[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE POLARITY OF THE CARBON-HALOGEN BOND
II. THE KINETICS OF THE ACID HYDROLYSIS OF HALOGEN PHENOLS AND HALOGEN NAPHTHOLS

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RECEIVED JULY 5, 1927 PUBLISHED NOVEMBER 5, 1927

The development of a quantitative method for the determination of relative rates of acid hydrolysis of positive halogens[1] has opened the way for a study of the kinetics of the reaction. In the present article an investigation is made on the effect of a change in both the hydrogen-ion concentration and the stannous chloride concentration upon the velocity of the reaction that has been used as a test for the determination of the degree of polarity of the halogen atoms in halogen phenols and halogen naphthols.

Effect of Hydrogen-Ion Concentration

The effect of a change in the hydrogen-ion concentration of the solution was first investigated. The total acidity of the stannous chloride solution used in Table I of the preceding article was determined by titration against a normal sodium hydroxide solution: 5.0 cc. of the stannous chloride solution neutralized 14.6 cc. of the normal sodium hydroxide. A solution of about one-seventh this total acidity was prepared by making up 50 g. of $SnCl_2.2H_2O$ and 80 g. of hydrochloric acid (37%) to 2960 cc. with 95% alcohol; 20.0 cc. of this solution neutralized 8.5 cc. of normal sodium hydroxide. The stronger acid solution removed 0.0260 g., or 14.85%, of the bromine from 1-bromo-2-hydroxynaphthalene in twenty minutes; the weaker acid solution removed 0.0072 g., or 4.1%, of the bromine in the same length of time.

It is not justifiable to draw any conclusions of a quantitative nature from these data on the relation between the hydrogen-ion concentration and the speed of the reaction, because the relation of the total acidity as determined to the actual hydrogen-ion concentration of the solutions is unknown. By taking advantage, however, of the qualitative relation, we were able to slow down the hydrolysis of the more positive halogen compounds found in Tables II, IV, VII and VIII, and to speed up the removal of the bromine from the less positive halogen compounds found in Tables III, V, VI and IX.

A possible mechanism for the acid hydrolysis of positive halogens has been formulated;[2] the role of the hydrogen ions in the reaction, however, is very likely catalytic. According to the theories of Lapworth[3] and more

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[1] Sampey, THIS JOURNAL, **49**, 2849 (1927).

[2] Nicolet, *ibid.*, **49**, 1810 (1927).

[3] Lapworth, *J. Chem. Soc.*, **107**, 857 (1915).

recently Rice,[4] it is the unhydrated hydrogen ions that catalyze reactions of this type. Experiments are planned to determine the effect of moisture on the rate of removal of the halogens by acids.

Effect of Stannous Chloride Concentration

The hydrolysis was further studied to determine the effect of a change in the concentration of the stannous chloride. In order to increase the acidity of the solution and at the same time not add so much water that half a gram of the organic halides would not dissolve readily, dry hydrogen chloride gas was passed into a solution containing 200 cc. of the 37% hydrochloric acid and two liters of 95% alcohol; 5.0 cc. of this solution neutralized 22.3 cc. of normal sodium hydroxide. This high concentration of acid caused more rapid hydrolysis. The following constants were obtained when the data were substituted in the equation for a first-order reaction: $1/t \times \log a/(a-x) = 0.4343k$, where a is the amount of removable bromine in the sample, and x is the amount of bromine removed.

