[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

CATALYSIS IN ACETAL FORMATION[1]

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In continuation of a study[2] of the factors that influence acetal formation, some 32 acetals have been prepared and a thorough investigation has been made of the relative efficiencies of ferric chloride, calcium chloride and hydrogen chloride as catalyst. Numerous other catalysts have been used in attempting to secure information as to the source and mechanism of catalytic power. The effects of water and of amount of catalyst have also been considered.

The effect of variation of the amount of salt catalyst upon the amount of acetal and methylal isolated is shown in Table I. In the preparation of methylal, paraformaldehyde equivalent to 1 mole of formaldehyde was heated at 100° with 2 moles of absolute methanol. In the case of acetal, 1 mole of acetaldehyde was allowed to react in a stoppered bottle with 2 moles of absolute ethanol. The reaction mixtures were allowed to stand for several days. It was shown that increased yields were not obtained in a longer time.

TABLE I

EFFECT UPON YIELD OF METHYLAL AND ACETAL OF VARIOUS AMOUNTS OF SALT CATALYSTS

$CaCl_2$, g	0.30	1.00	3.00	5.00	10.00	15.00	20.00	
Methylal, %	1.18	4.87	9.60	21.50	36.10	37.10	35.53	
$CaCl_2$, g	1.00	2.00	5.00	10.00	15.00	20.00	60.00	90.00
Acetal, %	16.65	19.50	36.30	47.20	53.50	54.60	53.60	46.30
$FeCl_3$, g	0.01	0.05	0.10	0.20	0.50	2.00	4.00	15.00
Methylal, %	28.70	42.10	54.60	69.50	89.00	93.50	97.00	91.90
$FeCl_3$, g	0.01	0.05	0.30	0.50	3.00	15.00		
Acetal, %	5.37	8.20	13.12	16.62	17.52	17.42		

It is apparent that in the case of either ferric chloride or calcium chloride, increase in the amount of catalyst within certain limits increases the amount of methylal or acetal that may be isolated. Increase in the amount of catalyst beyond the optimum amount for that salt and acetal is disadvantageous. Ferric chloride is very much the better catalyst for the production of methylal from paraformaldehyde, while calcium chloride is far superior for the production of acetal. The conditions for the formation of these two acetals are quite different, for in one case the catalyst must

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[1] This paper is an abstract of Part I of a dissertation presented by Elmer Wade Adams in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.—H. A.

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

depolymerize the paraldehyde, while in the other this is not necessary. The marked capacity of calcium chloride to abstract water from the acetal-alcohol mixture is of no avail in the formation of methylal, for the reaction goes nearly to completion irrespective of the presence of water. The tendency of calcium chloride to abstract water may be disadvantageous in fact, for it may thereby remove itself from the sphere of the reaction and hence can no longer promote the reaction. The optimum concentration of ferric chloride is very much lower than for the calcium chloride. Hydrogen chloride is as efficient as ferric chloride for the preparation of methylal from paraformaldehyde.

It seems worth while to examine reversible reactions to determine whether the point of equilibrium is affected by the catalyst used. The traditional view of physical chemistry is that it is not so affected, but there is enough evidence against this view to make it advisable, where possible, to examine experimental results critically. In the case of only 7 acetals was it possible to preserve a homogeneous solution when calcium chloride was used as a catalyst; hence the comparison is limited to these cases. Forty-five cc. of the alcohol and 5 cc. of the aldehyde were used in the case of the acetals and 42 cc. of alcohol and 8 cc. of the aldehyde in the case of the butylals. Either 0.01 g. of hydrogen chloride or 0.1 g. of calcium chloride was used. The first percentage given after the name of the acetal is that obtained with the hydrogen chloride catalyst, and the second with calcium chloride: ethyl acetal, 92.4 and 92.5%; *iso*propyl acetal, 55.4 and 56.5%; *n*-butyl acetal, 88.4 and 88.3%; methyl butylal, 92.3 and 93.2%; ethyl butylal, 86.6 and 86.5%; *iso*propyl butylal, 45.2 and 44.5%; and *n*-butyl butylal, 85.4 and 84.5%. The point of equilibrium was reached several times as rapidly with the hydrogen chloride as with the calcium chloride. Approximately the same amount of acetal was formed when hydrogen chloride was the catalyst as with calcium chloride.

