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

# THE CONDENSATION OF ALDEHYDES TO ESTERS BY ALKOXIDES[1]

BY W. C. CHILD AND HOMER ADKINS

RECEIVED JULY 14, 1924 PUBLISHED MARCH 5, 1925

In a continuation of the study of the Tischtschenko reaction, the effect of modifying the aldehyde, the solvent and the catalyst has been noted. The data are shown in Table I, the rate of disappearance of the aldehyde being indicated.

Benzaldehyde reacts much more slowly and the curve representing its rate is very different from that for the three aliphatic aldehydes. About three-fourths of the total reaction with these aliphatic aldehydes takes place the first hour, while only about one-seventh of the total reaction of benzaldehyde takes place during that period. However, the amount of benzaldehyde ultimately entering into reaction is only 12% less than in the case of butyraldehyde.

TABLE I

THE RATE OF DISAPPEARANCE OF ALDEHYDES UNDER VARIOUS CONDITIONS

The reaction mixtures consisted of 100 cc. of solvent, 0.045 mole of aldehyde and 0.0024 mole of alkoxide; temperature, 25°C. The values given in this paper have been duplicated within ±3%, or are the averages of several experiments which might show that large a derivation. Quantities of ester have been separated under each of the various conditions but only ethyl acetate has been quantitatively determined.

| Hours | 1/6<br>% | 1/3<br>% | 1/2<br>% | 1<br>% | 2<br>% | 8<br>% | 24<br>% |
|---|---|---|---|---|---|---|---|
| VARIOUS ALDEHYDES, CARBON TETRACHLORIDE AND ALUMINUM ETHOXIDE | | | | | | | |
| $C_6H_{13}CHO$ | 31 | .. | 60 | 80 | 93 | 99 | 100 |
| Acetaldehyde | .. | 45 | 60 | 79 | 91 | 98 | 100 |
| Butyraldehyde | 19 | .. | 45 | 62 | .. | 80 | 84 |
| Benzaldehyde | 5 | .. | 6 | .. | .. | 57 | 72 |
| Furfural | .. | .. | .. | 6 | .. | 12 | 13 |
| VARIOUS SOLVENTS, ACETALDEHYDE AND ALUMINUM ETHOXIDE | | | | | | | |
| Carbon tetrachloride | 21 | 45 | 58 | 78 | 90 | 98 | 100 |
| Heptane | 11 | .. | 28 | 42 | .. | 77 | 91 |
| Xylenes | 10 | 14 | 17 | 20 | .. | 49 | 65 |
| Ether or benzene | 7 | 10 | 13 | 19 | .. | 49 | 67 |
| Chloroform | 5 | .. | 10 | 15 | .. | 48 | 72 |
| VARIOUS ALKOXIDES, ACETALDEHYDE AND XYLENE | | | | | | | |
| Aluminum *iso*propoxide | 21 | 35 | 44 | 58 | .. | 82 | 97 |
| Aluminum butoxide | 15 | 27 | 36 | 53 | .. | 81 | 95 |
| Aluminum ethoxide | .. | 15 | 17 | 20 | .. | 49 | 65 |
| Titanium ethoxide | .. | .. | 9 | 11 | .. | 24 | 41 |

---

[1] This paper and a previous one on the same subject [(a) Child and Adkins, THIS JOURNAL, 45, 3013 (1923)], were abstracted from the doctor's dissertation of Dr. Child.—H. A.

Aluminum butoxide and *iso*propoxide give a much faster rate of reaction and greater final conversion than does the ethoxide and should be much better for the preparation of esters than is the ethoxide which has always been recommended and used. Titanium ethoxide is much less susceptible to the deleterious effects of water than is the aluminum compound because the first hydrolysis product of the alkoxide is soluble in organic solvents.[2]

Ether, benzene, xylene and chloroform give very similar rates of reaction, although in the latter the reaction goes more slowly at first but in the end goes farther than in the other solvents. The reaction in heptane is almost twice as rapid during the first hour. The reaction is by a good deal the most rapid in carbon tetrachloride and the conversion is 100%.

