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Berkeley, California
ISOTOPIC STUDIES ON THE RADIATION DECOMPOSITION OF CRYSTALLINE CHOLINE CHLORIDE

Richard M. Lemmon and Margaret A. Smith

December 1962
Isotopic Studies on the Radiation Decomposition of Crystalline Choline Chloride\(^1\)\(^2\)

Richard M. Lenahan and Margaret A. Smith

(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.


Abstract

Carbon-14- and deuterium-labeled choline chlorides were used to study the mechanism of the radiolysis of crystalline choline chloride. These studies demonstrate that, during the highly-sensitive radiation decomposition, (1) the carbino1 group of the ethanol moiety becomes the aldehyde group of the resultant acetalddehyde, (2) no hydrogens are transferred to or from the trimethylamine group, (3) the hydrogens of the ethanol moiety are highly mobile, and (4) intermolecular hydrogen transfers take place.
This paper is part of a continuing study of the extraordinary
radiation sensitivity of crystalline choline chloride, \([(CH_3)_2NCH_2CH_2OH]Cl^-
\), a compound that decomposes with G values as high as 55,000.\(^{3,4,5}\)


Earlier work had indicated the possibility of a symmetrical inter-
mediate between choline chloride and one of its principal radiolysis
products, acetaldehyde. Such a structure was based on the electron spin
resonance spectra obtained from selectively deuterated, irradiated choline
chloride. To test this possibility, in the present work \([(CH_3)_2NCH_2CD_2CH_2OH]Cl^-
\) was prepared and decomposed by electron irradiation. The distribution of
radioactivity was then determined in the resultant acetaldehyde.

The movements of hydrogen atoms during the radiation decomposi-
tion process were determined through experiments on the following deuterated
cholines: \([(CD_3)_2NCH_2CH_2OH]Cl^-, [(CH_3)_2NCH_2CD_2CH_2OH]Cl^-
\), \([(CH_3)_2NCH_2CD_2OH]Cl^-, [(CH_3)_2NCH_2CH_2OD]Cl^-
\), and \([(CH_3)_2NCH_2CD_2OD]Cl^-
\).

The resultant principal products, trimethylamine and acetaldehyde, were
purified by gas chromatography and their deuterium contents determined
by mass spectroscopy.

Experimental

Preparation of Labeled Compounds.--The method for the preparation of
\([(CH_3)_2NCH_2C^{14}H_2OH]Cl^-\) was the condensation of ethyl bromoacetate-\(^{14}Cl\)}
with dimethylamino to give the ethyl ester of N,N-dimethylglycine.
LiAlH₄ reduction of the latter compound to N,N-dimethylaminopentanol, and
quaternization with methyl iodide. The resultant choline iodide was
then converted to the chloride. Details of this preparation have been
given previously.⁶ The final product was recrystallized from ethanol-

(6) N. A. Smith and R. M. Lasmion, University of California Radiation
Laboratory Report No. UCRL-9208, June 1960, p. 27.

ether; its specific activity was 0.28 μc/mole. The elemental analysis
was: C, 43.45% (calculated 43.01); H, 9.77% (calculated 10.11); Cl,
25.07% (calculated 25.41).

The [(CD₃)₂NCH₂CH₂OH]⁺Cl⁻ and [(CH₃)₃NCD₂CH₂OH]⁺Cl⁻ used were
samples of the compounds whose preparations and properties were pre-
viously reported.⁵ ⁷

(7) R. O. Lindblom, University of California Radiation Laboratory Report
No. UCRL-9218, October 19, 1959.

The [(CH₃)₃NCH₂CD₂OH]⁺Cl⁻ was prepared following the same procedure
outlined above for the Cl¹⁴-labeled compound. In this case, no Cl¹⁴ was
involved, and LiAlH₄ (from Metal Hydrides, Inc., Beverly, Mass.) was
used in place of LiAlH₄. The NMR spectrum obtained on the product was
identical to that previously reported for deuterated choline chloride
in which the O-methylene proton contribution was missing and the
N-methylene peak was sharpened by the elimination of hyperfine interactions.³
The identity of the compound was also determined through satisfactory ele-
mental analyses.
\[
((\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OD})^+\text{Cl}^- \text{ and } ((\text{CH}_3)_3\text{NCH}_2\text{CD}_2\text{OD})^+\text{Cl}^- \text{ were prepared by dissolving undeuterated (or O-methylene deuterated) choline chloride in a large excess of 99\% D}_2\text{O. The solution was evaporated to dryness and the deuterated compound was recrystallized from H}_3\text{N-dimethylformamide. Before using this solvent for recrystallization, we established by } \text{NMR spectroscopy that the carbonyl-bound hydrogen atom of the solvent would not exchange with D}_2\text{O. The identities of the deuterated choline chlorides were established by C and H analysis. It was not possible to obtain a check of the purities by } \text{NMR spectroscopy since no suitable aprotic solvent could be found.}
\]

