88. *Stereospecificity in Thermal Elimination Reactions. Part II.* The Pyrolysis of (—)-Menthyl Chloride.*

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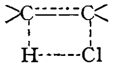
The pyrolysis of (—)-menthyl chloride to furnish a mixture of (+)-*p*-menth-2- and -3-enes and hydrogen chloride has been studied by both static and dynamic methods. In reactors coated with a carbonaceous film the reaction has been proved to be homogeneous and unimolecular in mechanism. The rate-constant equation can be represented by the expression $k = 10^{12\cdot6}e^{-45,000/RT}$ sec.$^{-1}$. The ratio of Δ^2- to Δ^3-olefin formed is approximately 1 : 3. The production of the latter hydrocarbon confirms the correlation previously propounded between stereospecificity of thermal elimination and reaction mechanism. In clean-walled reactors the much faster heterogeneous decomposition of (—)-menthyl chloride has been shown to follow a different reaction path.

In Part I * of this series it was concluded that thermal elimination reactions which were unimolecular † in mechanism should show, where the molecular structure was otherwise appropriate, a *cis*-stereospecificity of elimination. From the stereochemical point of view there was already at that time an adequate number of examples of *cis*-elimination in the pyrolysis of methyl xanthates and of benzoates (cf. Barton and Rosenfelder, *J.*, 1949, 2459; 1951, 1048) to substantiate our conclusion. However, up to the present, in no case has the *mechanism* of elimination been established for a thermal reaction of known stereospecificity. The examples already cited could, in principle, be heterogeneous reactions, in which case *no* theoretical conclusion as to the stereospecificity of elimination would have been justified.

Now, in a series of papers (Barton, Head, Howlett, Onyon, and Williams, *J.*, 1949, 148, 155, 165; *Trans. Faraday Soc.*, 1949, **45**, 725, 735; 1950, **46**, 114; *J. Amer. Chem. Soc.*, 1950, **72**, 988; *J.*, 1951, 2033, 2039) on the pyrolysis of saturated chlorinated hydrocarbons it has been shown that hydrogen chloride is smoothly eliminated with the formation of olefin or chlorinated olefin. There are three general mechanisms for these reactions : (i) heterogeneous decomposition (on glass), (ii) homogeneous unimolecular decomposition, (iii) homogeneous radical-chain decomposition. Normally, mechanism (i) is much faster than (ii) or (iii), but by using reactors coated with a carbonaceous film, it can be reduced to insignificance. The course of homogeneous reaction then followed depends only on the molecular structure of the substrate. If either the latter, or the products of reaction, are inhibitors for mechanism (iii), then the chlorinated hydrocarbon decomposes by the alternative unimolecular mechanism (ii). From these generalisations it can, for example, be concluded that (—)-menthyl chloride should be pyrolysed by the unimolecular mechanism, since the menthenes produced would be inhibitors for the radical-chain type of decomposition. In the unimolecular mechanism the four-centre transition state must be as represented in (*A*). As we have emphasised previously (Barton, *loc. cit.*), quantum-mechanical theory suggests that, for a minimisation of activation energy, the four centres should lie in one plane. In suitable *cyclo*hexane derivatives this implies that *cis*- should take preference over *trans*-elimination.



(*A*)

In this connection we were particularly interested in the pyrolysis of (—)-menthyl chloride (I) because the elegant work of Hückel, Tappe, and Legutke (*Annalen*, 1940, **543**, 191) has shown that the mixtures of (+)-*p*-menth-2- and -3-enes, (II) and (III), respectively, which would be formed in this reaction, are readily analysed by taking

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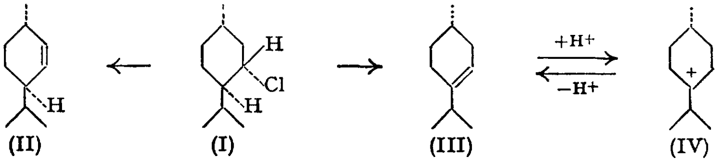
* The paper by Barton (*J.*, 1949, 2174) is regarded as Part I of this series.

† The term unimolecular is again used in the sense employed by physical chemists in dealing with gas-phase reactions, not in the sense commonly used for discussing heterolytic reactions.

advantage of the facile acid-catalysed racemisation of the Δ^3-isomer through the symmetrical carbonium ion (IV).