While the same equilibrium point is reached with the two catalysts if the reaction mixture remains homogeneous, this is by no means true if enough calcium chloride is used to cause the formation of an aqueous layer. By using 2 moles of ethanol and 1 mole of acetaldehyde with hydrogen chloride, 54% of the aldehyde was converted to acetal. When 20 g. of calcium chloride was used, 86% of the aldehyde was converted to acetal. (This value, obtained by direct titration, is higher than that calculated by Nissen.)

The equilibrium point was also reached from the acetal side using both hydrogen chloride and calcium chloride as the catalysts in the case of diethyl acetal. The results agreed with those obtained from the synthetic side.

The advantage of the use of calcium chloride in the preparation of acetal apparently lies to a considerable extent in its dehydrating action in removing water from the system. In the case of the higher alcohols and acetals the solubility of water is so much less that no salt is needed to separate the water from the sphere of reaction so that calcium chloride loses some of its value as compared with hydrogen chloride. (When hydrogen chloride is used as a catalyst it must be *quickly and completely* neutralized with carbonate or sodium ethoxide before the reaction mixture is diluted with water, else the reverse reaction sets in so rapidly that much acetal is lost.)

If the efficiency of calcium chloride is due to a combination of catalytic and dehydrating or salting out qualities it seemed that the same effect could be produced by using a small amount of calcium chloride and a large amount of a good dehydrating salt such as zinc chloride or sodium chloride. One g. of calcium chloride with 2 moles of ethanol and 1 mole of acetaldehyde gives a 17% yield of acetal. When 19 g. of zinc chloride is used with 1 g. of calcium chloride, the yield is 5%. Five g. of calcium chloride gives 36% of acetal, while the addition of 15 g. of zinc chloride gives no acetal. When 20 g. of calcium chloride is used the yield of acetal is 54% (uncorrected for losses in working up the product). The combination of sodium chloride with small amounts of calcium chloride is equally inefficient.

An increase in the amount of catalyst either of calcium chloride or of hydrogen chloride causes a marked increase in the rate of reaction. There is one exception to this general statement and that is in the case of the use of calcium chloride in the reaction of methanol and acetaldehyde. When 45 cc. of absolute methanol and 5 cc. of acetaldehyde are used with 0.1 g. or 0.5 g. of calcium chloride the reaction goes about 36% to completion in 20 hours, while with 3.0 g. of the salt it is 20% and with 5.0 g., 15% complete. The more usual case, however, is as in the reaction of ethanol and acetaldehyde. Under the same conditions the reaction is 17% complete with 0.1 g. of the salt, 21% with 0.5 g., 46% with 3.0 g. and 56% with 5 g. at the end of an hour and a half. Butanol and acetaldehyde react much more slowly; for example, 0.1 g. of calcium chloride gives 7% completion, 0.5 g. gives 24% and 1.3 g. gives 51% in 75 minutes. *iso*Butanol gives a similar rate. These alcohols require perhaps six days for the completion of the reaction, while ethanol requires considerably less than half this time with the same concentration of catalyst. Methanol is perhaps slower than the butanols in rate of reaction.

Butyraldehyde reacts more slowly than does acetaldehyde. The reaction of acetaldehyde with ethanol is 50% complete in six hours, while 24 hours is required with butyraldehyde for a like extent of conversion, 0.1 g. of calcium chloride being used. Under similar conditions, 5 days is required for a 55% reaction of butyraldehyde with butanol or *iso*butanol. Increasing the amount of catalyst ten times increases the rate by a similar amount.

