

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

THE CONDENSATION OF ALDEHYDES TO ESTERS BY ALUMINUM ETHOXIDE

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RECEIVED AUGUST 9, 1923

Aldehydes react to give polymers, esters, aldols or benzoines depending primarily upon the condensing agent employed and to a less extent upon the specific aldehyde involved. Since these reactions are so dependent upon the catalyst used it has seemed that their study together with that of acetal formation¹ offered an excellent point of attack upon the problem of the causation and mechanism of organic reactions. To that end an investigation of the condensation by aluminum ethoxide of acetaldehyde to ethyl acetate is being made. W. E. Tischtschenko² discovered that the reaction, $2 RCHO = RCO_2CH_2R$, was induced by aluminum or magnesium ethoxide and prepared esters from formaldehyde, acetaldehyde, benzaldehyde, *p*-nitrobenzaldehyde, chloral, α -bromo-*isobutyraldehyde*, heptylic, propionic, *isobutyric*, and *isovaleric* aldehydes. From 100 g. of acetaldehyde and 15 g. of aluminum ethoxide he obtained 69 g. of ethyl acetate. Through the use of lower concentrations of catalyst he believed that he obtained and identified aldol, β -hydroxyethyl butyrate, and its mono-acetic ester, β -butylene glycol and its diacetic ester, crotonic aldehyde, paraldehyde, acetal and ethyl alcohol. We have the utmost respect for Tischtschenko's work, since whenever we have duplicated his experiments we have substantiated his conclusions.³ So much cannot be said for the numerous patents.⁴ The patents claim advantages for the use of aluminum chloride, "chloroethylate," water, potassium alum, copper sulfate, or camphor with the catalyst, and for the melting of the catalyst and pouring it into xylene or on a cold slab to convert it into an "active form."

We have found that aluminum ethoxide exists in two allotropic forms, which we have designated as *alpha* and *beta*. The α form is soluble in

¹ Adkins and Nissen, *THIS JOURNAL*, **44**, 2749 (1922).

² Tischtschenko, *J. Russ. Phys. Chem. Soc.*, **38**, 355, 482 (1906); *Chem. Centr.*, **77**, 1309, 1552 (1906).

³ A translation of Tischtschenko's original articles was made by virtue of a grant from the University of Wisconsin and through the courtesy of the Library of the University of Michigan.

⁴ See p. 162 "Catalysis in Industrial Chemistry," by Henderson. Longmans, Green and Company, New York, 1919. (Consortium für Elektrochemische Industrie, Brit. pats. 26,825, 26,826 (1913), 1,288 (1915), 4,887 (1915); Ger. pats. 27,7111 (1912), 277,187, 277,188 (1913), 258,990, 286,812, 314,210, 218,898 (1914), 282,266, 308,043 (1915); French pat. 465,965 (1913); Norwegian pats., 30,419, 30,906 (1920); Swiss pats., 74,445 (1917). *C. A.* **8**, 3489 (1914); **9**, 695, 1226, 1829 (1915); **10**, 666, 1910, 2388 (1916); **11**, 2027 (1917); **13**, 1076 (1919); **14**, 2803 (1920); **15**, 1029 (1921).)

xylene to the extent of about 45 g. in 100 cc. of solution and is slowly soluble in ether. It slowly solidifies at a little above room temperature. The β form is soluble in xylene to the extent of 0.4 g. in 100 cc. It melts at 140° and is very slightly soluble in ether. The ethoxide as prepared by the method of Wislicenus is wholly α . Upon distillation it is partially converted to the β form. The extent of conversion varies from one-fourth to three-fourths, depending upon various factors. The β may be completely converted to the α by fusion in a sealed tube at 275° for 15 hours. When the temperature is 290° alumina and ether are produced. If alumina is already present in the ethoxide the temperature for the formation of ether is reduced to 275° or less.

The α is not converted into the β by heating at any temperature up to 250° . Hence the α is not converted to the β during distillation by the heating but during the vaporization and condensation. A sample of α in a sealed tube did not change to β during a period of 32 days.

