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# REARRANGEMENT IN THE HOMOGENEOUS ELIMINATION KINETICS OF 3-CHLORO-2,2-DIMETHYLPROPAN-1-OL IN THE GAS PHASE

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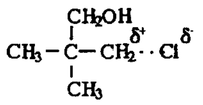
**3-Chloro-2,2-dimethylpropan-1-ol was pyrolysed in a static system at 410·0–459·1 °C and 62–179 Torr. The reaction, in a seasoned vessel and in the presence of the free radical suppressor propene, is homogeneous, unimolecular, and follows a first-order rate law. The rate coefficient follows the Arrhenius equation: log $k_1$ ($s^{-1}$) = (13·14 ± 0·15) – (218·8 ± 2.1) kJ mol$^{-1}$ $(2{\cdot}303RT)^{-1}$. The products are isobutene, formaldehyde and HCl gas. The exclusive intramolecular migration of the $CH_2OH$ group to the positively charged carbon atom, from the C—Cl bond polarisation, appears to proceed by way of an intimate ion-pair type of mechanism. The intermediate 3-methylbut-3-en-1-ol, under the reaction conditions, undergoes a six-centered decomposition characteristic of $\beta$-hydroxyalkenes to produce isobutene, formaldehyde and HCl. The pyrolysis of the deuterated substrate, 3-chloro-2,2-dimethylpropan-1-[$^2$H]ol, serves to support the mechanistic consideration assumed above.**

## INTRODUCTION

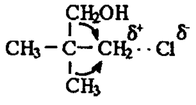
Just two aliphatic hydroxyalkyl chlorides have been examined in gas-phase pyrolytic eliminations. 2-Chloroethanol, at 430–496 °C, was believed to proceed via a 1,2-hydrogen shift for the formation of acetaldehyde and HCl gas.[1] However, when the chlorine atom is interposed by four $CH_2$ groups with respect to the OH, i.e. 4-chlorobutan-1-ol, pyrolysis[2] yielded tetrahydrofuran, propene, formaldehyde and HCl. These results imply that the hydroxy oxygen provides anchimeric assistance by way of an intimate ion-pair type of mechanism.

With this background, the present work was thought of interest for examining the gas phase elimination kinetics of 3-chloro-2,2-dimelylpropan-1-ol. This substrate cannot dehydrochlorinate through a four-membered cyclic transition state as in most alkyl halides, because of the lack of an adjacent $\beta$-hydrogen (**1**). An intramolecular migration or rearrangement may be expected (**2**), or the elimination of HCl could take place through a six-centred state mechanism (**3**). Anchimeric assistance of the hydroxyl oxygen through a four-membered structure (**4**) is not favourable in neighbouring group participation.[3] Consequently, consideration of this intermediate may be neglected.



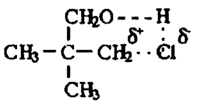
$$\mathrm{CH_3{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{C}}{-}\overset{\delta^+}{CH_2}\cdots\overset{\delta^-}{Cl}}$$

**1**



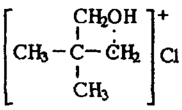
$$\mathrm{CH_3{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{C}}{-}\overset{\delta^+}{CH_2}\cdots\overset{\delta^-}{Cl}}$$

**2**



$$\mathrm{CH_3{-}\overset{\displaystyle CH_2O{-}{-}{-}H}{\underset{\displaystyle CH_3}{C}}{-}\overset{\delta^+}{CH_2}\cdots\overset{\delta^-}{Cl}}$$

**3**



$$\left[\mathrm{CH_3{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{C}}{-}\dot{C}H_2}\right]^+\mathrm{Cl^-}$$

**4**

## RESULTS

The elimination kinetics of 3-chloro-2,2-dimethylpropan-1-ol, in a static system seasoned with allyl bromide and in the presence of the free radical suppressor propene, was examined in the temperature range 410·0–459·6 °C and pressure range 62·0–179·0 Torr (1 Torr = 133·3 Pa). The stoichiometry of reaction (1) demands $P_f = 3P_0$, where $P_f$ and $P_0$ are the final and initial pressure, respectively. The actual average experimental value of $P_f/P_0$, was found at four

