to each other, one being a dissociated (or associated) form of the other and also that the associated form is likely a polymer of a ring type resulting from the mutual electrostatic neutralization of zwitterion structures.

## Summary

The rotatory dispersion of gelatin has been examined in various concentrations of sodium iodide at 0.5 and 40°, at five different wave lengths in the visible spectrum.

A single term Drude equation was shown to express the experimental results. From calculations it was shown that an absorption band at 2200 Å. governed the dispersion. Absorption spectrum data showed that gelatin has a high absorption in this region.

The rotatory dispersion constants of gelatin at 40° follow the linear equation $k_{40°} = 44.5170 - 6.220C_{\mathrm{NaI}}$.

The rotatory dispersion constants at 0.5° were found to be expressed by the sum of two equations

$$C_{\mathrm{NaI}} = \frac{1}{2.66}\log\left(\frac{a}{1-a}\right) - \log\left(\frac{1}{K}\right)$$

and the linear equation

$$K_{0.5°} = 46.3300 - 6.7605C_{\mathrm{NaI}}$$

It was concluded that the linear effect of salt concentration on the dispersion constant was due probably to a shift in the association of the solvent (hydrol–polyhydrol equilibrium) or an association between solvent and salt, and that the much greater effect of added salt at 0.5° was due to a dissociation or association of the gelatin molecule.

Based on the formulation of Lucas, it was shown that two and only two optically active species exist in gelatin solutions or gels.

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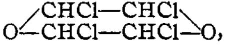
[CONTRIBUTION FROM THE DAIRY CHEMISTRY LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

# The Catalytic Chlorination of Dioxane[1]

BY J. J. KUCERA AND D. C. CARPENTER

According to recent investigations,[2] 1,4-dioxane and 2,3-dichlorodioxane on chlorination without catalysts give poor yields of the tetrachlorodioxanes and particularly of the symmetrical isomers  $\mathrm{O}\left\langle\begin{array}{c}\mathrm{CHCl{-}CHCl}\\ \mathrm{CHCl{-}CHCl}\end{array}\right\rangle\mathrm{O}$, which are valuable because of their quantitative yield of glyoxal on hydrolysis. Since preliminary experiments with copper, iron, manganese, nickel, tin and iodine chlorides showed that the two latter substances catalyzed the chlorination most vigorously, we have carried out carefully chlorinations using them.

Technical dioxane was purified by distillation, crystallization and a final distillation over sodium. The purified dioxane boiled at 101.5–101.7° and melted at 11°. The usual method of chlorination was employed, the amount of chlorine absorbed being calculated from the increase in weight of the reaction vessel.

Starting with 78.5 g. of dioxane and chlorinating at a temperature of 90°, a yield of 96.6% of the 2,3-dichlorodioxane was obtained, both with stannic chloride (added as 1 g. of $SnCl_2$) and with iodine chloride (added as 1 g. of I) catalyst. The amount of decomposition was negligible. This yield is considerably greater than that (69%) previously reported in the absence of a catalyst.[3]

In the chlorination of 47 g. of the 2,3-dichlorodioxane at 145° using stannic chloride as a catalyst (added as 0.5 g. of $SnCl_2$), the following unsymmetrical tetrachlorodioxanes were obtained: 37 g., b. p. 96° at 14 mm., and 1 g., m. p. 57–58°, together with symmetrical tetrachlorodioxanes: 12 g., m. p. 70° and 6 g., m. p. 143°. This corresponds to a total yield of 83% and a 32% yield of the symmetrical tetrachlorodioxanes. In the run with iodine chloride (added as 1 g. of I) as a catalyst at 145°, and starting with 81.8 g. of 2,3-dichlorodioxane, 68 g. of the unsymmetrical tetrachlorodioxane b. p. 96° at 14 mm., and 2 g., 21 g. and 10 g. of the symmetrical isomers melting respectively at 60, 70 and 143° were obtained. This corresponds to a total yield of 85% and a 33% yield of the symmetrical isomers. In

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[1] Approved by the Director of the New York Agricultural Experiment Station for publication as Journal Paper No. 98.

[2] Butler and Cretcher, THIS JOURNAL, **54**, 2987 (1932); Christ and Summerbell, *ibid.*, **55**, 4547 (1933); Baker, *J. Chem. Soc.*, 2666 (1932).

[3] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

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.

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[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]

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[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).