The rate of formation of the acetals increases rapidly with increase in the amounts of hydrogen chloride used as catalyst. With an amount of catalyst equal to 0.01 of the amount of alcohol used, the conversions are complete within five or ten minutes. With one-tenth as much catalyst as noted above the reaction in the case of acetal itself requires an hour or more. The butylals react much more slowly with the lower concentrations of catalyst. The reactions are almost instantaneous when 1% as much catalyst as alcohol is used.

A considerable amount of experimentation was done in attempting to carry out the acetal reaction in an inert solvent. Acetone would have been an ideal one to use but aldehyde cannot be conveniently determined in the presence of the ketone. Ether, xylene and toluene were used but it seemed impractical to preserve a homogeneous solution after reaction began. The separation of solid alcoholates and of aqueous layers in other experiments made the interpretation of results so complicated that no extended report of the results will be given.

A rather interesting correlation has been observed between the tendency of a salt to form an alcoholate and its ability to catalyze the formation of acetal. The following compounds are reported in the literature as forming alcoholates, and are also reported or have been observed in this Laboratory to catalyze the formation of acetal: calcium chloride, bromide and nitrate, lithium chloride, magnesium chloride and nitrate, aluminum chloride, manganese chloride, sodium iodide, thorium chloride, cupric chloride, arsenic trichloride, stannic chloride and nitric acid. The following compounds are reported or have been observed in this Laboratory to catalyze the acetal reaction but no report has been found in the literature as to whether they form alcoholates: cerium, ammonium, lithium, cuprous, ferric and zinc chlorides, cupric sulfate, ammonium bromide, sodium acid sulfate, monosodium phosphate, silver nitrate, calcium iodide, potassium acid sulfite, oxalic, tartaric, phosphoric, monochloro-acetic and hydrochloric acids. The following compounds have shown no catalytic activity for acetal formation when tested in this Laboratory and none of them have been reported as forming alcoholates: barium, sodium and potassium chlorides, calcium, sodium, cerium and silver sulfates, potassium, sodium and lead carbonates, sodium acid carbonate, potassium and sodium bromides, manganese and barium nitrates, trisodium phosphate, potassium iodide, calcium and sodium acetates and acetic acid. The following compounds are reported as forming alcoholates, but have never been tested for catalytic activity in acetal formation: thallium, lanthanum, neodymium, chromium, cobalt, antimony, platinum and titanium chlorides, magnesium bromide, magnesium and cobalt iodides, selenium dioxide and sodium sulfide.

No salt that has failed to produce acetal has been reported as forming an alcoholate. No salt so reported and which has been tried has failed to produce some acetal. One can hardly escape the conclusion that the ability to form an alcoholate is a prerequisite to the manifestation of catalytic action in acetal formation.

All of the substances that have been found to be catalysts for the formation of acetals are either acids or show an acid reaction when dissolved in water. Numerous reaction mixtures were tested for hydrogen-ion concentration by the colorimetric method and all of them showed a Sörensen (*P*H) value of less than 7; that is, they were acid in reaction. A sample of "calcium chloride" which gave very poor results in the preparation of acetal in the laboratory of the Eastman Kodak Company was found in this Laboratory to be mostly $CaCl_2.2H_2O$ with enough calcium hydroxide present to give a basic reaction. When this was dehydrated in a current of hydrogen chloride and the excess of the latter removed with air free from carbon dioxide, the product was as good as any calcium chloride. A very small amount of an alkali such as sodium carbonate greatly decreases the catalytic power of calcium chloride.

