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THE KINETIC DETERMINATION OF HYDROGEN-ION CONCENTRATIONS IN AQUEOUS SOLUTION

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1. Introduction

The principles of the various methods which have served for the determination of the concentration of hydrogen ions in aqueous solutions were originally developed with only slight consideration of the phenomenon known as "salt effect." However, as early as 1887 Arrhenius[2] showed that kinetic reactions were influenced by the presence of neutral salts. In his fundamental investigations on the measurement of hydrogen-ion concentrations and their significance in biochemical reactions, Sørensen[3] called attention to the effects of salts in the colorimetric and the kinetic methods, while the electrometric method was generally adopted as a standard method in which such influences were supposed to be absent. It was later realized as a consequence of the more recent aspects of the theory of salt solutions that electrometric measurements also are considerably affected by the presence of salts, but up to the present time the electrometric method seems still to be generally considered as the most reliable and the most suitable method for accurate determinations of hydrogen-ion concentration. Even if this be true in some cases, it should be noted that salt effects manifest themselves in a much simpler way in a catalytic reaction than in either electrometric or colorimetric determinations, and that, from this point of view, since salt effects form one of the most serious sources of error in hydrogen-ion measurements, the kinetic method stands out as marked by considerable advantages.

The most rational method for the elimination of the errors to which these salt effects may lead is, obviously, to compare by the method adopted the solution under examination with a reference solution of which the hydrogen-ion concentration is known from the stoichiometric amount of completely ionized acid present and which exhibits as nearly as possible the same medium effect as the solution of unknown hydrogen-ion concentration. Kinetic methods based on this principle have rendered particularly satisfactory service in the determination of the acidity of a number of aquo-ions.[4] However, it has not always been easy to prepare a reference solution which as regards its medium effect is sufficiently close to the test solution. Hence, in addition to throwing light on the general

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[1] Fellow of the American-Scandinavian Foundation, 1928–1929.

[2] Arrhenius, *Z. physik. Chem.*, **1**, 110 (1887).

[3] Sørensen, *Medd. från Carlsberg lab.*, **8**, 1 (1910).

[4] Brönsted and Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

kinetics of the effects of salts, an extensive examination of all these phenomena should contribute considerably to the problem of accurate hydrogen-ion determination.

For the solution of this problem it is, of course, very important to possess a number of suitable catalytic reactions of varied sensitivity which may be subject to accurate and easy experimental examination. As a result of extensive experimental investigations, Skrabal[5] and his co-workers have recently brought to light a large number of catalytic reactions many of which seem very useful for this purpose. It has also been shown[6] that several of these reactions can be investigated by a simple dilatometric method.

In using the catalytic method for the determination of hydrogen-ion concentrations, there is, however, a point which requires special consideration. According to a recent extension of the theory of acid and basic catalysis,[7] the catalysis by hydrogen ion—which is actually not the free proton, but a chemical compound H_3O^+— is to be looked upon only as a special case of general acid catalysis. If the solution in which the concentration of hydrogen ion is to be determined contains acids other than H_3O^+, the catalytic action exhibited by the solution may be a compound effect in which all the acids present take part. Also the solvent itself by virtue of its acid–basic character may be catalytically active. The catalytic relations involved in such cases seem to be of a certain simplicity and are discussed elsewhere. However, for the exact determination of hydrogen-ion concentrations, it is preferable that those catalytic reactions be selected in which general acid–basic effects of this kind are absent or are at least proved to be negligible as compared with the effect of the hydrogen ion itself. Fortunately, there seems to be no difficulty in finding reactions which fulfil these simple conditions.

In the above-mentioned paper by Brönsted and Wynne-Jones[6] the use of diethyl acetal and similar compounds was suggested as a means of determining hydrogen-ion concentrations. With a view to making a further investigation of hydrolytic reactions and of their use in the determination of hydrogen ions at fairly high concentrations, with particular reference to the effect of salts, we have in the present study investigated the hydrolytic reactions of several acetals less sensitive to hydrogen ions than diethyl acetal.

