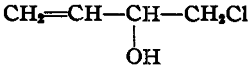
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PITTSBURGH PLATE GLASS CO., COLUMBIA CHEMICAL DIVISION]

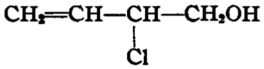
The Hydrolysis Rates of the Three Butadiene Monochlorohydrins

BY RICHARD G. KADESCH

The addition of one molecule of hypochlorous acid to butadiene might possibly yield any of the three chlorohydrins, I, II and III.


$CH_2{=}CH{-}CH(OH){-}CH_2Cl$

I


$CH_2{=}CH{-}CH(Cl){-}CH_2OH$

II

$ClCH_2{-}CH{=}CH{-}CH_2OH$

III

These isomers offer some interesting variations in structure; I is an α-chlorohydrin, III an allylic chloride and II has both of these structural features.

The kinetics of the hydrolysis of a few α-chlorohydrins have been studied by previous workers. The reactions of ethylene chlorohydrin,[1a] propylene chlorohydrin[1] and glycerol α-chlorohydrin[2] with hydroxide ion have been reported to be second order. The hydrolysis of propylene chlorohydrin by water is stated to be bimolecular.[3] The hydrolysis of allyl type chlorides in basic media has been shown to involve simultaneous unimolecular (S_N1) and bimolecular (S_N2) mechanisms,[4,5] the relative amounts of which depend on the structure and the reaction conditions.

Of the chlorohydrins studied in the present work I and III were prepared directly from butadiene and hypochlorous acid[6,7] while II was prepared by the addition of hydrochloric acid to 3,4-epoxy-1-butene.[6b,7]

In the present work the hydrolysis rates were determined in aqueous solution, generally with the chlorohydrin and sodium hydroxide (when used) at 0.1 *M*, the reaction being followed by the determination of chloride ion. With I and sodium hydroxide several different relative concentrations were used without any appreciable change in the second order *k*'s. Results of one of these experiments are shown in Table I, the extreme speed of the reaction preventing a better constancy in the *k*'s due to the relatively large time required in withdrawing the samples for analysis. In the case of hydrolysis of I by base at 25° and of II at 0° the *k*'s are even greater and only rough values may be given. For example, the hydrolysis of 0.03 *M* II by 0.03 *M* sodium hydroxide at 0° was about 65% complete after one minute.

In the hydrolysis of II by water at 70° the plot of chloride ion against time was asymptotic with the line corresponding to 92% hydrolysis. It was concluded that there was 8% of a relatively inert impurity, probably I,[8] present. This was deducted in order to get the true initial concentration of II for the calculation of *k*. One of the runs is shown in Table II. All of the results are summarized in Table III.

It was possible to isolate 3,4-epoxy-1-butene

TABLE I

HYDROLYSIS OF 1-CHLORO-3-BUTEN-2-OL (I) IN AQUEOUS SODIUM HYDROXIDE AT 0°

Initial I = NaOH = 0.0948 mole/liter

Time, min.	Cl^- concn.	2nd order *k*, $min.^{-1}$ g. $moles^{-1}$ liter
0	0.0000	..
2.5	.0292	1.88
7	.0495	1.52
15	.0659	1.57
30	.0782	1.71
		Mean 1.67

TABLE II

HYDROLYSIS OF 2-CHLORO-3-BUTEN-1-OL (II) IN WATER AT 30°

Initial II = 0.0940 mole/liter

Time, hr.	Cl^- concn.	1st order $k \times 10^3$, $min.^{-1}$
0	0.0000	...
8.00	.0290	0.768
25.17	.0634	.731
72.12	.0904	.753
		Mean .751

TABLE III

HYDROLYSIS OF BUTADIENE MONOCHLOROHYDRINS

Chlorohydrin	Temp., °C.	Hydrolysis by	1st ord. *k*	2nd ord. *k*
I	0	NaOH	....	1.7
I	25	NaOH	....	30
I	70	Water	5.5×10^{-6}	...
II	0	NaOH	....	70
II	30	Water	7.51×10^{-4}	...
II	50	Water	0.0094	...
II	60	Water	.0282	...
II	70	Water	.068	...
III	30	Water	.0012	...
III	30	NaOH	....	0.89
III	50	Water	.022	...

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[1] (a) Smith, Holm and Svenonius, *Z. physik. Chem.*, **152**, 153 (1931); (b) Smith, *et al.*, *Ber.*, **55B**, 3143 (1922), and earlier papers.