Most of the above facts could be correlated by the assumption that the real catalyst is the hydrogen ion. It appears to us, however, that the ability of a substance to produce hydrogen ions in water and its ability to catalyze acetal formation are coexistent rather than that the latter depends on the former. There is no apparent relationship between the acidity of a salt and its efficiency as an acetal catalyst. For example, zinc chloride is more acidic than is calcium chloride, yet it is not so good a catalyst. The rate of acetal formation with 0.5000 g. of calcium chloride is about twice as great as with 0.0011 g. of hydrogen chloride. It appears questionable whether that amount of calcium chloride would produce so many more hydrogen ions (through hydrolysis and ionization of the hydrochloric acid formed) under the conditions of experiment than would the hydrogen chloride. Then, too, the very condition that is most harmful to the rate of the reaction is the very one that is conducive to ionization. As will be shown in a later paper, the velocity "constants" for the acetal reaction fall off rapidly as water accumulates in the reaction mixture. When 0.055 mole of water was added to 1 mole of ethanol and 0.091 mole of acetaldehyde about 7% of the aldehyde was converted at the end of an hour while if no water had been added 30% would have been converted. The final yield of acetal is reduced only 4% through the effect of the water.

It seems probable that the seat of catalytic activity is to be found around the anion end of the undissociated acid or salt rather than in dissociated hydrogen ions.

Experimental Part

Catalysts.—The salts used were of the usual c. p. grade unless otherwise specified. Hydrogen chloride was prepared from sodium chloride and sulfuric acid. Its concentration was determined by titration with standard alkali or by the Volhard method.

Aldehydes.—Acetaldehyde was fractionated from a commercial product and then boiled at 21.0°. It contained 99% of acetaldehyde as shown by the modified Seyewetz-Bardin method.[3] Propionic, *iso*butyric and cinnamic aldehydes and *m*-nitrobenzaldehyde were obtained from the Eastman Kodak Company. Butyric aldehyde was fractionated from the commercial product and dried over anhydrous copper sulfate; b. p., 72–73°. Heptaldehyde, furfural and benzaldehyde were prepared by fractionation under reduced pressure.

Alcohols.—Methanol, ethanol, *n*-propanol, *iso*propanol, *n*-butanol and *iso*butanol were dried over calcium oxide and showed correct boiling points within 1°. Secondary butanol boiling from 98–100° was obtained by drying over quicklime and fractionating a commercial product made from the butylene resulting from the cracking of petroleum.

Tertiary butanol was made from *iso*butanol by a slight modification of the method described by Read and Priestly in the abstracts of the Organic Division of the American Chemical Society, September, 1923. *isoButanol* was dehydrated over alumina at 450°. The *iso*butylene so formed was collected in carbon tetrachloride held below 0° by an ice-salt pack. The saturated solution was then gradually forced into 50% sulfuric acid, held below 0°. During this operation and thereafter for several hours the mixture was vigorously agitated, the temperature in the meantime being allowed to rise gradually to that of the room. The upper aqueous layer was separated and placed in a large evaporating dish. The sulfuric acid was neutralized with sodium carbonate decahydrate. After complete neutralization a supernatant layer of oil on a small amount of water was in evidence. This was best removed from the large mass of salt cake by immediate centrifuging and subsequent decantation and separation of the two layers. This oil was purified by dehydration with excess lime, treatment with metallic sodium, and re-dehydration with lime. The product boiled at 81° (uncorr.) and melted at 25°. Approximately 100 cc. of pure *tert.*-butanol was obtained from 500 cc. of *iso*butanol. It was found that small amounts of alcohol were obtained by repeated fractionations of the remaining aqueous layer after the supernatant oil had been separated. A small additional amount of alcohol was obtained, by washing the carbon tetrachloride again with water and salting out with anhydrous potassium carbonate.

The *iso*-amyl alcohol boiled at 131–135°. *tert.-Amyl alcohol* was supplied by Merck and Company. After dehydration with lime the whole amount boiled constantly at 101° uncorrected. Pure *γ-phenyl-propyl alcohol* was obtained by the method suggested by Conant and Kirner.[4] The technical grade supplied by the Eastman Kodak Company was the source. It was also found that a fair grade could be obtained by fractionation under reduced pressure without converting it into the half phthalic ester. The *benzyl* and *phenyl-ethyl* alcohols were supplied by the Eastman Kodak Company.