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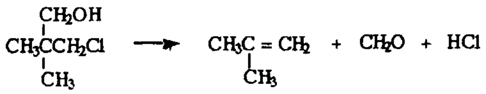
Table 1. Stoichiometry of the reaction

| Temperature (°C) | $P_0$ (Torr) | $P_f$ (Torr) | $P_f/P_0$ |
|---|---|---|---|
| 419·7 | 82·5 | 235·5 | 2·86 |
| 441·0 | 85·0 | 237·0 | 2·79 |
| 448·5 | 80·0 | 222·5 | 2·78 |
| 459·6 | 93·5 | 264·0 | 2·82 |

Table 2. Pressure change versus isobutene and HCl analyses at 448·5 °C

| Time (min) | 2 | 4 | 6 | 8 |
|---|---|---|---|---|
| Reaction (%) (pressure) | 21·7 | 38·0 | 49·3 | 61·2 |
| Isobutene (%) (GC analysis) | 22·7 | 41·5 | 51·1 | 61·7 |
| HCl (%) (titration) | 24·7 | 42·3 | 54·7 | 65·5 |

different temperatures and ten half-lives to be 2·81 (Table 1).


$$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_2OH}}{\mathrm{CH_3CCH_2Cl}}} \longrightarrow \underset{\mathrm{CH_3}}{\mathrm{CH_3C=CH_2}} + \mathrm{CH_2O} + \mathrm{HCl}$$
(1)

The small departure of the required stoichiometry was found to be due to slight polymerization of product formaldehyde. However, further verification of the stoichiometry of equation (1), up to 50–60% reaction, was made by comparing the substrate decomposition from pressure measurements with those obtained by the quantitative gas chromatographic (GC) analysis of isobutene and by the titration of HCl gas product with 0·05 M sodium hydroxide solution (Table 2).

The substrate 3-chloro-2,2-dimethylpropan-1-ol yielded, within the range of the rate determinations, isobutene (98·9%), formaldehyde and HCl gas. However, very small amounts of $CH_4$ (0·2%), $CH_3CH_3$ (0·7%) and $CH_3Cl$ (0·3%) were also detected. The homogeneity of this pyrolytic elimination was examined in a vessel with a surface-to-volume ratio 6·0 times greater than that of a normal vessel. The packed and unpacked, clean and seasoned Pyrex vessels showed, within experimental error, no effect on the rate coefficients (Table 3).

The lack of a free radical process in this elimination reaction was demonstrated by carrying out several runs in the absence or presence of the inhibitor propene (Table 4). No induction period was observed.

Table 3. Homogeneity of the reaction at 431·0 °C

| $S/V$ (cm$^{-1}$) | $10^4 k_1$ (s$^{-1}$)[a,b] | $10^4 k_1$ (s$^{-1}$)[a,c] |
|---|---|---|
| 1 | 7·78 | 7·95 |
| 6·0 | 7·55 | 8·21 |

[a] $k$ Values were estimated by quantitative GC analysis of isobutene.
[b] Clean Pyrex vessel.
[c] Seasoned with allyl bromide.

Table 4. Effect of the inhibitor propene on rates at 431·0 °C

| $P_s$ (Torr)[a] | $P_i$ (Torr)[b] | $P_i/P_s$ | $10^4 \times k_1$ (s$^{-1}$) |
|---|---|---|---|
| 41·0 | — | — | 8·03 |
| 101·0 | 61·0 | 0·6 | 7·86 |
| 63·0 | 97·5 | 1·6 | 7·88 |
| 85·0 | 188·0 | 2·2 | 8·03 |
| 62·0 | 245·0 | 4·0 | 7·99 |

[a] $P_s$ = pressure of substrate.
[b] $P_i$ = pressure of inhibitor.