It was shown in the first paper of the series that the reaction goes more rapidly in a very concentrated xylene solution than it does in the dilute solutions used in these experiments. In such a concentrated solution the reaction would go to completion, within ten or fifteen minutes. It is then probably more correct to say that carbon tetrachloride, for example, cuts down the reaction less than does xylene, rather than to say that carbon tetrachloride promotes the reaction. There is no apparent correlation between the effect of the solvents upon the rate of the reaction and their other characteristics such as enolizing power, or physical constants.[3]

### Various Proportions of Catalyst and Aldehyde

Four sets of experiments were made. In one set 0.09 mole of aldehyde and 0.0048 mole of catalyst were used, in another the amount of catalyst was halved, in another the aldehyde was cut to one-half, and in the fourth set both aldehyde and catalyst were halved in amount. One hundred cc. of xylene was used in each experiment. The change in rate on doubling the amount of aldehyde or of catalyst is surprisingly small. A 100% increase in aluminum ethoxide content causes about a 4.5% increase in rate and yield, and a 100% increase in the amount of aldehyde added causes a 3% increase. A 100% increase in both catalyst and aldehyde increases the rate by about 20%. Some work done in xylene solution indicates that not until the catalyst is cut down to about one-third the amount here used is there any considerable falling off in rate. With 0.0008 mole about half the rate is obtained as when 0.0024 mole is used.

### The Use of Promoters

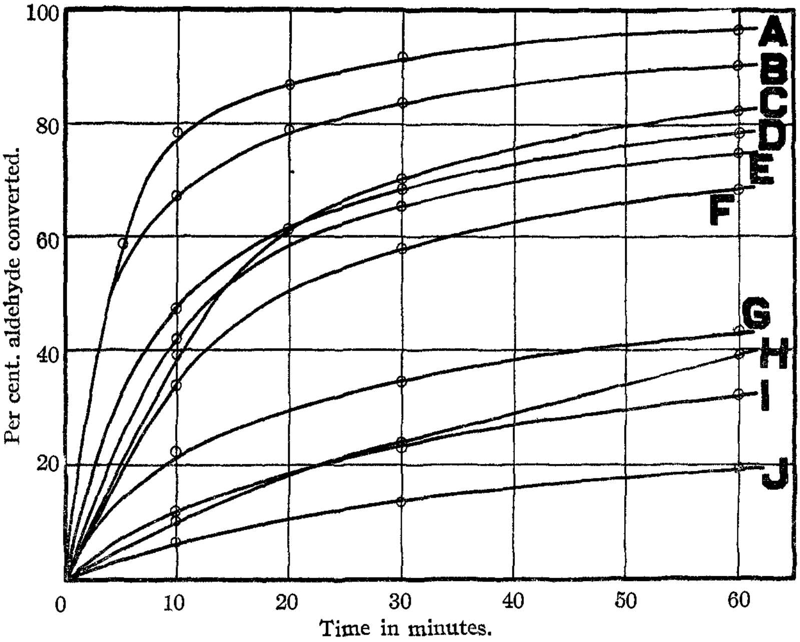
The metallic chlorides are such important catalysts for organic reactions and show such diversified effects that it seems of the utmost importance to a knowledge of the mechanism of organic reactions that they be carefully compared as to their effects. It has been previously shown that certain

---

[2] Bischoff and Adkins, THIS JOURNAL, **46**, 256 (1924).

[3] Compare Michael and Hibbert, *Ber.* **41**, 1080 (1908); "Theories of Organic Chemistry," Henrick-Johnson-Hahn, John Wiley and Sons, New York, **1922**, p. 251.

metallic chlorides very markedly increase the rate and extent of conversion of acetaldehyde by aluminum ethoxide. The experiments involved the use of xylene as a solvent and in most cases the promoter was introduced in a small amount of ethanol. So few salts are soluble in xylene that it was thought wise to use ether as a solvent and thus be able to employ a wider range of salts, avoid the use of the inhibitor, ethanol, and vary the concentrations of promoter over as wide a range as possible.



A. 0.0012 $ZnCl_2$ (100%). B. 0.0019 $AlCl_3$ (100%). C. 0.013 $HgCl_2$ (100%). D. 0.0003 $ZnCl_2$ (97%). E. 0.0015—0.0019 $FeCl_3$ (97%). F. 0.0011 $AlCl_3$. G. 0.00038 $FeCl_3$ (73%). H. 0.0013 $HgCl_2$ (81%). I. 0.00006 $ZnCl_2$ (73%). J. No promoter (67%).

