions—in this case for a typical ester decomposition. In particular the results justify our previous assumptions (Barton, *loc. cit.*; Barton and Rosenfelder, *loc. cit.*) with regard to benzoate pyrolyses.

We thank the Government Grants Committee of the Royal Society, the Central Research Fund of London University, and Imperial Chemical Industries Limited for financial assistance. This work was carried out during the tenure of a D.S.I.R. Maintenance Grant (A. J. H.) and a Courtaulds' Postgraduate Scholarship (R. J. W.).

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[Received, February 11th, 1953.]

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