Table 5. Invariability of rate coefficients with initial pressure at 431·0 °C

| $P_0$ (Torr) | 62·0 | 67·5 | 85·0 | 101·0 | 179·0 |
|---|---|---|---|---|---|
| $10^4 k_1$ (s$^{-1}$) | 7·99 | 8·11 | 8·03 | 7·86 | 8·09 |

The rate coefficients were found to be independent of the initial pressure of the substate. A plot of $\log(3P_0 - P_t)$ against time $t$, from the equation $k_1 = (2{\cdot}303/t)\log[2P_0/(3P_0 - P_t)]$, gave a good straight line up to 50–60% reaction (Table 5). The $k$ values were reproducible with a relative standard deviation not greater than 5% at a given temperature. The variation of the first-order rate coefficient with temperature is given in Table 6. The data were fitted to the Arrhenius equation shown where 90% confidence coefficients from a least-squares procedure are quoted.

## DISCUSSION

Prior to establishing a plausible mechanism for the chlorodimethylpropanol pyrolysis, with the consideration that $C^{\delta+} \cdots Cl^{\delta-}$ bond polarization is rate determining, three possible pathways may be assumed

Table 6. Temperature dependence of rate coefficients

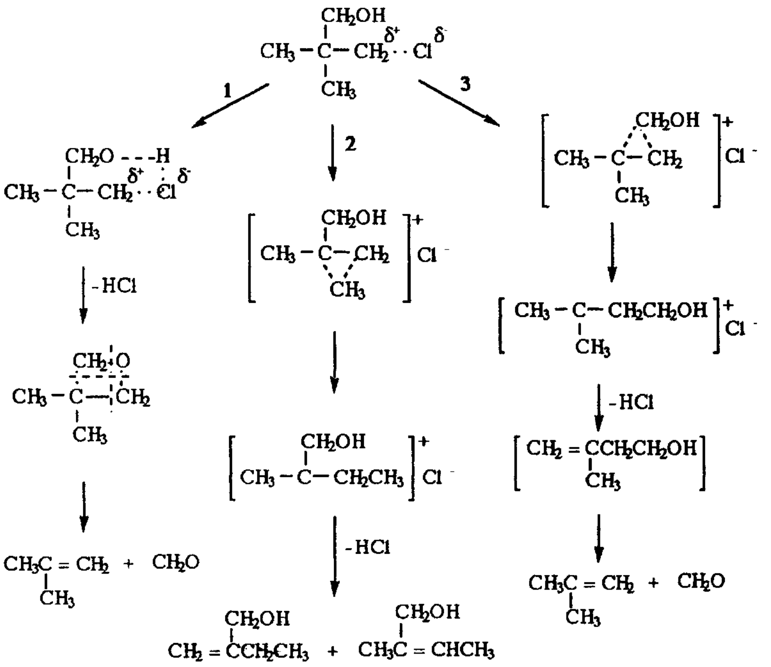
| Temperature (°C) | 410·0 | 419·7 | 431·0 | 441·0 | 450·3 | 454·3 | 459·6 |
|---|---|---|---|---|---|---|---|
| $10^4 k_1$ (s$^{-1}$) | 2·60 | 4·40 | 7·95 | 13·56 | 21·88 | 26·88 | 35·20 |
| Rate equation | $\log k_1$ (s$^{-1}$) = (13·14 ± 0·15) − (218·8 ± 2·1) kJ mol$^{-1}$ $(2{\cdot}303RT)^{-1}$ | | | | | | |

[equation (2)]: path **1**, an intramolecular displacement of the chlorine atom by the hydrogen of the OH group through a six-membered cyclic transition state; path **2**, the migration of the $CH_3$ by a 1,2-shift to the positive carbon intermediate; and path **3**, migration of the $CH_2OH$ to the positive carbon intermediate. An additional consideration is that a competitive migration of the $CH_3$ and $CH_2OH$ may also occur.