Fig. 1.—The rate of disappearance of acetaldehyde with various kinds and amounts of promoters. The reaction mixture consisted of 100 cc. of ether, 0.045 mole of acetaldehyde, 0.0024 mole of aluminum ethoxide and a promoter in the amount indicated above. The amount of promoter is given in equivalents of chlorine. If this value is divided by two in the case of the divalent metals or by three in the case of the trivalent metals the amount of the promoter in moles will be obtained. The percentage of aldehyde reacted at the end of 24 hours is given in the parentheses.

In Fig. 1 the effect upon the rate of the disappearance of aldehyde during the first hour of various amounts and kinds of promoters is represented. About 25 different sets of conditions were used and the nine shown in the figure were selected to bring out the more important facts.

Apparently aluminum chloride and ferric chloride are similar in activity, with regard to (1) the speed of reaction, (2) the final yield of ester and (3) the relation between the amount of promoter and catalyst necessary to give the same result. Both promoters show their maximum effect at a concentration slightly less than that required to form the complexes $AlCl_3.3Al(OEt)_3$ and $FeCl_3.3Al(OEt)_3$.

Zinc chloride gives the most rapid promotion during the first hour and is effective in the lowest concentration. It requires approximately four times as much aluminum chloride as zinc chloride (stated in equivalents of chlorine) to give the same speed of reaction. No concentration of aluminum chloride gives as good promotion as does the best concentration of zinc chloride.

Mercuric chloride is the least active of the promoters during the first hour, and to produce the same conversion necessitates 40 times the molecular concentration required with zinc chloride.

The use of the best concentration of zinc chloride causes the conversion of eleven times as much aldehyde during the first ten minutes as does the unpromoted catalyst. At the end of an hour, about five times as much has been converted and at the end of 24 hours about one-half more aldehyde has been converted and about twice as much ester has been actually formed. Although a much higher concentration of mercuric chloride must be used, it will give about the same conversion as will the zinc chloride. The yield of ester is 10 to 15% lower than the percentage of aldehyde converted.

The data in Table II show another aspect of the variation in amount and kind of promoter used. The amount of aldehyde converted at the end of 24 hours and the amount of ester formed under the same conditions is given.

There is a very marked difference between zinc and mercuric chloride and aluminum and iron chloride. The first two salts do not act as polymerizing

Table II

The Percentages of Acetaldehyde Reacted and of Ester Formed at the End of 24 Hours with Various Promoters

The reaction mixtures consisted of 100 cc. of ether, 0.045 mole of acetaldehyde, 0.0024 mole of aluminum ethoxide and the various amounts of promoters indicated in the first column of the table. The amounts of the latter are expressed as in Fig. 1; temperature, 25°.

| | $ZnCl_2$ | | $HgCl_2$ | | $FeCl_3$ | | $AlCl_3$ | |
|---|---|---|---|---|---|---|---|---|
| Equivalents of chlorine | Ald. % | Ester % | Ald. % | Ester % | Ald. % | Ester % | Ald. % | Ester % |
| None | 66 | 41 | 66 | 41 | 66 | 41 | 66 | 41 |
| 0.0004 | 96 | 80 | .. | .. | .. | 60 | .. | .. |
| .0010 | 100 | 87 | 79 | 68 | .. | .. | .. | 73 |
| .0015 | ... | .. | .. | .. | 94 | 84 | 96 | 84 |
| .0020 | ... | .. | .. | .. | 96 | 80 | 100 | 88 |
| .0025 | 100 | 93 | .. | .. | 40 | 40 | 41 | 40 |
| .0030 | 100 | 93 | 89 | 82 | 54 | 10 | 38 | 15 |

catalysts when they are present in excess of the amount necessary to form the compounds of the type $ZnCl_2.2Al(OC_2H_5)_3$ while if ferric or aluminum chloride are used in excess of the amount necessary to form a compound of the type $AlCl_3.3Al(OC_2H_5)_3$ they cause polymerization. Hence the formation of ester does not fall off when excess of zinc and mercury chlorides are used as promoters.