Analysis for alumina in either α or β form varied from 31.26 to 31.87% and from 85.06 to 83.1% for alcohol. The calculated percentage for $\text{Al}(\text{OC}_2\text{H}_5)_3$ is alumina 31.52%, alcohol 85.13%.

When aluminum ethoxide is heated in an open tube at 350° decomposition takes place⁵ according to the equations: $2 \text{Al}(\text{OC}_2\text{H}_5)_3 \longrightarrow \text{Al}_2(\text{OC}_2\text{H}_5)_4\text{O} + (\text{C}_2\text{H}_5)_2\text{O}$; $\text{Al}_2(\text{OC}_2\text{H}_5)_4\text{O} \longrightarrow 2 \text{Al}(\text{OC}_2\text{H}_5)\text{O} + (\text{C}_2\text{H}_5)_2\text{O}$; $2 \text{Al}(\text{OC}_2\text{H}_5)\text{O} \longrightarrow \text{Al}_2\text{O}_3 + (\text{C}_2\text{H}_5)_2\text{O}$. At the end of an hour the fusion material is very viscous and a mixture of products is obtained which is extremely soluble in xylene. This product which is hereafter referred to as Henle's ethoxide contained by analysis 50.52% of alumina and 60.8% of alcohol. This analysis agrees very closely with the formula $\text{Al}_6(\text{OC}_2\text{H}_5)_8\text{O}_5$, but the product is probably a mixture of the basic ethoxides formulated in the equations above. Henle did not carry his fusion so far and hence obtained mixtures which gave less alumina and more alcohol than did ours.

More than a hundred experiments were made in attempting to ascertain whether there was any difference in catalytic activity between the α , β and Henle's ethoxide. The α form and Henle's are of course much better than the β if the catalyst is used in the solid state, for they are more readily soluble in the ethyl acetate. The important question was as to whether they were equal in activity when solutions containing the same amount of aluminum were used. The most careful comparisons have established that the α and β ethoxides are identical in their catalytic activity. Henle's ethoxide is 91.2% as active as either α or β . This comparison was made between solutions which had the same aluminum content, 62% as much $\text{Al}_6(\text{OC}_2\text{H}_5)_8\text{O}_5$ being present as $\text{Al}(\text{OC}_2\text{H}_5)_3$. The conclusion to be drawn from this is that the catalytic activity is not solely a function of the number of aluminum atoms in an alkoxy deriva-

⁵ Henle, *Ber.*, **53**, 719 (1920).

tive in solution but is dependent upon the nature of the molecule. The fact that the α and β ethoxide gave the same activity cannot be explained by supposing that the one form changes into the other in solution, for the β was obtained by dissolving a mixture of α and β in hot xylene and then cooling the solution until the β separated. The α was then removed by decantation and washing with xylene. The α was also compared with mixtures of α and β and found to have an identical activity.

The effect of water upon the reaction is very marked. It was shown that when the aldehyde and ethoxide were mixed in the absence of a solvent, water cut down the reaction to a much greater extent than was expected from the decrease in the amount of ethoxide. It was also observed that water in the aldehyde was more disadvantageous than an equal amount of water added to the catalyst. In both cases the effect of water is not only to destroy part of the ethoxide but to cover its surface with a film of hydrated alumina, thus greatly retarding solution.

In studying the effect of water upon the reaction in xylene, the former was added as a 0.03% solution in xylene. It was found that the rate of reaction and yield were lowered in almost direct proportion to the amount of water added, the comparison being made with the amount of water necessary to react with all the ethoxide. Water sufficient to react with as much as 23% of the ethoxide was added, yet no precipitate appeared, although the reaction was reduced by 28%. Observations under the ultramicroscope showed, however, that there were present particles too large for Brownian movement yet too small to settle out or to be visible. It is evident that three molecules of water remove one molecule of ethoxide as hydrated alumina and that there are no soluble partial hydrolysis products.