[2] Drozdov and Cherntzov, *J. Gen. Chem.* (*U. S. S. R.*), **4**, 1305 (1934); *C. A.*, **29**, 3306 (1935); Smith, *et al.*, *Ber.*, **61**, 1709 (1928), and earlier papers.

[3] Kedrinskii and Merson, *C. A.*, **31**, 6092 (1937).

[4] Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[5] Young and Andrews, THIS JOURNAL, **66**, 421 (1944).

[6] (a) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 131 (1938); *C. A.*, **32**, 4524, 5369 (1938); (b) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 991 (1941); *C. A.*, **37**, 1699 (1943).

[7] R. G. Kadesch, THIS JOURNAL, **68**, 41 (1946).

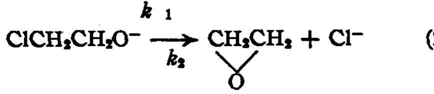
[8] The impurity is regarded as I because of the method of preparation (addition of hydrochloric acid to 3,4-epoxy-1-butene) and because the boiling points of I and II at 30 mm. lie only 3° apart.

in 87% yield after the treatment of 2.5% aqueous I with sodium hydroxide at room temperature.

Discussion

The second order kinetics for the α-chlorohydrin → epoxide conversion observed in the present work and elsewhere[1,2] is consistent with the mechanism

$$\mathrm{ClCH_2CH_2OH + OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ClCH_2CH_2O^- + H_2O} \quad (1)$$



$$\mathrm{ClCH_2CH_2O^-} \xrightarrow[k_2]{} \mathrm{CH_2CH_2 + Cl^-} \quad (2)$$

which has been suggested by Winstein and Lucas.[9b] The extreme speed of the reaction and the occurrence of inversion[9] are a consequence of the intramolecular nucleophilic ($S_N{}^2$) displacement of step 2. Nucleophilic displacement reactions in general involve Walden inversion[10] and the rapidity of this displacement arises from the close proximity in space of the reacting groups in the intermediate alkoxide ion.

The rate expression derived from this mechanism is

$$\frac{d(\mathrm{Cl^-})}{dt} = \frac{k_1k_2(\mathrm{Chl.})(\mathrm{OH^-})}{k_{-1}(\mathrm{H_2O})} = k(\mathrm{Chl.})(\mathrm{OH^-})$$

which indicates that the over-all rate depends both on the acidity of the chlorohydrin (k_1/k_{-1}, the equilibrium constant of step 1) and on k_2.[11]

The available data are listed below in the order of decreasing k.

$R_1CH(OH)CHR_2Cl$ R_1	 R_2	k min.$^{-1}$ g. moles^{-1} l.	Temp., °C.	Ref.
H	$CH_2{=}CH$ (II)	70	0	Present work
$CH_2{=}CH$	H (I)	1.7	0	Present work
CH_3	H	6.5	18	1
H	H	0.62–0.68	25	1
H	H	0.54	25	Present work

Attempts to interpret these data on the basis of the usual effects of substituents R_1 and R_2 on the acid strength of organic molecules and on the rates of $S_N{}^2$ type reactions were only partially successful. It may be that substituents also exert a steric influence[12] on the formation of the three-membered epoxide ring in a manner similar to that postulated by Thorpe, Ingold, *et al.*, for certain ring closures to give cyclopropane derivatives.[13]

The pronounced increase in the rate of hydrolysis of III in the presence of alkali is similar to the behavior observed for allyl and crotyl chlorides.[4,5] The latter has been shown to hydrolyze by the simultaneous operation of the $S_N{}^1$ and $S_N{}^2$ mechanisms.[5] Whether or not alkali would bring the $S_N{}^2$ mechanism into play for II, thus increasing its hydrolysis rate (which it does not do in the case of a close analog, 3-chloro-1-butene, that hydrolyzes solely by the $S_N{}^1$ mechanism[4,5]) cannot be determined since extremely rapid epoxide formation intervenes.

Experimental

Preparation of 1-Chloro-3-buten-2-ol (I).—I was obtained by the addition of hypochlorous acid to butadiene as already described.[7] This was refluxed with an equal volume of water for five hours to remove small amounts of hydrolyzable chlorine-containing impurities.[14] The lower chlorohydrin layer, which contains about 15% of water, was distilled through a 2 × 43-cm. Fenske column packed with 0.25-inch glass Raschig rings. After the fore-runs containing water there was obtained I at 76° (60 mm.), n^{20}D 1.4643.

Preparation of 2-Chloro-3-buten-1-ol (II).—This was prepared by the reaction of hydrochloric acid with 3,4-epoxy-1-butene[7] and redistilled through a 1.7 × 75-cm. Fenske column packed with $^1/_8$-inch glass helices, b. p. 69.5–70.0° (30 mm.), n^{20}D 1.4665.