Table I

Hydrolysis of Half-Gram Samples

Time, min.	Cc. of $SnCl_2$[a] soln.	Cc. of 0.1 N I_2 soln.	a	x	$k \times 10^{-2}$
		1-Bromo-2-hydroxynaphthalene			
5	20.00	15.93	0.1793	0.0203	2.39
10	20.00	10.82	.1793	.0432	2.52
15	20.00	6.49	.1793	.0580	2.60
18	20.00	5.27	.1793	.0629	2.39
20	20.00	3.80	.1793	.0688	2.41
					Mean 2.46
		1,6-Dibromo-2-hydroxynaphthalene			
					$k \times 10^{-2}$
20	20.00	14.03	0.1324	0.0279	1.17
40	20.00	9.39	.1324	.0464	1.07
60	20.00	6.05	.1324	.0599	1.00
					Mean 1.08
		2,4-Dibromo-1-hydroxynaphthalene			
					$k \times 10^{-3}$
40	20.00	15.25	0.2649	0.0230	2.26
50	20.00	14.10	.2649	.0276	2.19
60	20.00	11.95	.2649	.0362	2.44
					Mean 2.29

[a] 20.00 cc. of this $SnCl_2$ solution was equivalent to 21.00 cc. of 0.1 N iodine.

The rate of removal of the halogens by the acid solution is apparently independent of the concentration of the stannous chloride; the evidence therefor is still more conclusive in Tables IV–IX below, where the range of concentration over which the reaction is studied is wider. Nicolet[2] has used in his interpretation of the mechanism of the removal of positive

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[4] Rice, This Journal, **45**, 2808 (1923).

halogens this significant fact of the independence of the concentration of the stannous chloride on the rate of hydrolysis.

If we wish to determine how far, relatively, the bonding pair of electrons has been drawn from any positive halogen, it is more significant to use that weight of each compound which will lose the same weight of halogen on complete hydrolysis than it is to employ the same weight of each halogen phenol and naphthol. In the next two tables of data the halogen atoms that were not removed were not counted in when determining the equivalent weights to be used; for instance, 0.25 g. of 2,4-dibromo-1-hydroxynaphthalene was taken and 0.5 g. of 1,6-dibromo-2-hydroxynaphthalene, because in the latter only one bromine atom is removed. The weight of bromine lost on complete hydrolysis of 1,6-dibromo-2-hydroxynaphthalene was taken as the standard in the calculations for the amount of other halogens to be used. Due to the large differences in the rates of hydrolysis of the compounds, as shown in the preceding article of this series, it was necessary to prepare two stannous chloride solutions with different hydrogen-ion concentrations; the solution with the weaker hydrogen-ion concentration was used with those compounds whose halogens were more positive. The solution used in Table II was prepared by passing dry hydrogen chloride gas into 95% alcohol; 30 g. of SnCl$_2$.-

TABLE II

HYDROLYSIS OF EQUIVALENT QUANTITIES IN WEAK ACID

Sample, g.	Time, min.	Cc. of SnCl$_2$[a] soln.	Cc. of 0.1 N I$_2$ soln.	a	x	$k \times 10^3$
1-Bromo-2-hydroxynaphthalene						
0.3690	20	30.00	18.15	0.1324	0.0185	7.46
.3690	30	30.00	16.10	.1324	.0267	7.46
.3690	45	30.00	13.40	.1324	.0375	7.38
						Mean 7.43
1-Iodo-2-hydroxynaphthalene						
0.2815	5	30.00	7.72	0.1324	0.0954	2.55
.2815	6.5	30.00	5.94	.1324	.1067	2.52
.2815	8	30.00	4.45	.1324	.1162	2.62
						Mean 2.56
1,4-Dibromo-2,3-dihydroxynaphthalene						$k \times 10^{-2}$
0.2631	12	30.00	13.00	0.1324	0.0390	2.90
.2631	16	30.00	9.90	.1324	.0514	3.06
.2631	20	30.00	8.70	.1324	.0562	2.76
						Mean 2.90
1,4,6,7-Tetrabromo-2,3-dihydroxynaphthalene						$k \times 10^{-2}$
0.3940	12	30.00	12.15	0.1324	0.0424	3.21
.3940	16	30.00	9.75	.1324	.0520	3.11
.3940	22	30.00	7.35	.1324	.0616	2.84
						Mean 3.05

[a] 30.00 cc. of this SnCl$_2$ solution was equivalent to 22.75 cc. of 0.1 N iodine.

