corresponding runs without catalysts total yields of 83 and 33% of the symmetrical isomers were obtained. These experiments show that these catalysts have no influence on either the total yield or the total yields of the symmetrical isomers. This is presumably due to the fact that because of the more elevated temperature required for this reaction, the stannic chloride and the iodine monochloride are volatilized and lost from the reaction mixtures despite the presence of a condenser.

Summary

Iodine and tin chlorides are suitable catalysts for the chlorination of dioxane to 2,3-dichlorodioxane, the yield being almost quantitative. Their use is not adapted to the further chlorination of 2,3-dichlorodioxane to tetrachlorodioxane on account of the high temperatures required for the latter reaction at ordinary pressures. The yields of the various tetrachlorodioxanes produced have been recorded.

GENEVA, NEW YORK RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF TORONTO]

The Sourness of Acids

BY R. M. BEATTY[1] AND L. H. CRAGG

Many attempts have been made in the past to relate the sourness of acids to various other properties such as their hydrogen-ion concentration, normality, vapor pressure, surface tension, etc., but with little success. A fairly complete survey of the literature up to the year 1926 was made by Dietzel.[2] Several important papers were missed in that discussion and further work has been done on the subject since 1926.[3]

In a preliminary paper, F. B. Kenrick[4] showed that the proportion of a phosphate buffer required to bring the *p*H of various acids of the same molar concentration to a fixed value of about 5 is roughly proportional to the sourness of the various acids alone, the sourness being defined as the normality of the hydrochloric acid solution of equal sourness. From this work it appeared that the sourness of an acid might be determined roughly by titration with a phosphate buffer to the shade of bromcresol green indicator corresponding to *p*H 5. To obtain the relative sourness of the acids Kenrick made use of the table of threshold values given by Paul and Bohnen (see Dietzel[2]) and assumed on the basis of a few experiments that the relative sourness of equimolar solutions was roughly independent of the concentration.

The present research was undertaken to test (a) the validity of this assumption, and (b) the accuracy of the conclusion drawn from the preliminary experiments. The *p*H's and total phosphate concentrations of the buffers used were within the ranges of the values possessed by most physiological fluids, such as saliva and blood serum.

Procedure

Equally sour solutions of various acids were prepared and the *p*H's of these solutions with addition of varying proportions of buffer were determined.

In all experiments (with the exception of those in section 2) hydrochloric acid was used as the standard and each of the other acids was altered in concentration until it had the same sourness as the hydrochloric acid.

The following precautions were taken in tasting the solutions in order to make the comparisons as accurate as possible.

(a) The nose was closed by a pair of balance forceps to prevent the interference of odors.

(b) For the more dilute acids 20 cc. of solution was taken into the mouth for each test and between each the mouth was rinsed with distilled water; in the case of acids which were sour enough to "set the teeth on edge" the tongue was dipped into a crucible of the liquid.

(c) In the final comparisons the effect of personal equation was reduced by placing the solutions in two tubes indistinguishable except for a hidden marking, and recording the decisions before re-identifying the tubes. These comparisons were continued until after seven tests there was no definite preponderance of choice of one as the sourer.[5]

---

(1) Holder of a Bursary from the National Research Council of Canada, 1931.

(2) Dietzel, *Kolloid-Z.*, **40,** 174 (1926).

(3) Special reference might be made to the following: Corin, *Arch. biol.*, **8,** 121 (1888); Becker and Herzog, *Z. physiol. Chem.*, **52,** 496 (1907); Liljestrand, *Arch. neerland. physiol.*, **7,** 532 (1922); Taylor, *Protoplasma*, **10,** 98 (1930).

(4) F. B. Kenrick, *Trans. Roy. Soc. Can., III,* [3] **25,** 227 (1931).

(5) Opinions as to the sourness of an acid vary slightly but definitely from one taster to another; consequently, although with accumulated experience (Cragg) small differences such as that between values for acetic acid equisour to 0.0025 *M* HCl (0.0070 in 3b and 0.0065 in 1) can now be reduced, it has been thought advisable to confine the data to the observations of one individual (Beatty in 1931).

