2. Tertiary compounds add one or two molecules of the base to one molecule of the benzenesulfonylchloride.
3. Light promotes all of these reactions.
4. The reactions are non-ionic.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE RELATIVE STABILITY OF HALOGEN SUBSTITUTED ALIPHATIC ACIDS IN WATER SOLUTION.

BY W. A. DRUSHEL AND G. S. SIMPSON.

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Among the investigators who have studied the stability of a few of the halogen substituted acids under various conditions are Buchanan,[1] Schwab,[2] Wislicenus,[3] Kastle,[4] DeBarr,[5] Bischoff,[6] Lossen,[7] Slator,[8] Bevan,[9] Senter,[10] Euler,[11] Clark,[12] Madsen,[13] and Johanssen.[14] In general the method of investigation has been to determine the rate of replacement of the halogen atom by certain groups. Since hydrolysis offers a method which is easy in manipulation and which is not complicated by side reactions it has been used by several investigators of this problem. This reaction in which the halogen atom is replaced by the hydroxyl group has been called hydroxylation by Frankland.[15]

The most extensive work in this field has been done by DeBarr and by Senter. DeBarr has shown that many of these compounds are very stable toward water at the ordinary temperatures. In his experiments he found that secondary reactions accompanied the hydrolysis of several α-, β-, and γ-halogen substituted acids at 150°. Senter has conducted a series of important experiments in which he has studied the mechanism of the hydrolysis of the substituted aliphatic acids. Most of his work has been done on the α-brom substituted acids or their salts. He has shown that halogen acids act as negative catalysts. By means of a derived equation

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[1] *Ber.*, **4**, 863 (1871).

[2] *Etades de Dyn. Chem.*, **1884**, 20.

[3] *Ann.*, **212**, 239 (1882).

[4] *Am. Chem. J.*, 14, 586 (1892); **15**, 471 (1893).

[5] *Ibid.*, **22**, 333 (1899).

[6] *Ber.*, **32**, 1748 (1899).

[7] *Ann.*, **342**, 112 (1905).

[8] *Trans. Chem. Soc.*, **87**, 482 (1905); **95**, 93 (1909).

[9] *Proc. Camb. Phil. Soc.*, **13**, 269 (1906).

[10] *Trans. Chem. Soc.*, **91**, 466 (1907); **95**, 1827 (1909); **99**, 1049 (1911).

[11] *Ber.*, **39**, 2726 (1906).

[12] *Trans. Chem. Soc.*, **97**, 416 (1910).

[13] *Ibid.*, 103, 965 (1913).

[14] *Ber.*, **48**, 1262 (1915).

[15] *Trans. Chem. Soc.*, **103**, 713 (1913).

he has been able to determine the influence of this catalyst as the reaction progresses. The work of Johanssen is interesting because he has found a convenient method of making β-lactones which are intermediate products in the hydroxylation of β-substituted halogen acids under certain temperature conditions.

In this investigation we have studied the relative stability of several of the halogen substituted aliphatic acids. This paper includes only the work on halogen substituted acetic acids. In a later paper several substituted acids of the propionic and butyric series will be discussed. The work of DeBarr has shown that it is impractical to hydrolyze the acids themselves, but Senter's experiments have suggested the possibility of using their sodium salts.

Preparation of Materials.

The chloroacetic, dichloroacetic, and trichloroacetic acids in stock were sufficiently pure for use in this investigation.

The bromoacetic ester was prepared by the method of Zelinsky.[1] The bromoacetyl bromide was formed by treating glacial acetic acid with bromine in the presence of red phosphorus. This was converted to the ester by adding to chilled absolute alcohol. After washing, drying and distilling the fraction boiling between 157° and 159° was considered sufficiently pure.

The iodoacetic acid was made from chloroacetic acid by boiling it in alcohol with an excess of potassium iodide, by the method of Abderhalden and Guggenheim.[2]

The sodium salts of these acids were prepared by treating cooled alcoholic solutions of the free acids or their esters with the theoretical amount of strong sodium hydroxide solution free from carbonate. At this point in the process the sodium bromoacetate separated out pure from the alcoholic solution as described by Kastle.[3] This salt was washed with chilled alcohol and ether, pressed on a porous plate and dried in a desiccator. In all other cases it was necessary to evaporate the alcoholic solutions to a small volume at room temperature until the salt began to separate out and then its separation was completed by chilling. The salt was filtered off, washed and dried as described above. This method has the disadvantage that varying and undetermined amounts of water of crystallization are not completely removed.

Procedure.

These salts were dissolved in water forming approximately 0.1 N solutions which were hydrolyzed at 70° whenever convenient. In a few cases it was necessary to use a higher temperature due to the low velocity

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[1] *Ber.*, 20, 2026 (1887).