The effect of adding various salts, alcohols and excess of aluminum ethoxide is represented graphically in Fig. 1. The reaction was followed by means of aldehyde titrations. The amount of ester formed was shown to be very closely parallel to the amount of aldehyde that disappeared. In each of the experiments, the data for which are plotted in Fig. 1, 100 cc. of xylene, 2.0 g. of acetaldehyde and 0.3 g. of aluminum ethoxide were used. To this basic charge various materials were added as noted. All of the experiments were duplicated at least once and most of them many times. The percentage of ester titrated at the end of 24 hours is given in parentheses below (Fig. 1). It is to be noted that Curve IV represents two distinct experiments, in one of which *isobutyl* and in the other *normal butyl* alcohol was used. Curve VIII represents three different experiments, that is 1 cc. of ethyl alcohol + 0.05 g. of mercuric chloride gives exactly the same rate as 0.025 g. of mercuric chloride or an additional 0.3 g. of aluminum ethoxide.

The alcohol was used with the salts because with the exception of mer-

curic chloride they are not sufficiently soluble in xylene and hence must be introduced in an alcoholic solution.

An inspection of Fig. 1 shows that the rate of the reaction and the final yield of ester are very susceptible to the addition of small quantities of various substances. All the alcohols containing five or less carbon atoms cut down the rate of reaction, though the amyl alcohols have a very slight effect. The inhibiting effect decreases with increase in number of carbon atoms. One cc. of ethyl alcohol introduced into the reaction mixture

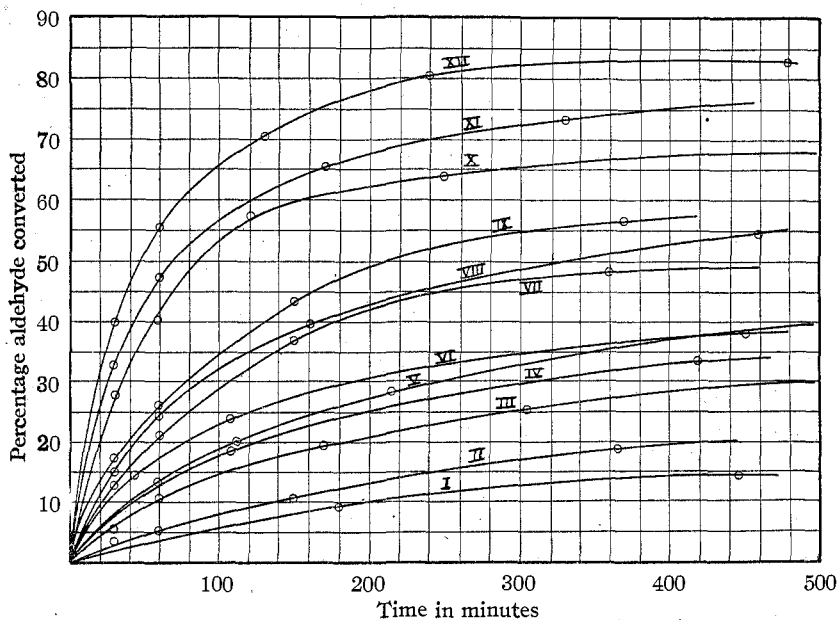


Fig. 1.—Effect of various substances upon the rate of reaction

(I) 1 cc. of methyl alcohol (17%); (II) 1 cc. of ethyl alcohol (26%); (III) 1 cc. of *isopropyl* alcohol (37%); (IV) 1 cc. of *n*-butyl alcohol (44%); (V) 1 cc. of *isobutyl* alcohol (44%); (VI) nothing added (53%); (VII) 0.05 g. of CaCl_2 + 1 cc. of ethyl alcohol (57%); (VIII) 0.05 g. of HgCl_2 + 1 cc. of ethyl alcohol (55%); (IX) 0.3 g. of aluminum ethoxide (75%); (X) 0.025 g. of HgCl_2 (62%); (XI) 0.04 g. of AlCl_3 + 1 cc. of ethyl alcohol (65%); (XII) 0.075 g. of HgCl_2 (87%); (XII) 0.075 g. of HgCl_2 (87%).

