STUDIES OF CONJUGATED SYSTEMS. IX. THE ADDITION OF HYPOCHLOROUS AND HYPOBROMOUS ACIDS TO VINYLACRYLIC ACID

BY IRVING E. MUSKAT AND LESLIE HUDSON

In a recent paper Muskat and Northrup[1] have developed a theory to interpret the addition reactions of conjugated systems. This theory is based on the supposition that conjugated systems differ from non-conjugated systems only in so far as the former may exhibit 1,3-rearrangement, while the latter cannot exhibit this phenomenon. It further assumes that the addition of both components of the addendum to an ethylenic double bond does not occur simultaneously but rather, as has been suggested by Stieglitz,[2] that the essential feature is the attraction of the positive substituting group to the negative carbon valences irrespective of complete saturation. By the application of this theory these authors have shown that in the halogenation of vinylacrylic acid a 1,3-rearrangement is not possible and consequently only 3,4-halogenation can occur. This is in accord with the work of Muskat, Becker and Lowenstein,[3,4] who have shown that in the chlorination and bromination of vinylacrylic acid only 3,4-addition products are formed. As a corollary to the mechanism proposed by these authors, the hypohalous acids should add to vinylacrylic acid in exactly the same manner as do the halogens. The work reported in this paper was undertaken to test this point and contains the results of an investigation on the addition of hypochlorous and hypobromous acids to vinylacrylic acid.

Thiele[5] proved that vinylacrylic acid is reduced, by means of sodium amalgam in alkaline medium, in the 1,4-positions, and not in the 1,2-positions as claimed by Doebner.[6] Ingold and Burton[7] have shown that if vinylacrylic acid is reduced by means of sodium amalgam in acid medium, then 18% of the vinylacrylic acid is reduced in the 1,2-positions while the remainder is reduced in the 1,4-positions. Muskat and Knapp[8] have recently shown that vinylacrylic acid is hydrogenated catalytically in the 3,4-positions. These last investigators have proposed a theory to interpret these varying reduction reactions of conjugated systems.

[1] Muskat and Northrup, THIS JOURNAL, **52**, 4043 (1930).

[2] Stieglitz, *ibid.*, **44**, 1304 (1922).

[3] Muskat, Becker and Lowenstein, *ibid.*, **52**, 326 (1930).

[4] Muskat and Becker, *ibid.*, **52**, 812 (1930).

[5] Thiele, *Ber.*, **35**, 2320 (1902).

[6] Doebner, *ibid.*, **35**, 1136 (1902).

[7] Ingold and Burton, *J. Chem. Soc.*, 2022 (1929).

[8] Muskat and Knapp, *Ber.*, **64**, 779 (1931).

Kohler and Butler,[9] while studying the relative ease of 1,4- and 1,6-addition, showed that sodium malonic ester combines with the esters of vinylacrylic and sorbic acids to give 1,6-addition products, while phenylmagnesium bromide reacts with the same esters to give first the corresponding ketones, which react further to give 1,4-addition products.

Muskat, Becker and Lowenstein[10] have studied the chlorination and bromination of vinylacrylic acid and found that both chlorine and bromine are absorbed in the 3,4-positions.   They also found that 3-chloro- and 3-bromovinylacrylic acids absorb chlorine and bromine, respectively, in the 3,4-positions.   These are the only addition reactions of vinylacrylic acid that have been reported in the literature.

Mokiewsky[11] was the first investigator to study the addition of hypohalous acids to conjugated systems.[12]   He prepared the dichlorohydrin and dibromohydrin of isoprene but did not determine the structure of these compounds.   Muskat and Grimsley[13] have made a detailed study of the addition of hypochlorous and hypobromous acids to phenylbutadiene. They have found that these acids are added to phenylbutadiene in the 3,4-positions to give 3-hydroxy-4-chloro-1-phenylbutadiene and 3-hydroxy-4-bromo-1-phenylbutadiene, respectively.   They also prepared the dichlorohydrin and dibromohydrin of phenylbutadiene.

