ON TWO DIRECTIONS OF THE DEHYDROCHLORINATION REACTION OF LOWER ALKYLENE CHLOROHYDRINS

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Abstract

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ON TWO DIRECTIONS OF THE DEHYDROCHLORINATION REACTION OF LOWER ALKYLENE CHLOROHYDRINS

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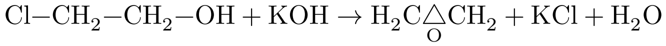
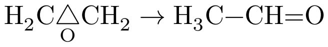
In 1959 it will be one hundred years since A. Wurtz described the reaction of dehydrochlorination of ethylene chlorohydrin in an alkaline medium, as a result of which a new compound—ethylene oxide—was obtained for the first time (1):



$$Cl{-}CH_2{-}CH_2{-}OH + KOH \rightarrow H_2C\underset{O}{\triangle}CH_2 + KCl + H_2O$$

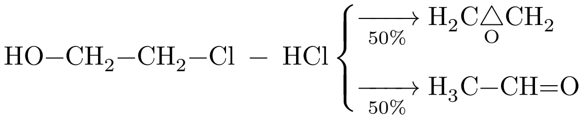
At the present time this reaction underlies the industrial preparation of ethylene oxide from ethylene with the aid of chlorine (2). In carrying out this reaction with lime milk, in practice ethylene oxide is always obtained with an admixture of acetaldehyde in an amount of approximately 1-2% (3). Until very recently no significance was attached to this circumstance, or it was assumed that small impurities of aldehyde could be formed through a secondary isomerization reaction of ethylene oxide:



$$H_2C\underset{O}{\triangle}CH_2 \rightarrow H_3C{-}CH{=}O$$

In 1939 a French patent was published (4) on the formation of considerable quantities of aldehydes (or ketones) along with α-oxides during the dehydrochlorination of aliphatic chlorohydrins in a medium of "magnesia milk." The subject of the patent did not draw the attention of chemists to the dual reactivity of a simple compound—ethylene chlorohydrin.

Several years ago (5) we undertook a detailed study of the process of dehydrochlorination of ethylene chlorohydrin (ECH) in various media and under various conditions. We showed that the presence in the medium of the ordinarily used "lime milk" of artificially added calcium chloride increases the yield of acetaldehyde in the decomposition of ECH to 3-4%. We also examined the process of dehydrochlorination of ECH in a medium of "magnesia milk" at boiling. Under the conditions of our experiments, up to 98% of the ECH taken was dehydrochlorinated; of this, up to 35% with formation of ethylene oxide and up to 50% with formation of acetaldehyde; about 15% of the ECH was converted into ethylene glycol. We specially demonstrated that ethylene glycol is formed only by hydration of the ethylene oxide formed initially. Taking the latter into account, it may be said that, upon dehydrochlorination of ECH in a medium of boiling magnesia milk (10%), as a result of the elimination of hydrogen chloride, ethylene oxide and acetaldehyde are formed in approximately equal amounts:



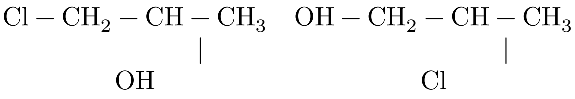
$$HO{-}CH_2{-}CH_2{-}Cl\ -\ HCl \begin{cases} \xrightarrow[50\%]{} H_2C\underset{O}{\triangle}CH_2 \\ \xrightarrow[50\%]{} H_3C{-}CH{=}O \end{cases}$$

In the course of further investigations it was found (⁵) that, in the dehydrochlorination of ECH in a medium of a boiling aqueous suspension of nickel hydroxide hydrate (10% $Ni(OH)_2$), acetaldehyde is formed practically as the sole reaction product, with yields based on ECH of up to 98%, while ethylene oxide is present as an "impurity" in insignificant amount.

Thus, the fact is confirmed that even such a simple compound as ECH, depending on the nature of the reagent acting on it $(Ca(OH)_2, Mg(OH)_2, Ni(OH)_2)$, exhibits a clearly expressed dual reaction capacity.

It is of interest to study the features of the dehydrochlorination reaction of ECH. The first supposition in this connection is that ethylene oxide in all the cases considered above is the primary product, while the aldehyde is formed from it by isomerization to one degree or another (depending on the reagent).