Table III

The Rate of Reaction of Acetaldehyde with Various Promoters in an Ether-Butanol Solution

The reaction mixture consisted of 90 cc. of ether, 10 cc. of butanol, 0.045 mole of acetaldehyde, 0.0024 mole of aluminum ethoxide and 0.0018 equivalent of the promoter; temperature, 25°.

| Promoter | $^1/_6$ hour | $^1/_3$ hr. | $^1/_2$ hr. | 1 hr. | 24 hr. |
|---|---|---|---|---|---|
| $FeCl_3$ | 33 | 42 | 48 | 52 | 75 |
| $AlCl_3$ | 9 | 14 | 18 | 22 | 64 |
| $ZnCl_2$ | .. | 10 | 15 | 20 | 75 |
| $CuCl_2$ | 6 | 8 | 10 | 18 | 70 |
| None | .. | .. | 8 | 9 | 39 |
| $HgCl_2$ | 4 | 5 | 7 | 8 | 65 |

In all these runs some precipitate was formed, immediately in the case of the zinc, aluminum and ferric chlorides, but not for several minutes after the run was started in the case of the mercuric chloride. The amount of complex that was actually left in solution at the end of 24 hours and, in the case of the aluminum complex, for shorter periods of time, was determined. The figures for the aluminum complex show that the precipitations, especially with the low concentrations of chloride, are very slow, that even at the end of 24 hours, the greater part is still in solution. Since the main part of the reaction is over within an hour or so in these promoted solutions, we are observing the effect of practically all the promoter added. This is true for the lower concentrations of the aluminum, zinc and mercuric chlorides. With the higher concentrations (above 0.0024 mole) and with all concentrations of ferric chloride, this is not so, for the amount of precipitation is considerable. It will be pointed out later that in a solvent in which the ferric complex is soluble, the ferric chloride proves to be the best promoter. It is because of this precipitation that it does not appear to be the best promoter in this case.

These precipitates proved to be $AlCl_3.Al(OEt)_3$, $FeCl_3.3Al(OEt)_3$, $ZnCl_2$, $2Al(OEt)_3$, and $HgCl_2.2Al(OEt)_3$ which had been partially hydrolyzed. That these compounds are the real catalysts is proven by the fact that when 1 cc. of alcohol was added to a reaction mixture the rate was actually increased although as previously pointed out, alcohol is a strong inhibitor of the reaction. The alcohol increases the solubility of the complex so much that an actual increase in the yield of ester was observed.

In view of the complicating factor of the insolubility of the catalyst-promoter complex in ether, promoter action was also studied by adding the promoter in 10 cc. of butyl alcohol to the ether solution of the aldehyde. In this way, the precipitation of the complex was delayed for six to ten hours and the effect of all the promoter added was studied. The results are shown in Table III. With butyl alcohol present, ferric chloride behaves very differently from the other promoters in that for the first hour it is three times as active as any of the others. The final yield of ester is similar to that obtained with zinc, mercury and copper chlorides. The aluminum chloride causes the reaction to go towards the formation of paraldehyde and with the formation of very little ester. Ferric chloride was also found to be the best promoter (though not so markedly so) when it was introduced in an ethanol solution into a reaction mixture in which xylene was the solvent.

We must conclude therefore that if the solvent is such that the complex is not thrown from the solution, ferric chloride is the best of the promoters if the proper amount is used. Zinc chloride has the advantage, however, in that it is impossible to put in too much, as the yield is not cut down with an excess of it, as is the case with ferric chloride. Zinc chloride gives as high a yield as is possible, but with the proper amount of ferric chloride the maximum conversion is obtained more rapidly.

## Discussion of Results

Since the rate of this reaction depends so little on concentration of catalyst and aldehyde, it appears that the speed of formation of some sort of an aldehyde-catalyst complex is very rapid while the speed of its decomposition into ester and alkoxide is slow. Anything, therefore, that will hasten this decomposition should hasten the ester condensation, while anything that retards the decomposition should retard the reaction, even though there be an excess of active catalyst present.

None of these reactions reaches a true equilibrium; they appear to go to completion or until the catalyst is killed, that is, until it becomes inactive due to precipitation by water or the retarding effect of the other by-products of the reaction such as those noted by Tischtschenko. Reaction velocity "constants" are constant for a short time only, then fall off very rapidly.

A high rate of reaction always leads to a high yield of ester. The side reactions are evidently slow and rather independent of the concentration of the catalyst. If the ester is formed quickly, a large amount will be formed before the catalyst becomes inactive. The proportion of byproducts is thus decreased.