\text{Irradiations.--The C}^{14}_4\text{-labeled crystalline choline chloride was irradiated with the electron beam of a 3-5 Mev linear accelerator. The deuterium-labeled cholines were irradiated with Co}^{60} \text{ rays; the irradiation techniques have been described previously. There is little difference between the effects of electron beams and } \lambda \text{ rays in the radiolysis of choline chloride. The choice of the radiation is merely one of convenience. In all experiments the radiation dose given (2-5 } \times 10^6 \text{ rads) was sufficient to cause approximately 10\% decomposition. Direct determinations of the amounts of decomposition were not made.}
\]

\text{Acetaldehyde-C}^{14}_4 \text{Degradations.--After an irradiation the sealed tube containing the choline chloride was opened and the contents dissolved in water at 0^\circ. Inactive acetaldehyde was added as carrier, and the resultant solution was refluxed for two hours while a stream of helium passed through it, carrying the acetaldehyde into a liquid nitrogen-cooled trap. The trap and contents were then placed in an ice bath and cold, dilute, basic KMnO}_4 \text{ was added. After the solution}
was stirred for an hour, excess KMnO₄ was decomposed with FeSO₄, and the mixture was acidified with H₂SO₄ and steam distilled. The distillate was titrated to neutrality with standard NaOH (thus giving the yield of acetic acid) and evaporated to dryness.

The resultant sodium acetate was decomposed into CO₂ and methylamine with NaOH and H₂SO₄ (Schmidt reaction—details given previously⁶). The evolved CO₂ was swept by helium into a trap cooled by liquid oxygen. The CO₂ was transferred to a vacuum line where it was dried (passage through a trap at ~80⁰) determined manometrically, and transferred to an ionization chamber for radioactivity measurement. This determination was made by using a vibrating-reed electrometer and the "rate of charge" method.

The methylamine was recovered by making the solution (from which the CO₂ had been generated) basic and codistilling water and methylamine into a cold trap. The phenylmethylthiocarbamide of the methylamine was then prepared by allowing the latter compound to diffuse into a flask containing an aqueous solution of phenyl isothiocyanate.⁸ The crystals of phenyl-


methyurea (identity established by melting point and elemental analysis) were washed with hexane, dried, and their specific activity determined by liquid scintillation counting.

Purification of the Evolved Acetaldehyde and Trimethylamine.—The irradiated choline chloride sample tube was cooled in liquid nitrogen and opened. It was then attached to a vacuum line and volatile components vacuum-distilled into a trap suitable for introducing the sample into a
gas chromatograph (Milliken, Model A-350, 10' by 1/4" dimethylsulfolane on firebrick column). Using helium as the carrier gas, with a flow rate of 90 cc per minute, at room temperature, the acetaldehyde is cleanly separated (retention time: 11 minutes) from all other volatile materials (very small amounts of methyl chloride and ethyl ether).

Trimethylamine was recovered, after the acetaldehyde was removed, by making alkaline the solution of the irradiated choline. The volatile trimethylamine was also swept over into a cold (-196°C) trap from which it was introduced into a gas chromatograph. Using the same chromatographic conditions as described above for acetaldehyde (with the exception only of a flow rate of 60 cc per minute) the trimethylamine is also cleanly separated (retention time: 3.5 minutes) from other volatile compounds (traces of dimethylamine and acetaldehyde).

Deuterium Contents of Evolved Acetaldehyde and Trimethylamine.--

The amounts of deuterium in the chromatographically-purified gases were determined by observations of the enhancements, or lack of it, of such mass peaks as 46 (CH$_2$DCDO), 45 (CH$_2$DCHO), and 39 (CD$_2$O) for acetaldehyde. Appearance of deuterium in trimethylamine would result in enhancement of mass peak 59 (53 is the major peak for ordinary trimethylamine). An additional check of the deuterium in the methyl group of acetaldehyde was made by photolyzing part of the acetaldehyde, in the presence of iodine vapor, following the procedure of Blacet and Heldman. The resultant methyl iodide contains the methyl group of the acetaldehyde and the presence of deuterium is reflected in the appearance of peaks

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(9) F. E. Blacet and J. B. Heldman, J. Am. Chem. Soc. 64, 889 (1942).
at mass 148 and above. The methyl iodide was also purified by gas chromatography (on dimethysulfolane and Apiezon columns).