The pH's of the various solutions were determined electrometrically with a Leeds and Northrup potentiometer and a cell of the type

Hg/HgCl, KCl (satd.)/acid solution + quinhydrone/Pt

In some of the experiments a gold electrode was used; it was found that platinum and gold gave the same results, but the platinum required cleaning less frequently.

Experimental Results

1. **Various Acids.**—Solutions of chloroacetic, tartaric, acetic and malic acids were adjusted by dilution to a sourness equal to that of 0.0025 M hydrochloric acid (M = moles per liter). These solutions were titrated with a phosphate buffer of pH 6.9, made up as follows: 3.240 g. of sodium dihydrogen phosphate $NaH_2PO_4 \cdot H_2O$, 0.480 g. of disodium hydrogen phosphate $Na_2HPO_4 \cdot 12H_2O$, 10 cc. of approximately normal sodium hydroxide solution, made up to one liter with distilled water. The results are given in Fig. 1.

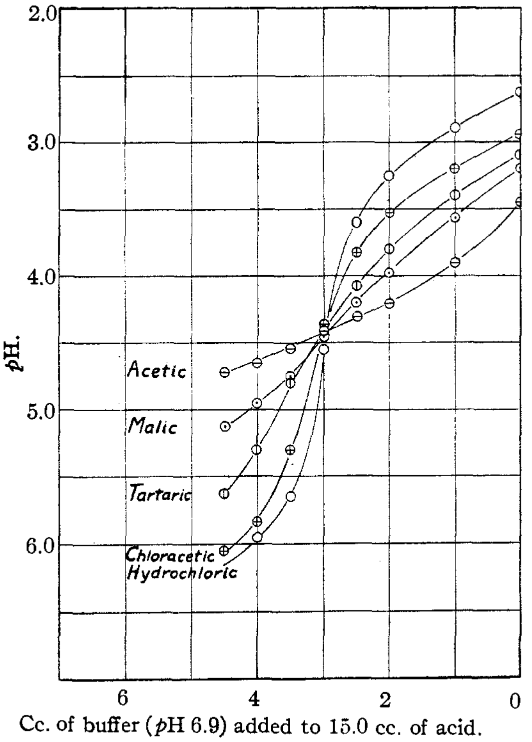


Fig. 1.—Concentration M: hydrochloric, 0.0025; chloroacetic, 0.0028; tartaric, 0.0016; malic, 0.0021; acetic, 0.0065.

2. **Saturated Carbon Dioxide Solution.**—When comparing hydrochloric acid and carbon dioxide solutions it was found advantageous to adjust the concentration of the hydrochloric acid solution. As the very peculiar taste of carbon dioxide solutions made comparison difficult, attempts were made to imitate the prickling sensation by adding thymol, chloroform, capsicum, oil of cloves, etc., to the hydrochloric acid. Although the prickling could be duplicated to a certain extent in this way, it was found that the sensation gradually increased in intensity so that when enough of the substance in question was added to imitate the immediate sensation characteristic of carbon dioxide solution, the liquid in a few seconds became too painful to retain in the mouth; when less was added the effect was too slow in coming. Attempts to imitate this sensation by supersaturating the hydrochloric acid with nitrous oxide were also unsuccessful. Finally, however, 0.0013 M hydrochloric acid was chosen as having about the same sourness as a saturated solution of carbon dioxide (0.0361 M from solubility data). The buffer used was the same as in section 1.

The results are shown in Fig. 2. Each point on the curve for carbonic acid was determined with a freshly made solution.