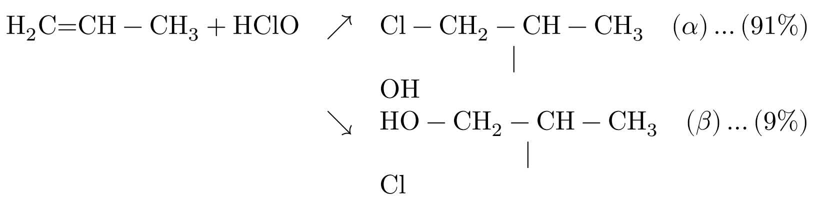
In order to facilitate the experimental verification of such a supposition, we turned to the dehydrochlorination reaction of propylene chlorohydrin (PCH), taking into account that the latter exists in two isomeric forms:



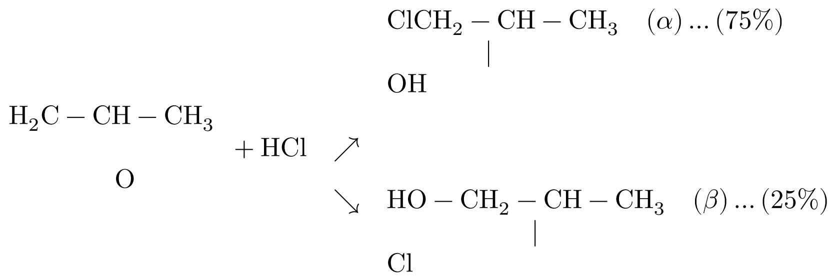
$$\underset{\substack{\text{I} \\ (\alpha\text{-form})}}{Cl - CH_2 - \underset{\substack{|\\ OH}}{CH} - CH_3} \qquad \underset{\substack{\text{II} \\ (\beta\text{-form})}}{OH - CH_2 - \underset{\substack{|\\ Cl}}{CH} - CH_3}$$

The dehydrochlorination reaction of PCH, proceeding under the same conditions and just as readily as for ECH, usually does not lead to yields of propylene oxide above 85%. The reasons for the reduced yields of propylene oxide in the dehydrochlorination of PCH remain unclear to this day.

Propylene chlorohydrin can be prepared in two ways: by hypochlorination of propylene and by hydrochlorination of propylene oxide. We made use of the circumstance that both these routes lead to the formation of mixtures of PCH isomers that differ appreciably in composition (⁶).

I


$$H_2C{=}CH-CH_3+HClO \begin{array}{l} \nearrow\ Cl-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \quad (\alpha)\ldots(91\%) \\ \searrow\ HO-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \quad (\beta)\ldots(9\%) \end{array}$$

II


$$\underset{\displaystyle O}{H_2C-CH}-CH_3+HCl \begin{array}{l} \nearrow\ ClCH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \quad (\alpha)\ldots(75\%) \\ \searrow\ HO-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \quad (\beta)\ldots(25\%) \end{array}$$

On decomposition of PCH of any origin in boiling "lime milk," we obtained identical yields of propylene oxide (84-85%). The amount of propionaldehyde corresponded to 2-3% of PCH; more than 10% of PCH was converted into propylene glycol. We showed that the conversion of PCH into glycol, just as in the case of ECH, does not proceed by direct saponi-

of chlorine, but through the propylene oxide formed as an intermediate and its subsequent hydration. The yield of propylene glycol here is greater than that of ethylene glycol in the dehydrochlorination of ECH because propylene oxide is more readily hydrated than ethylene oxide (7). In full accordance with this, the yield of propylene oxide in the dehydrochlorination of PCH is lower than the corresponding yield of ethylene oxide.

In Table 1 we give the results of dehydrochlorination of two mixtures of PCH isomers in an excess medium (up to 300% of the stoichiometric amount) of boiling "milk of magnesia" (about 15% $Mg(OH)_2$).

Table 1

Dehydrochlorination of mixtures of propylene chlorohydrin isomers in a boiling aqueous suspension of $Mg(OH)_2$

Isomeric composition of PCH, %	Isomeric composition of PCH, %	Yield in % based on the initial PCH	Yield in % based on the initial PCH	Yield in % based on the initial PCH	Yield in % based on the initial PCH	Yield in % based on the initial PCH	$\frac{PO + PG}{PA + AS}$
α	β	unconverted PCH	propylene oxide (PO)	propylene glycol (by difference) (PG)	allyl alcohol (AS)	propionaldehyde (PA)	
91	9	7.5	62.5	22.2	1.9	5.9	11.2
91	9	7.1	52.0	33.4	1.9	5.6	11.4
91	9	6.5	61.6	24.6	1.7	5.6	11.8
91	9	6.8	60.7	23.0	2.3	6.4	9.7
75	25	1.0*	64.5	9.8	0.3	24.4	3.0
75	25	1.3*	67.2	6.3	0.2	25.0	2.9

* The milk of magnesia was stronger (up to 30% $Mg(OH)_2$), and its amount relative to PCH was larger (up to 500%).