The mass spectroscopy was done on a Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer.

Results

Distribution of Activity in Acetaldehyde from \([\text{[(CH}_3\text{)}_3\text{NCH}_2\text{C}^{14}\text{H}_2\text{OH}]^{+}\text{Cl}^-}\)

Two samples of irradiated choline chloride were analyzed. The results of the acetaldehyde degradations are presented in Table I.

Table I

<table>
<thead>
<tr>
<th>Degradations of Acetaldehyde from Irradiated ([\text{[(CH}_3\text{)}_3\text{NCH}_2\text{C}^{14}\text{H}_2\text{OH}]^{+}\text{Cl}^-})</th>
<th>Activity per mmole CO(_2)</th>
<th>Activity per mmole C(_2\text{H}_6\text{NHCSNHCH}_3)</th>
<th>Activity in C-1 of CH(_3\text{CHO}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>4.07 x 10(^{-2}) µc</td>
<td>7.1 x 10(^{-5}) µc</td>
<td>99.3</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.82 x 10(^{-2}) µc</td>
<td>4.8 x 10(^{-5}) µc</td>
<td>99.5</td>
</tr>
</tbody>
</table>

The results given in Table I demonstrate that there is no symmetrical two-carbon species in the mechanism yielding acetaldehyde from irradiated crystalline choline chloride. The carbinol carbon atom of choline chloride is the aldehydic carbon in the acetaldehyde.
Acetaldehyde from [(CD₃)₂NCH₂CH₂OH]⁺Cl⁻.--The mass spectral data are presented in Table II.

Table II

<table>
<thead>
<tr>
<th>Mass (m/e)</th>
<th>CH₃CHO A.P.I.</th>
<th>CH₃CHO Census</th>
<th>Deuterated Acetaldehyde Expt. 1</th>
<th>Deuterated Acetaldehyde Expt. 2</th>
<th>Deuterated Acetaldehyde Expt. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>1.1</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>43</td>
<td>26.7</td>
<td>30.1</td>
<td>28.3</td>
<td>25.9</td>
<td>27.8</td>
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<tr>
<td>44</td>
<td>45.7</td>
<td>54.0</td>
<td>50.2</td>
<td>49.7</td>
<td>49.5</td>
</tr>
<tr>
<td>45</td>
<td>1.2</td>
<td>1.3</td>
<td>2.6</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>46</td>
<td>0.1</td>
<td>0.1</td>
<td>v. small</td>
<td>v. small</td>
<td>v. small</td>
</tr>
</tbody>
</table>

%Relative peak heights

**Reagent grade, after CLC purification on dimethylsulfolane

The data of Table II clearly indicate that there is little, if any, involvement of the methyl protons in the radiolysis of crystalline choline chloride. The mass spectrum of the acetaldehyde is almost identical to that of the acetaldehyde from ordinary choline. There is a slight enhancement of the mass 45 peak, but this increase is so small as to be of dubious significance.

Acetaldehyde from [(CH₃)₂NCD₂CH₃OH]⁺Cl⁻.--The mass spectral data are presented in Table III.

Table III

<table>
<thead>
<tr>
<th>Mass (m/e)</th>
<th>CH₃CHO A.P.I.</th>
<th>CH₃CHO Census</th>
<th>Deuterated Acetaldehyde Expt. 1</th>
<th>Deuterated Acetaldehyde Expt. 2</th>
<th>Deuterated Acetaldehyde Expt. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>30</td>
<td>1.1</td>
<td>1.1</td>
<td>4.8</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>43</td>
<td>26.7</td>
<td>11.6</td>
<td>11.9</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>45.7</td>
<td>26.4</td>
<td>28.5</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>1.2</td>
<td>30.2</td>
<td>23.9</td>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>0.1</td>
<td>14.8</td>
<td>14.4</td>
<td>23.3</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>--</td>
<td>2.8</td>
<td>2.5</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

%Relative peak heights
The data of Table III show: (1) There is a small fraction at mass 39; thus some CD₃ is formed. (2) The major peak is at mass 45, not 46. Therefore, there is more CH₂CHO than CH₂CD₂CHO formed (by a factor of nearly 2). (3) The appearance of a small peak at mass 47 indicates the formation of acetaldehyde with three deuterium atoms. This is evidence of intermolecular hydrogen transfers during the radiolysis.