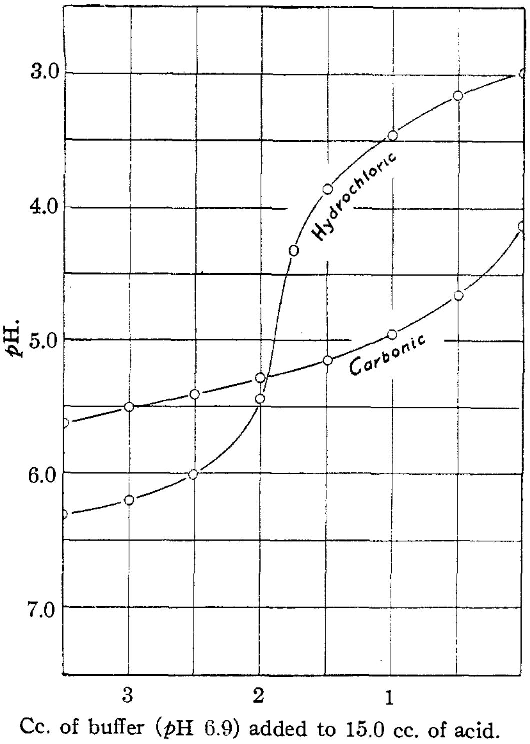


Fig. 2.—Concentration M: hydrochloric, 0.0013; carbonic, 0.0361.

3. **Equisour Acid Solutions at Various Concentrations.**—In these experiments equisour hydrochloric, acetic and tartaric acid solutions (representative of strong and weak monobasic acids and dibasic acids, respectively) were used

with a buffer of *p*H 7.4, ten times as dilute as that of section 1.[6]

In each set of experiments the concentrations of acetic and tartaric acids were chosen so that the acids were equisour to the hydrochloric acid used in that set. The acids were added to a measured volume of buffer.

The results are summarized in Figs. 3a, b, c, d and e.

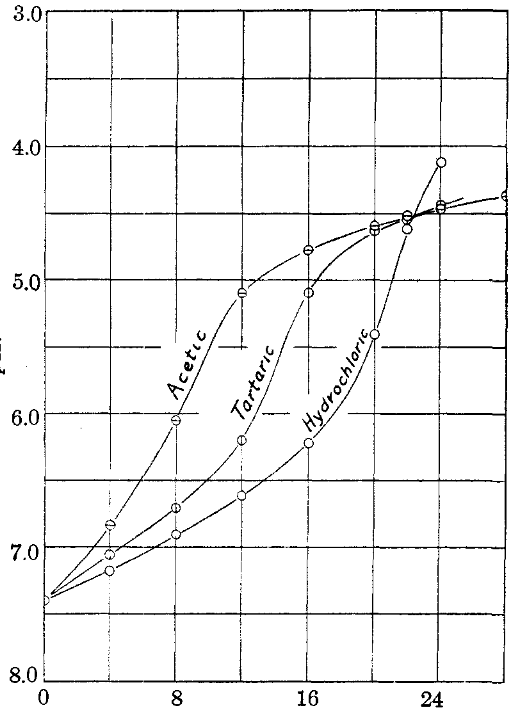


Fig. 3(a).—Concentration *M:* hydrochloric, 0.0010; tartaric, 0.0006; acetic, 0.0022.

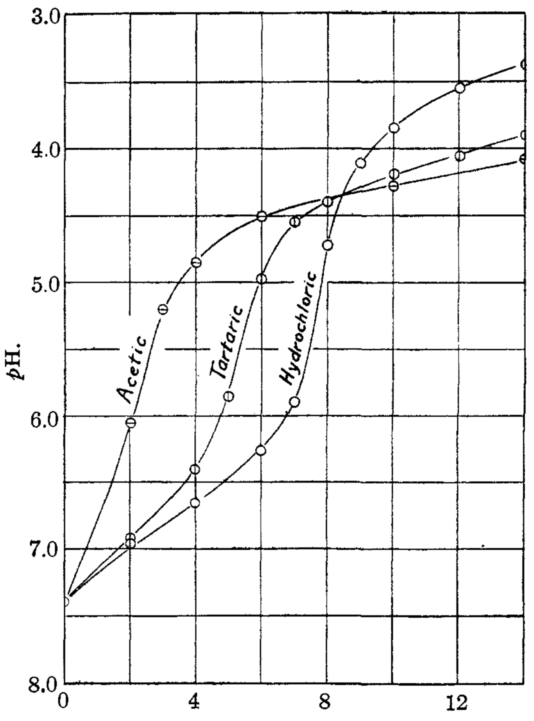


Fig. 3(b).—Concentration *M:* hydrochloric, 0.0025; tartaric, 0.0016; acetic, 0.0070.