Braun[14] recently attempted to add hypochlorous acid to vinylacrylic acid and reported that "vinylacrylic acid is easily oxidizable with hypochlorous acid."   However, he did not isolate any products.   In our investigation we had no difficulty in preparing and isolating crystalline monohalogenhydrins and dihalogenhydrins of vinylacrylic acid.

The addition of hypochlorous acid to vinylacrylic acid was first studied. It was found that vinylacrylic acid very readily absorbs one molecule of hypochlorous acid to form a monochlorohydrin, m. p. 71–74°.   The structure of the monochlorohydrin was determined by ozonization.   Six monochlorohydrins are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the relative positions of the Cl and OH groups.

$$\begin{array}{ccccc} 4 & 3 & 2 & 1 \\ H_2C{=}CH{-}CH{=}CH{-}COOH^{15} \\ + & - & + & - & + \end{array}$$
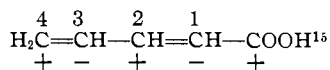
[9] Kohler and Butler, THIS JOURNAL, **48**, 1036 (1926).

[10] Muskat, Becker and Lowenstein, *ibid.*, **52**, 326, 812 (1930); see also Farmer and Healy, *J. Chem. Soc.*, **130**, 1060 (1927).
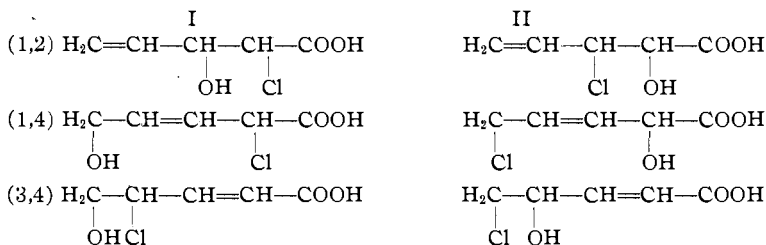
[11] Mokiewsky, *J. Russ. Phys.-Chem. Soc.*, **30**, 885 (1898).

[12] We refer here to conjugated systems of carbon atoms C=C—C=C but not to those containing the carbonyl group in conjugation with an ethylene linkage, such as C=C—C=O.

[13] Muskat and Grimsley, THIS JOURNAL, **52**, 1574 (1930).

[14] Braun, *ibid.*, **52**, 3188 (1930).

[15] The plus and minus signs do not imply a complete transfer of an electron from

$$
\text{I}
$$

(1,2) $H_2C=CH-\underset{\underset{OH}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-COOH$

(1,4) $H_2C-CH=CH-\underset{\underset{Cl}{|}}{CH}-COOH$ with $\underset{\underset{OH}{|}}{H_2C}$

(3,4) $H_2C-\underset{\underset{OH\,Cl}{|\ \ |}}{CH}-CH=CH-COOH$

$$
\text{II}
$$

$H_2C=CH-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-COOH$

$H_2C-CH=CH-\underset{\underset{OH}{|}}{CH}-COOH$ with $\underset{\underset{Cl}{|}}{H_2C}$

$H_2C-\underset{\underset{Cl\ \ OH}{|\ \ \ |}}{CH}-CH=CH-COOH$

However, since in all of its addition reactions hypochlorous acid reacts as if it has the electronic structure $\overset{-}{HO}\ \overset{+}{Cl}$, and since the electronic structure of vinylacrylic acid has been shown to be $\overset{+}{CH_2}=\overset{-}{CH}-\overset{+}{CH}=\overset{-}{CH}-\overset{+}{COOH}$,[4] it seems altogether probable that the structure of the monochlorohydrin is represented by series I rather than by series II.

On ozonizing the vinylacrylic acid monochlorohydrin it was possible to isolate oxalic acid as one of the oxidation products. This proves that hypochlorous acid adds to vinylacrylic acid in the 3,4-positions to give the chlorohydrin $CH_2OH-CHCl-CH=CH-COOH$.

On distilling the monochlorohydrin under reduced pressure, decomposition occurred with the elimination of water. A lower-boiling fraction distilled over but it was not possible to identify any definite products.