The Method of Experimentation for all the aldehydes except formaldehyde was essentially that used by Nissen. When hydrogen chloride was the catalyst the method was modified in that the reactants were cooled to a temperature several degrees below zero before mixing. At the end of 15 or 20 hours the reaction mixture was transferred to a liter beaker and enough solid sodium carbonate added to neutralize the acid present. The reaction mixture was then treated with an equal volume of a sodium carbonate solution, and extracted with ether. The etherial solution was dried over potassium carbonate and fractionated.[5] When ferric chloride was used for the preparation of acetal, Nissen's procedure was modified in that

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[3] Seyewetz and Bardin, *J. Soc. Chem. Ind.*, **25,** 202 (1906).

[4] Conant and Kirner, THIS JOURNAL, **46,** 232 (1924).

[5] Fischer and Giebe, *Ber.*, **30,** 3053 (1897).

sodium carbonate in an amount double that of the ferric chloride used was added to the reaction mixture after 10 or 12 hours. After the acid was neutralized and the ferric hydroxide precipitated, 100 cc. of water was added, the upper layer separated and washed with two 50cc. portions of water. The oil was then worked up in the usual manner.

In the case of paraformaldehyde the procedure was as follows. Two moles of absolute methanol was placed in a bottle having a spring-held stopper, with an amount of paraformaldehyde corresponding to one mole of formaldehyde. The proper amount of the desired catalyst was then added and the flask heated on a water-bath at 100° for 15 to 25 hours, or until the solid had disappeared. The contents were then placed in a 500cc. round bottom Pyrex flask, a Vigreux column was attached and two fractions were collected at 42–45° and 45–70°. The higher-boiling fraction was then placed in a clean, dry flask and redistilled, the portion boiling from 43° to 45° being added to the first low-boiling portion. These combined distillates were then refractionated through a similar apparatus and the portion boiling from 42° to 45° considered to be methylal.[6]

Determination of the Amount of Acetal Formed from the Amount of Aldehyde Reacting.—It is difficult and tedious to compare different catalysts and different aldehydes and alcohols as to their effects upon acetal formation entirely by means of the process of isolating the pure acetal. A more rapid and accurate method was needed. Preliminary experiments indicated that such a method was to be found in the titration of the unchanged aldehyde by a modified Seyewetz-Bardin method. The method used was as follows.

Five cc. of the mixture in which aldehyde was to be determined was pipetted into 40 cc. of a slightly alkaline (to phenolphthalein), 10% solution of sodium sulfite held at a temperature near 0°. The alkalinity developed was titrated against N sulfuric acid. The end-point was taken as the point at which the color of the sample being titrated was of the same tint as that of 40 cc. of the sodium sulfite also held near 0° and to which the same amount of indicator had been added. One cc. of N acid is equivalent to 0.044 g. of acetaldehyde.

Experiments showed that the catalysts used did not cause polymerization of the aldehyde during the usual time involved in the acetal reactions and hence that no large error was introduced into the results because of this reaction. The method was found to be accurate against furfural, acetaldehyde, propionic, butyric, *iso*butyric, heptylic and cinnamic aldehydes. In the case of the latter, 1 cc. of N sulfuric acid is equivalent to 0.0005 mole of the aldehyde, for two moles of the bisulfite add to one mole of the aldehyde, addition taking place at the olefinic as well as the carbonyl linkage.

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[6] Trillat and Gambier, *Bull. soc. chim.*, [3] **11**, 752 (1894).