cuts down the yield to less than one-half of what it otherwise would be. Aluminum, calcium, mercuric, and zinc chlorides are all promoters. Upon a weight basis zinc chloride is the most active of the salts, but upon a molecular basis mercuric chloride is of about equal activity. Zinc chloride was also the most active when used with the solid catalyst and pure aldehyde. The small amount of promoter required to give an increase in reaction equal to a large increase in catalyst is shown in Curve VIII. The same rates of reaction were obtained by using 0.6 g. of ethoxide as

by using 0.3 g. of ethoxide and 0.025 g. of mercuric chloride; that is, adding $\frac{1}{2}$ as much promoter as additional catalyst gave the same increase in rate. The inhibiting effect of ethyl alcohol is also shown in Curve VIII, for 0.05 g. of mercuric chloride plus 1 cc. of alcohol gave the same rate as half that quantity of promoter in the absence of alcohol; 0.05 g. of mercuric chloride in the absence of alcohol gives a much higher rate, as shown in Curve X. Calcium chloride was not found to be a promoter when the solid catalyst was used but is a weak promoter in xylene solution. Curves VIII, X and XII illustrate the effect of increasing the amount of mercuric chloride from 0.025 to 0.050, to 0.075 g. One cc. of butyl iodide, phenyl bromide, or camphor had no effect upon the reaction. One g. of phenol cut down the reaction by two-thirds.

Aluminum chloride is an excellent promoter for the reaction, and so various concentrations of it were used in xylene solution. The chloride was prepared by the action of chlorine upon aluminum powder, and was dissolved in alcohol to give a solution that contained 0.95 g. of the halide per cc. Various amounts of aluminum chloride were then used as a promoter in 100 cc. of xylene, 2.0 g. of acetaldehyde, 0.3 g. of ethoxide and 1 cc. of alcohol being used in each case. The percentage of aldehyde that had reacted at the end of 24 hours and the percentage of ester formed with different concentrations of promoter are plotted in Fig. 2. Increasing the amount of promoter from zero up to 0.04 g. gives a rapid increase in the rate of reaction of the aldehyde and a corresponding increase in the amount of ester formed. The two curves do not coincide and the difference between them represents the amount of other reactions presumably the formation of paraldehyde. Increasing the amount of promoter above 0.04 g. cuts down the rate of reaction of aldehyde and the amount of ester formed until with 0.12 g. of promoter no ester is formed and paraldehyde is the only product. Further increase in the amounts of aluminum chloride increases the rate of paraldehyde formation, but no ester is formed.

When 0.04 g. of aluminum chloride in 1 cc. of alcohol with no aluminum ethoxide is added to a 100 cc. of solution of 2 cc. of aldehyde there is a precipitate of aluminum chloride, no ester is formed, and the aldehyde disappears very slowly. When half the xylene is replaced by absolute alcohol, no precipitation occurs, no ester is formed, and 90% of the aldehyde disappears in an hour to form paraldehyde. The aluminum chloride is only slightly soluble in xylene and so attacks the aldehyde but slowly in the first case. The aluminum chloride is soluble in a 50-50 mixture of alcohol and xylene and therefore converts it rapidly to paraldehyde.

When aluminum ethoxide is present, 0.08 g. of aluminum chloride is not precipitated, while even 0.04 g. is precipitated in the absence of the

ethoxide. A soluble complex of the ethoxide and chloride must be formed. This is further shown by the fact that when 0.04 g. of aluminum chloride is added with aluminum ethoxide in a 50-50 alcohol-xylene solution, practically no paraldehyde or ester is formed. Ester formation is prevented by the alcohol present and the production of paraldehyde by the fact that the aluminum chloride is tied up with aluminum ethoxide. The catalytic activity of the ethoxide is increased by the formation of the complex