There appears to be no valid reason for assigning to these intermediate compounds or "polymolecules" any specific structural formula. Such an assignment has no basis in experimental work and can only confuse the matter. It seems certain that addition compounds of catalyst, aldehyde, promoters and solvent are formed, for the variation in any of these modifies the rate of the reaction. One is justified in saying that this "polymolecule" is of the type usually referred to as a molecular compound.

However much one may hesitate to adopt Lachman's conception[4] of the mechanism of the reaction in terms of a rigid application of the structural theory, there can be no doubt of the importance of the phenomenon that he calls metakliny, that is, the tendency of adjacent carbon atoms to undergo auto-oxidation-reduction as in the glycollic acid rearrangement.

$$\mathrm{CHO.CHO + HOH \longrightarrow CH_2OH.COOH}$$

As Miss Edith Usherwood[5] has pointed out there is no essential difference between the migration of hydrogen within one molecule and its migration between two molecules. That is, there is no fundamental difference between the reversible tautomerization, $\mathrm{CH_3COCH_2COOEt \leftrightarrows CH_3CH(OH)CHCOOEt}$, and the reversible aldolization, $\mathrm{CH_3CHO{+}HCH_2CHO \rightleftarrows CH_3CH(OH)CH_2CHO}$. The function of the catalyst in the latter case is probably in part to orient the two molecules with respect to each other so that the migration may take place over spaces that are no greater than are involved in the migration of hydrogen in the enolization of aceto-acetic ester.

In the Tischtschenko reaction, one function of the catalyst is probably so to orient the two molecules of aldehyde that the auto-oxidation-reduction may take place without involving any greater distances than are involved in the similar oxidation reduction of the two parts of the same molecule of glyoxal as illustrated above.

This function of the catalyst is obviously not the only one. Its second function is, in terms of Michael's terminology, contributing to the polymolecule sufficient "free chemical energy" to overcome the forces that have hitherto prevented reaction. Or in terms of the electronic conception of matter, we may say that the catalyst dislocates the electronic system of the aldehyde so that the rearrangement of the two molecules into the ester may ensue. The catalyst, solvent and promoter probably do this by combining with the aldehyde to form a compound whereby the electronic system of the latter is shifted from its "resting" state to one where metakliny may take place.

## Experimental Part

**Preparation of the Aldehydes.**—Furfural was purified by repeated fractional distillation under reduced pressure. This gave a product titrating practically 100% by the sulfite method. Butyraldehyde was purified by forming the bisulfite addition compound and decomposing it with sodium carbonate after washing thoroughly with ether. On distillation it all passed over between 72° and 74°. It was then dried by repeatedly

---

[4] Lachman, This Journal, **45**, 2356 (1923).

[5] Usherwood, *J. Chem. Soc.*, **123**, 1717 (1923).

distilling it at reduced pressure through a large tube of calcium chloride placed just above the condenser. Benzaldehyde was shaken with sodium carbonate and fractionally distilled under reduced pressure. The heptaldehyde was donated by the Research Laboratory of the Eastman Kodak Company. It was dried over calcium chloride and fractionally distilled.

**Analysis of the Promoter-Ethoxide Complexes.**—The precipitates formed in the promoted runs in ether were filtered out on Gooch crucibles, washed with dry ether, dried over concd. sulfuric acid under reduced pressure and analyzed for aluminum, zinc, iron and chloride. The results were as follows.

*Anal.* (zinc complex). Calcd. for $ZnCl_2.Al(OEt)_3$: Zn, 14.1; Al, 11.6; Cl, 15.4. Calcd. for $ZnCl_2.Al(OEt)2^1/_2\ O$: Zn, 16.9; Al, 14.0; Cl, 18.4. Found: Zn, 16.1; Al, 12.1; Cl, 14.6.

*Anal.* (mercury complex). Calcd. for $HgCl_2.2Al(OEt)_3$: Al, 9.1; Cl, 11.9. Calcd. for $HgCl_2.2Al(OEt)2^1/_2\ O$: Al, 10.4; Cl, 13.6. Found: Al, 12.1; Cl, 12.8.