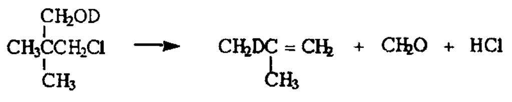
The actual experimental results described in equation (1) ruled out path **2** of equation (2). This is because the products 2-ethyl-2-propen-1-ol and 2-methyl-2-buten-1-ol were not obtained. The yields of isobutene, formaldehyde and HCl gas as final products suggest either the six-membered cyclic transition state of path **1**, or the intimate ion-pair intermediate of path **3**.

In order to establish which of the two paths **1** and **3** takes place, the hydrogen of the OH group was deuterated. The NMR spectra of the pyrolysis product exhibited a signal at $\delta$ 1·7 ($3H, s, CH_3$), 2·1 ($2H, s, CH_2D$) and 4·7 ($2H, s, {=}CH_2$). The mass spectra showed very abundant ions at *m*/*e* 57·1 ($M^+ + 1$) and 58·1 ($M^+ + 2$). These data suggest the presence of a deuterated isobutene product at one of the $CH_3$ groups. Therefore, path **1** of equation (2) may not be one of the assumed mechanisms shown in equation (4).

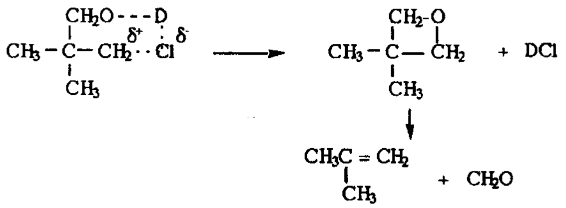
In addition to the above-mentioned results, DCl gas was not obtained when trapped in dimethylamine. This solid showed neither evidence of N–D stretching in the infrared spectra nor a detectable fragment of *m*/*e* 38 (DCl) in the mass spectrometer. 3,3-Dimethyloxetane has been reported to pyrolyse over the temperature range



(2)



$$CH_3\underset{CH_3}{\overset{CH_2OD}{C}}CH_2Cl \longrightarrow CH_2D\underset{CH_3}{C}{=}CH_2 + CH_2O + HCl \qquad (3)$$



(4)

Table 7. Rearrangements of substituent Z in $(CH_3)_2\,(Z)CCH_2Cl$ at 450·0 °C

| Z | $10^4k_1$ $(s^{-1})$[a] | $10^4k_\Delta$ $(s^{-1})$[b] | Rel. rate | $E_a$ (kJ mol$^{-1}$) | Log[$A$ $(s^{-1})$] | $\sigma_I$[c] | Ref. |
|---|---|---|---|---|---|---|---|
| $CH_3$ | 0·12 | 0·12[d] | 1 | 258·7 ± 8·4 | 13·78 ± 0·60 | −0·04 | 7 |
| $C_6H_5$ | 10·23 | 9·72[e] | 81 | 227·8 ± 6·9 | 13·47 ± 0·49 | 0·10 | 8 |
| $CH_2OH$ | 21·38 | 21·14[f] | 176 | 218·8 ± 2·1 | 13·13 ± 0·15 | 0·23 | This work |

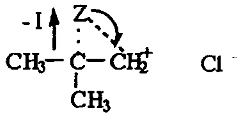
[a] $k_1$ = overall rate.
[b] $k_\Delta$ = rate of rearrangement.
[c] Ref. 9.
[d] 98% $CH_3$ migration.
[e] 95% $C_6H_5$ migration.
[f] 98·8% $CH_2OH$ migration.

400–450 °C,[4] and the rate coefficient for elimination into isobutene and formaldehyde was expressed as $k_1 = (3{\cdot}8 \pm 0.1)10^5 \exp(-60{,}700/RT)\ s^{-1}$. Consequently, our working temperatures make it difficult to detect the oxetane intermediate. The actual result is the formation of a deuterated isobutene described in equation (3). An early publication on the pyrolysis of a deuterated $\beta$-hydroxyolefin, $PhCH{=}CHCH_2C(OD)(CH_2CH_3)_2$,[5] gave via a six-membered cyclic transition state the corresponding deuterated alkene [3-$^2$H]-3-phenylprop-1-ene and pentan-3-one. This work appears to support the assumed mechanism described in path 3 of equation (2).