It is true that the formation of *two* olefins from the pyrolysis implies that two different transition states must be involved. However, both reactions would be expected to have the same, unimolecular, mechanism and to exhibit first-order kinetics. The difference in the rate-constant equation for the two reactions would be too small to be detected experimentally as a curved Arrhenius plot (cf. Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988). It should be mentioned that, since *cis*-elimination towards, usually takes preference over *cis*-elimination away from, a bridge-head (cf. Barton, *loc. cit.*) the (+)-*p*-menth-3-ene should be the preponderant reaction product.

The aim of the present work, then, was (*a*) to confirm that the mechanism of pyrolysis of (−)-menthyl chloride (in coated reactors) was unimolecular, and (*b*) to show that this led to the formation of a mixture of (+)-*p*-menth-2- and -3-enes in which the latter predominated. Although both hydrocarbons would be formed through a transition state of type (*A*), only the formation of the Δ^3-isomer would constitute an unambiguous demonstration of *cis*-elimination of hydrogen chloride. If *trans*-elimination were the preferred mode of reaction, as in (say) alkoxide-induced elimination (Hückel *et al.*, *loc. cit.*), then (+)-*p*-menth-2-ene alone would be formed.

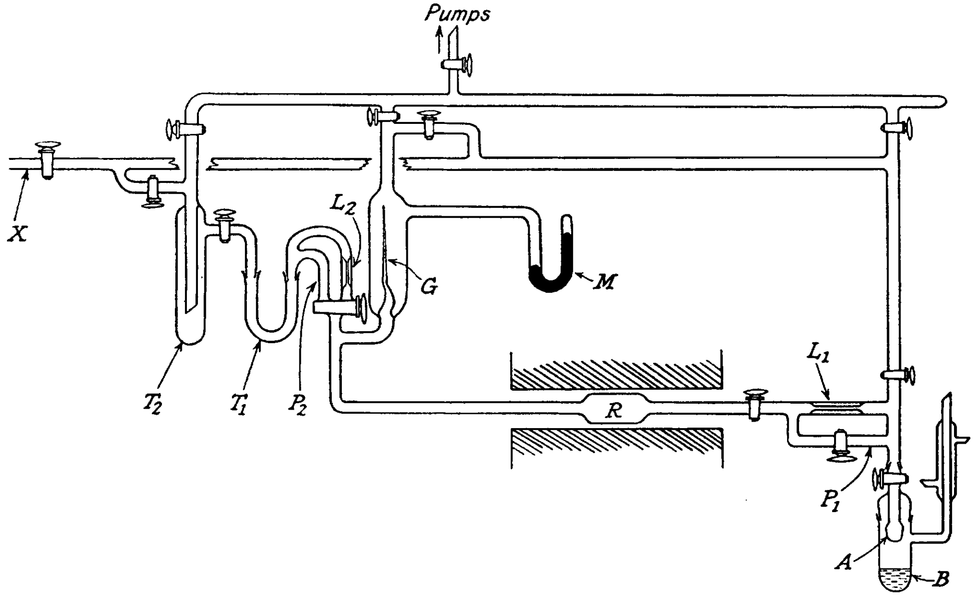
EXPERIMENTAL

Materials.—(−)-Menthyl chloride was prepared according to the directions of Hückel and Pietrzok (*Annalen*, 1939, **540**, 250). It had b. p. 88·5°/12·5 mm., n_D^{22} 1·4634, d_4^{26} 0·9349, $[\alpha]_D$ −50·2° (homogeneous). This material was used for the static experiments. For the dynamic work a slightly less pure fraction, $[\alpha]_D$ −48·4° (homogeneous), was employed in the majority of the experiments.

Apparatus.—(i) *Static experiments.* The apparatus and general technique have already been described in detail by Barton and Howlett (*J.*, 1949, 155). Because of the lower vapour pressure of (−)-menthyl chloride it was found advantageous to modify the ordinary storage trap by incorporating a 250-ml. bulb, the whole being immersed in a heated oil-bath. This provided a larger reservoir of heated vapour and, with the oil-bath at 110°, it was easily possible to introduce 20 mm. of the (−)-menthyl chloride vapour. All connecting tubes from the trap to the reactor and the necessary taps were, of course, electrically heated as before. Some modification of the method of measuring pressure was also introduced. The spoon gauge, still used as a null-point instrument, was made more sensitive, and the differential pressures were measured by using a small closed-limb manometer in conjunction with a cathetometer. In all experiments mercury was employed as thermostatic vapour. The kinetics of the reaction were elucidated by following the increase in pressure at constant volume as in our previous work on chlorinated hydrocarbon pyrolysis.