Preparation of 1-Chloro-2-buten-4-ol (III).—While still cold the butadiene–hypochlorous acid (0.57 mole) reaction mixture from another preparation was extracted immediately five times with one-fifth its volume of methylene chloride. The combined extracts were dried over anhydrous potassium carbonate and the methylene chloride distilled off. The remainder was distilled through a 25-cm. column packed with a wire spiral. The main fraction was 1-chloro-3-buten-2-ol, b. p. 66–69° (33 mm.), 30.5 g., 50% yield. An intermediate fraction of 1.5 g. came over at 64° (15 mm.) to 64° (5 mm.) and then the 1-chloro-2-buten-4-ol at 67–69° (4–5 mm.), 11.3 g., 18.6% yield. A residue of 5.4 g., remained. Some 1-chloro-2-buten-4-ol was redistilled, b. p. 64–65° (2 mm.), n^{20}D 1.4845.

Anal. Calcd. for C_4H_7OCl: Cl, 33.3; unsat. equiv.. 106.5. Found: Cl, 32.9; unsat. equiv., 104 (bromate-bromine method).

Conversion of I to 3,4-Epoxy-1-butene (Performed by Mr. Henry Stevens).—To 0.47 mole of 2.5% aqueous 1-chloro-3-buten-2-ol was added 40 g. of 50% aqueous sodium hydroxide at room temperature. Distillation at 20 mm. pressure enabled the recovery of 87% of 3,4-epoxy-1-butene from the mixture.

Rates of Reaction of Butadiene Monochlorohydrins with Sodium Hydroxide and with Water.—Into a 100-ml. volumetric flask was weighed the chlorohydrin. This was placed in the thermostat (temperature within 0.1° as determined by Bureau of Standards thermometer) and brought to temperature. In the hydrolyses with water alone, the water, previously brought to temperature, was quickly added to the mark. In the hydrolyses with sodium hydroxide the alkali and chlorohydrin were made up to the mark in separate volumetric flasks and quickly mixed. Or, if the chlorohydrin was quite reactive to water alone (II, III), it was diluted as much as possible with water, the desired amount of standard aqueous sodium hydroxide quickly added and the final volume adjustment made. Aliquot portions were withdrawn at intervals and run into very dilute nitric acid and ice before titrating for chloride ion by the Volhard method.

Hydrolysis of II in Water at 70°.—2-Chloro-3-buten-1-ol was hydrolyzed in water (0.01022 mole/liter) at 70° as described above. The extent of hydrolysis after 0.37, one, three and six hours was 73.5, 90.1, 91.4 and 91.7%, respectively.

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(9) (a) Wilson and Lucas, THIS JOURNAL, 58, 2396 (1936); (b) Winstein and Lucas, *ibid.*, 61, 1576 (1939); (c) Lucas, Schlatter and Jones, *ibid.*, 63, 22 (1941); (d) Winstein and Henderson, *ibid.*, 65, 2196 (1943); (e) Revlos and Tellier, *C. A.*, 39, 926 (1945).

(10) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, Chap. VI.

(11) This results from the reasonable expectation that $k_2 \ll k_{-1}$.

(12) This was suggested by Dr. S. G. Cohen.

(13) Watson, "Modern Theories of Organic Chemistry," 2nd ed., Oxford University Press, New York, N. Y., 1941, p. 230.

(14) Unless the material is given this treatment, it becomes yellow to light brown after standing a few days. Several redistillations of such colored material will also produce a product which will remain water-white.

Acknowledgment.—The author is grateful to Dr. A. Pechukas who suggested this work and to Drs. F. Strain and W. E. Bissinger for helpful discussions.

Summary

1. The rate constants for the hydrolysis of the three butadiene monochlorohydrins by water and by base have been determined.

2. The conversion of the two butadiene α-chlorohydrins to the epoxide by base is extremely rapid. Their second order rate constants have been compared with those of ethylene and propylene chlorohydrins and have been discussed with regard to the mechanism involved.

