Radiolysis of chloroalkanes: 1,2-dichloroethane

Stanisław Truszkowski, Aleksander Chostenko

Abstract The stable products of radiolysis of 1,2-dichloroethane (12DCE) $\gamma$-irradiated in an oxygen-free atmosphere were investigated. The pure products of radiolysis were separated by preparative gas chromatography and identified by $^1$H, $^{13}$C NMR and mass spectroscopy as well as quantitative gas chromatography. In the gas phase we have obtained H$_2$ and HCl; in the liquid phase: chloroethane, 1,1-dichloroethane, 1,1,2-trichloroethane, 1,2,4-trichlorobutane and 1,2,3,4-tetrachlorobutanes (dl- and meso-: [2R,3R] or [2S,3S] and [2R,3S]-isomers). On the basis of the results obtained a preliminary scheme for the formation of the stable products is proposed.

Key words 1,2-dichloroethane • chloroalkanes • radiolysis products

Introduction

Radiolysis of 1,2-dichloroethane (12DCE) has been studied by many workers. However, it is reported only some aspects of this process. Ueda [6] has analysed especially unsaturated products in irradiated neat 12DCE and with scavengers. Katz, Baruch and Rajbenbach [2] have reported the kinetics of the radiation induced free radical chain reactions of 12DCE in cyclohexane in the temperature range 150–250°C. Sumiyoshi, Sugita, Watanabe and Katayama [3] have reported the observation of radical cations of 12DCE (CH$_2$ClCH$_2$Cl$^+$, CH$_2$ClCH$^+$) by means of pulse radiolysis and the rate constants of charge transfer for various cation scavengers. Hasegawa, Symons and Shiotani confirmed the formation of CH$_2$CICHCl$^+$ cation radical in detailed ESR analysis [1]. The stable and transient products of $\gamma$-radiolysis of 12DCE (and other chloroalkanes) have not been studied systematically till now.

The present paper is a continuation of our work on chlorosubstituted aliphatic hydrocarbons [4].

Experimental

Materials

The investigated compound 12DCE (POCh, Gliwice, Poland product) was fractionated twice over using a 0.5-m column filled with Rasching rings under normal pressure. The purity of each fraction was determined by gas chromatography. The 12DCE of > 99.9% purity was obtained and subsequently used for the investigations. Remainder < 0.1% was an unidentified compound (resistant to $\gamma$-irradiation).

Irradiation

Before irradiation, samples of the investigated compound were carefully de-aerated in an air-tight cell by blowing...
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nitrogen (N₂ was purified to remove oxygen and water). The samples were then irradiated in a RHM-γ-20 Co-60 unit. The dose rate determined by a Fricke dosimeter was from 0.60 up to 0.64 kGy·h⁻¹ during experiments.

Measurements

The radiolytic changes were determined, as in our earlier work [5], by potentiometric titration, analytical and preparative gas chromatography, ¹H as well as ¹³C NMR, ESR and mass spectroscopy.

In the potentiometric determination of HCl a chloro-silver indicator electrode and a reference silver electrode in AgNO₃ solution were used: Ag/AgCl, Cl⁻ → Ag⁺/Ag.

The identification and quantitative determination of hydrogen was performed by chromatographic analysis, as described elsewhere [5]. The identification was made by comparison of the retention time of a pure hydrogen sample and the analysed gas product. The quantitative determinations were done using standard line for pure H₂ of a known concentration.

The chromatographic analysis of liquid products was performed using the columns described in a previous work [5]. The isothermal analysis was carried out during 10 min at 353 K then the temperature was linearly increased up to 553 K at a rate of 8 deg/min. Products were fractionated under reduced pressure and volatile fractions collected at 176 K (solid methanol). Non-volatile fraction (in a small amount) was not analysed. Some pure products of radiolysis were isolated by preparative gas chromatography and collected in a trap at 176 K. The isolated products of radiolysis were identified by ¹H and ¹³C NMR spectroscopy. Some products were identified by GC-MS technique on the basis of various published data, catalogues of spectra and analysis of standard substances.

Results

The gaseous products of radiolysis, HCl and H₂, were formed linearly with the dose in the dose range up to 110 (HCl) and 150 (H₂) kGy. The radiation yields were: G(HCl) = 5.67 ± 0.08 and G(H₂) = 0.18 ± 0.01.

In the liquid phase at least 18 products were formed. The chromatogram of irradiated 12DCE with a dose of 192 kGy is presented in Fig. 1. We have determined six products I–VI at retention times of 2.8, 4.2, 10.7, 22.4, 25.5, and 26.8 minutes, respectively. Peaks I–III were determined using chromatographic reference compounds and MS, peaks IV–VI by ¹H, ¹³C and ¹³C DEPT NMR. The results of the identification are shown in Table 1.