Acetaldehyde from [(CH₃)₂CHCD₂CH]⁺Cl⁻.—Consistent mass spectral data on the acetaldehyde from the O-methylene deuterated choline chloride proved difficult to obtain. The acetaldehyde mass spectrum was taken after thirteen different radiolysis experiments, including those from three different preparations of the deuterated compound. Mass 30 was always the largest peak; however, the mass 45/mass 46 ratio varied all the way from 2.75 to 0.43; the average was 0.89. That this was not due to varying amounts of water present in the crystals was shown by our obtaining similar mass spectra regardless of whether the crystals were handled with rigorous exclusion of water or in the presence of atmospheric moisture.

The major products, occurring in about equal amounts, appear to be CH₃CHO and CH₂CD₂CO. The mass 47 peak is no greater than is the mass 45 peak for ordinary acetaldehyde; therefore, there is no evidence of CD₃CHO or CD₂HCDO.

Typical mass spectral data follow:
Table IV

Mass Spectral Data* for CH$_2$CHO (A.P.I. Catalog) and for Acetaldehyde from [(CH$_3$)$_2$NCH$_2$CD$_2$OH]$^+Cl^-$

<table>
<thead>
<tr>
<th>Mass (m/e)</th>
<th>CH$_2$CHO</th>
<th>Deuterated Acetaldehyde**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt. 1</td>
<td>Expt. 2</td>
</tr>
<tr>
<td>29</td>
<td>100.0</td>
<td>11.6</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>100.0</td>
</tr>
<tr>
<td>43</td>
<td>26.7</td>
<td>14.7</td>
</tr>
<tr>
<td>44</td>
<td>45.7</td>
<td>10.9</td>
</tr>
<tr>
<td>45</td>
<td>1.2</td>
<td>33.8</td>
</tr>
<tr>
<td>46</td>
<td>0.1</td>
<td>16.8</td>
</tr>
<tr>
<td>47</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*Relative peak heights  
**Representative data from a total of 13 experiments

Acetaldehyde from [(CH$_3$)$_3$NCH$_2$CH$_2$OD]$^+Cl^-$—The mass spectral data are presented in Table V.

Table V

Mass Spectral Data* for CH$_2$CHO (A.P.I. Catalog) and for Acetaldehyde from [(CH$_3$)$_3$NCH$_2$CH$_2$OD]$^+Cl^-$

<table>
<thead>
<tr>
<th>Mass (m/e)</th>
<th>CH$_2$CHO</th>
<th>Deuterated Acetaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt. 1</td>
<td>Expt. 2</td>
</tr>
<tr>
<td>29</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>2.5</td>
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<tr>
<td>43</td>
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<td>22.3</td>
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<tr>
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<td>45.7</td>
<td>43.0</td>
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<tr>
<td>45</td>
<td>1.2</td>
<td>20.7</td>
</tr>
<tr>
<td>46</td>
<td>0.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*Relative peak heights

There are three conclusions to be drawn from the data of Table V:  
(1) There is a small, but definite, fraction of deuterium appearing in the aldehyde group (mass 30)—that is, a small amount of CHO is formed;  
(2) a considerably greater fraction appears in the methyl group (mass 45 =
CH₂DCHO)₅ and (3) the increase of mass 45 (= CHD₂CHO) shows that intermolecular hydrogen transfer occurs during the radiolysis.

Acetaldehyde from [(CH₃)₂NCH₂CD₂OD]⁺Cl⁻—The mass spectral data for the acetaldehyde from this triply-deuterated choline is presented below.

Table VI

<table>
<thead>
<tr>
<th>Mass (m/z)</th>
<th>CH₃CHO</th>
<th>Deuterated Acetaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>100.0</td>
<td>7.1</td>
</tr>
<tr>
<td>30</td>
<td>1.1</td>
<td>100.0</td>
</tr>
<tr>
<td>43</td>
<td>26.7</td>
<td>6.2</td>
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<tr>
<td>44</td>
<td>45.7</td>
<td>10.5</td>
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<tr>
<td>45</td>
<td>1.2</td>
<td>17.1</td>
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<tr>
<td>46</td>
<td>0.1</td>
<td>24.5</td>
</tr>
<tr>
<td>47</td>
<td>--</td>
<td>15.5</td>
</tr>
<tr>
<td>48</td>
<td>--</td>
<td>4.9</td>
</tr>
</tbody>
</table>

*Relative peak heights

The peak at mass 48 shows that some perdeuterio-acetaldehyde is formed. This is further evidence (added to that presented in Tables III and IV) that intermolecular hydrogen transfers take place during the radiation decomposition process.