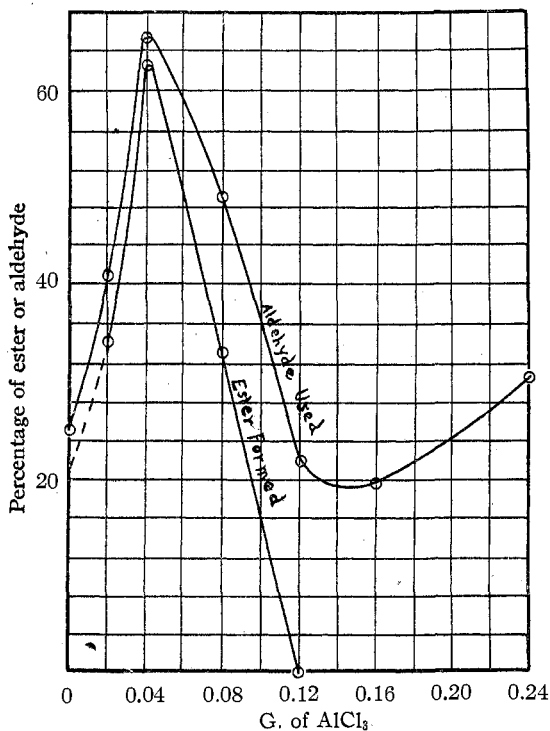


Fig. 2.—Effect of using various amounts of aluminum chloride as a promoter. The ordinate shows the percentage of aldehyde converted (upper curve) or of ester formed (lower curve) at the end of 24 hours

with aluminum chloride, but the latter loses its own ability to form paraldehyde (or acetal). Parenthetically, it may be said that in other work addition compounds, such as $2\text{Al}(\text{OC}_2\text{H}_5)_3 \cdot \text{ZnCl}_2$, have been isolated.

In making a rather extensive study of the reaction of pure aldehyde and solid aluminum ethoxide, 2.25 g. of the latter was fused at $168\text{--}172^\circ$ for 10 minutes, 0.225 g. of promoter added, and the fusion continued for 5 minutes. The mass was then cooled for 15 minutes, crushed and added to 15 g. of acetaldehyde. It is impracticable to follow closely the course of the reaction in this system, which approximates the *preparational*

method. However, by observing how long the solution boiled and the amount of aldehyde and ester present after 10 and 25 minutes, certain statements are justified. In all cases investigated the reaction was 90–97% complete within 25 minutes. Zinc chloride is the best promoter, and with it the reaction is 97% complete in 10 minutes. Aluminum chloride and mercuric chloride are not quite so good, but are positive promoters. Camphor and calcium sulfate have no effect upon the reaction. Lithium, sodium and calcium chlorides and alumina are apparently inhibitors, and alcohol is quite markedly so. In considering the use of the solid catalyst, one must carefully differentiate between those factors which increase the rate of solution (and hence reaction) and true promoters. Destroying the film of hydrated alumina by previously melting the catalyst or dissolving it in xylene comes under the first case.

In using pure aldehyde and aluminum ethoxide it seemed necessary to add 7% as much ethoxide as aldehyde in order to obtain a 90% yield of ester. If, however, the ethoxide was used in a concentrated xylene solution (0.09 g. per cc.) a 93% yield was secured with 2.85% as much ethoxide as aldehyde. The yield falls off very rapidly if less than this proportion of catalyst to aldehyde is used. An increase in the proportion of the catalyst above this amount speeds up the reaction but does not materially increase the yield of ester.

Dilution of the reaction mixture with xylene decreases the yield markedly. For example, when 2 g. of aldehyde and 0.3 g. of catalyst are used in 100 cc. of xylene the yield is about 53%, yet the amount of catalyst used is 15% of the aldehyde and this is five times as much as would be necessary to obtain more than a 90% yield provided only a few cubic centimeters of xylene were present. This is not due to any water introduced in the xylene for our best xylene gave the same results, and no hydrated alumina was precipitated. It is not due to the aldehyde being converted to other products because the titration with bisulfite indicates that almost 47% of the aldehyde is present as such. It is evidently due to the poisoning of the catalyst by products of the reaction, for the alkoxide is still present in the solution.

Two types of experiments were made to discover whether the reaction was taking place in a homogeneous or heterogeneous system. A number of runs were made in which the reaction mixture was from time to time during the run placed in the cell of an ultramicroscope. In no case was there any evidence of a colloidal solution. Since it was possible that a colloid might be present having an index of refraction so close to that of xylene that it could not be detected in the ultramicroscope, similar experiments were carried out in ether solution, with negative results. Any colloid present would have shown in one solvent, if not in both, since their indices of refractions are so different. A few large particles of

hydrated alumina were present during the latter part of the reaction, and of course a large apparent Tyndall effect was noticed, due to the fluorescence of the xylene.