Quantitative analysis of the identified products of radiolysis was carried out by means of the chromatographic method, drawing calibration lines for the majority of compounds analysed. The concentration of products increased linearly with the dose in the full dose range for 11DCE, 124TCB, dl- and meso-1234TeCB. However, the yields of CE and 112TCE showed a slow decrease with the dose. The results are presented in Table 2.

Discussion

For investigated compound, the formation of hydrogen and hydrogen chloride has been confirmed. The mechanism was discussed in our previous works [4, 5].

In the irradiated 12DCE chloroethane was also formed. The dechlorination can be explained by the rupture of the C-Cl bond in the excited molecule (1) or dissociative electron capture (2) resulting in the formation of alkyl radicals and followed by the detachment of hydrogen (3):

\[
\begin{align*}
\text{(1)} \quad & \text{CH}_2\text{CICH}_2\text{Cl} \rightarrow \text{CH}_2\text{CICH}_2\text{Cl}^+ \rightarrow \\
& \quad \rightarrow \text{CH}_2\text{CICH}_2^+ + \text{Cl}^- \quad \text{(or CH}_2\text{CICHCl}^+ + \text{H)} \\
\text{(2)} \quad & \text{CH}_2\text{CICH}_2\text{Cl} + \text{e}^- \rightarrow \text{CH}_2\text{CICH}_2^+ + \text{Cl}^- \\
\text{(3)} \quad & \text{CH}_2\text{CICH}_2^+ + \text{RH} \rightarrow \text{CH}_2\text{CICH}_3 + \text{R}^*
\end{align*}
\]

Among the products of radiolysis, we have not found vinyl chloride. One can explain this by many reactions: the addition to double bond, polymerization and others. For example, the addition of HCl (via ionic mechanism) to vinyl chloride leads to 1,1-dichloroethane (4), which is one of the products of radiolysis (G = 2.03):

\[
\text{(4)} \quad \text{CH}_2 = \text{CHCl} + \text{HCl} \rightarrow \text{CH}_2\text{CHCl}_2
\]

whereas the addition of Cl atoms forms initial compounds (5):

\[
\begin{align*}
\text{(5)} \quad & \text{CH}_2 = \text{CHCl} + \text{Cl}^- \rightarrow \\
& \quad \rightarrow \text{CH}_2\text{CICHCl}^- \rightarrow \text{CH}_2\text{CICH}_2\text{Cl}
\end{align*}
\]

The formation of vinyl chloride is possible in one step dehydrochlorination reaction of the analysed compound: 12DCE → HCl + CH₂ = CHCl or in a disproportionation of radicals (formed in eqs. (1) and (2)): 2CH₂CICHCl⁻ → CH₂ = CHCl + CH₂CICH₃.

Among the stable products of radiolysis of the 12DCE, we have determined the 112TCE. This compound can be formed as a result of recombination of the radical from reaction (1) with a chlorine atom:

\[
\text{(6)} \quad \text{CH}_2\text{CICHCl}^- + \text{Cl}^- \rightarrow \text{CH}_2\text{ClCHCl}_2
\]

or in a reaction with the primary compound
Radiolysis of chloroalkanes: 1,2-dichloroethane

\[
\text{CH}_2\text{ClCHCl}^+ + \text{CH}_2\text{ClCH}_2\text{Cl} \rightarrow \text{CH}_2\text{ClCHClCH}_2\text{Cl} + \text{CH}_2\text{Cl}^+
\]

G-values of 1CE and 112TCE were high and slightly decreased with dose. This one can explain throughout secondary reaction under irradiation the chlorination of CE and dechlorination of 112TCE leads, in both cases, to parent 12DCE. Dimers of the initial compounds with various chlorine contents were formed with high efficiency (G = 7.57). Most probable is the recombination of radicals created by a detachment of hydrogen or chlorine atom from the primary molecule (1). The reactions (8) and (9) are given as the more representative ones:

\[
\text{(8)} \quad \text{CH}_2\text{ClCHCl}^+ + \text{CH}_2\text{ClCH}_2\text{Cl} \rightarrow \text{CH}_2\text{ClCHClCH}_2\text{Cl}
\]

\[
\text{(9)} \quad \text{CH}_2\text{ClCHCl}^+ + \text{CH}_2\text{ClCHCl}^+ \rightarrow \text{CH}_2\text{ClCHClCHClCH}_2\text{Cl}
\]

In the case of 124TCB, the addition of the CH2ClCHCl radical to a double bond of vinyl chloride seems to be also probable:

\[
\text{(10)} \quad \text{CH}_2 = \text{CHCl} + \text{CH}_2\text{ClCHCl}^+ \rightarrow \text{CH}_2\text{ClCHClCH}_2\text{Cl} + \text{HCl}
\]

We have determined two isomers of 1,2,3,4-tetrachlorobutane. The mechanism of formation dl- and meso-isomers is still not clear, but one can explain it by different structural conditions of recombinating radicals.