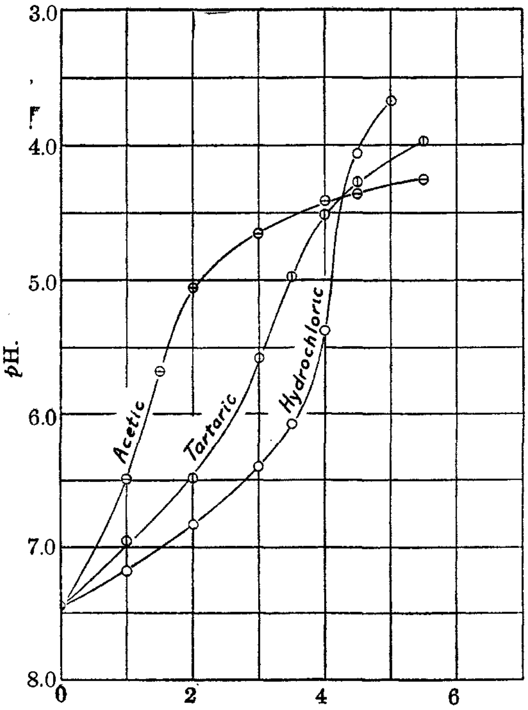


Fig. 3(c).—Concentration *M:* hydrochloric, 0.0050; tartaric, 0.0030; acetic, 0.0140.

Discussion

When 0.0025 *M* hydrochloric acid and the various equisour acid solutions are titrated with buffer of *p*H 6.9, the titration curves cross at a *p*H of 4.40 to 4.45 (see Fig. 1), *i. e.*, it requires the same amount of buffer to bring the *p*H of the different acids to *p*H 4.4. The position of this point is not affected by moderate changes in the *p*H and concentration of the buffer, for from Fig. 3b the curves still cross at *p*H 4.4 when acids of the same concentration as were used in section 1 are titrated with a buffer ten times as dilute and with a *p*H of 7.4. Furthermore, its position is constant even when the concentrations

[6] 0.3240 g. of $NaH_2PO_4 \cdot H_2O$, 0.0480 g. of $Na_2HPO_4 \cdot 12H_2O$, and 2.0 cc. of approximately normal NaOH solution, all made up to one liter with distilled water.

of the acids used are varied over almost the whole range of taste perception (see Table I).

TABLE I

Fig. no.	Concn. of HCl (standard), M	pH at intersection
3a	0.0010	4.5
3b	.0025	4.4
3c	.0050	4.4
3d	.0075	4.4
3e	.0100	4.2–4.4[a]

[a] The unpleasant sensation caused by acids of this concentration in the mouth makes judgment uncertain and it is very difficult to make an accurate comparison with the tongue dipping into the liquid.

It will be noted that the titration curves for hydrochloric acid and equisour carbon dioxide solution do not cross at pH 4.4, but at 5.3. We do not know whether this deviation indicates an exception to the rule or is due to the difficulty in tasting carbon dioxide solutions referred to in Section 2.

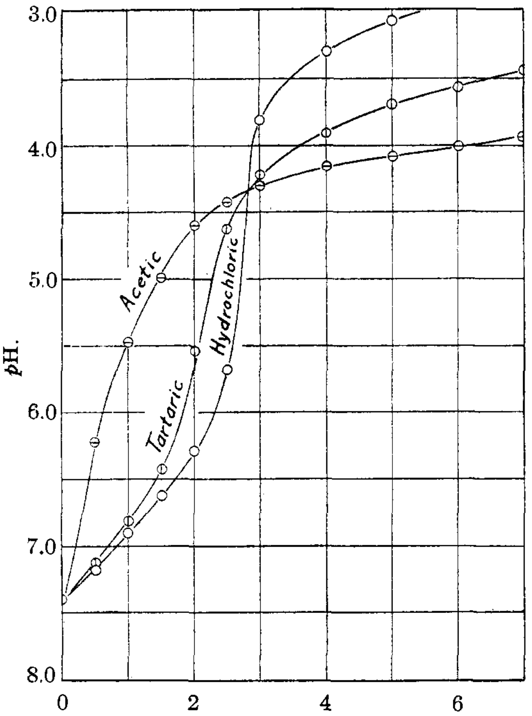


Fig. 3(d).—Concentration M: hydrochloric, 0.0075; tartaric, 0.0043; acetic, 0.024.