Trimethylamine from Deuterated Cholines—The data of Table VII establish the failure of hydrogens to transfer from the ethanol moiety to the trimethylamine during the radiolysis.
Table VII

Mass Spectral Data\textsuperscript{a} for (CH\textsubscript{3})\textsubscript{3}N (A. P. I. Catalog and Our Data) and for Trimethylamine from Deuterated Choline Chlorides\textsuperscript{b, c}

<table>
<thead>
<tr>
<th>Mass (m/z)</th>
<th>(CH\textsubscript{3})\textsubscript{3}N A. P. I.</th>
<th>Trimethylamine from Deuterated Choline Chlorides\textsuperscript{d}</th>
<th>$\text{CH}<em>{3}\text{CD}</em>{3}\text{Cl}$</th>
<th>$\text{CH}<em>{3}\text{CD}</em>{2}\text{OH}$</th>
<th>$\text{CH}<em>{3}\text{CH}</em>{2}\text{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>6.3</td>
<td>6.8</td>
<td>4.9</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>33.7</td>
<td>43.0</td>
<td>37.1</td>
<td>35.0</td>
<td></td>
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<tr>
<td>16</td>
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<td>1.1</td>
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<td>0.7</td>
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<td>17</td>
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<tr>
<td>19</td>
<td>30.7</td>
<td>43.7</td>
<td>46.0</td>
<td>45.0</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.3</td>
<td>1.6</td>
<td>1.6</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Relative peak heights

\textsuperscript{b}Trimethylamine, from the radiolysis of ordinary choline chloride, after GLC purification on dimethylsulfoxolane

\textsuperscript{c}Representative data only—either two or three experiments were done on each deuterated choline. For each compound, the separate determinations of trimethylamine mass spectra were in good agreement.

Deuterium Contents of CH\textsubscript{3}I from CH\textsubscript{3}CHO.—The deuterium contents in the methyl group of acetaldehyde products were checked by measurements of the mass spectra of the CH\textsubscript{3}I obtained from aliquots of the different acetaldehydes. This was done in seven different experiments and, in all cases, the deuterium found in the CH\textsubscript{3}I (ratios of masses 142:143:144:145) followed closely that found in CH\textsubscript{3}CHO (ratios of masses 44:45:46:47).

The finding of significant mass 145 (\textsuperscript{14}D\textsubscript{3}I) from the acetaldehyde from N-methylenone deuterated choline is further substantiation of our conclusion that intermolecular hydrogen transfer is occurring.

Summary and Conclusions

The results presented in this paper have increased our understanding of the mechanism of the unique radiation decomposition of crystalline choline chloride. Unfortunately, however, we still have no understanding of why choline chloride is so sensitive to ionizing radiation. What we now further know about the mechanism, as a result of the present work, is
the following:

(1) The carbon atoms of the ethanol moiety maintain their identities during the mechanism leading to the production of acetaldehyde—i.e., the oxygen atom remains attached to the same carbon, and there is no symmetrical intermediate.

(2) None of the hydrogen atoms of the three methyl groups of choline chloride appear in the radiolytically-produced acetaldehyde.

(3) The five hydrogen atoms of the ethanol moiety show considerable mobility during the radiolysis. It is difficult to give quantitative values for these hydrogen transfers, but the following intramolecular processes do occur:

(a) Unexpectedly, protons are often lost from the N-methylene group during its transition to the methyl group of the acetaldehyde. Sometimes N-CH₂ hydrogens appear in the CH₃ group of the acetaldehyde. More often, a detached N-CH₂ hydrogen is simply eliminated (to appear as HCl).

(b) O-methylene hydrogens appear to have about equal probabilities of elimination and of appearance in the acetaldehyde methyl group.

(c) Hydroxyl hydrogens usually are eliminated, but their elimination probability is only about twice that of their appearance in the acetaldehyde methyl group. This latter appearance is, in turn, about ten times as probable as appearance in the acetaldehyde CH₃ group.

(d) Although they are only minor processes, intermolecular hydrogen transfers do take place. Transfers to another molecule occur in the cases of the N-methylene and hydroxyl hydrogens, but do not involve O-methylene hydrogens.