An ethereal solution of the monochlorohydrin was treated with phosphorus pentoxide. Water was eliminated, as could be easily seen, by the warming of the solution and the appearance of the phosphoric anhydride. A polymer was obtained which appeared to be the polymer of 3-chlorovinylacrylic acid but no definite proof could be obtained.
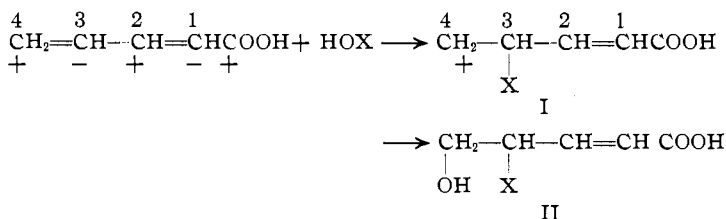
The monochlorohydrin of vinylacrylic acid readily absorbs a molecule of hypochlorous acid to form a dichlorohydrin, m. p. 143°. Its structure was not determined but it most probably had the structure $CH_2OH-CHCl-CHOH-CHCl-COOH$.

The addition of hypobromous acid to vinylacrylic acid was then studied. It was found that vinylacrylic acid readily absorbs one molecule of hypobromous acid to form a monobromohydrin, m. p. 92–93°. The structure of the monobromohydrin was determined in a manner entirely analogous to that used for the chlorohydrin. The isolation and identification of oxalic acid as one of the oxidation products of the bromohydrin proved that it also was a 3,4-addition product of vinylacrylic acid.

Vinylacrylic acid bromohydrin readily absorbs a molecule of hypobromous acid to form a dibromohydrin, m. p. 148–149ˇ. Its structure was not determined but it most probably had the structure $CH_2OH-CHBr-CHOH-CHBr-COOH$.

one atom to another. They indicate merely a displacement of the pair of valence electrons from the central position.

The addition of the hypohalous acids to vinylacrylic acid in the 3,4-positions therefore confirms the theory of Muskat and Northrup[1] regarding the addition reactions of conjugated systems.   The first step in the addition of $\overset{-\,+}{HOX}$ to vinylacrylic acid, is the addition of the positive halogen X^+ to the 3-carbon atom to give the intermediate I.

$$
\begin{array}{cccc}
4 & 3 & 2 & 1 \\
\end{array}
$$

$$
\underset{+\quad -\quad +\quad -\ +}{CH_2=CH-CH=CHCOOH} + HOX \longrightarrow \underset{+}{CH_2}-\underset{\underset{X}{|}}{CH}-CH=CHCOOH
$$

I

$$
\longrightarrow \underset{\underset{OH}{|}}{CH_2}-\underset{\underset{X}{|}}{CH}-CH=CH\ COOH
$$

II

This intermediate cannot undergo a 1,3-rearrangement, and the negative hydroxyl group must therefore add to the terminal carbon atom to give the 3,4-addition product, II.

Experimental Part

Vinylacrylic Acid Chlorohydrin.—Vinylacrylic acid was prepared according to the method of Muskat, Becker and Lowenstein,[3] by the condensation of acrolein with potassium bisulfite and treatment of the resulting addition product with malonic acid.   Hypochlorous acid was prepared according to the method of Reformatsky,[16] by passing chlorine into a finely divided suspension of mercuric oxide in water at about $-5°$. The hypochlorous acid was distilled under reduced pressure to free it from dissolved mercuric salts.   A 3–5% solution of hypochlorous acid, free from chlorine, was used in these experiments.
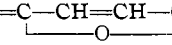
Vinylacrylic acid in chloroform solution was treated with one mole of a dilute hypochlorous acid solution.   The hypochlorous acid must be added very slowly and under continuous stirring and cooling in an ice-bath; otherwise, the reaction becomes too violent.   The hypochlorous acid is absorbed almost instantaneously.   The reaction mixture was then extracted several times with chloroform, in which vinlyacrylic acid is very soluble but the chlorohydrin of vinylacrylic acid is insoluble.   The water solution was then thoroughly extracted with ether, the ethereal solution dried over anhydrous sodium sulfate, and the ether removed by vaporization.   A yellowish oil remained which crystallized on standing.   The crystals were brought onto a porcelain suction filter and thoroughly washed with a chloroform–benzene (3–1) solution.   The crystals melted at 71–74°.   The chlorohydrin is soluble in water, alcohol, acetone, glacial acetic acid, ethyl acetate, pyridine, ether, benzene and toluene.   It is insoluble in ligroin, chloroform and carbon tetrachloride.