2. The Reactants and their Preparations

Skrabal,[5] reviewing the extensive work of himself and his co-workers on the hydrolytic reactions of esters, acetals, etc., states that, in general, for a given aldehyde, the sensitivity of the corresponding acetals to hydrogen-ion catalysis of hydrolysis increases with the complexity of the

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[5] Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

[6] Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[7] Brönsted, *ibid.*, 24, 63 (1928).

alcohol involved and that, conversely, for a given alcohol, the sensitivity of its acetals increases with the complexity of the aldehyde used in their preparation. Skrabal and Sawiuk,[8] on the basis of roughly quantitative measurements, give tables for the relative rates of hydrolysis as the numbers of carbon atoms in the alcohol chain and in the aldehyde chain are increased. From these tables it appears that the acetal of methyl alcohol should give a convenient velocity of hydrolysis in the hydrogen-ion range around 0.001 to 0.005 equivalent per liter and that dimethyl *iso*butyral should cover a slightly higher range. Accordingly, these substances were prepared and tested.

Dimethyl acetal was prepared from methyl alcohol and 95% acetaldehyde by the method suggested by Adkins and Nissen[9] using calcium chloride as a catalytic dehydrating agent.

Twenty grams of anhydrous neutral calcium chloride was dissolved in seventy grams of methyl alcohol in a stout 250-cc. bottle with a tightly-fitting glass stopper. After thoroughly cooling in an ice-bath, fifty cc. of 95% acetaldehyde was poured carefully down the side of the bottle so as to form a separate layer. The bottle was then tightly stoppered and thoroughly shaken. A reaction, resulting in a considerable evolution of heat, took place immediately. The bottle was shaken overnight in a continuous shaker to complete the reaction. Upon standing in a separatory funnel for a few minutes, the acetal rose to form a light separate layer and was separated from the salt solution. It was washed several times with concentrated calcium choride solution and once with water. It then stood for several hours, during which time considerable water separated. The pure acetal was decanted from the water and was then dried over anhydrous potassium carbonate and purified by fractional distillation through an efficient column. The product used boiled at 63.5 to 64.5° (uncorrected).

Carrying Skrabal's ideas as to decreasing sensitivity with decreasing complexity a step further, the acetal of ethylene glycol should be even less sensitive to H_3O^+ catalysis of hydrolysis than is dimethyl acetal, even though the difference of but two hydrogen atoms may be rather slight.

This acetal, otherwise known as ethylene ethylidene oxide, was prepared in a manner similar to that used for the preparation of dimethyl acetal, also using calcium chloride as catalyst. Since it shows a high reciprocal solubility with water, it was washed only with concentrated calcium chloride solution three or four times. Most of the water was removed by allowing the acetal to stand for some time over anhydrous calcium chloride, after which the drying was completed over anhydrous potassium carbonate. After purification by fractional distillation, the acetal boiled at 82.5 to 83° (uncorrected).

3. Experimental Method

As the hydrolysis of the acetals here dealt with is accompanied by a considerable volume change, expansion in the case of dimethyl acetal

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[8] Skrabal and Sawiuk, *Z. physik. Chem.*, **122**, 357 (1926).

[9] Adkins and Nissen, THIS JOURNAL, **44**, 2749 (1922).

and of dimethyl *iso*butyral and contraction in the case of ethylene acetal, the course of the reaction may be followed by the dilatometric method used by Brönsted and Wynne-Jones.[6] In fact, the same dilatometers were used, one having a bulb holding 115 cc. and a capillary with a cross section of 0.32 mm. and the other a bulb holding 165 cc. and a capillary with a cross section of 0.13 mm. A calibration of these capillaries showed a uniformity of cross section within 1%. A convenient volume change was obtained with an acetal concentration of 0.01 to 0.04 molal.

The dilatometers were placed in electrically heated and controlled water thermostats maintained at 20 ± 0.01°.

The velocities of reaction were calculated by the method described by Guggenheim,[10] and are expressed as $k = -\mathrm{d}\ \ln c/\mathrm{d}t$ in min.$^{-1}$ using natural logarithms.

4. Standardization of Acetals

The first work undertaken was the verification of the strict dependence of the velocity of hydrolysis upon the H_3O^+ concentration in solutions of strong acids. To this end, the velocity of hydrolysis of dimethyl acetal was measured in solutions of perchloric acid ranging from 0.001 to 0.005 molar, and the constant $k_{H_3O^+}$ for molal acid calculated therefrom.