$2H_2O$ was added to the 2800 cc. of solution; 5.0 cc. of this solution neutralized 13.8 cc. of normal sodium hydroxide. For the solution used in Table III it was necessary to add about 300 g. of 37% hydrochloric acid along with the dry hydrogen chloride gas and alcohol in order to prevent the escape of hydrogen chloride fumes when the temperature was raised to 70 degrees (an alcoholic hydrogen chloride solution fumes at a lower concentration than an aqueous hydrogen chloride solution). Five cc. of this solution neutralized 21.9 cc. of normal sodium hydroxide. 1-Bromo-2-hydroxynaphthalene was hydrolyzed by both solutions in order to furnish a means for the comparison of the rates of the halogen removal in the two solutions.

TABLE III

HYDROLYSIS OF EQUIVALENT QUANTITIES IN STRONG ACID

Sample, g.	Time, min.	Cc. of $SnCl_2$[a] soln.	Cc. of 0.1 N I_2 soln.	a	x	$k \times 10^{-3}$
		1,6-Dibromo-2-hydroxynaphthalene				
0.5000	30	30.00	10.00	0.1324	0.0160	4.28
.5000	45	30.00	7.85	0.1324	0.0246	4.56
.5000	60	30.00	6.40	0.1324	0.0304	4.34
						Mean 4.39
		1-Bromo-2-hydroxynaphthalene				
						$k \times 10^{-2}$
0.3690	10	30.00	10.45	0.1324	0.0142	1.13
.3690	15	30.00	9.08	.1324	.0197	1.07
		2,4-Dibromo-1-hydroxynaphthalene				
						$k \times 10^{-3}$
0.2500	60	30.00	10.46	0.1324	0.0142	1.88
		4,6-Dibromoresorcinol				
						$k \times 10^{-3}$
0.2217	45	30.00	11.95	0.1324	0.0082	1.42
.2217	60	30.00	11.40	.1324	.0104	1.36
.2217	75	30.00	10.70	.1324	.0132	1.40
						Mean 1.36

[a] 30.00 cc. of this solution was equivalent to 14.0 cc. of 0.1 N iodine.

By the use of equivalent quantities the interesting fact appears in Table II that the 1,4-bromine atoms in the two dihydroxynaphthalenes are removed at approximately the same rate; such a relation could not be drawn from any preceding results. In view of this relation, it is surprising to find in Table III that the bromine atom in the 6 position of 1,6-dibromo-2-hydroxynaphthalene exerts a decided influence upon the bromine in the 1 position.

In the final series of runs[5] the effect of a wide range of concentration of the stannous chloride was determined. The method of hydrolysis was slightly changed: in each case 25.0 cc. of stannous chloride solution was

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[5] The results set forth in Tables IV–IX were obtained in the Chemical Laboratory of Howard College.

heated to the temperature of the thermostat before the organic halide was introduced. The oxygen of the atmosphere was kept out by keeping the tube from the cylinder of nitrogen below the neck of the Erlenmeyer flask when the sample was introduced. In order to control the rate of the hydrolysis a stannous chloride solution of different hydrogen-ion concentration was used for each compound; for the more positive halogens a solution of low acidity was used. The weight of organic halide used first in Tables IV–VI was sufficient to oxidize on complete hydrolysis 25.0 cc. of 0.1 *N* stannous chloride solution; in the last three tables that weight of sample was used which would oxidize all of the stannous chloride present on complete removal of the positive halogens. The solutions used in Tables IV–IX were made as follows.

Table IV: 160 g. of HCl (37%) and 14 g. of $SnCl_2.2H_2O$ made up to a volume of one liter with 95% alcohol.

Table V: 435 g. of HCl (37%) and 25 g. of $SnCl_2.2H_2O$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 23.0 cc. of *N* NaOH.

Table VI: 175 g. of HCl (37%) and 15 g. of $SnCl_2.2H_2O$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 10.4 cc. of *N* NaOH.