(ii) *Dynamic experiments.* The apparatus employed is illustrated in Fig. 1. It was constructed throughout in Pyrex glass. The (−)-menthyl chloride was stored in a detachable trap, *A*, which was heated by the reflux apparatus, *B*. In all experiments steam was used as thermostatic vapour; the temperature of the (−)-menthyl chloride remained constant to 0·1° in any run. The (−)-menthyl chloride vapour was passed through the previously calibrated capillary leak L_1 (to which a by-pass P_1 was also attached) and then into the reaction vessel R, which was heated as indicated in an electric furnace. The reactor itself was constructed of two long 2-mm. bore lengths of tubing attached to a short length of 30-mm. bore tubing which constituted the main reactor volume. The length and position of the latter were so adjusted that the main reactor volume was at constant temperature (within 1°) and placed at the position of maximum temperature in the furnace. On either side of the main reactor volume the temperature fell off quite rapidly. The main reactor volume comprised 21·6 ml. In order to allow for any reaction occurring in the narrow-bore connecting tubing the lengths of connecting tubing (and hence the volumes) were observed at which, by calculation, it was known that the reaction would proceed at an average of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, etc., of the velocity in the main reactor volume. By weighting these volumes accordingly, it was computed that the effective volume of the whole reactor was 22·7 ml. Although this method of computation is only approximate, the errors involved in the estimate of the extra 1·1 ml. are so small relative to the main reactor volume (21·6 ml), that the effect of the approximations is negligible. The temperature of the furnace was manually controlled and measured by a base-metal thermocouple. The gases issuing from the furnace were passed through a second, previously calibrated capillary leak L_2, then through a trap T_1 cooled in solid carbon dioxide–alcohol mixture, which served to condense the menthenes and any unchanged (—)-menthyl chloride, and finally through a liquid-nitrogen-cooled trap T_2 in which the hydrogen chloride was condensed. Oxygen-free nitrogen was admitted through X when required. During a run the apparatus was pumped continuously by a two-stage mercury pump backed by an oil pump, the pumps being attached as indicated. In order to facilitate evacuation of the reactor itself, a by-pass P_2 was used. The pressure in the reactor during a run was measured by a spoon gauge G which was employed as a null-point instrument. The actual pressure readings were obtained with the aid of the closed-limb mercury manometer M which was read (to 0·1 mm.) with a cathetometer. Other connections and taps were as indicated in Fig. 1 All taps and joints in contact with vapours were lubricated with silicone high-vacuum grease. All tubing and taps, the spoon gauge, and other parts of the apparatus in contact with (—)-menthyl chloride vapour or its decomposition products, but not heated by the furnace, were heated by suitable nichrome-wire windings to such a temperature (at least 100°) as to prevent any condensation.

FIG. 1.



The technique for conducting experiments was as follows. (—)-Menthyl chloride was introduced into the storage trap and thoroughly outgassed by repeated freezing and evacuation. The (—)-menthyl chloride trap was then weighed and replaced on the apparatus. The apparatus was evacuated with both by-passes open, and the null-point of the spoon gauge determined. The by-pass P_2 was closed, and the run commenced by opening the tap of the (—)-menthyl chloride trap, and then closing the by-pass P_1. At the end of the run the tap of the (—)-menthyl chloride trap was closed and all gases in the reactor tubing were rapidly pumped (<5 secs.) into the collecting traps T_1 and T_2, the by-passes being used. The traps A and T_1 were detached, cleaned, and weighed. The hydrogen chloride collected in trap T_2 was swept out by a stream of nitrogen into water and titrated with N/20-potassium hydroxide. At the temperature of trap T_1 the vapour pressure of liquid hydrogen chloride is about 2 atm. This made it unlikely that any hydrogen chloride would be condensed in T_1, but this was confirmed in two ways.

First, at the end of a run the traps T_1 and T_2 were left open to each other in the evacuated state to ensure complete equilibration. Secondly, the hydrogen chloride in a typical run [92% decomposition of the (−)-menthyl chloride] collecting in trap T_1 was determined and found to be negligible [less than 0·09 mg. for the decomposition of 303 mg. of (−)-menthyl chloride]. The success of the technique depends, however, on seeing that all parts of the apparatus are thoroughly dry. The average flow rate of (−)-menthyl chloride was about 150 mg. per hour, and runs were made for 2—3 hours in each case.