Anal.   Calcd. for $C_5H_7O_3Cl$:   Cl, 23.56.   Found: Cl, 23.70, 23.59.   Calcd. for $C_5H_7O_3Cl$: mol. wt., 150.5.   Found (by acid–base titration): mol. wt., 156.0.
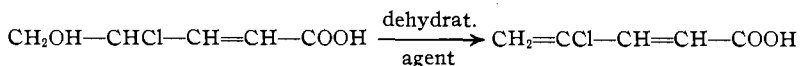
The vinylacrylic acid chlorohydrin, dissolved in water, was subjected to ozonization for twenty-four hours.   The process of ozonization and the method of working up the oxidized fractions are amply described by Muskat and Becker.[4] It was possible to isolate oxalic acid from the ozonization products, which proved that hypochlorous acid had added to vinylacrylic acid in the 3,4-positions.   A number of ozonizations were made,

[16] Reformatsky, J. prakt. Chem., 40, 396 (1889).

using glacial acetic acid as the solvent for vinylacrylic acid. In every case oxalic acid was the only product that was isolated.

A portion of the vinylacrylic acid chlorohydrin was distilled under reduced pressure. Decomposition occurred with the elimination of water. A lower boiling fraction (100–130° under 12 mm. pressure) distilled over, from which a small amount of a solid, m. p. 137–141°, was isolated. It appeared to be the γ-lactone, $CH_2{=}C{-}CH{=}CH{-}C{=}O$,
$\underset{\text{O}}{\rule{3cm}{0.4pt}}$
which was obtained by the distillation of the dichloride and dibromide of vinylacrylic acid. However, this was not verified.

An anhydrous ethereal solution of the chlorohydrin was shaken with phosphorus pentoxide. The reaction mixture became quite warm and the phosphorus pentoxide became sticky and gave all the indications of having taken up water from the chlorohydrin. The solution was filtered, and the ether was removed by vaporization. A solid remained which appeared to be the polymer of 3-chlorovinylacrylic acid. However, this could not be verified.

$$CH_2OH{-}CHCl{-}CH{=}CH{-}COOH \xrightarrow[\text{agent}]{\text{dehydrat.}} CH_2{=}CCl{-}CH{=}CH{-}COOH$$

A number of efforts were made to chlorinate the vinylacrylic acid chlorohydrin, but with no success. Only a small amount of chlorine seemed to be absorbed. This fact is of interest since the 3.4-dichloride of vinylacrylic acid would not absorb chlorine to form the tetrachloride of vinylacrylic acid.[4]

Vinylacrylic Acid Dichlorohydrin.—Vinylacrylic acid chlorohydrin, in water solution, was treated with one mole of a dilute hypochlorous acid solution. Absorption took place fairly readily and the solution became warm. The water solution was extracted a number of times with ether. The ethereal solution was dried over anhydrous sodium sulfate and the ether was removed by vaporization. A yellowish oil remained which crystallized on standing. The crystalline mass was triturated with a small amount of ether and filtered by means of suction. Snow white crystals remained on the filter. The pure crystals melted sharply at 143°. The dichlorohydrin is very soluble in alcohol, acetone and hot water; moderately soluble in ether; and insoluble in ligroin, benzene, chloroform and carbon tetrachloride.

Anal. Calcd. for $C_5H_8O_4Cl_2$: Cl, 34.936. Found: Cl, 34.89, 34.62. Calcd. for $C_5H_8O_4Cl_2$, mol. wt., 202.98. Found (by acid–base titration): mol. wt., 205.99.