Several experiments were made in which solid ethoxide was kept in the reaction flask. The rate of reaction was no greater in these cases than in the absence of the solid. The reaction apparently takes place only in a homogeneous system. It was also shown that the reaction proceeded as rapidly in the dark as in the light.

Temperature Coefficient of the Reaction.—A considerable number of the experiments were carried out in a thermostat held constant to within a few hundredths of 25°. Small changes in temperature, however, have so little effect as compared with other factors that in many cases comparative runs were made at "room temperatures." The speed of the reaction was repeatedly determined at 0° and 30°. The reaction mixture consisted of 100 cc. of xylene, 0.3 g. of aluminum ethoxide and 2.0 g. of acetaldehyde. The reaction was followed by aldehyde titrations. The value of the velocity constant ($\times 1000$) for a monomolecular reaction in the interval 20 to 60 minutes at 0° was 1.55, 1.49, 1.58, 1.55 and 1.60; at 30° it was 3.74, 3.48, 3.63, 3.73. Considering the average of these values the temperature coefficient was calculated to be 1.30 for a rise of 10°. After an hour and a half the values for the "constant" fall off rapidly. For example, in the experiment noted above the value after 7 hours was 0.77 for 0°, and 0.83 for 30°.

Experimental Part

Preparation of Acetaldehyde.—The acetaldehyde was made from paraldehyde by a modification of McLeod's method.⁶ Five cc. of 20% sulfuric acid was added to 100 g. of paraldehyde and the acetaldehyde distilled through a Vigreux fractionating column wrapped in a cloth soaked in ice water. From this fractionating column the acetaldehyde passed through a tube, 30 cm. in length, filled with calcium chloride and then was condensed in a 91cm. straight condenser surrounded with ice water. On re-distillation, the aldehyde boiled at 20–21.5°. After two or three distillations through the calcium chloride, it was distilled once with the calcium chloride tube removed. The aldehyde was then sucked out of the receiver through a 3-way stopcock into a pipet, the stopcock reversed and the measured portion (2 g.) discharged into a glass tube in which it was sealed. It was protected at all points from the moisture of the air.

Determination of Aldehyde.—The sulfite method for titrating the aldehyde was used.⁷ About 80 cc. of a 10% solution of sodium sulfite was taken, two drops of phenolphthalein added, and then enough acid to reduce the color to a faint pink. There was no sharp end-point. The solution, ice-cold, was divided into two equal parts in two Erlenmeyer flasks, surrounded with ice water, and the aldehyde sample added to one. Standard sulfuric acid was then very slowly added until the color was brought back nearly to that of the blank. Water neutral to phenolphthalein was added to the blank to bring its volume up to that of the other. The titration was then

⁶ McLeod, *Am. Chem. J.*, 37, 27 (1907).

⁷ Seyweetz and Bardin, *J. Soc. Chem. Ind.*, 25, 202 (1906).

continued until the color exactly matched that of the blank. One molecule of sulfuric acid is equivalent to two of aldehyde. When a reaction in xylene or other solvent was being followed, 5 cc. of the solution was transferred to the sulfite solution and titrated with 0.1 *N* sulfuric acid. To the blank was added 5 cc. of the solvent containing the same amount of aluminum ethoxide that the run contained.

Titration of Ester.—The ester formed in this reaction was saponified in pressure bottles with an excess of standard sodium hydroxide solution, and the excess titrated back with standard sulfuric acid. Of the two determinations, that of the aldehyde is much more accurate and dependable, since an excess of aldehyde absorbs sodium hydroxide.

Analysis for Alcohol and Alumina.—The ethoxyl content of the ethoxides was determined by distilling the aluminum compounds directly into weighed test-tubes; the tubes were then broken and dropped into a solution of potassium hydroxide, the alcohol was distilled and determined by the density of the distillate. Alumina was determined by precipitation with ammonium hydroxide and weighed as the trioxide.