The analysis of the mixture of menthenes and (−)-menthyl chloride in trap T_1 was carried out as follows. The liquid contents were rinsed quantitatively with chloroform into a 10-ml. volumetric flask and made up to the mark. The rotation of this solution was then measured in a 1-dm. tube. From this determination, and with a knowledge of the percentage decomposition of (−)-menthyl chloride (see above) and hence the amount of (−)-menthyl chloride condensed in trap T_1, it was possible to compute the amounts of (+)-*p*-menth-2- and -3-enes formed, it being assumed, of course, that no racemisation had occurred. Since, however, the rotation of (+)-*p*-menth-2-ene ($[\alpha]_D$ +132°) is rather close to that of (+)-*p*-menth-3-ene ($[\alpha]_D$ +109°) (see Hückel *el al.*, *loc. cit.*) this procedure was not very accurate. A more reliable measure of the (+)-*p*-menth-3-ene content was obtained by racemisation. This was effected by Hückel *et al.* (*loc. cit.*) by refluxing with toluene-*p*-sulphonic acid in ethanol solution. We found that the following procedure was more convenient. Its accuracy was checked by using the toluene-*p*-sulphonic acid method.

Approximately 5 ml. of the above-mentioned chloroform solution were placed in a graduated tube, one drop of water added, and hydrogen chloride gas passed through for 30 minutes. Most of the hydrogen chloride (and some of the chloroform) was then removed *in vacuo*; the turbidity of the solution was destroyed by adding a small piece of anhydrous calcium chloride and leaving the whole to stand. The dried chloroform solution was transferred to a further graduated tube with adequate rinsing and made up to the original mark, and the rotation determined again. In numerous preliminary experiments it was established (*a*) that the chloroform had to be saturated with water to ensure racemisation (thorough drying led to no, or only partial, racemisation) and (*b*) that repetition of the treatment specified above caused no further change in optical rotation.

The rotation after racemisation was due to (−)-menthyl chloride (of known amount and $[\alpha]_D$), of racemised (+)-*p*-menth-3-ene, and of (+)-*p*-menth-2-ene (of unknown amount, but of known $[\alpha]_D$). It was possible therefore to calculate the amounts of the two hydrocarbons present. Furthermore, from the rotation of the solution before racemisation, and the information obtained from the racemisation, the rotation of the (+)-*p*-menth-3-ene originally produced in the pyrolysis could be calculated. This procedure assumed that the rotations of the (+)-*p*-menth-2- and -3-enes were the same in chloroform and in the homogeneous state. This was checked by measurements on mixtures of menthenes (see later) and on (−)-menthyl chloride.

RESULTS

Static Experiments.—(i) *Stoicheiometry.* By analogy with previous work in our series of papers on the pyrolysis of chlorinated hydrocarbons (see, especially, Barton, *J.*, 1949, 148; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *ibid.*, 1950, **46**, 114) it was expected, with some certainty, that (−)-menthyl chloride would decompose according to the equation

$$C_{10}H_{19}Cl \longrightarrow C_{10}H_{18} + HCl \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

to furnish a mixture of (+)-*p*-menth-2- and -3-enes and hydrogen chloride. This was confirmed in the static experiments when it was shown (Table 1) that the final pressure (p_f) in the reactor after a long run was close to twice the initial pressure (p_0). A more extensive justification of this stoicheiometry is given below.

TABLE 1.*

Temp., °K.	614	614	614	624	624	624
p_0, mm.	16·7	16·7	18·7	12·5	14·2	14·9
p_f/p_0	2·09	2·05	2·05	2·03	2·17	2·09
Temp., °K.	624	624 †	624	624	624	—
p_0, mm.	15·6	16·5	19·4	26·3	26·7	—
p_f/p_0	2·10	2·21	2·04	2·11	2·06	—

* Reaction time 15 hours in each case unless stated to the contrary, except where denoted by †, where it was 45 hours.

(ii) *Kinetics.* The kinetics of the decomposition were studied in both empty and packed reactors, the latter having an approximately five-fold increase in surface area/volume ratio. As with our previous experience in the pyrolysis of chlorinated hydrocarbons (see, especially, Barton and Onyon, *loc. cit.*), the decomposition of (—)-menthyl chloride was fast and of indefinite kinetic order in clean-walled glass reactors. This heterogeneous mode of decomposition was slowly repressed by repeated experiments and, after about 60 runs, reproducibility was finally attained. The reaction then showed first-order kinetics as illustrated in Fig. 2, with no indication of induction periods. It was generally found more satisfactory to avoid thorough evacuation of the reactor, the products of a run being left in until just before the next run. The reactor was then evacuated for 4—5 minutes to a pressure of 10^{-2} mm. This procedure is comparable with that employed by Brearly, Kistiakowsky, and Stauffer (*J. Amer. Chem. Soc.*, 1936, **58**, 43) in studying the pyrolysis of *tert.*-butyl chloride. Within the limited pressure range accessible, the first-order rate constant was independent of initial pressure (see Table 2). The rate-constant data over the temperature range 592·9° to 623·9° K are summarised in Table 3

TABLE 2.*

p_0, mm.	5·9	14·4	23·3	31·5
$k \times 10^3$, sec.$^{-1}$	0·44	0·40	0·40	0·40

* All experiments at 608·2° K in the packed reactor.

