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# Gas-phase Eliminations. Part VIII.† The Effect of β-Methylation on the Pyrolysis of some t-Alkyl Chlorides

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A series of t-alkyl chlorides (t-butyl, 1,1-dimethylpropyl, 1,1,2-trimethylpropyl, and 1,1,2,2-tetramethylpropyl) have been pyrolysed to form hydrogen chloride and the appropriate olefin. The kinetics follow a first-order law; the reactions were homogeneous and indifferent to the presence of inhibitors. It is concluded that all these compounds undergo elimination by a unimolecular mechanism; the Arrhenius parameters reported are consistent with this. Rate constant ratios are shown to have the same trend as has been observed in  $S_N$  solvolysis. The implications of this finding with regard to the nature of the transition state in gas-phase eliminations are discussed.

ONE of the most effective methods of investigating the nature of transition states is to study a series of structurally related molecules in which substitution is effected at or near the seat of reaction. In view of the marked effect of *a*-methyl substitution on the rates of pyrolyses of organic halides,<sup>1</sup> we investigated the effect of  $\beta$ -methyl substitution in a tertiary series. This series has the advantage that three methyl groups may be progressively substituted on a  $\beta$ -carbon atom of t-butyl chloride. If on the one hand, the rate constant progressively increases from that for t-butyl to that for 1,1,2-trimethylpropyl chloride and then drops for 1,1,2,2-tetramethylpropyl chloride, the effect may be interpreted as a first-order effect on the  $\beta$ -carbon-hydrogen bond. If on the other hand it continuously increases throughout the series, then the effect is better interpreted as a second-order effect on the carbon-chlorine bond.

The primary series of  $\beta$ -methylated chlorides, namely ethyl,<sup>2-7</sup> n-propyl,<sup>4,8</sup> and isobutyl<sup>4,9,10</sup> chlorides has already been investigated. The rate constant ratios are 1:3.6:5.1 at  $440^{\circ}$ . t-Butyl chloride, at the time this work was done, had been investigated by two groups of workers; the Arrhenius parameters 11,12 obtained were as follows:  $\log A = 14.20$  and 12.40sec.<sup>-1</sup>; E = 45.0 and 41.4 kcal. mole<sup>-1</sup>. Subsequent investigations have been made; these will be referred to in the discussion section. The former workers also report the Arrhenius parameters for 1,1-dimethylpropyl chloride: <sup>11</sup>  $\log A = 14.65$  sec.<sup>-1</sup> E = 46.0kcal. mole<sup>-1</sup>, which gave a rate ratio of 2.37:1.

In view of the small effect of  $\beta$ -methylation upon the rate, we reinvestigated t-butyl and 1,1-dimethylpropyl chlorides, so that any differences in experimental

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conditions over the series of four compounds would be minimised. Further, it was deemed important to verify, by the use of an inhibitor, the unimolecular nature of the 1,1-dimethylpropyl chloride decomposition.

# EXPERIMENTAL

Commercial t-butyl chloride was shaken thoroughly with concentrated sulphuric acid until no further colour developed. It was washed with sodium hydrogen carbonate solution, then with water, dried (CaCl<sub>2</sub>), and fractionated; b.p. 50·8°/764 mm.,  $n_{\rm D}^{25}$  1·3828 (lit., <sup>13</sup> b.p. 50·7°/760 mm.,  $n_{\rm D}^{25}$  1·3828). Commercial 1,1-dimethylpropyl chloride was shaken with concentrated hydrochloric acid, washed, and dried (CaCl<sub>2</sub>). After fractionation it had b.p. 46°/200 mm.,  $n_{\rm D}^{19}$  1·4058 (lit.,<sup>14</sup> b.p. 51°/238 mm.,  $n_{\rm D}^{20}$  1·4055). 1,1,2-Trimethylpropyl chloride was prepared by treating 2,3-dimethylbutan-2-ol with concentrated hydrochloric acid. After being washed, dried, and fractionated it had b.p.  $67.3^{\circ}/180$  mm.,  $n_{\rm D}^{25}$  1.4168 (lit.,<sup>15</sup> b.p. 68/185 mm., lit.,<sup>16</sup>  $n_{\rm D}^{20}$  1·4192) (Found: Cl, 29·1. Calc. for C<sub>6</sub>H<sub>13</sub>Cl: 29·4%). 1,1,2,2-Tetramethylpropyl chloride was prepared from the corresponding alcohol by the action of thionyl chloride.<sup>15</sup> After vacuum distillation it had m.p. 135° (lit.,<sup>15</sup> 133°) (Found: Cl, 26.3. Calc. for C<sub>7</sub>H<sub>15</sub>Cl: 26.3%). The pure chloride was stored in liquid nitrogen to prevent decomposition

The kinetics of the reactions were followed by the technique previously described; the reaction vessel was seasoned with allyl bromide. As the dead space was less than 1%, no correction was considered necessary.<sup>17</sup> In no case was it possible to check the stoicheiometry by a comparison of the percentage reaction as estimated from  $100[(P_t - p_0)/p_0]$  with that determined by direct titration of the hydrogen chloride produced, because of rapid recombination of the products when condensed. The