Table VII: 135 g. of HCl (37%) and 26 g. of $SnCl_2.2H_2O$ made up to one liter with 95% alcohol; 5.0 cc. of this solution neutralized 7.7 cc. of *N* NaOH.

Table VIII: 160 g. of H_2SO_4 (concentrated) and 30 g. of $SnCl_2.2H_2O$ made up to one liter with 95% alcohol; 200 cc. of water was added in an attempt to dissolve the heavy precipitate of tin salts; 5.0 cc. of this solution neutralized 12.6 cc. of *N* NaOH.

Table IX: 435 g. of H_2SO_4 (concentrated), 35 g. of $SnCl_2.2H_2O$ and 150 cc. of water were made up to a volume of one liter with 95% alcohol.

TABLE IV

HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	a	x	$k \times 10^{-2}$
0.3359	10	19.6	0.1580	0.0596	4.73
.3359	15	16.0	.1580	.0826	4.92
.3359	20	13.4	.1580	.0989	4.92
.3359	30	9.5	.1580	.1237	5.09
.4738	10	14.9	.2229	.0894	5.13
.4738	15	10.3	.2229	.1186	5.13
.4738	20	6.8	.2229	.1408	4.97
.4738	30	1.4	.2229	.1751	5.13

[a] 29.0 cc. of this 0.1 *N* iodine was equivalent to 25.0 cc. of $SnCl_2$ solution.

TABLE V

HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	a	x	$k \times 10^{-2}$
0.2787	10	33.0	0.1000	0.0340	4.15
.2787	15	30.2	.1000	.0452	4.01
.5574	10	25.2	.2000	.0652	3.94
.5574	15	20.7	.2000	.0832	3.58
.8361	10	18.7	.3000	.0912	3.60

[a] 41.5 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of the $SnCl_2$ solution.

TABLE VI

HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	*a*	*x*	$k \times 10^{-3}$
0.2787	40	18.0	0.1000	0.0124	3.30
.2787	50	17.3	.1000	.0152	3.29
.5574	30	16.6	.2000	.0180	3.14
.5574	40	15.6	.2000	.0220	2.91

[a] 21.1 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of $SnCl_2$ solution.

TABLE VII

HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE

Sample g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	*a*	*x*	$k \times 10^{-2}$
0.5395	10	25.0	0.2538	0.0825	3.93
.5395	15	20.3	.2538	.1122	3.90
.5395	20	17.1	.2538	.1327	3.70
.5395	30	10.3	.2538	.1733	3.82
.5395	45	4.6	.2538	.2121	4.01
.2697	15	29.2	.1269	.0559	3.85
.8092	5	28.4	.3807	.0609	3.48
.8092	15	14.5	.3807	.1492	3.31

[a] 38.0 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of $SnCl_2$ solution.

TABLE VIII

HYDROLYSIS OF 4,6-DI-IODORESORCINOL

Sample, g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	*a*	*x*	$k \times 10^{-2}$
0.2260	15	16.1	0.1586	0.0527	2.69
.2260	30	10.0	.1586	.0914	2.90
.4520	12	11.4	.3172	.0825	2.51
.4520	20	4.8	.3172	.1244	2.49

[a] 24.4 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of $SnCl_2$ solution.

TABLE IX

HYDROLYSIS OF 1-BROMO-2-HYDROXYNAPHTHALENE

Sample, g.	Time, min.	Cc. of 0.1 *N* I_2[a] soln.	*a*	*x*	$k \times 10^{-2}$
0.4454	15	26.5	0.1598	0.0580	3.00
.4454	30	18.9	.1598	.0884	2.68
.2227	15	33.7	.0799	.0292	3.02
.2227	30	29.1	.0799	.0476	2.88

[a] 41.0 cc. of this 0.1 *N* iodine solution oxidized 25.0 cc. of $SnCl_2$ solution.

Summary

1. The rate of removal of positive halogens from halogen phenols and halogen naphthols increases strikingly with the acid concentration.

2. The rate of hydrolysis in acid solution is independent of the concentration of the stannous chloride.

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