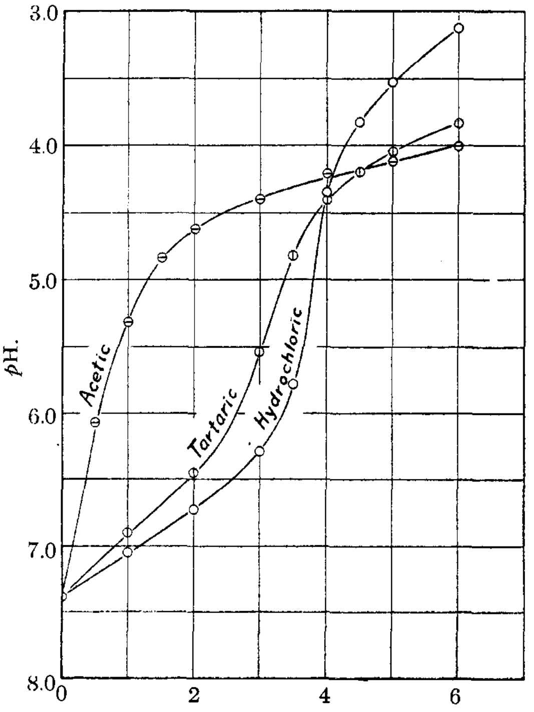
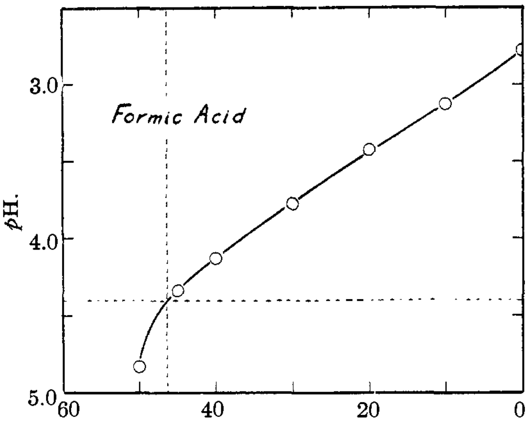


Fig. 3(e).—Concentration M: hydrochloric, 0.0100; tartaric, 0.0055; acetic, 0.045.



Cc. of buffer (pH 6.9) added to 60 cc. of acid solution.

Fig. 4.

These results show the very considerable degree of accuracy of the statement that the volume of buffer required to bring a given volume of an acid to a pH of 4.4 (Kenrick said "about 5") is proportional to its sourness. This is illustrated for acetic, tartaric and hydrochloric acids in Table II.

Acids more sour than 0.0100 M hydrochloric and less sour than 0.0010 M hydrochloric[7] cannot be compared by taste measurements, so that these results cover the whole range of measurable sour taste. They may be summed up by the formula $S = x/470$, where S is the sourness of the acid and x is the volume in cc. of the buffer required to bring 1 cc. of the acid to pH 4.4.

(7) Paul and Bohnen (see Dietzel[2]) consider this the threshold value for hydrochloric acid.