Table II

Various Acetals

Acetal	Method of preparation	Boiling point °C.	Yield %	Analyses				Notes
				Calcd.		Found		
				% H	% C	% H	% C	
n-Propyl	1	143–144	..	...	...	...	...	A
*iso*Propyl	2	122	..	12.33	65.75	12.54	65.57	B
n-Butyl	2	186	69	12.64	68.96	12.59	68.94	..
*iso*Butyl	2	175–176	68	...	...	...	...	C
sec.-Butyl	2	171	..	12.64	68.96	12.66	68.82	..
Methyl butylal	2	114	30	11.86	61.01	11.91	61.17	..
Ethyl butylal	2	143	50	12.33	65.75	12.39	65.69	..
n-Propyl butylal	1	182	..	12.64	68.96	12.85	68.82	..
*iso*Propyl butylal	2	164	26	12.64	68.96	12.71	68.79	..
n-Butyl butylal	2	213	50	...	...	...	...	D
*iso*Butyl butylal	2	203	46	12.87	71.29	12.98	71.14	..
Ethyl propylal	1	124	..	...	...	...	...	E
*iso*Propyl propylal	1	146.5	..	12.50	67.50	12.55	67.40	..
Ethyl *iso*butylal	1	138	..	12.33	65.75	12.58	65.70	..
*iso*Propyl *iso*butylal	1	158	..	12.64	68.96	11.80	68.80	..
Methyl furfurylal	1	178	..	7.04	59.15	7.0	58.9	F
Ethyl furfurylal	1	191–192	..	...	...	...	...	G
*iso*Propyl furfurylal	1	201	..	9.09	66.66	8.63	65.61	..
Ethyl heptal	1	209	..	...	...	...	...	H
*iso*Propyl heptal	1	240	..	13.2	72.22	13.26	71.98	..
Ethyl cinnamal	1	279	..	...	...	...	...	I
Methyl benzal	2	207	..	...	...	...	...	J
Ethyl benzal	2	221	28	...	...	...	...	K
*iso*Propyl benzal	1	234	..	9.62	75.0	9.76	74.9	L
n-Butyl benzal	2	262	17	10.17	76.22	10.21	76.1	..
*iso*Butyl benzal	2	255	15	10.17	76.22	10.21	76.1	..
Ethyl *m*-nitrobenzal	1	167 (23 mm.)	..	...	...	...	...	M

Notes: A. Reported as boiling at 146–148°. B. Crude product previously reported, Reichert, Bailey and Nieuwland [This Journal, **45**, 1552 (1923)]. C. B. p., 168–170° [Claus and Trainer, *Ber.*, **19**, 3004 (1886)]. D. B. p., 105–109° (18 mm.) [Van Resseghem, *Bull. soc. chim. Belg.*, **28**, 335 (1919)]. E. B. p., 122–128° (744 mm.) [Fischer and Giebe, *Ber.*, **30**, 3053 (1897)]. F. Ten moles of alcohol, 1 mole of aldehyde and 0.0046 mole of hydrogen chloride were used. The unreacted aldehyde was removed after three days with a 20% sodium sulfite solution, the alkalinity being not quite all neutralized to phenolphthalein. G. B. p., 189–191° (uncorr.), when prepared by use of orthoformic ester [Claisen, *Ber.*, **31**, 1015 (1898); **40**, 3903 (1907)]. H. B. p., 204–205° [Fischer and Giebe, *ibid.*, **30**, 3053 (1897); **31**, 545 (1898)]. I. B. p., 264–266°, when prepared from orthoformic ester (Claisen, Note G, above). J. 0.1% of hydrogen chloride was added to the reaction mixture of alcohol, aldehyde and calcium chloride. The unreacted aldehyde was extracted with acid sodium sulfite. K. B. p., 222° [Fischer and Giebe, Note H, above. MacKenzie, *J. Chem. Soc.*, **79**, 1213 (1910)]. L. No product was obtained through the use of calcium chloride as a catalyst. M. B. p., 162–164° (19 mm.) [Claisen, *Ber.*, **31**, 1015 (1898)].

*iso*Propyl cinnamal and *tert.*-butyl, *iso*-amyl, β-phenyl-ethyl and benzyl acetals were also formed but were not purified on account of the small quantities available.