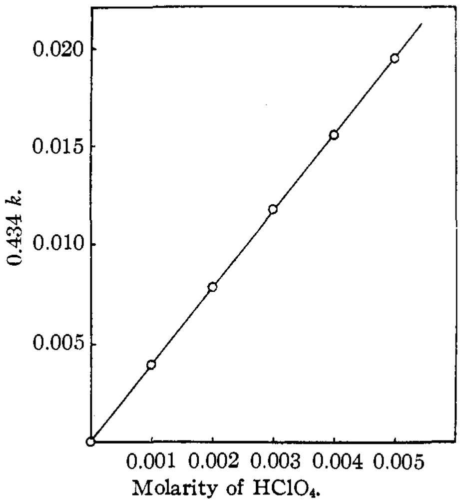

Fig. 1.—The hydrolysis of dimethyl acetal in perchloric acid solutions (t = 20°).

As will be seen from the constancy of $k_{H_3O^+}$ and from Fig. 1, there is a straight line relationship between the velocity of hydrolysis and the H_3O^+ concentration of the hydrolyzing medium. Since the concentrations are so low, no detectable salt effect due to the acid can be expected.

The work on dimethyl *iso*butyral never passed the preliminary stage, since it was found to cover approximately the same range of H_3O^+ concentrations as the more readily obtainable dimethyl acetal. Preliminary experiments showed the following results for the hydrolysis in solutions of perchloric acid.

It is apparent that for a given H_3O^+-concentration the *iso*butyral hydrolyzed about 1.1 times as rapidly as the corresponding acetal. Skrabal and Sawiuk reported 0.69 for the same ratio.

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[10] Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

TABLE I

HYDROLYSIS OF DIMETHYL ACETAL

Molarity of $HClO_4$	0.001	0.001	0.002	0.002	0.003	0.003
$0.434\ k \times 10^3$	3.91	3.98	7.77	7.86	11.82	11.76
$0.434\ k_{H_3O^+}$	3.91	3.98	3.89	3.93	3.94	3.92
Molarity of $HClO_4$	0.004	0.004	0.005	0.005		
$0.434\ k \times 10^3$	15.67	15.94	19.31	19.37		
$0.434\ k_{H_3O^+}$	3.92	3.90	3.86	3.87	Mean value, 3.92	

TABLE II

HYDROLYSIS OF DIMETHYLISOBUTYRAL

Molarity of $HClO_4$	0.003	0.004
$0.434\ k \times 10^3$	12.7	17.7
$0.434\ k_{H_3O^+}$	4.22	4.42

In the case of the ethylene acetal, the hydrolysis is so insensitive to hydrogen ions that—at reasonable velocities—the concentration of the acid in the hydrolyzing medium may have an appreciable salt effect. In fact, this effect is quite noticeable and the curve showing the relationship of the velocity constant of hydrolysis to the H_3O^+ concentration, instead of being a straight line, is convex downward as shown by Fig. 2. The velocities of hydrolysis of ethylene acetal in solutions of perchloric acid are as follows.

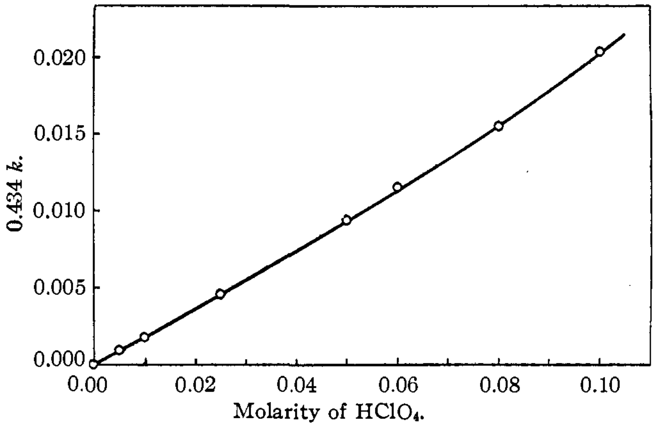

Fig. 2.—Velocity of hydrolysis of ethylene acetal in perchloric acid solutions (t = 20°).