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stoicheiometry, arrived at from previously studied chlorides was assigned in the following way. First, the ratio  $P_t/p_0$ was 2 in all cases, as demanded by equation (1). Second,

$$C_n H_{2n+1} Cl \longrightarrow C_n H_{2n} + HCl$$
(1)

no gases were produced in the reaction that could not be condensed in liquid nitrogen. Third, if at a given point, a run was stopped by condensing out the remaining reactant and the products, reintroduction of the mixture gave a pressure-time curve superimposable on the original one after a shift of time-scale. And fourth, good first-order plots, up to 70% decomposition, were obtained in all cases. Investigation of the products by g.l.c., after the hydrogen chloride had been removed by passage of the gaseous mixture over soda-lime, showed in the case of 1,1-dimethylpropyl and 1,1,2-trimethylpropyl chlorides that the product was predominantly the Saytzeff one, namely 2-methylbut-2-ene and 2.3-dimethylbut-2-ene, respectively. In the cases of t-butyl and 1,1,2,2-tetramethylpropyl chlorides, a unique product was observed, isobutene and 2,3,3-trimethylbut-1-ene, respectively.

By analogy with the kinetics of the pyrolysis of other alkyl chlorides, the reaction was expected to follow the first-order law. Rate coefficients calculated from  $k_1 =$  $(2\cdot303/t) \ln p_0/(2p_0 - P_t)$  are shown in Table 1. In no case is there any systematic variation of  $k_1$  with initial pressure.

TABLE 1

The lac	k of de	penden	ce of $k_1$	on pres	sure	
1,1	-Dimeth	ylpropy	l chlorid	e (315°)		
$p_0 \text{ (mm.) } \dots $	$\begin{array}{c} 34 \\ 25 \cdot 0 \end{array}$	$57 \\ 25.1$	$83 \\ 25 \cdot 6$	$114 \\ 25 \cdot 0$	$134 \\ 25.5$	$155 \\ 25 \cdot 0$
1,1,2-Trimethylpropyl chloride (306°)						
$p_0 \text{ (mm.) } \dots $	$51 \\ 25 \cdot 3$	$78.5 \\ 25.7$	$93 \\ 25 \cdot 3$	$119 \\ 25.7$	$\begin{array}{c} 148 \\ 26 \cdot 4 \end{array}$	$220 \\ 26 \cdot 1$
1,1,2,2-Tetramethylpropyl chloride (280°)						
$p_0 \text{ (mm.) } \dots $	$23.5 \\ 17.5$	80 17·6	$\frac{118}{17\cdot 5}$	$\begin{array}{c} 153\\ 17\cdot 4\end{array}$	172 17·3	$\begin{array}{c} 202 \\ 17 \cdot 7 \end{array}$

### TABLE 2

The temperature variation of the rate constants

	1	t-Butyl	chlorid	le (I)			
Temp	$290^{\circ}$	<b>3</b> 00°	$310^{\circ}$	<b>319</b> ·8°	330·8°		
No. of runs	6	6	6	7	7		
$10^4k_1$ (sec. <sup>-1</sup> )	2.05	4.11	8.06	15.5	<b>31</b> ·0		
1,1-Dimethylpropyl chloride (II)							
Temp	280·1°	289·9°	$298^{\circ}$	306·6°	310·9°	$315^{\circ}$	$320^{\circ}$
No of runs	7	7	9	7	7	12	6
$10^{4}k$ (sec. <sup>-1</sup> )	2.24	4.75	8.12	14.5	18.8	25.3	34.9
1,1,2-Trimethylpropyl chloride (III)							
Temp	$270^{\circ}$	$282^{\circ}$	$287^{\circ}$	$296 \cdot 9^{\circ}$	$306 \cdot 1^{\circ}$	311°	
No. of runs	6	7	6	6	8	6	
$10^4k_1$ (sec. <sup>-1</sup> )	$2 \cdot 29$	5.46	7.55	14.7	25.7	35.6	
1,1,2,2-Tetramethylpropyl chloride (IV)							
Temp	$250.2^{\circ}$	260°	$270.2^{\circ}$	$280^{\circ}$	$290^{\circ}$	$295^{\circ}$	
No. of runs	4	6	12	13	11	4	
$10^4k_1$ (sec. <sup>-1</sup> )	2.02	4.21	8.91	17.5	34.5	48.2	