Preparation of Aluminum Ethoxide.—The compound may be prepared by Gladstone and Tribe's method⁸ using aluminum and iodine, or by Hillyer's method⁹ using aluminum and stannic chloride, or by Wislicenus and Kaufmann's method¹⁰ using aluminum amalgam. The first two methods give a product which may contain several per cent. of an aluminum halide. This would be advantageous if one simply desired to prepare esters from aldehydes but is obviously not suitable for our purposes. The directions used by us have recently been published.¹¹

Other Chemicals.—The xylene was of a c. p. grade boiling at 137.5–140° and was dried over sodium. The alcohols were dried over lime. Ethyl alcohol was also dried over aluminum ethoxide. The salts were of the c. p. grade and dried. The aluminum chloride was prepared as noted above. Other reagents were dried over calcium chloride or potassium carbonate.

Method of Experimentation.—In one series of experiments, the solid

⁸ Gladstone and Tribe, *J. Chem. Soc.*, 39, 1 (1881).

⁹ Hillyer, *Am. Chem. J.*, 19, 37 (1897).

¹⁰ Wislicenus and Kaufmann, *Ber.*, 28, 1323 (1895).

¹¹ Adkins, *THIS JOURNAL*, 44, 2178 (1922).

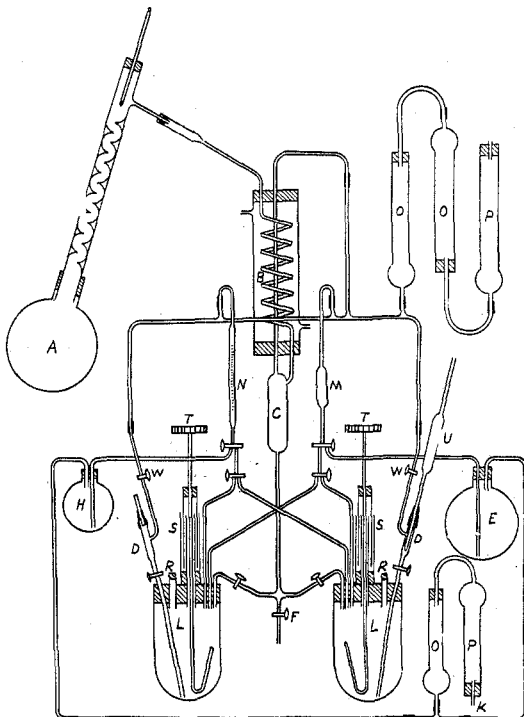


Fig. 3

catalyst and the aldehyde were mixed in a flask under a reflux condenser and samples were removed from time to time by means of a water-jacketed pipet.

In the experiments where a solvent was used, the aldehyde and the catalyst were dissolved in the solvent, the solutions mixed in a 500cc. flask provided with a stopper bearing (1) a stirring device in a mercury seal, (2) a small opening bearing a tiny stopper through which aldehyde, xylene or any other desired liquid might be introduced, (3) a sampling device so designed that portions of the reaction mixture could be measured and removed without the escape of aldehyde vapors or the entrance of moist air. This apparatus served fairly well but in making very exact comparisons it was found necessary to use an apparatus such that the solvent might be distilled directly into it out of contact with moist air and all operations carried out so that moisture in flasks, solvent, promoters or catalysts might be rigorously excluded. Such an apparatus is illustrated in Fig. 3.

Dried xylene and sodium are placed in A distilled through the Vigreux column, condensed in B, the first part of the distillate is discarded through F, the dried xylene collected in C and later run into the reaction tubes. A solution of the catalyst is in E, and of the promoter in H. By forcing air in through K the solution of the catalyst or promoter may be forced into the pipets M or N, respectively, where they may be measured and later allowed to flow into either of the reaction flasks L. The aldehyde is then introduced through the tube R by breaking the tip from one of the sealed containers. The reaction mixture is agitated, and a sample removed by means of the sampling device D and titrated for aldehyde. The reaction flasks are equipped with mercury seals S and stirring devices T. O and P are drying tubes containing phosphorus pentoxide and calcium chloride, respectively.