TABLE III

HYDROLYSIS OF ETHYLENE ACETAL

Molarity of $HClO_4$	0.005	0.010	0.025	0.050 (HCl)	0.050
$0.434\ k \times 10^3$	0.912	1.82	4.62	9.35	9.40
$0.434\ k_{H_3O^+}$	0.182	0.182	0.185	0.187	0.188
Molarity of $HClO_4$	0.060	0.080	0.100	0.100	0.100
$0.434\ k \times 10^3$	11.50	15.58	20.3	20.4	20.2
$0.434\ k_{H_3O^+}$	0.192	0.195	0.203	0.204	0.202

That the increase in the velocity constant is a linear salt effect is shown in Fig. 3 by the straight line relationship of $k_{H_3O^+}$ to the H_3O^+ concentrations. The molar velocity constant for the catalytic hydrolysis of ethylene acetal is given by the equation

$$0.434\, k_{H_3O^+} = 0.180 + 0.19c$$

where c is the concentration of the acid producing the salt effect.

5. Absence of Acid Catalysis

As already pointed out, if one proposes to use the rate of reaction as a measure of the H_3O^+-concentration, troublesome complications are introduced if there are present in the solution under examination substances which have a similar catalytic effect large enough to be apparent above the limit of experimental error. It is important, therefore, to ascertain whether such a general acid effect is present in the reaction studied or not.

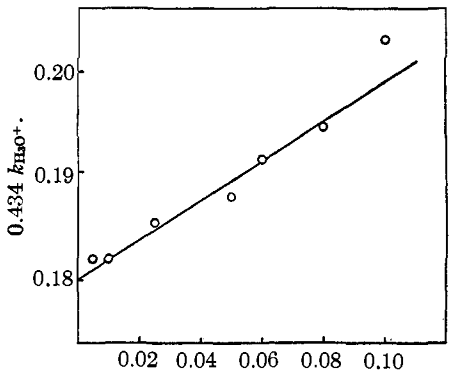

Fig. 3.—Salt effect of perchloric acid upon the hydrolysis of ethylene acetal (t = 20°).

It was previously found by Brönsted and Wynne-Jones that diethyl acetal shows no general acid catalysis. It is probable, therefore, that such an effect is also absent in the hydrolysis of dimethyl acetal. Furthermore, it has been shown, in connection with the generalized theory of acid and basic catalysis, that in order to show a detectable catalysis by acids in general, a reaction catalyzed by H_3O^+ ions must also have a detectable "spontaneous" reaction. Hence the absence of a detectable "spontaneous" reaction of hydrolysis of these acetals should indicate the absence of any detectable acid catalysis.

In order to detect any possible spontaneous reaction, 0.08 molal solutions of the acetals in distilled water neutral to brom thymol blue were prepared and placed each in a sealed dilatometer, being allowed to stand in the thermostat at 20° for forty-five days. At the end of that time, in each dilatometer, the meniscus was, within the error of reading, in its original position, indicating the absence of any spontaneous reaction with a velocity constant above 5×10^{-8} and the probable absence of any detectable "acid catalysis."

This conclusion was corroborated by other experiments. The dimethyl acetal was allowed to hydrolyze in solutions 0.00294 molar in perchloric acid and containing different amounts of the weak acid phenol. These results are as follows.

TABLE IV

HYDROLYSIS OF DIMETHYL ACETAL IN THE PRESENCE OF PHENOL

Molarity of phenol	0.00	0.10	0.20
0.434 *k*	0.01160	0.01154	0.01156

Even if a slight catalytic effect of the phenol may have been masked by a simultaneous counteracting medium effect, the conclusion that there is no detectable general acid catalysis in the hydrolysis of dimethyl acetal seems well justified.

It was somewhat more difficult to show the absence of general acid catalysis of ethylene acetal because of the difficulty of obtaining a buffered solution giving a suitable hydrogen-ion concentration or of finding a weak acid whose dissociation in a solution of perchloric acid of suitable strength would give a definitely known hydrogen-ion concentration. The second method was finally adopted and acetic and monochloro-acetic acids, whose dissociation constants are rather definitely known, were used as the weak acids to be added to the solutions of perchloric acid used as a hydrolyzing medium. From the dissociation constants of these weak acids, the H_3O^+ concentrations of the solutions used were calculated with an accuracy comparable with that of the experiment.

In calculating from the dissociation constant of a weak acid the H_3O^+ concentration of a solution containing definite amounts of a weakly and of a completely ionized acid, the ionization of the weaker will be repressed by the H_3O^+ of the stronger to such an extent that it will furnish only a small part of the H_3O^+ present. Hence, although it is necessary to make an approximation in determining the value of the dissociation constant of the weak acid in the particular solution being used, any slight uncertainty in this estimation will cause only a very small percentage error in the calculated value of the total H_3O^+ concentration to be measured. This method was used in calculating the H_3O^+ concentrations given in the second column of Table V as those to be expected if there is no general acid catalysis. The velocity constant corresponding to this H_3O^+ concentration (taken from Table III) was then compared with that found with the following results.

