[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD COLLEGE]

THE POLARITY OF THE CARBON-HALOGEN BOND. III. THE INHIBITORY EFFECT OF WATER ON THE ACID HYDROLYSIS OF HALOGEN NAPHTHOLS[1]

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The inhibitory effect of water upon reactions catalyzed by hydrogen ions has been studied intensively, although the number of different types of reactions investigated has been limited. The theories postulated to explain the phenomenon are almost as numerous as the number of investigators working in the field. A comprehensive review of the literature has appeared recently.[2] In the present investigation data are presented to show the inhibitory effect of water on another type of reaction catalyzed by hydrogen ions.

1-Iodo-2-hydroxynaphthalene was the compound selected for the determination of the effect of moisture on the rate of removal of the iodine by hydrogen ions. The method of hydrolysis was the same as that developed for the study of the relative rates of reduction of aromatic nitro compounds.[3] The alcoholic hydrochloric acid solutions used in Table I were prepared as follows.

Solution A	37% HCl, 10.00 cc.	....	Abs. alc. to 500.00 cc.
Solution B	37% HCl, 10.00 cc.	Water, 50.00 cc.	Abs. alc. to 500.00 cc.
Solution C	37% HCl, 10.00 cc.	Water, 190.00 cc.	Abs. alc. to 500.00 cc.

The insoluble nature of $SnCl_2 \cdot 2H_2O$ in absolute alcohol did not permit us to make a more anhydrous solution than Solution A; 0.3375 g. of the iodonaphthol and 0.3000 g. of $SnCl_2 \cdot 2H_2O$ (equivalent to 25.00 cc. of $N/10$ iodine solution) were added to each 50.00-cc. portion of the above solutions in the hydrolyses. The constants reported in Table I were obtained when the data were substituted in the equation for a first order reaction.[4]

TABLE I

EFFECT OF WATER ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE IN ALCOHOLIC HYDROCHLORIC ACID SOLUTION

	Soln. A		Soln. B		Soln. C	
0.1 N iodine used in titrn., cc.	15.2	15.0	20.3	20.5	21.7	21.7
$k \times 10^{-2}$	3.32	3.40	1.38	1.32	0.94	0.94

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[1] The author is indebted to Dr. A. W. Homberger of the University of Louisville, in whose laboratory the major portion of this research was completed during the summer of 1928.

[2] Brönsted, *Chemical Reviews*, **5**, 231 (1928).

[3] Sampey, THIS JOURNAL, **52**, 88 (1930).

[4] Sampey, *ibid.*, **49**, 2853 (1927).

When acetic acid was used as the solvent in place of the alcohol the inhibitory effect of water was even more pronounced. The acetic acid solutions were made as follows

Solution A	37% HCl, 5.00 cc.	....	Gl. HAc, to 500.00 cc.
Solution B	37% HCl, 5.00 cc.	Water, 10.00 cc.	Gl. HAc, to 500.00 cc.
Solution C	37% HCl, 5.00 cc.	Water, 30.00 cc.	Gl. HAc, to 500.00 cc.
Solution D	37% HCl, 5.00 cc.	Water, 50.00 cc.	Gl. HAc, to 500.00 cc.
Solution E	37% HCl, 5.00 cc.	Water, 100.00 cc.	Gl. HAc, to 500.00 cc.

The same weights of iodonaphthol and stannous chloride were used as in the previous hydrolyses.

TABLE II

EFFECT OF WATER ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE IN ACETIC ACID SOLUTION

	Soln. A		Soln. B		Soln. C		Soln. D		Soln. E	
Time, minutes	5	5	5	5	5	5	10	10	10	10
0.1 N I_2, cc.	11.0	11.1	8.0	8.3	12.4	12.4	11.1	11.2	20.3	20.0
$k \times 10^{-1}$	1.64	1.62	2.27	2.20	1.40	1.40	0.81	0.80	0.20	0.22

It will be noted that in Solution B the rate of removal of the iodine is faster than in Solution A, although the former contains more water. This may be explained by the observation that at the end of the five-minute period Solution A was strongly colored by iodine; this color disappeared *immediately* upon the addition of ten cubic centimeters of water. Presumably the iodine was removed more rapidly in Solution A than in Solution B, but because of the nearly anhydrous conditions existing in the former, the stannous chloride was unable to react with the liberated iodine, with the result that part of the iodine resubstituted in the naphthol. When iodine and stannous chloride were dissolved in glacial acetic acid containing a small amount of hydrochloric acid, the iodine color did not disappear until more water was added. This phenomenon made it impossible to determine the effect of small amounts of water on the rate of removal of the iodine from the iodonaphthol.

Neutral Salt Effect.—The effects of neutral salts on the reactions catalyzed by hydrogen ions have received considerable attention. In Table III some observations are recorded of the action of several inorganic salts upon the rate of hydrolysis of the positive halogen in 1-iodo-2-hydroxynaphthalene. The alcoholic solution used had to contain a large proportion of water in order to dissolve the salts, and also a large amount of hydrochloric acid to bring about the removal of the halogen from the aqueous solution; after a considerable number of solubility determinations, the solution that was used was prepared by making up 100.00 cc. of 37% hydrochloric acid and 475.00 cc. of water to exactly one liter with 95% alcohol. The amounts of iodonaphthol and stannous chloride were the same as in the previous tables. Sufficient quantities of the dry salts were added to give a half molar concentration.

TABLE III

EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE

Salt	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$
...	15	12.7	4.51	15	12.7	4.51
KCl	15	11.3	5.29	15	11.2	5.35
NaCl	15	10.8	5.59	15	10.8	5.59
KBr	15	10.5	5.78	15	10.6	5.72
NaBr	15	10.1	6.04	15	10.2	5.98
LiCl	15	10.0	6.10	15	10.2	5.98
$SnCl_4$	15	10.4	5.84	15	10.2	5.98

Stannic chloride is not a neutral salt but it was added to the list because in the former method of preparing standard solutions of stannous chloride[3] there were always appreciable quantities of this salt present due to the oxidation of the stannous chloride during storage. We were not able to include sodium or potassium iodide in Table III, because they decomposed quite rapidly with the liberation of free iodine.

Summary

1. Water decreases the rate of hydrolysis of 1-iodo-2-hydroxynaphthalene in alcoholic and acetic acid solutions of hydrochloric acid.
2. Stannous chloride and iodine do not react appreciably in hydrochloric acid solutions of acetic acid containing little moisture.
3. Neutral salts increase the rate of hydrolysis of positive halogens.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND COLUMBIA UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF REACTIONS IN SOLUTION

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The generally accepted explanation for the temperature coefficient of reactions in general is essentially the Arrhenius hypothesis of activated molecules. This has been worked out rather completely for gaseous reactions on the assumption that there is a whole series of such active molecules in statistical equilibrium with the inactive molecules and that the active molecules differ from the inactive molecules only in their energy content; each of these active molecules has a finite probability of reacting which depends upon this energy content. On this hypothesis the energy of activation is the difference of the mean energy of the molecules which react and the mean energy of all the molecules.[1] It is generally supposed that the temperature coefficients of reactions occurring in solution has a similar explanation but so far there has been no theory generally

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[1] Tolman, THIS JOURNAL, **47,** 2652 (1925).