Summary

It has been shown that aluminum ethoxide exists in two allotropic forms, α and β , and that the β is converted into the α by fusion in a closed tube at 275° and the α partially into the β during distillation. These forms do not differ in their catalytic activity if the difference in their solubility is taken into consideration. The de-etherated alkoxide as prepared by fusion of the ethoxide at 350° is 91.2% as effective as the latter. Yields of esters of from 90 to 95% may be obtained by the use of an amount of catalyst equivalent to 2.85% of the weight of the aldehyde, provided the catalyst is used in a concentrated solution of xylene. It is necessary to use 7% of catalyst if the solid is introduced into the aldehyde. Zinc, mercuric and aluminum chlorides are promoters. Camphor, butyl iodide, and phenyl bromide have no effect upon the reaction. Listed in the order of decreasing effect, phenol, methyl, ethyl, *isopropyl*, butyl and amyl alcohols are "anticatalysts."

In certain concentrations aluminum chloride is an excellent promoter, but in slightly higher concentrations it acts entirely as a polymerizing

catalyst. In the lower concentrations the aluminum chloride is not present as such but as a complex with the ethoxide and if the ester reaction is inhibited by alcohol no polymerization takes place. Aluminum ethoxide is thus an "anticatalyst" for the polymerization reaction under these conditions. The reaction takes place in a homogeneous system and is not dependent upon colloidal solutions.

Three moles of water react quantitatively with one mole of catalyst and destroy its catalytic activity.

The temperature coefficient of the reaction in xylene is approximately 1.30 for a rise of 10° in the vicinity of room temperatures.

The patent claims in regard to the use of camphor and the conversion of the catalyst to an "active form" by melting are baseless except in so far as melting destroys a film of hydrated alumina and hence increases the rate of solubility.

The study of this reaction is being continued. The correlation of the results with those obtained with other reactions of aldehydes and an interpretation of them will be given in a later paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

ALIPHATIC ARSENO COMPOUNDS. I

ARSENO-ACETIC ACID AND TETRA-ARSENO-ACETIC ACID

BY CHARLES SHATTUCK PALMER¹

RECEIVED AUGUST 11, 1923

Aliphatic arsenicals such as "arrhenal"² and "mon-arsone"³ have found a limited application in therapy, but the superiority of the aromatic arsenic compounds seems to have been accepted as definitely proved. In

¹ National Research Fellow in Chemistry.

² (a) Sodium methylarsonate, $\text{CH}_3\text{AsO}_3\text{Na}_2$. (b) Meyer, *Ber.*, **16**, 1440 (1888). (c) Klinger and Kreutz, *Ann.*, **249**, 149 (1888). (d) Gautier, *Compt. rend.*, **134**, 329 (1902). (e) Astruc, *ibid.*, **134**, 660 (1902). (f) Adrian and Trillat, *ibid.*, **134**, 1231 (1902). (g) D'Emilio, Jr., *Boll. Chim. Farm.*, **41**, 633 (1902); *Chem. Zentr.*, **1902**, II, 1277. (h) Mouneyrat, *Compt. rend.*, **136**, 696 (1903). (i) Auger and Billy, *ibid.*, **137**, 925 (1903). (j) Dehn, *Am. Chem. J.*, **33**, 136 (1906); *THIS JOURNAL*, **28**, 347 (1906). (k) Moore, Nierenstein and Todd, *Ann. Trop. Med.*, **2**, 269 (1908). (l) Castelli, *Arch. Schiffs Tropen-Hyg.*, **16**, 605 (1913). (m) Fabrel, *Bull. sci. pharmacolog.*, **20**, 337 (1913). (n) Launoy, *Compt. rend. soc. biol.*, **81**, 164 (1918). (o) Voegtlin and Smith, *J. Pharmacol.*, **15**, 475 (1920); **16**, 449 (1921). (p) Quick with Adams, *THIS JOURNAL*, **44**, 805 (1922).

³ Sodium ethylarsonate, $\text{C}_2\text{H}_5\text{AsO}_3\text{Na}_2$. (a) La Coste, *Ann.*, **208**, 34 (1881). Ref. 2j. (b) Valeur and Delaby, *Bull. soc. chim.*, [4] **27**, 366 (1920). Ref. 2o. (c) Wright, Kennell and Hussey, *Med. Record*, **97**, 607 (1920). (d) Nichols, *J. Am. Med. Assoc.*, **76**, 1335 (1921). (e) Council on Pharmacy and Chemistry, *ibid.*, **76**, 1781 (1921). Ref. 2p.