*Anal.* (aluminum complex). Calcd. for $AlCl_3.3Al(OEt)_3$: Al, 17.7; Cl, 23.2. Calcd. for $AlCl_3.3Al(OEt)_3$: Al, 17.4; Cl, 17.2. Calcd. for $AlCl_3.3Al(OEt)2^1/_2\ O$: Al, 21.2; Cl, 21.0. Found: Al, 22.4; Cl, 20.0.

*Anal.* (iron complex). Calcd. for $FeCl_3.3Al(OEt)_3$: Fe, 8.6; Al, 12.5; Cl, 16.7. Calcd. for $FeCl_3.3Al(OEt)2^1/_2\ O$: Fe, 10.2; Al 14.8; Cl, 19.5. Found: Fe, 9.2; Al, 14.7; Cl, 17.8.

The data for the aluminum complex are the averages of two determinations, and for the others, of three determinations each. Entirely different ratios of catalyst to promoter were used in making the precipitates for the several analyses. Due to the great instability of the complexes and their reactivity with water it was found impossible to check closer than 1 or 2% (5 to 10% on a 100% basis). In spite of the inaccuracies, the results show that the precipitates were $AlCl_3.3Al(OEt)_3$, $FeCl_3.3Al(OEt)_3$, $ZnCl_2.2Al(OEt)_3$ and $HgCl_2.2Al(OEt)_3$ which had been partially hydrated. Whether this hydration took place before precipitation or on preparing the sample for analysis is not known. On attempting to obtain better results on the zinc complex it was found possible to get the reagents so dry that no precipitate would form. The addition of a trace of water would partially throw it out. There are apparently definite complexes formed between the aluminum ethoxide and the metal chloride in which there is one molecule of the ethoxide to each chlorine atom in the chloride.

**Purification of the Solvents.**—Xylene was shaken with concd. sulfuric acid, washed with water, and distilled from sodium: b. p., 136–138° (730 mm.). Benzene when similarly purified boiled at 79.1–79.3° (740 mm.). Chloroform was shaken with concd. sulfuric acid and with dil. sodium hydroxide solution, and distilled from phosphorous pentoxide; b. p., 60.9° (737 mm.). Carbon tetrachloride was allowed to stand over solid potassium hydroxide for a number of days and was then distilled from phosphorous pentoxide; b. p., 76.0° (740 mm.). Ether was extracted with water, allowed to stand for 24 hours over calcium chloride, and distilled from sodium. Heptane from the Jeffrey pine was supplied by Prof. E. Kremers of this University. Dry hydrogen chloride was passed into it and it was allowed to stand in the ice box for a week. The heptane was then decanted from the precipitated resins, it was washed with water and dried over sodium; b. p., 97.3–97.6° (740 mm.).

**Preparation of the Alcohols.**—These substances were dried over lime. Ethyl alcohol was also dried over aluminum ethoxide and butyl alcohol over aluminum butoxide, but this treatment apparently gave no better product than did the lime.

**Preparation of the Salts.**—C.P. zinc chloride was fused in a test-tube and allowed to stand stoppered in a desiccator until cold. The tube was then broken and the chloride dropped into the ether. After a short time two liquid layers were formed, the lower a solution of ether in zinc chloride, and the upper about a 9% solution of zinc chloride in ether. Aluminum chloride was made by passing chlorine over aluminum wire. Ferric chloride was purified by resubliming a good grade of the anhydrous salt. Mercuric chloride was recrystallized from water, dried at 110° for a short time, and then allowed to stand for several days over concd. sulfuric acid. Titanium ethoxide was prepared as by Bischoff.[6] The preparation of all other reagents and the method of experimentation has been previously described.[1a]

## Summary[7]

Acetaldehyde, butyraldehyde, heptaldehyde, benzaldehyde and furfural have been converted into the corresponding esters by the use of aluminum ethoxide as a catalytic agent. The cyclic aldehydes have a slower rate of condensation than the aliphatic, the order being furfural, benzaldehyde, butyraldehyde, acetaldehyde and heptaldehyde. The furfural was very much slower than the benzaldehyde, while the acetaldehyde and the heptaldehyde had almost identical rates.

Titanium ethoxide, aluminum ethoxide, aluminum *iso*propoxide and aluminum butoxide have been used to convert acetaldehyde into ethyl acetate. They are listed above in order of increasing activity with the exception of the last two which showed identical rates. Both of these catalysts are *much more* effective than the ethoxide.