[2] *Ibid.*, 41, 2853 (1909).

[3] *Am. Chem. J.*, 15, 471 (1893).

of the reaction at 70°. These values, determined experimentally at higher temperatures, were converted by means of the temperature coefficients to corresponding values for 70°. It will be shown in a later paper that in some cases secondary reactions disturb the main reaction at higher temperatures. In the work described in this paper, however, this discrepancy is negligible.

A thermostat with a bath of commercial paraffin was used and found satisfactory for several weeks at these high temperatures. The temperature of the bath was maintained constant within 0.01° by means of a mercury-steel regulator which was made by C. A. Kraus of Clark University.[1] This thermoregulator with the usual electrical connections operated a 200-ohm relay on a dry battery circuit of 4.8 volts. The thermostat was heated by an electro-gas unit of the Hahn[2] type which was controlled by the relay. The temperature of the bath was maintained uniform throughout the thermostat by a screw stirring device.

The hydrolytic reaction was carried out in a series of sealed tubes made from a very good grade of American glass. Into each tube properly cleaned were introduced 15 cc. of 0.1 *N* solution of the salt. These tubes were simultaneously submerged in the bath by means of a wire frame about fifteen minutes before the first reading was taken. In this way the solutions reached the temperature of the thermostat before the initial concentration was determined. After allowing this action to continue for definite time intervals, the tubes were removed and placed in ice water to stop the reaction. The end point of the reaction was determined by allowing the last tubes of the series to remain in the bath several days after the last time interval. Each reaction was carried out in duplicate.

The general equation for the action of water on the sodium salts of these halogen substituted acids may be expressed thus:

$$R'CHX - R - COONa + H_2O = R'CHOH - R - COOH + NaX$$

Previously most experimenters have followed the course of the reaction by determining merely the amount of acid formed by titrating with standard alkali. The work of Johanssen[3] has shown that this method does not measure the true amount of hydrolysis and so the following procedure has been adopted: After opening each tube the contents were washed into a flask and titrated with 0.1 *N* solution of sodium hydroxide using phenolphthalein as an indicator. This sodium hydroxide, prepared from metallic sodium, contained no carbonate. The free halide was then determined by titrating the neutral solution with 0.1 *N* solution of silver

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[1] This regulator will be described in detail by Dr. Kraus in the near future.

[2] *Z. physik. Chem.*, **44**, 525 (1903).

[3] *Ber.*, **48**, 1262 (1915).

nitrate which had been made to exactly the same molar concentration as the alkali. A few drops of a concentrated solution of potassium chromate served as an indicator. This titration was very difficult in the presence of an iodide due to the color of silver iodide which was formed.

The values of the velocity constants K_1 of a monomolecular reaction and K_2 of a bimolecular reaction were calculated by the usual titration formula given below. In all of this work the figures are based on the silver nitrate used for 15 cc. portions of the 0.1 *N* solutions of the salts.

$$K_1 = \frac{2.3}{t_n}\,[\log_{10}(T_\infty - T_0) - \log_{10}(T_\infty - T_n)].$$

$$K_2 = \frac{1}{t_n}\left[\frac{T_n - T_0}{(T_\infty - T_n)(T_\infty - T_0)}\right].$$

The hydrolysis of sodium chloroacetate has been previously studied by Senter[1] and others. The salt was hydrolyzed at 90° and the values for K_1 determined. These were converted to constants at 70° by means of the factor 3.2 which Senter[2] had previously determined as the temperature coefficient for each 10°.

In this table are included the time intervals in minutes, the number of cc. of sodium hydroxide used in neutralizing the solution, the number of cc. of silver nitrate necessary to precipitate the halide and the values for K_1 at 90° and 70°.

TABLE I.

Sodium Chloroacetate in 0.1 *N* Solution.

t (min.).	Cc. of NaOH.	Cc. of $AgNO_3$.	10^5K_1 at 90°.	10^5K_1 at 70°.
0	1.63	1.65	...	6.6
60	2.08	2.15	68.0	6.6
360	3.43	3.55	44.0	4.3
1200	6.08	6.25	42.0	4.1
1900	8.40	8.84	42.0	4.1
3420	9.85	10.35	39.0	3.8
7020	12.18	12.64	29.0	2.9
∞	13.93	14.25	...	..

Sodium bromoacetate has been hydrolyzed by Kastle[3] and by Senter[4] but at different temperatures. It will be noted that the values for K_1 at 70° are not as constant as those given by Senter at 52.4°. A satisfactory explanation of this irregularity will be given in a later paper dealing with certain homologues of acetic acid.

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[1] *Trans. Chem. Soc.*, **91**, 466 (1907).