The data given in Table 1 provide grounds for the conclusion that the composition of the products formed depends on the isomeric composition of the initial PCH.

Thus, when this composition changes from $\frac{\alpha}{\beta} = 10 : 1$ to $\frac{\alpha}{\beta} = 3 : 1$, the ratio of the products formed also changes approximately, as is seen from the last column of Table 1. Apparently, the aldehyde and the alcohol are formed only from the β-isomer or, at least, predominantly from it.

We next turned to experiments on the dehydrochlorination of a mixture of PCH isomers in a boiling aqueous suspension of nickel oxide hydrate. As indicated above, in such a medium ($Ni(OH)_2$) ECH is dehydrochlorinated almost entirely in the direction of formation of acetaldehyde. In the experiments a 20% suspension of $Ni(OH)_2$ was taken, with a 200% excess relative to the stoichiometric amount.

The data given in Table 2 support to an even greater degree the suggestion stated above, namely that propionaldehyde is formed only from the β-isomer of PCH. This becomes still more evident if the yield of propionaldehyde is calculated only on the β-isomer: it amounts on average to about 85%.

We isolated from the reaction mixture (Table 2) the PCH that had not entered into reaction. Obviously, it must have consisted entirely of the α-isomer, since the β-isomer had been completely dehydrochlorinated in the $Ni(OH)_2$ medium.

With this PCH (the α-isomer) we repeated the experiment on its dehydrochlorination under the former conditions, i.e., in an excess of a boiling aqueous suspension of $Ni(OH)_2$. As could be expected, the reaction did not proceed at all; no noticeable amounts of dehydrochlorination products were detected. We carried out in parallel, dehydrochlorination of another portion of the same PCH, but in a boiling aqueous suspension of $Ca(OH)_2$; in the latter case a high yield of propylene oxide (about 85%) was obtained.

Table 2

Dehydrochlorination of mixtures of propylene chlorohydrin isomers in a boiling aqueous suspension of $Ni(OH)_2$

Isomeric composition of PCH, %	Isomeric composition of PCH, %	Yield, % based on initial PCH	Yield, % based on initial PCH	Yield, % based on initial PCH	Yield, % based on initial PCH	Yield, % based on initial PCH
α	β	unreacted PCH	propylene oxide	propylene glycol	propionaldehyde	allyl alcohol
75	25	69.2	4.2	4.8	21.3	0.1
75	25	69.8	3.6	4.3	21.6	0.1
75	25	71.8	4.6	5.0	18.3	0.5

Conclusions

1. Propionaldehyde is formed in appreciable amounts during the dehydrochlorination of PCH only in suitable media, such as an aqueous suspension of magnesium hydroxide and especially nickel hydroxide. In this respect the same regularity is observed as in the dehydrochlorination of ECH.
2. Propionaldehyde is formed during the dehydrochlorination of PCH in a suitable medium ($Ni(OH)_2$) only from the β-isomer. Under the same conditions the α-isomer not only does not form aldehyde, but in general does not undergo dehydrochlorination.
3. The α-isomer of PCH, like its β-isomer, is dehydrochlorinated with equal ease in basic media: $(NaOH, KOH, Ca(OH)_2)$, with formation of propylene oxide. Propionaldehyde arises under the conditions of PCH dehydrochlorination not through isomerization of propylene oxide.
4. During the dehydrochlorination of ECH in media of $Mg(OH)_2$ and $Ni(OH)_2$, acetaldehyde is formed not as a result of isomerization of ethylene oxide, but arises as a consequence of an independent process directly from ECH.

5. Such simple compounds as ECH and PCH, upon dehydrochlorination, exhibit dual reactivity, depending on the composition of the medium in which the dehydrochlorination reactions are carried out: in one case, as a result of elimination of a molecule of hydrogen chloride, α-oxides are formed; in the other, carbonyl compounds (aldehydes) are formed.

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Note: Figure translations are in progress. See original paper for figures.

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