TABLE II

Fig. no.	Concentration, M Acetic	Tartaric	Sourness = normality of equisour HCl, M	Vol. buffer to bring 1 cc. acid to pH 4.4 Calcd. from figs.	$\frac{\text{Vol. buffer}}{\text{Sourness}}$
	M = moles per liter				
3a	0.0022	0.0006	0.0010	0.463	46 × 10
3b	.0070	.0016	.0025	1.18	47
3c	.0140	.0030	.0050	2.35	47
3d	.024	.0043	.0075	3.54	47
3e	.045	.0055	.0100	5.0 approx.	50[a]

[a] When checking the pH curves of 3e it was found that it required 4.15 cc. of buffer to bring 20 cc. of 0.0100 M hydrochloric acid to pH 4.4 rather than 4.0 cc., thus making the constant 480 approximately. The curves however still did not cross at a common point. This was attributed to the difficulty of making taste comparisons at this concentration. After trying acetic acid solutions of various concentrations, it was estimated that a solution 0.0038 M would give a titration curve crossing at pH 4.4, approximately. It is interesting to note that when plotted on Fig. 5, this point gives a continuation of the curve for acetic acid more similar in shape to that for tartaric acid.

Since it has been shown that changing the concentration and pH of the buffer within certain limits does not affect the validity of this relation the formula can be extended to take account of small variations in the buffer used; thus $S = x/K$ where K is a constant characteristic of the buffer.

Example: To Measure a Sourness by Titration.—Formic acid was chosen because it had not been used in the preceding experiments. The constant K for the buffer of pH 6.9 used in Sec. 1 can be calculated from the results in Fig. 1: $S = 0.0025$, $x = 3/15$ and therefore $K = x/S = 80$.

A formic acid solution (0.0090 M) was titrated with the buffer of pH 6.9 with the results shown in Fig. 4. From this curve it is seen that 60 cc. of acid required 46.5 cc. of buffer, and $S = 46.5/(60 \times 80) = 0.0097$. The actual sourness of this formic acid solution was measured by Beatty in 1931 and found to be 0.0100. Thus even for a sourness as high as 0.0100, the two values agree to within 3%.

These results also enable us to verify the assumption that the relative sourness of equimolar solutions is independent of concentration. Fig. 5 is plotted from the data of 3a, b, c, d and e. The curves give the sourness of acetic and tartaric acids at various molar concentrations. It is obvious that if these curves were straight lines the assumption would be exactly true. As it is the curves differ very little from straight lines up to a sourness of 0.0075, beyond which tasting becomes difficult. The assumption is therefore approximately true over the whole range of accurate tasting.

This research was carried out at the suggestion and under the direction of Dr. F. B. Kenrick.

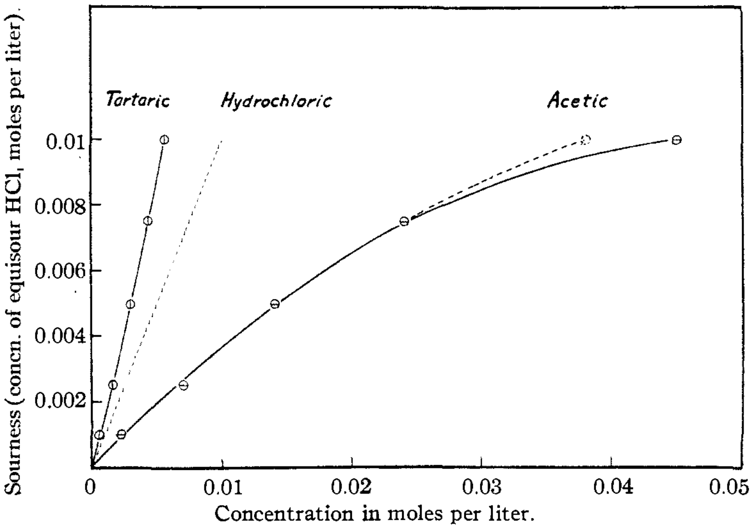


Fig. 5.—Sourness of acetic and tartaric acid solutions (Beatty).

Summary

The sourness of a solution being defined as the normality of an equally sour hydrochloric acid, it has been established for several typical acids that the sourness of an unbuffered acid solution is expressed by x/K, where x is the volume of a phosphate buffer required to bring a unit volume of the acid to a pH of 4.4 and K is a constant characteristic of the buffer used.

This relation has been verified for buffers of pH from 6.9 to 7.4 and of total concentration of anhydrous sodium phosphates from 0.04 to 0.35% by weight—within which ranges most physiological liquids lie.

TORONTO, ONTARIO, CANADA RECEIVED APRIL 30, 1935