The reactions are thus of the first order. This was not verified for t-butyl chloride, since both previous groups of workers had reported the reaction to be of the first order. The homogeneity of the reactions was verified by comparing the rates in the unpacked vessel (s/v ca. 1) with those in a packed vessel (s/v ca. 2). In the cases of 1,1-dimethyl-, 1,1,2-trimethyl-, and 1,1,2,2-tetramethyl-propyl chlorides the mean of at least four results gave  $5\cdot32 \times 10^{-4}$  sec.<sup>-1</sup> (calc.  $5\cdot33 \times 10^{-4}$  sec.<sup>-1</sup>, 292°),  $10\cdot4 \times 10^{-4}$  sec.<sup>-1</sup> ( $10\cdot5 \times 10^{-4}$  sec.<sup>-1</sup>, 292°) and  $8\cdot92 \times 10^{-4}$  sec.<sup>-1</sup> ( $8\cdot91 \times 10^{-4}$  sec.<sup>-1</sup>, 270°). The reactions are thus homogeneous. In order to test for the presence of reaction chains, runs were done in the presence of varying partial pressures of propene. These gave for the same three compounds  $10\cdot8 \times 10^{-4}$  sec.<sup>-1</sup> ( $10\cdot9 \times 10^{-4}$  sec.<sup>-1</sup>,  $302^{\circ}$ ),  $3\cdot44 \times 10^{-4}$  sec.<sup>-1</sup> ( $3\cdot48 \times 10^{-4}$ sec.<sup>-1</sup>,  $276^{\circ}$ ) and  $17\cdot8 \times 10^{-4}$  sec.<sup>-1</sup> ( $17\cdot5 \times 10^{-4}$  sec.<sup>-1</sup>,  $280^{\circ}$ ). The rate constants are thus independent of propene pressure and the reactions may be taken to be unimolecular.

The temperature variation of the rate constants is shown in Table 2. These values lead to the Arrhenius parameters tabulated in Table 3.

## DISCUSSION

All the reactions are homogeneous and unimolecular, the Arrhenius parameters are shown in Table 3, together with the rate ratios,  $k_{\rm I} = 1$ , at 280°. A number of workers have investigated t-butyl chloride, and the Arrhenius parameters obtained are shown in Table 4. With the exception of the value given in ref. 12,

#### TABLE 3

#### Arrhenius parameters

log A (sec. <sup>-1</sup> )	(I)	(II)	(III)	(IV)
E (kcal. mole <sup>-1</sup> )	13.77	13.82	13.38	13.80
$k_{\rm X}/k_{\rm I}$ (280°)	<b>45</b> ·0₄	$44 \cdot 2$	$42 \cdot _{3}$	41·9
	1	$2\cdot\overline{3}$	<b>4</b> ·7	18

#### TABLE 4

Arrhenius parameters for the t-butyl chloride pyrolysis

<sup>a</sup> R. L. Failes and V. R. Stimson, Austral. J. Chem., 1967, 20, 1553. <sup>b</sup> Wing Tsang, J. Chem. Phys., 1964, 40, 1171. <sup>c</sup> Wing Tsang, J. Chem. Phys., 1964, 40, 1498. <sup>d</sup> B. Roberts, Ph.D. Thesis, University of London, 1961.

there is general agreement between the various results. The mean values are  $\log A = 13.73 \text{ sec.}^{-1}, E = 45.0 \text{ kcal.}$  mole<sup>-2</sup>. The value reported here for 1,1-dimethylpropyl chloride is in reasonably good agreement with that reported earlier.<sup>11</sup>

The interesting point to emerge from Table 3 is the continual augmentation of the rate as the number of  $\beta$ -methyl groups is increased from zero to three. This shows that the effect of  $\beta$ -methyl substitution is indeed second-order on the carbon-chlorine bond and not a first-order effect on the  $\beta$ -carbon-hydrogen bond. This conclusion has already received some support from the observation of Thomas <sup>18</sup> that 4-bromopent-1-ene is pyrolysed at 380° at about the same rate as s-butyl bromide, despite the allylic weakening of the  $\beta$ -carbon-hydrogen bond in the former compound.

<sup>18</sup> P. J. Thomas, J. Chem. Soc., 1959, 1192.

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It is of interest to examine the results reported here in the light of the analogy proposed by Thomas and one of us <sup>19</sup> between the gas-phase elimination reaction and the  $S_{\rm N}$  or E1 reactions of the corresponding substrates in polar solvents. Thus Hughes et al.<sup>20</sup> have commented upon the relative insensitivity of the  $S_N l$  mechanism to β-methyl substitution. Winstein and Marshall<sup>21</sup> have

<sup>19</sup> A. Maccoll and P. J. Thomas, *Nature*, 1955, **176**, 392.
 <sup>20</sup> E. D. Hughes, C. K. Ingold, R. L. Marton, and O. F. Meigh, *Nature*, 1950, **166**, 679.

investigated the solvolysis of the series of secondary *p*-bromobenzenesulphonates corresponding to the chlorides listed in Table 3, in formic acid at 25°. The rate constant ratios found were 1: 2.5: 14.4: 14.4; these figures bear a strong resemblance to those of Table 3. Our results have thus further supported the proposed analogy.

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<sup>21</sup> S. Winstein and H. Marshall, J. Amer. Chem. Soc., 1952, 74, 1120.