FIG. 2.

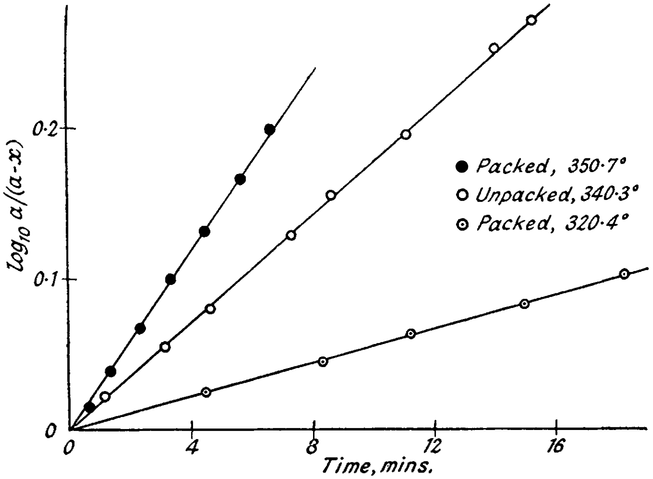


TABLE 3.

Temp., ° K	No. of runs	Mean $k \times 10^3$, sec.$^{-1}$	% Standard deviation of mean k *
Unpacked reactor.			
603·3	5	0·383	0·7
613·9	13	0·720	1·4
Packed reactor.			
592·9	22	0·209	1·4
608·8	13	0·464	1·4
623·9	21	1·26	4·0

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

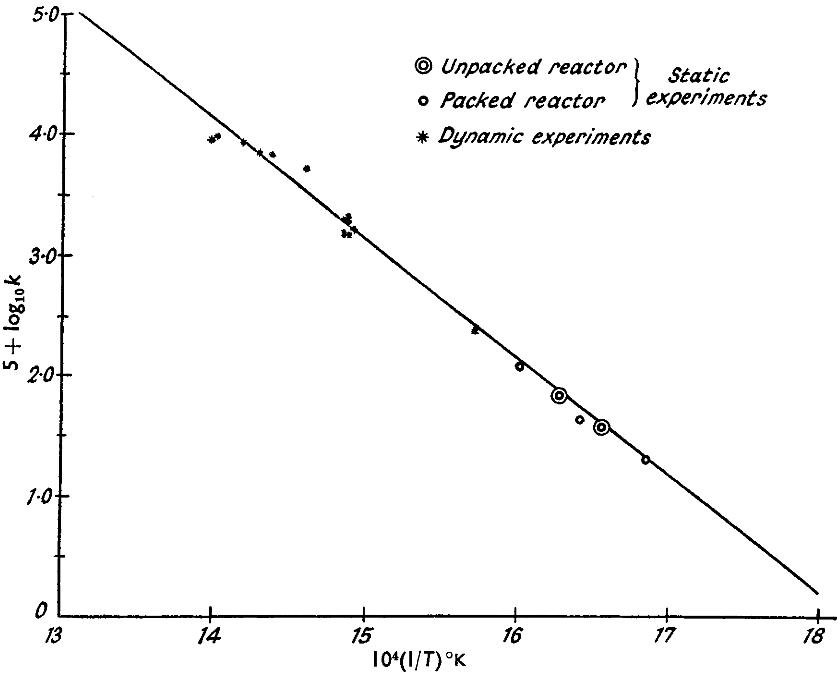
TABLE 4.

p_0, mm., of (—)-menthyl chloride	p_0, mm., of C_3H_6	C_3H_6, %	$k \times 10^3$, sec.$^{-1}$	p_0, mm., of (—)-menthyl chloride	p_0, mm., of C_3H_6	C_3H_6, %	$k \times 10^3$, sec.$^{-1}$
Unpacked reactor at 613·9° K.				Packed reactor at 609·2° K.			
—	0	0	0·720	—	0	0	0·420
14·2	5·4	38	0·720	16·7	11·4	68	0·425
11·4	6·4	56	0·725	15·5	13·8	89	0·420

and illustrated graphically in Fig. 3. The best straight line through the points, drawn by visual inspection, indicated an approximate rate constant equation of $10^{12\cdot0}e^{-42,600/RT}$ sec.$^{-1}$. The homogeneity of the reaction is clearly demonstrated and, having regard to the experimental difficulties of the study, the reproducibility of the results must be regarded as satisfactory. The addition of propylene, even in major amounts, had no effect on the rate of decomposition (see Table 4) in either the packed or the unpacked reactors.