Vinylacrylic Acid Bromohydrin.—Vinylacrylic acid was treated with one mole of a dilute hypobromous acid solution. Its method of preparation is identical with that described for the preparation of the chlorohydrin. It is essential in this preparation that the hypobromous acid be distilled under reduced pressure to free it from dissolved mercuric salts. The bromohydrin may easily be recrystallized from benzene. The pure bromohydrin melts at 92–93°. It is very soluble in ether, alcohol, glacial acetic acid; somewhat soluble in hot benzene, chloroform, carbon tetrachloride, water; and insoluble in cold benzine and ligroin.

Anal. Calcd. for $C_5H_7O_3Br$: Br, 40.99. Found: Br, 40.94, 40.78.

The vinylacrylic acid bromohydrin, in water solution, was subjected to ozonization and the ozonide thus formed was worked up in a manner entirely analogous to that described for the chlorohydrin. It was possible to isolate oxalic acid as one of the oxidation products which was identified by its melting point and the melting point of a mixture with a sample of known origin. It was not possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1.2- or 1,4-addition of hypobromous acid.

Vinylacrylic Acid Dibromohydrin.—Vinylacrylic acid bromohydrin, in ethereal

solution, was treated with one mole of a dilute hypobromous acid solution. Its method of preparation is identical with that described above for the dichlorohydrin. The pure crystalline dibromohydrin melts at 148–149°. It has approximately the same solubilities as the monobromohydrin.

Anal. Calcd. for $C_5H_8O_4Br_2$: Br, 54.76. Found: Br, 54.84.

Summary

1. Vinylacrylic acid absorbs hypochlorous and hypobromous acid in the 3,4-positions to form 3-chloro-4-hydroxyvinylacrylic acid and 3-bromo-4-hydroxyvinylacrylic acid, respectively.

2. Vinylacrylic acid chlorohydrin absorbs a molecule of hypochlorous acid to give a dichlorohydrin. In the same way vinylacrylic acid bromohydrin absorbs a molecule of hypobromous acid to give a dibromohydrin.

3. These addition reactions of vinylacrylic acid are found to be in perfect agreement with the general theory on the addition reactions of conjugated systems as previously developed.

CHICAGO, ILLINOIS

NOTES

A Simplified Method of Preparation of Alpha Amino Acid Amides.[1]— It has been generally recognized by investigators of the chemistry of alpha amino acids that good yields of the amides of these acids are difficult to obtain. Fischer,[2] Koenigs[3] and Bergell[4] were leaders in this field of work. The Fischer method and that of Koenigs for obtaining the amides consists in treatment of the alpha amino acid esters with liquid ammonia in sealed tubes at room temperature for from ten days to three months. Bergell, Heintz,[5] and others obtained the amides by treatment of the alpha halogen fatty acid esters or amides with alcoholic ammonia at fairly high temperatures. The yields of amides obtained by the use of these methods were not particularly satisfactory.

The authors undertook the preparation of certain alpha amino acid amides as a preliminary to the study of the chemistry of their biuret reactions.[6] A simplification of the older methods for obtaining the amides was accomplished. The esters of glycine, *d*-alanine and *dl*-leucine were treated separately in a shaking device with methyl alcohol which had been saturated previously with ammonia at 0°. The reactions were allowed

[1] The contents of this paper were reported at the National Meeting of the American Chemical Society held at Cincinnati, September, 1930.

[2] E. Fischer, "Untersuchungen über Aminosäuren, Polypeptide und Proteine," Julius Springer, Berlin, 1906.

[3] E. Koenigs and B. Mylo. *Ber.*, **41**, 4427 (1908).

[4] P. Bergell and T. Brugsch. *Z. physiol. Chem.*, **67**, 97 (1910).

[5] W. Heintz, *ibid.*, **64**, 348 (1910).

[6] Mary M. Rising and C. A. Johnson, *J. Biol. Chem.*, **80**, 709 (1928); Mary M. Rising, J. S. Hicks and G. A. Moerke, *ibid.*, **89**, 1 (1930).