Variations in the relative amounts of aldehyde and catalyst used have a very small effect on the rate of reaction. An aldehyde-catalyst complex is evidently formed rapidly and then decomposes but slowly into ester and catalyst.

Solvents decrease the rate of the reaction. Carbon tetrachloride having the least effect while heptane, chloroform and xylene in order have a greater influence. Ether and benzene are similar in effect to xylene.

Aluminum chloride, ferric chloride, zinc chloride and mercuric chloride react with aluminum ethoxide to give, respectively, the complexes $AlCl_3.3Al(OEt)_3$, $FeCl_3.3Al(OEt)_3$, $ZnCl_2.2Al(OEt)_3$ and $HgCl_2.2Al(OEt)_3$ which are partially precipitated from an ether solution. These complexes are very much more active for the ester condensation than is aluminum ethoxide itself. When more than enough ferric chloride or aluminum chloride to form these complexes is added to the aluminum ethoxide, the rate of reaction is cut down due to paraldehyde formation promoted by the un-

---

[6] Bischoff and Adkins, THIS JOURNAL, 46, 256 (1924).

[7] It was stated in a previous paper that the temperature coefficient of the velocity constant of the *conversion of the aldehyde* was about 1.30 for a rise of 10° in the vicinity of room temperatures. This is approximately correct if the amount of catalyst is quite low, *i. e.*, less than 0.0007 mole (not 0.0019 mole as stated in the original paper), as with this concentration of catalyst the side reactions are important. The temperature coefficient for the *formation of ester* from acetaldehyde is always less than one, *i. e.*, 0.89 to 0.94, no matter what is the amount of catalyst. If there is as much as 0.0024 mole of catalyst, 0.045 mole of aldehyde and 100 cc. of xylene, the temperature coefficient for the *conversion of aldehyde* also becomes less than unity.

combined chloride. Mercuric and zinc chloride do not form any polymerization products and, since zinc chloride is much more active than mercuric chloride, it is the best promoter of all the salts in an ether solution.

Ferric chloride is the most potent of all the salts studied in the promotion of the Tischtschenko reaction. This conclusion was reached through a study of the reaction in butanol-ether and ethanol-xylene solutions.

The aldehyde-catalyst-promoter compound is probably held together by secondary valence forces and cannot be assigned any definite configuration. The authors believe that the experimental work is not in accord with the interpretation of the mechanism of the reaction variously advanced by Nef, Claissen and Lachman.

MADISON, WISCONSIN

---

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

# ORGANIC REACTIONS AT THE SURFACE OF TITANIA ADSORPTION OF CERTAIN GASES BY TITANIA

BY FRITZ BISCHOFF[1] AND HOMER ADKINS

RECEIVED JULY 14, 1924 PUBLISHED MARCH 5, 1925

The work reported below was carried on with titania along lines analogous to those previously followed in this Laboratory with alumina catalysts. The principal method of attack has been to study a series of reactions with the same titania catalyst and a series of titania catalysts with the same reaction. Particular attention has been paid to the changes in the catalyst that modify the proportion of two simultaneous reactions, that is, to selective activation.

The reactions of formic acid, acetic acid, a mixture of formic and acetic acids, ethanol, butanol, butanol and ammonia, ether and ethyl acetate have been studied for the titanias obtained from the alkyl titanates, titanic acid, sodium titanate and titanous hydroxide. A few experiments were performed with acetone, acetaldehyde, butyraldehyde and propionic acid.

The adsorptions, by three varieties of titania, of certain products of the catalytic reactions have been measured in attempting to discover the relationship that has been supposed to exist between the adsorptive power of substances and their catalytic activity.

**The Reported Reduction of Acetic Acid by Formic Acid.**—Sabatier and Mailhe[2] stated that mixtures of formic acid and a higher aliphatic acid, when passed over titania at 300°, gave excellent yields (40 to 90%) of aldehydes; and that it was but natural that this should be the case, since

---

[1] Dr. Bischoff held a DuPont Fellowship for the year 1923–24. This paper and one entitled "The Alkyl Titanates" were abstracted from his dissertation submitted in candidacy for the degree of Doctor of Philosophy.—H. A.

[2] Sabatier and Mailhe, *Compt. rend.*, **154**, 561 (1912).