[2] *Proc. Chem. Soc.*, **24**, 89 (1908).

[3] *Am. Chem. Jour.*, **15**, 484 (1893).

[4] *Loc. cit.*

TABLE II.

Sodium Bromoacetate in 0.1 *N* Solution.

t (min.).	Cc. of NaOH.	Cc. of $AgNO_3$.	10^5K_1 at 70°.
0	1.90	1.93	...
60	2.86	2.90	(132.0)
240	4.10	4.42	90.6
600	6.70	7.30	89.8
1320	10.38	10.88	89.1
2010	12.03	12.70	88.6
2570	13.20	13.48	88.0
4020	14.10	14.40	85.3
...	14.80	14.85	...

Apparently the hydrolysis of sodium iodoacetate has not been studied before. It is more stable than the analogous bromine compound. These experiments have been repeated several times and the results of one hydrolysis are given below. No satisfactory explanation can be given at this time why it should be more stable than bromoacetic acid which is contrary to the usual rules of analogous bromine and iodine compounds.

TABLE III.

Sodium Iodoacetate in 0.1 *N* Solution.

t (min.).	Cc. of NaOH.	Cc. of $AgNO_3$.	10^5K_1 at 70°.
0	0.1	0.1	...
60	0.35	0.40	34.1
240	1.05	1.15	29.1
1440	4.85	5.15	29.0
2460	6.95	7.53	28.3
4080	9.73	10.10	27.6
6960	12.45	12.65	27.0
11280	13.95	14.00	22.9
...	14.90	14.90	...

Beckurts and Otto[1] and others in a qualitative study of the hydrolysis of sodium dichloroacetate found glyoxalic acid, sodium chloride and dichloroacetic acid as products. The following equation represents this as a bimolecular reaction:

$$2CHCl_2COONa + H_2O \longrightarrow CHOCOOH + CHCl_2COOH + 2NaCl$$

It would seem probable that there are two consecutive reactions which may be expressed thus:

$$(a)\quad CHCl_2COONa + H_2O \longrightarrow CHOCOOH + NaCl + HCl$$

$$(b)\quad CHCl_2COONa + HCl \longrightarrow CHCl_2COOH + NaCl$$

As reaction (*b*) should be instantaneous, we might expect that the hydrolysis of this salt should give constant values for a first order reaction.

Sodium dichloroacetate is very stable toward water, so it was hydrolyzed at 90° and 100°. The temperature coefficient for each 10° was

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[1] *Ber.*, 14, 576 (1881).

found to be 3.16 for a first order reaction and 3.40 for a second order reaction.

The results of this hydrolysis would tend to show that the reaction is apparently neither monomolecular nor bimolecular. At first it was thought that this might be due to the difference in the rate of substitution of the two chlorine atoms. Subsequent work has shown that this irregularity is found in the hydrolysis of salts of several halogen substituted acids which can only be monomolecular reactions. This will be discussed in detail in a later paper from which it will appear that the hydrolysis of sodium dichloroacetate is a first order reaction.

TABLE IV.

Sodium Dichloroacetate in 0.1 *N* Solution.

t (min.).	Cc. of NaOH.	Cc. of $AgNO_3$.	10^6K_1 at 90°.	10^5K_1 at 70°.	10^6K_2 at 70°.
0	0.10	0.30	..	...	....
1440	3.83	4.13	9.1	0.91	0.026
2880	6.83	7.13	8.6	0.86	0.027
4320	9.25	9.48	8.1	0.81	0.028
7200	13.10	13.40	7.8	0.78	0.029
11520	16.95	17.23	6.8	0.68	0.030
17280	20.55	20.80	6.3	0.63	0.031
24480	23.70	24.10	5.9	0.59	0.037
....	31.05	31.40	..	...	....

In these tables it will be noted that a difference exists between the titration of the free acid and the halide liberated. Both Senter[1] and Johanssen[2] have previously discussed this point. Senter believed that bromoacetoglycollic acid was formed as an intermediate product in the hydrolysis of sodium bromoacetate. This on subsequent hydrolysis produced glycollic acid. Although Senter has never been able to isolate his intermediate product, he has prepared a similar compound, acetoglycollic acid, by adding sodium acetate to his solution of sodium bromoacetate.

$$CH_3COONa + BrCH_2COONa = CH_3COOCH_2COONa + NaBr.$$

The formation of a lactide or lactone was first suggested by Holmberg[3] but it was not until the work of Johanssen[4] that the β-lactone was isolated during the hydrolysis of β-chlorobutyric acid. Since the formation of a lactide has been found by Kastle,[5] Walden[6] and others in the hydrolysis of α-halogen substituted acids under certain conditions it may be considered an intermediate product in these reactions. Apparently this is

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[1] *Trans. Chem. Soc.*, **101**, 2535 (1912).

