Rate Constants and Reaction Products of the Alkaline Hydrolysis of Ethylene and Trimethylene Chlorohydrins with Alkyl Substituents

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The hydrolysis of the two series of alkyl-substituted ethylene chlorohydrins of the types

$RCHOHCH_2Cl$ and $RCHClCH_2OH$

have been kinetically investigated at 20.00 °C in alkaline aqueous solution. As with other ethylene chlorohydrins that have been investigated, these gave good second-order constants, and the reaction products were found to be the corresponding oxides. The following constants (k_{20} mole litre^{-1} min^{-1}) were obtained in the two series.

CH_2OHCH_2Cl	$k_{20} = 0.332$
$CH_3CHOHCH_2Cl$	$k_{20} = 7.85$
$C_2H_5CHOHCH_2Cl$	$k_{20} = 9.60$
n-$C_3H_7CHOHCH_2Cl$	$k_{20} = 9.50$
i-$C_3H_7CHOHCH_2Cl$	$k_{20} = 12.3$
$CH_2CHClCH_2OH$	$k_{20} = 2.65$
$C_2H_5CHClCH_2OH$	$k_{20} = 2.41$
n-$C_3H_7CHClCH_2OH$	$k_{20} = 2.71$
i-$C_3H_7CHClCH_2OH$	$k_{20} = 1.14$

The chlorohydrins of the type $RCHOHCH_2Cl$ were prepared by Grignard syntheses from chloroacetaldehyde and alkyl bromides. The chlorohydrins of the type $RCHClCH_2OH$ were prepared from the corresponding chlorosubstituted acid chlorides by reduction with lithium aluminium hydride.

In order to investigate the corresponding reactions of the trimethylene chlorohydrins, compounds of the types

$RCHOHCH_2CH_2Cl$ and $RCHClCH_2CH_2OH$

were synthesized using the same methods as in the case of the ethylene chlorohydrins. — The compounds $RCHOHCH_2CH_2Cl$ from alkylmagnesium bromides and β-chloropropionaldehyde and the compounds $RCHClCH_2CH_2OH$ by lithium aluminium hydride and β-chlorosubstituted acid chlorides.

They were also found to give good second-order constants, but the rates of the alkaline hydrolysis were much slower than for the corresponding ethylene chlorohydrins. The rate constants were therefore measured at 80.07° C (k_{80} mole litre^{-1} min^{-1}). At that temperature there is also a first-order reaction with water (hydrolysis, yielding hydrochloric acid) that must be measured in pure water in order to calculate the second-order constants from the measurements in the alkaline solution.

$CH_2OHCH_2CH_2Cl$	$k_{80} = 0.0212$
$CH_3CHOHCH_2CH_2Cl$	$k_{80} = 0.049$
$C_2H_5CHOHCH_2CH_2Cl$	$k_{80} = 0.071$
n-$C_3H_7CHOHCH_2CH_2Cl$	$k_{80} = 0.069$
i-$C_3H_7CHOHCH_2CH_2Cl$	$k_{80} = 0.12$
$CH_3CHClCH_2CH_2OH$	$k_{80} = 0.45$
$C_2H_5CHClCH_2CH_2OH$	$k_{80} = 0.79$
n-$C_3H_7CHClCH_2CH_2OH$	$k_{80} = 0.79$
i-$C_3H_7CHClCH_2CH_2OH$	$k_{80} \sim 1.5$

As in the case of the ethylene chlorohydrins, the unsubstituted trimethylene chlorohydrin and the chlorohydrins of the type $RCHOHCH_2CH_2Cl$ gave the corresponding trimethylene oxides in alkaline aqueous solution. The chlorohydrins of the type $RCHClCH_2CH_2OH$ gave no oxides but were decomposed with the formation of formaldehyde and an alkene as shown in the equation.

$$RCHClCH_2CH_2OH + OH^- \longrightarrow RCH{=}CH_2 + CH_2O + H_2O + Cl^-$$

Thus in alkaline solution the carbon chain of the compounds $RCHClCH_2CH_2OH$ is cleaved. The alkenes were identified through their boiling-points (in the case of propylene, also through the bromo addition-compound), and the formaldehyde through the color reactions with orcinol [1] and resorcinol [2]. The compounds of the type $RCHOHCH_2CH_2Cl$ gave no alkenes and no reaction of formaldehyde.

After the termination of this investigation a publication by Searles and Gortatowski [3] appeared in which the alkaline hydrolysis of 3-bromo-2,2-dimethyl-propanol was discussed. According to their investigations this compound gave oxide and simultaneously *iso*butylene and formaldehyde in alkaline solution. I have found also that 3-chloro-2,2-dimethyl-propanol gave formaldehyde when it was treated with alkali.

A more detailed report on these reactions will be published in the near future.

1. Sumner, J. B. *J. Am. Chem. Soc.* **45** (1923) 2378.
2. Walker, J. F. *Formaldehyde*, New York, 1953, p. 370.
3. Searles, S., and Gortatowski, M. J. *J. Am. Chem. Soc.* **75** (1953) 3031.

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Chemical Analysis of a New Mineral, Bøggildite, from Ivigtut, Greenland

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In 1950 the late Richard Bøgvad, chief geologist to "Kryolitselskabet Øresund A/S", discovered a hitherto unknown mineral in the cryolite mine at Ivigtut. Bøgvad published a provisional notice [1] of this mineral of which he had prepared a thorough investigation. His plans were brought to an end by his sudden death on August 7, 1952; but not before Bøgvad had named the new mineral "bøggildite" in honour of O. B. Bøggild, professor emer. of the University of Copenhagen.

In January 1951 Bøgvad handed over to me 4.4 g of pulverised bøggildite. Of this material a sample was sent to the Central Laboratory of "Bolidens Gruvaktiebolag", Sweden, for spectrographic estimations. The results of these were in reasonable agreement with the chemical-analytical data. — 0.5 g were reserved for X-ray and crystaloptic investigations. — The rest of the material I have used for quantitative analyses, the results of which are given below.

As regards the purity of the material Bøgvad stated that "the material for analysis only contains a very slight trace of quartz and "ivigtite". Further, traces were found of presumed sphalerite in particles about 1 μ large. Otherwise it is very pure".

Chlorine, zinc, and cerium were sought for by microanalytical methods, but were not detected. The alkalies were determined by the method of Wells and Stevens [2].

Formula for bøggildite: $Na_2Sr_2Al_2(PO_4)F_9$. Mol.wt. calculated from the analysis = 543.3.

On heating in a glass tube over a Bunsen burner the mineral melts and deposits a small quantity of white sublimate.

Chemical Analysis of Bøggildite from Ivigtut.

	Weight %	Ionic ratios		Number of ions
Al	10.04	0.372	0.373	2.01
Fe	0.06	0.001		
Sr	31.89	0.364	0.379	2.04
Ba	0.35	0.003		
Mg	0.18	0.007		
Ca	0.20	0.005		
Mn	trace	—		
Na	8.60	0.374	0.378	2.03
K	0.15	0.004		
Li	trace	—		
PO_4	17.63	0.186	0.186	1.00
F	31.70	1.668	1.668	8.97
$H_2O\pm$	none	—		
Total	100.80			

1. Bøgvad, R. *Medd. Dansk Geol. Foren.* **12** (1951) 109; Bøggild, O. B. *The Mineralogy of Greenland. Medd. Grønland* **149** No. 3 (1953) 439.
2. Wells, R. C., and Stevens, R. E. *Ind. Eng. Chem. Anal. Ed.* **6** (1934) 439.

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