The sulfite method of titration of aldehydes is not satisfactory for the estimation of benzaldehyde and *m*-nitrobenzaldehyde in the presence of their acetals as the end-point is indistinct. The method described below gave excellent results with these aldehydes. Twenty cc. of 0.8561 *N* sodium hydroxide solution was placed in a 150cc. Erlenmeyer flask which was covered with a watch glass and placed in an oven held at 65–70°. When the standard alkali had reached this temperature 30 cc. of 3% hydrogen peroxide was added and followed quickly by the sample of benzaldehyde (approximately 1 cc. either as pure benzaldehyde or in a 5cc. reaction mixture) and 5 cc. of 95% ethyl alcohol. The latter greatly shortens the time necessary for complete oxidation of the aldehyde. The aldehyde was always found to be completely in solution after 20 to 25 minutes and the odor but faint. At this point 10 cc. more of hydrogen peroxide was added and the flask returned to the oven for 10 to 15 minutes. The flask was then removed and the excess of alkali titrated while warm with 1.1175 *N* sulfuric acid, using phenolphthalein as indicator.

The data obtained in the preparation of a number of acetals are summarized in Table II. The method of preparation involving the use of hydrogen chloride as a catalyst is called "1" in the table. The acetals so prepared were chiefly isolated from a reaction mixture of 1 mole of the alcohol and 0.091 mole of the aldehyde, which was used in work described in another paper. The method involving the use of calcium chloride is referred to as "2," and is the same as that previously described. The time necessary for the complete reaction varies from a few hours to several days. The acetals were best purified by shaking them with an alkaline solution of hydrogen peroxide at about 65° (oven) to remove the excess of aldehyde. They were then washed with water, dried over anhydrous potassium carbonate and finally over sodium before distillation.

Summary

Ferric chloride is a most efficient catalyst for the production of methylal from paraformaldehyde and methanol. A yield of 97% of the calculated amount of methylal may be obtained by the use of the reactants in the proportion of 2 moles of methanol, 1 mole of trioxymethylene and 4 g. of the catalyst. Ferric chloride is much superior to calcium chloride in the preparation of methylal although the latter is much more efficient in the preparation of acetal.

Calcium chloride and hydrogen chloride cause the production of the same amount of acetals if the homogeneity of the reaction mixtures is maintained by the use of excess alcohol or of small amounts of the salt catalyst. When, however, sufficient calcium chloride is used to cause the separation of an aqueous salt layer the percentage of acetal formed may be, in some cases, almost double that obtained with hydrogen chloride. The advan-

tage in the use of calcium chloride becomes less marked with the higher alcohols and aldehydes.

The butylals are formed much more slowly than the acetals and butanol reacts more slowly than ethanol. A few tenths of a g. of hydrogen chloride will give a much more rapid reaction than will 20 g. of calcium chloride. Water inhibits this reaction out of all proportion to the extent to which it lowers the equilibrium point.

A close correlation has been pointed out between the ability of a salt to form an alcoholate and its ability to catalyze acetal formation. Apparently, the first but by no means the only prerequisite for a catalytically active salt is that it be able to form a compound with the alcohol.

All known catalysts for the acetal reaction give an acidic solution when dissolved in water, but the evidence is against the assumption that the real catalyst is the hydrogen ion. The seat of catalytic activity is probably at the anion end of the undissociated salt or acid, although the efficiency of this portion of the molecule is profoundly modified by the element at the other end of the molecule.

Methods of preparation and purification have been given for 17 hitherto undescribed acetals and for 11 acetals that have previously been prepared. Four other new acetals were obtained but not in sufficient quantities for analysis.

The Seyewetz-Bardin method for the determination of acetaldehyde has been extended to the quantitative estimation of furfural, propionic, butyric, *iso*butyric, heptylic and cinnamic aldehydes. Benzaldehyde and *m*-nitrobenzaldehyde have been quantitatively determined by oxidation with hydrogen peroxide in a solution of known alkalinity.

A method for the preparation of *tert.*-butanol, m. p., 25°, from *iso*butanol has been given.

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