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[CONTRIBUTION FROM THE DIVISION OF COTTON AND OTHER FIBER CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, SOILS, AND AGRICULTURAL ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Identity of Some Electrodialyzable Constituents of Cotton Root Bark

BY DAVID R. ERGLE, L. E. HESSLER AND J. E. ADAMS

The Soil Fertility unit of the present Bureau of Plant Industry, Soils, and Agricultural Engineering for several seasons studied the effects of soils and fertilizer treatment on the composition of the cotton plant in relation to the incidence of phymatotrichum root rot. This paper presents the results of a systematic attempt, quantitatively to isolate and identify definite organic compounds, principally nitrogenous, from the dialyzates of cotton root bark. Electrodialysis[1,2,3] was used to separate the nitrogen that was subsequently determined as ammonia, amide, amino and basic nitrogen. While these experiments were not completed with respect to determining the relationship to root rot resistance of these organic constituents, it is felt that a record of the occurrence of the indicated compounds in the cotton plant may be of value to other workers.

Experimental[4]

One kilogram of oven-dry, finely ground root bark from mature upland cotton plants was electrodialyzed.[1] The catholyte, containing practically all of the dialyzable organic nitrogen, was investigated for nitrogenous compounds while the anolyte was examined to a limited extent for solid organic acids. The relative importance of the two fractions as investigative materials is shown by their organic nitrogen contents; the catholyte yielded 12.07 g. of nitrogen while the anolyte contained only 0.20 g.

Fractionation of the catholyte into groups suitable for isolation studies was accomplished by methods used by Vickery.[5] Only enough of the methods are given to ensure clarity of presentation.

A partial segregation and concentration of the catholyte nitrogen was effected with aqueous mercuric acetate. The precipitate, after decomposition with hydrogen sulfide, contained the following amounts of nitrogen

Nitrogen	Grams
Ammonia	0.474
Amide	2.978
α-Amino	2.746
Basic	1.049
Other	2.133
Total	9.380

Purines.—The purine fraction contained only 0.024 g. of nitrogen from which no crystalline isolate was made. If either adenine or guanine was present, the amount was small.

Histidine.—Histidine was present as indicated by the diazo reaction,[6] but actual isolation was not accomplished. The nitrogen content of this fraction was 0.104 g.

Arginine.—The amount of nitrogen, 0.707 g., in this group was relatively large and from it arginine was obtained as the monoflavianate, equivalent to 0.555 g. of free arginine.

Anal. Calcd. for $C_{16}H_{20}O_{10}N_6S$: S, 6.56. Found: S, 6.45.

Lysine.—This fraction, containing 0.138 g. of nitrogen, failed to give a crystalline product when treated with picric acid in the conventional manner.

Asparagine.—The solution left after separation of the lysine fraction, when freed of phosphotungstic acid and barium, was concentrated by evaporation and ethanol added until a slight turbidity developed. After standing at 8–10° for several days, asparagine monohydrate separated as transparent rhombic prisms. Total yield of the recrystallized product was 26.5 g. Identification was made both by analysis and by preparation of copper asparaginate.

Anal. (1) Calcd. for $C_4H_8O_3N_2$: N, 21.20. Found: N, 21.21.

Anal. (2) Calcd. for $C_8H_{14}O_6N_4Cu$: N, 17.20. Found: N, 17.11.

Betaine.—The filtrate from the mercuric acetate precipitation, after removal of mercury, contained 1.360 g. of nitrogen. Of this amount, precipitation with phosphotungstic acid accounted for 1.03 g. of basic nitrogen. After removal of reagents and concentrating, part of the betaine was isolated as the picrate. For the remaining betaine, a second and better method was the precipitation of betaine from an alcoholic solution with mercuric chloride. Betaine hydrochloride in fairly pure form was thus obtained after removal of mercury and evaporation to dryness. The combined yield of free betaine by the two methods was 4.46 g. Identification was made by analysis of both derivatives.

Anal. (1) Calcd. for $C_5H_{12}O_2NCl$: N, 9.12. Found: N, 9.25.

Anal. (2) Calcd. for $C_{11}H_{14}O_9N_4$: N, 16.18. Found: N, 16.17.

As shown in Table I these isolations accounted for 46.87% of the total organic nitrogen content of the catholyte.

Oxalic Acid.—The anolyte was examined for solid organic acids amenable to separation by differential solubility of their copper salts.

Concentrated to 150 ml. by evaporation at reduced pressure, the anolyte was treated while hot with a slight

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[1] Collins, *et al.*, *Soil Sci.*, **44**, 217–229 (1937).

[2] Adams, *et al.*, *Proc. Soil Sci. Soc. Am.*, **4**, 329–332 (1939).

[3] Hessler, *et al.*, *J. Am. Soc. Agron.*, **31**, 528–540 (1939).

[4] All melting points uncorrected.

[5] Vickery, *Agr. Exp. Sta. Bull.* (Conn.), **339**, 639–645 (1932).

[6] Kapeller-Adler, *Biochem. Z.*, **271**, 206–208 (1934).