In relation to path 3, where there is no $\beta$-hydrogen adjacent to the C—Cl bond, the mechanism for chlorodimethylpropanol may be rationalized in terms of an intimate ion-pair intermediate with the exclusive migration of the $CH_2OD$ group to the positively charged atom as described in equation (5).

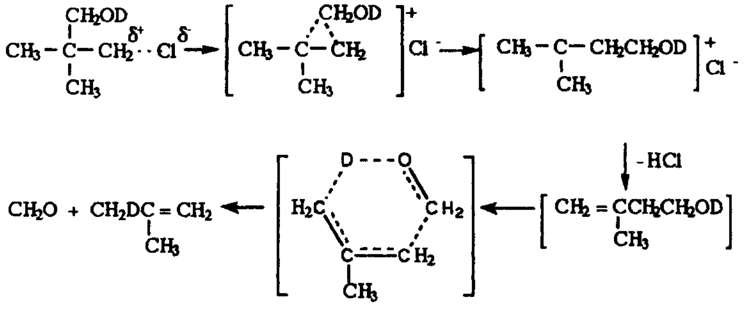
Apparently, 3-methylbut-1-en-1-[$^2$H]ol as the intermediate, under the reaction conditions, undergoes a six-membered cyclic transition state similar to that described for $PhCH{=}CHCH_2C(OD)(CH_2CH_3)_2$[5] to give deuterated isobutene and formaldehyde. The present consideration may be related to the elegant work of August *et al.*[6] on the mechanism of thermal eliminations of $\beta$-hydroxyalkenes, where 3-methylbut-3-en-1-ol was found to give, at 343·5–403·1 °C, isobutene and formaldehyde. In our work, the elimination reaction is carried out at much higher temperatures, 410·0–459·6 °C, which means that the intermediate 3-methylbut-3-en-1-[$^2$H]ol must have decomposed rapidly to $CH_2O$ and $CH_2DC(CH_3){=}CH_2$.

These results lead to an interesting comparison of the migration aptitude of substituents in the gas-phase Wagner–Meerwein rearrangement of some alkyl halides without a $\beta$-hydrogen adjacent to the C—Cl bond. Table 7 suggests that the greater the electonegative nature or electron-withdrawing effect of the substituent Z in $(CH_3)_2(Z)CCH_2Cl$, the faster is the 1,2-intramolecular migration. That is, the electron-withdrawing power of Z, as reflected through the inductive substituent constant $\sigma_I$—values (Table 7), assists migration to the positive carbon intermediate **5**.



**5**

In conclusion this work has provided an additional result of a Wagner–Meerwein rearrangement in gas-phase pyrolysis of an akyl halide and supports the intimate ion-pair type of mechanism.



(5)

## EXPERIMENTAL

3-Chloro-2,2-dimethylpropan-1-ol of 99·3% purity (GLC column, 10% Dow Corning 200/100 Chromosorb W AW DMCS, 80–100 mesh) was acquired from Aldrich. The primary pyrolysis product isobutene (Matheson) was determined quantitatively in a column of Carbopack-C (80–100 mesh) with 0·19% picric acid. HCl gas was determined by titration with 0·05 M NaOH solution.

The identities of the substate and products were confirmed by mass and NMR spectrometry.

3-Chloro-2,2-dimethylpropan-1-[$^2$H]ol was obtained by stirring the hydroxy compound with 99·9% $D_2O$ (Aldrich). In the FTIR spectrum, the O–D stretching vibration was found to be at 2495·8 $cm^{-1}$ (4·0 µm).

The substrate was pyrolysed in a static system and in the presence of at least a twofold excess of the free radical inhibitor propene. The reaction vessel was seasoned with the product of decomposition of allyl bromide. The rate coefficients were determined by pressure increase. The temperature was controlled by a Shinko DIC-PS resistance thermometer temperature controller maintained within ±0·2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. Different points along the reaction vessel showed no temperature gradient, and the substrate was injected directly into the vessel with a syringe through a silicone-rubber septum.

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