Dynamic Experiments.—(i) *Stoicheiometry.* As further evidence for the stoicheiometry of equation (1), the dynamic experiments were conducted in such a way as to furnish a materials balance. The results, summarised with other data in Table 5, show that in no case was more than 2·5% of material lost. For the purposes of calculation the loss was assumed to be in the menthene fraction which, in most experiments, was the major product of the reaction. As mentioned above, the results permit the calculation of the rotation of (+)-*p*-menth-3-ene. The fact that this is in fair agreement (see p. 461) with the best literature values supports the stoicheiometry assumed in the calculation. Finally an ultra-violet spectroscopic examination (with the Unicam S.P. 500 Spectrophotometer) revealed no indication of conjugated menthadienes or of *p*-cymene in the reaction products. The same result was obtained with the products from the heterogeneous decomposition (see further, p. 459).

FIG. 3.



(ii) *Kinetics.* The first runs in a clean-walled reactor, not unexpectedly, showed rates much above those calculated from the rate-constant equation of the static experiments. This effect was eliminated by leaving approximately 15 mm. of (—)-menthyl chloride in the reactor overnight at 500°, a slight carbonaceous film then being slowly deposited on the reactor walls. After approximately 20 runs, the rates of decomposition became reproducible and the rate constants were in fair agreement with those calculated by extrapolation from the static experiments. The rate constants were calculated, first-order kinetics being assumed, by the equation already given (*J.*, 1949, 148). The results for 16 consecutive runs, omitting two only, are summarised in Table 5 and further in Fig. 3. The overall rate-constant equation for both static and dynamic runs (see Fig. 3) can be represented by the expression $k = 10^{12\cdot6}e^{-45,000/RT}$, in good agreement with the equation deduced solely on the basis of the static experiments.

(iii) *Experiments on the heterogeneous decomposition of* (—)-*menthyl chloride.* These experiments were carried out in a packed reactor of effective residual volume 20·2 ml. The surface area/volume ratio was six times that in the unpacked reactor. The whole apparatus and

TABLE 5. *Homogeneous mechanism of decomposition.*

Run no.	Temp., °K.	p, mm.	Contact time, sec.	Decomp., %	$k \times 10^2$, sec.$^{-1}$	% lost	(+)-p-Menth-2-ene, %	$[\alpha]_D$ of (+)-p-menth-3-ene, calc.
22	672	9·7	22·0	37·6	2·14	2·1	—	—
23	671	10·7	24·5	33·8	1·68	1·3	—	—
24	672	11·0	25·7	39·8	1·97	0·7	—	—
25	673	10·3	22·6	33·5	1·53	0·0	—	—
26	672	13·1	20·8	33·9	1·53	1·9	—	—
27	673	10·6	22·3	38·5	1·62	0·2	—	—
28	673	11·0	23·9	38·5	2·04	0·9	—	—
30	705	12·3	22·4	86·1	8·8	0·0	26	+ 88°
31	714	11·8	21·3	87·2	9·6	1·7	29	+106
32	700	11·7	21·9	78·8	7·1	0·0	28	+ 96
33	716	12·3	24·2	89·0	9·2	1·1	29	+105
35	636	9·6	22·8	5·4	0·24	1·4	—	—
36	696	12·7	24·1	81·3	7·0	2·5	30	+124
37	685	12·6	23·6	72·8	5·5	0·9	25	+109

packing were of clean Pyrex glass. The aim of the experiments was to study the nature of the products formed in the heterogeneous decomposition. The results are summarised in Table 6. As a means of summarising the results the data have been calculated as if the reaction followed first-order kinetics. Although this is probably only approximately the case (cf. Barton