TABLE V

HYDROLYSIS OF ETHYLENE ACETAL IN VARIOUS ACID MIXTURES

Concn. of acids		Calcd. H_3O^+	Corresponding *k*	*k* Found
0.05 $HClO_4$	0.10 $ClCH_2COOH$	0.0545	0.01030	0.01033
0.05 $HClO_4$	0.20 CH_3COOH	.0505	.00951	.00950
0.075 $HClO_4$	0.10 $ClCH_2COOH$	.0787	.01525	.01533

From these results it is apparent that there is no general acid catalysis of the hydrolysis of ethylene acetal great enough to be shown above the limit of experimental error of these experiments. Thus we may conclude that the velocities of hydrolysis of these two acetals are, in the absence of salts, dependent only upon the H_3O^+ concentrations of the hydrolyzing media.

6. Salt Effects

The hydrolytic reactions of the acetals are particularly suitable for a study of primary salt effects, since the reactions are sufficiently insensitive to hydrogen ion to be measured in solutions in which the acidity is well defined by the presence of strong acids only. The study of the primary salt effect may, therefore, be carried out in solutions containing no weak electrolytes and the complications introduced by a concurrent secondary salt effect are avoided.

The results of a series of experiments on the effects of various salts upon the velocity of hydrolysis of dimethyl acetal in perchloric acid solutions are given in Table VI. The velocities found for the salt solutions are given as decimal fractions of that found in the presence of the same concentration of pure perchloric acid with no salt present. The experiments were made at various H_3O^+ concentrations. In a number of cases, the recorded values are the average of several concordant experimental results.

TABLE VI

SALT EFFECT UPON THE HYDROLYSIS OF DIMETHYL ACETAL

		Equivalent concentration				
	Salts[a]	0.05	0.10	0.15	0.20	0.30
1	NaCl	1.058	1.123	...	1.235	...
2	$NaClO_4$	...	1.133	...	1.27	...
3	$NaNO_3$	...	1.092	...	1.175	...
4	$NaOC_6H_2(NO_2)_3$	0.992	0.980	0.974	...	...
5	$NaSO_3C_2H_5$	1.023	1.060	1.093	1.133	1.196
6	$NaSO_3C_6H_5$	1.041	1.070	...	1.140	1.195
7	$NaSO_3C_{10}H_7$	1.020	1.043	1.084	1.110	...
8	KNO_3	...	1.100	...	1.180	...
9	NH_4Cl	...	1.110	...	1.200	...
10	$BaCl_2$	1.082	1.193	...	...	...

[a] Salt 4 is picrate, No. 5 is ethyl sulfonate and No. 7 is naphthalenesulfonate.

In the case of ethylene acetal, the salt effect was determined only for sodium perchlorate and sodium nitrate, all measurements being made at a perchloric acid concentration of 0.05 *M;* the acid concentration was kept constant in this case since it is large enough itself to exhibit a considerable salt effect. The figures in Table VII are, as before, the ratio of the velocities in the salt-containing solutions to that in a solution 0.05 *M* in perchloric acid and containing no salt.

TABLE VII

SALT EFFECT UPON THE HYDROLYSIS OF ETHYLENE ACETAL

		Equivalent concentration			
	Salt	0.05	0.10	0.15	0.20
1	$NaClO_4$	...	1.165	1.239	1.326
2	$NaNO_3$	1.039	1.080	1.123	1.172

These results are illustrated graphically by Fig. 4 and Fig. 5. It will readily be seen that, for these two acetals, the increase in velocity of hydrolysis in the presence of increasingly large amounts of salt is, up to a salt concentration of 0.2 *M*, directly proportional to the concentration of the salt. The individual nature of the salt has, however, a very great influence; for instance, sodium perchlorate in the hydrolysis of dimethyl acetal shows an effect two to three times as great as that of the least effective salt, sodium naphthalenesulfonate. The negative values recorded for sodium picrate are undoubtedly due to the incomplete dissociation of picric acid and are not to be looked upon as a real primary effect. However, the dissociation constant of picric acid cannot be calculated from these data since the actual salt effect of the picrate is unknown.