[2] *Ber.*, **48**, 1262 (1915).

[3] *Ibid.*, **14**, 1713 (1912).

[4] *Ibid.*, **48**, 1262 (1915).

[5] *Am. Chem. Jour.*, **15**, 431 (1893).

[6] *Ber.*, **26**, 262 (1893).

the most satisfactory explanation of the difference in the alkali and silver nitrate titrations.

It has been shown by Lossen[1] and others that the hydrolysis of sodium trichloroacetate produces chloroform and sodium bicarbonate according to this equation:

$$CCl_3COONa + H_2O \longrightarrow CHCl_3 + NaHCO_3$$

It is obvious that the course of the reaction must be followed by estimating the amount of sodium bicarbonate formed during the different time intervals. No good method could be found for the direct estimation of the bicarbonate in such dilute solutions so the following method has been adopted:

The tubes containing the reaction mixture were taken from the thermostate and placed in ice water several minutes before opening them in order to prevent the decomposition of the bicarbonate into sodium carbonate and carbon dioxide. In this way all the pressure within the tubes was removed and the mechanical loss of part of the solution on opening was prevented. The contents of the tubes were washed into a filter flask containing 25 cc. of 0.1 *N* sulfuric acid. The flask was closed and attached to a vacuum pump which reduced the pressure to 2 mm. Several blank experiments with known concentrations of sodium bicarbonate proved that all of the carbon dioxide was removed by this treatment. Then the excess of sulfuric acid was titrated with sodium hydroxide, using phenolphthalein as an indicator. This method has proved fairly successful as shown by these results.

TABLE V.

Sodium Trichloroacetate in 0.1 *N* Solution.

t (min.).	Cc. of 0.1 *N* $NaHCO_3$ formed.	10^5K_1 at 70°.
0	0.0	....
120	1.50	99.0
300	3.57	104.0
540	5.93	110.0
840	8.37	118.0
1200	9.73	110.0
1800	11.33	106.0
2760	12.05	86.0
...	13.28	...

This work shows that the sodium salts of the halogen substituted acetic acids have a relative stability in water solutions at 70° as follows: Trichloroacetic acid, 1.0; bromoacetic acid, 1.2; iodoacetic acid, 3.6; chloroacetic acid, 26.0; dichloroacetic acid, 120.

This shows that chloroacetic acid is more stable than bromoacetic acid and iodoacetic acid, while iodoacetic acid is more stable than bromoacetic acid. It also shows that the introduction of the second halogen

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[1] *Ann.*, 342, 122 (1905).

atom makes the acid much more stable toward water. We might expect that the introduction of the third chlorine atom would also have this same effect but in this case the hydrolysis is not a true hydroxylation. From the table it is evident that trichloroacetic acid is the most unstable of the acids discussed in this paper.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

BROMOHYDROXYNAPHTHOQUINONES.[1]

BY A. S. WHEELER AND V. C. EDWARDS.

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In our study of the 1,4,5,6-tetrahydroxynaphthalene we proved that this compound is a quinone as well as a phenol, since it readily forms a semicarbazone, a phenylsemicarbazone and similar characteristic ketone derivatives. A somewhat analogous case is found in the hydrojuglons. When juglon is reduced with zinc dust to hydrojuglon, the product is almost wholly a trihydroxyphenol and this can be converted by melting almost wholly into the keto form. Willstätter and Wheeler[2] cleared up the constitution of these hydrojuglons by showing that they present a case of keto enol isomerism. The tetrahydroxynaphthalene, which is obtained by the reduction of naphthazarine by stannous chloride, presents a somewhat different case in that the two isomeric forms cannot be separated from each other, resembling in this respect phloroglucinol. The tetrahydroxynaphthalene was known to give readily a tetracetate and we have shown in Part I that it gives readily a series of ketone derivatives.

With a view to a deeper study of this case of tautomerisn, we attacked the problem of the bromination of naphthalene. This has opened up a very interesting field and in spite of one or two unsettled questions in the work so far done, it becomes necessary to publish our results because one of us[3] has entered the industrial field, thus severing permanently our coöperation.

The chart represents the various series of reactions, the derivatives of tetrahydroxynaphthalene being indicated by numbers and those of naphthazarine by letters. The naphthazarine derivatives were prepared with the expectation that they, being identical or similar, would act as checks upon the other series.

By representing the tetrahydroxynaphthalene 1 in the chart as a qui-

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[1] This paper forms Part II of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of North Carolina. Part I is found in THIS JOURNAL, **38**, 387 (1916).

[2] *Ber.*, **47**, 2796 (1914).

[3] V. C. Edwards.