Table 1. Identification of liquid products of radiolysis of 1,2-dichloroethane.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Bands</th>
<th>ppm</th>
<th>Groups</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td>chloroethane (CE)</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
<td></td>
<td>1,1-dichloroethane (11DCE)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C2H4Cl m/e = 63, CHCl2 m/e = 83, C2H5Cl m/e = 97</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td></td>
<td></td>
<td>1,1,2-trichloroethane (112TCE)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>molecular ion C2H3Cl m/e = 132, CHCl3 m/e = 97, CHCl2 m/e = 83, CHCl m/e = 61, CH2Cl m/e = 49</td>
</tr>
<tr>
<td>IV</td>
<td>1H NMR</td>
<td>multiplet</td>
<td>2.13</td>
<td>-CH2-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>multiplet</td>
<td>2.44</td>
<td>-CH2-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>multiplet</td>
<td>3.75</td>
<td>-CHCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>multiplet</td>
<td>4.33</td>
<td>-CHCl-</td>
</tr>
<tr>
<td></td>
<td>13C NMR</td>
<td></td>
<td>37.836</td>
<td>CH (C4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41.055</td>
<td>CH (C3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48.002</td>
<td>CH2 (C1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>57.527</td>
<td>CH (C2)</td>
</tr>
<tr>
<td>V</td>
<td>1H NMR</td>
<td>triplet</td>
<td>3.80</td>
<td>-CHCl</td>
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<tr>
<td></td>
<td>13C NMR</td>
<td></td>
<td>47.041</td>
<td>CH</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>59.813</td>
<td>CH</td>
</tr>
<tr>
<td>VI</td>
<td>1H NMR</td>
<td>multiplet</td>
<td>4.05</td>
<td>-CHCl</td>
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<tr>
<td></td>
<td>13C NMR</td>
<td></td>
<td>47.054</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>59.838</td>
<td>CH</td>
</tr>
</tbody>
</table>

*Four doublets of doublets (16 bands) – protons are not magnetically equivalent.

The identification of products V and VI seems to be confirmed by the differences in retention times corresponding to differences in the boiling points of identified compounds (383.2 - 384.2 K – dl-isomer and 403.2 - 407.2 K – meso-isomer).

Table 2. Concentration and radiation yields (G) of stable products formed in γ-irradiated 1,2-dichloroethane.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>CE</th>
<th>G(CE)</th>
<th>11DCE</th>
<th>112TCE</th>
<th>G(112TCE)</th>
<th>124TCB</th>
<th>dl-1234-TeCB</th>
<th>meso-1234-TeCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.9</td>
<td>12.2</td>
<td>11.9</td>
<td>2.3</td>
<td>7.58</td>
<td>7.43</td>
<td>3.5</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>30</td>
<td>29.7</td>
<td>9.52</td>
<td>6.3</td>
<td>15.8</td>
<td>5.09</td>
<td>10.9</td>
<td>7.5</td>
<td>5.4</td>
</tr>
<tr>
<td>60</td>
<td>56.5</td>
<td>9.08</td>
<td>12.1</td>
<td>21.8</td>
<td>3.51</td>
<td>19.1</td>
<td>14.1</td>
<td>11.1</td>
</tr>
<tr>
<td>80</td>
<td>71.7</td>
<td>8.70</td>
<td>16.3</td>
<td>28.8</td>
<td>3.47</td>
<td>28.5</td>
<td>19.4</td>
<td>17.1</td>
</tr>
<tr>
<td>105</td>
<td>85.0</td>
<td>7.81</td>
<td>22.4</td>
<td>34.5</td>
<td>3.11</td>
<td>37.4</td>
<td>25.0</td>
<td>21.0</td>
</tr>
<tr>
<td>147</td>
<td>105.4</td>
<td>6.92</td>
<td>29.9</td>
<td>42.7</td>
<td>2.80</td>
<td>50.1</td>
<td>33.0</td>
<td>27.4</td>
</tr>
</tbody>
</table>

G = 2.03 ± 0.10 3.35 ± 0.14 2.33 ± 0.12 1.89 ± 0.12

Table 2. Concentration and radiation yields (G) of stable products formed in γ-irradiated 1,2-dichloroethane.
Radical mechanism of the formation of the above mentioned isomers is more probable because of well known stereochemistry of ionic and radical reactions. Radicals, usually, change their configuration during reaction leading to a mixture of the stereoisomers. In our system at least two radicals have been formed – CH₂ClCH⁻ and CH₂ClCHCl⁺. ESR spectrum was complex and has not been resolved in detail till now. We have determined nearly equal concentrations of the meso- and dl-isomers. This confirms a radical mechanism of the dimerization of 12DCE in liquid phase under γ-irradiation.

References