TABLE 6. *Heterogeneous mechanism of decomposition.*

Run no.	Temp., °K.	p, mm.	Contact time, sec.	Decomp., %	$k \times 10^2$, sec.$^{-1}$	% lost	(+)-p-Menth-2-ene, %	$[\alpha]_D$ of (+)-p-menth-3-ene, calc.	$k/k_{calc.}$
Runs in clean glass reactor with no coating.									
1	645	11·6	21·3	88·8	10·3	—	7	+19	24
2	647	11·6	20·7	92·2	12·3	2·2	8	+ 5	26
3	645	12·6	21·2	92·3	12·1	1·5	—	—	28
After being coated overnight with 15 mm. of (—)-menthyl chloride at 743° K.									
4	661	12·5	20·3	76·5	7·1	1·9	17	+27	7
Coated overnight as before.									
5	691	13·1	19·8	88·9	11·5	2·2	19	+37	2·7
6	679	12·2	23·4	87·6	8·9	0·0	20	+18	3·7
Coated for 3 days at 773—803° K.									
7	692	12·0	20·5	81·8	8·3	0·0	20	+40	1·8
Coating destroyed with oxygen at 773° K.									
8	663	12·5	21·0	93·2	12·8	1·3	—	—	12

TABLE 7.

Treatment of menthene mixture	Temp., °K.	p, mm.	Contact time, sec.	$[\alpha]_D$ of product in $CHCl_3$
Experiments under homogeneous conditions.				
Before treatment	—	—	—	+43·1° (c, 0·64) *
Passed through furnace alone	694	9·9	18·1	+44·5° (c, 2·70)
Passed through furnace alone, but 101 mol. % of hydrogen chloride "bled in" after second capillary leak	695	9·5	18·9	+44·0° (c, 2·60)
Passed through furnace together with 100 mol. % of hydrogen chloride "bled in" after first capillary leak	694	11·5	23·8	+45·4° (c, 2·30)
Experiments under heterogeneous conditions.				
Passed through furnace with reactor surface giving heterogeneous decompn. 28 times as fast as homogeneous reaction	655	10·6	17·5	+44·1° (c, 3·80)
Passed through furnace with reactor surface giving heterogeneous decompn. 12 times as fast as homogeneous reaction together with 560 mol. % of hydrogen chloride "bled in" after first capillary leak	663	15	69	+43·3 (c, 1·60)

* $[\alpha]_D$ +43·2° ± 0·2° (homogeneous).

and Onyon, *loc cit.*), it serves to show that the heterogeneous rate of decomposition is much greater than the homogeneous rate. The final column in Table 6 gives the ratio of k for a particular run to $k_{\text{calc.}}$, the calculated rate constant (from Fig. 3) for the homogeneous mode of decomposition.

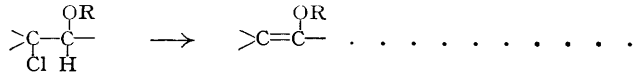
(iv) *Racemisation experiments.* As discussed in greater detail on p. 461, it was of importance to establish whether (+)-*p*-menth-3-ene would be racemised under the experimental conditions used. For this purpose a mixture of menthenes obtained as a by-product (Hückel *et al.*, *loc. cit.*) in the preparation of (—)-menthyl chloride was employed. By racemisation analysis (see above) this mixture contained 5% of (+)-*p*-menth-2-ene, 33% of (+)-*p*-menth-3-ene, and 62% of racemised *p*-menth-3-ene. The mixture was passed (*a*) through the empty reactor used for the homogeneous experiments of Table 5, and (*b*) through the packed reactor used for the heterogeneous experiments of Table 6. The results are summarised in Table 7. In no case was there any significant racemisation of the (+)-*p*-menth-3-ene.

DISCUSSION

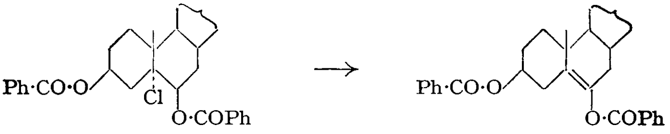
The thermal decomposition of (—)-menthyl chloride in reactors coated with a carbonaceous film follows first-order kinetics, the rate constants *not* varying with the initial pressure. The reaction is homogeneous, exhibits no induction periods even at the lowest temperatures studied, and is totally unaffected by the addition of propylene. All these experimental features are identical with those established previously for ethyl chloride, 1 : 1-dichloroethane, *n*- and *iso*-propyl chlorides, *n*- and *tert.*-butyl chlorides, and 1 : 2-dichloropropane (Barton and Howlett, *J.*, 1949, 165; Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725; Barton and Head, *ibid.*, 1950, **46**, 114; Barton, Head, and Williams, *J.*, 1951, 2039), and, without repeating the arguments in detail, we regard them as adequate to prove that (—)-menthyl chloride decomposes by the unimolecular mechanism. As additional support for this conclusion it should be mentioned that the rate constant equation of $10^{12 \cdot 6}e^{-45{,}000/RT}$ sec.$^{-1}$, established for both static and dynamic experiments, is in good agreement with the linear $\log_{10} A$ versus E relationship reported to hold for the unimolecular mode of decomposition of chlorinated hydrocarbons by Barton, Head, and Williams (*loc. cit.*).