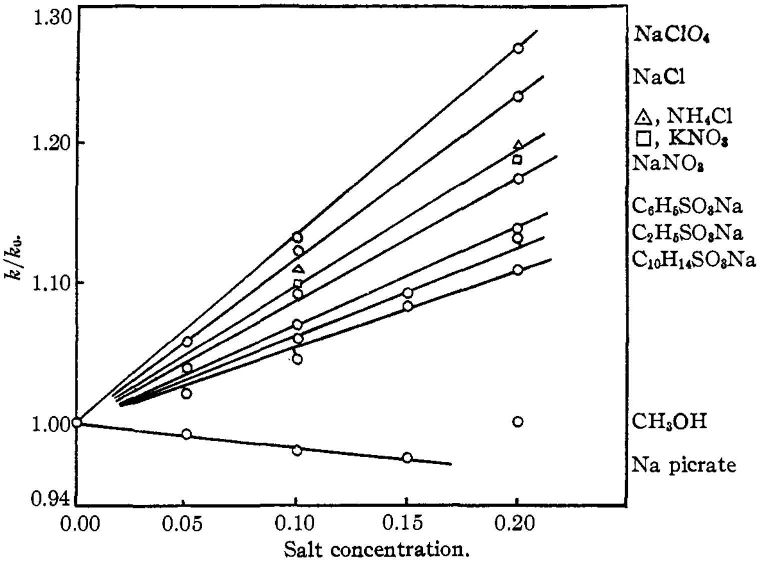

Fig. 4.—The primary salt effects upon the catalytic hydrolysis of dimethyl acetal (t = 20°).

It will be seen from Tables III and VII and from Figs. 3 and 5 that the salt effect of perchloric acid upon the hydrolysis of ethylene acetal is lower than the effect of sodium perchlorate. Methyl alcohol at a concentration of 0.20 *M* showed no measurable effect upon the hydrolysis of dimethyl acetal.

For the general applicability of the reactions here studied, the considerable salt effect demonstrated above is, of course, a complicating factor, unless the salt concentration is below 0.01 or the identity and concentration of any salts present are known. In many reactions, as for instance the inversion of cane sugar and the mutarotation of glucose, the salt effect is much smaller. It is to be hoped that reactions may be found which will combine insensitiveness to salts with the marked practical advantages of the reactions studied in the present investigation.

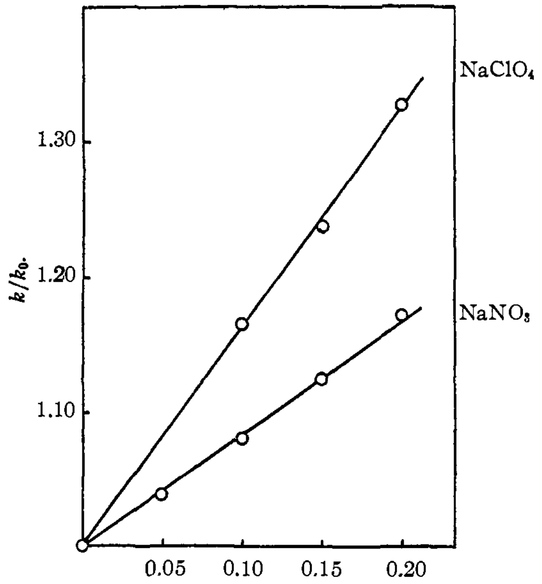

Fig. 5.—Salt effect on the hydrolysis of ethylene acetal (t = 20°).

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7. Summary

1. Dimethyl acetal and ethylene acetal have been prepared and their velocities of hydrolysis have been measured in solutions of perchloric acid at different concentrations. The velocity of hydrolysis is found to be directly proportional to the H_3O^+ concentration of the hydrolyzing medium. It is proposed to use the hydrolysis of these acetals for the measurement of hydrogen-ion concentrations.
2. It has been shown that these hydrolyses are not catalyzed to a detectable extent by acids other than H_3O^+.
3. The primary salt effect of various salts upon the catalytic hydrolyses of these acetals has been studied and is shown to be, up to a salt concentration of 0.2 M, a linear function of the concentration.
4. The magnitude of the primary salt effect is largely a function of the individual nature of the salt.

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