As demonstrated on p. 459, the homogeneous unimolecular thermal decompositions of (—)-menthyl chloride furnishes a mixture of (+)-*p*-menth-2- and -3-enes in the ratio of approximately 1 : 3. The formation of the latter compound is a clear demonstration of the correctness of our general thesis of the relationship between *cis*-elimination and unimolecularity of mechanism in thermal elimination reactions. The proportion of the Δ^2- to Δ^3-isomer is approximately the same as that given by the decomposition of the methyl xanthate (Hückel *et al.*, *loc. cit.*) although the mechanism of the latter reaction has not been rigidly established.

It seems probable that the related *cis*-elimination of hydrogen chloride in the pyrolysis of suitable *trans*-chlorohydrin derivatives according to (2) will prove a general phenomenon :



$$>\underset{\text{Cl}}{\text{C}}-\overset{\text{OR}}{\underset{\text{H}}{\text{C}}}- \longrightarrow >\text{C}=\overset{\text{OR}}{\text{C}}- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$



(V) (VI)

As a specific example we mention the smooth pyrolysis of 5α-chlorocholestane-3β : 6β-diol dibenzoate (V) to furnish cholest-5-ene-3β : 6-diol dibenzoate (VI) (Lettré and Muller, *Ber.*, 1937, **70**, 1947; Petrow, Rosenheim, and Starling, *J.*, 1938, 677).*

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* In a recent communication (Davis and Petrow, *J.*, 1949, 2536) it was stated that this reaction is best interpreted as *trans*-elimination of hydrogen chloride from 5β-chlorocoprostane-3β : 6β-diol dibenzoate, although there is, in fact, already ample evidence in the literature as to the correct stereochemistry of (V). In a personal communication Dr. V. Petrow has kindly indicated that he now withdraws his interpretation of *trans*-elimination in this pyrolysis.

From the experimental data summarised in Tables 5 and 6 it is possible to calculate the rotation of the (+)-*p*-menth-3-ene produced in each dynamic run. The rotations calculated for the homogeneous pyrolysis (Table 5) show a considerable scatter, though the mean value of +105° for $[\alpha]_D$ is in good agreement with the best literature value of +109° (see Hückel *et al.*, *loc. cit.*). To a certain extent this scatter is explained by the fact that all the errors, both of assumption for calculation purposes and of experimental technique, are concentrated in these figures. Further explanations would be provided if the reaction produced a small proportion of racemised *p*-menth-3-ene or if the latter hydrocarbon were racemised in the apparatus before analysis. The second alternative was excluded by the experiments summarised in Table 7. The first alternative, however, is a reasonable one as shown by the following evidence.

The much faster heterogeneous decomposition of (—)-menthyl chloride on clean, or only partly coated, glass walls (Table 6) afforded a menthene fraction which, if the usual analytical technique be applicable, contained somewhat less (+)-*p*-menth-2-ene than in the homogeneous decomposition, and a large proportion of racemised *p*-menth-3-ene. As the walls of the reactor were progressively coated and the rate of decomposition approached that of the homogeneous reaction, the content of non-racemised *p*-menth-3-ene increased. Again, various experiments with the latter hydrocarbon (see Table 7) demonstrated that the racemisation was *not* brought about after its genesis. The racemisation must therefore be an integral part of the heterogeneous reaction mechanism. The somewhat erratic values for the calculated $[\alpha]_D$ of (+)-*p*-menth-3-ene in the homogeneous decomposition (Table 5) may, therefore, be due in part to the intrusion of a minor percentage of heterogeneous decomposition.

We would emphasise, however, that we advance the thesis that the heterogeneous mode of decomposition on glass affords racemised *p*-menth-3-ene with reserve, because it is conceivable that other olefins are formed in this process. Thus the stereochemistry and conformation (cf. Barton, *Experientia*, 1950, **6**, 316) of (—)-menthyl chloride are suited to rearrangement to a five-membered-ring olefin. Be this as it may, these aspects of the heterogeneous decomposition reinforce our conclusion that, in the coated-wall reactors, we have indeed been studying a homogeneous reaction.

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