

9/16/54

Org. Chem. -
2,4-D + 2, H, S-T
process

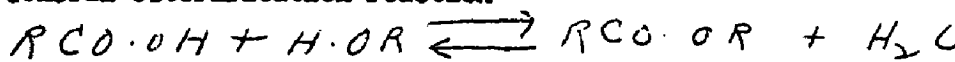
ESTERS

I. ESTERIFICATION PROCESS

A. General description: Refer to flow sheet and accompanying descriptive matter.

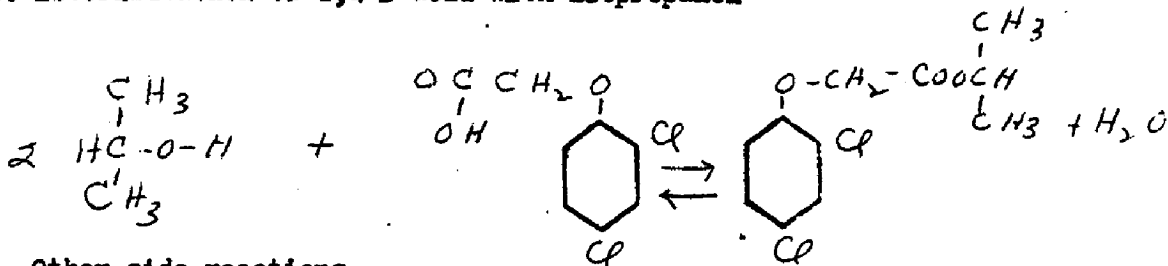
B. Chemistry of process:

1. General esterification reaction

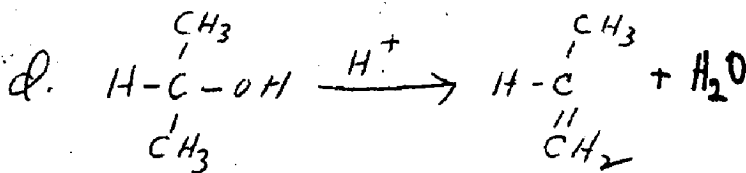
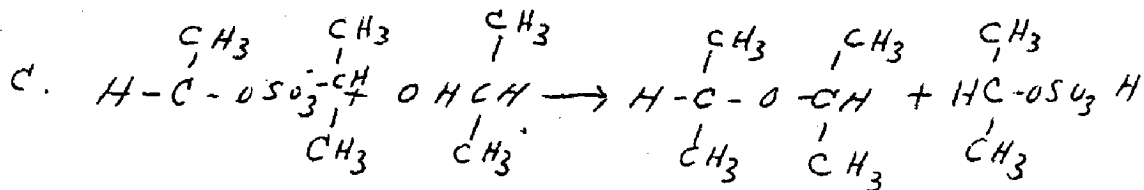
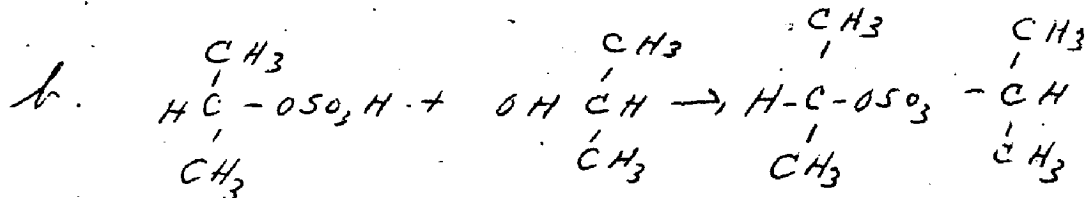
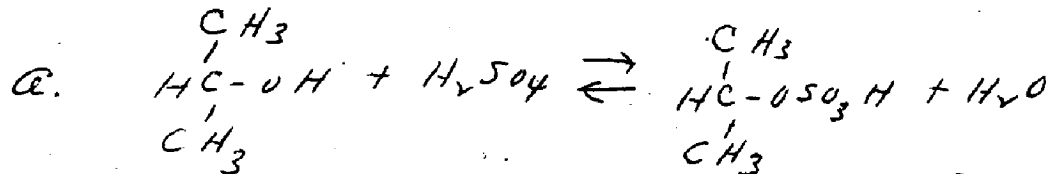


Note points of bond cleavage

2. Esterification of 2,4-D acid with isopropanol



3. Other side reactions



DS00011724

C. Speeding up esterification

1. Catalysis

Mineral acids such as hydrochloric acid or sulfuric are the strongest esterification catalysts but also tend to cause decomposition, especially at higher temperatures. In addition, mineral acids are more corrosive than organic acids.

2. Temperature

Reaction rate increases as the temperature rises approximately doubling for every 10° rise in temperature. The limiting factors here are the type of heating equipment available, and, in the case of low boiling alcohols, the excessive loss of alcohol by overheating.

3. Use of a primary alcohol rather than a secondary if possible. For example, the change from secondary butyl alcohol to normal butyl alcohol made here about 2 years ago cut the esterification approximately in half or from 36 hours to 18 hours. In general, primary alcohols, resist more effectively the side reactions that cause loss of alcohol such as were shown above.

4. Pressure

Increasing the pressure under which an esterification runs will decrease reaction time, but usually calls for more expensive equipment and safeguards.

D. Completing Esterification

The esterification reaction is a reversible one, i.e., it comes to a stop when a certain percentage of ester has been produced usually a relatively small percentage. For example, acid plus alcohol \rightleftharpoons Ester plus water

The equilibrium $K = \frac{(\text{Ester}) \times (\text{Water})}{(\text{Acid}) \times (\text{Alcohol})}$ is a fixed quantity for a particular acid and alcohol at a fixed temperature and pressure. If either the ester or the water is removed the equilibrium is upset and a more acid and alcohol react, forming more ester and water until the constant K is reestablished.

Thus in order to obtain a complete a conversion of the 2,4-D acid to ester as possible at least one of the two products has to be removed. In the case of 2,4-D and 2,4,5-T esters it is easier to remove water than ester. Two methods are used in plant practice.

DS00011725

1. Azeotrope

An azeotrope is a constant boiling mixture of two or more liquid compounds. Both isopropyl alcohol and normal butyl alcohol form azeotropes with water and thus we are able to remove water from an esterification by continuously distilling over the azeotrope, separating the alcohol from the water and returning the alcohol to the esterification reaction. Although isopropyl alcohol forms an azeotrope with water it is also completely soluble in water, this is not the case with normal butyl alcohol. To reduce the loss of isopropyl alcohol in water going to sewer, benzol is added to the isopropyl esterification. Thus a three component azeotrope consisting of water, isopropyl alcohol and benzol is formed which upon cooling separates into a water phase containing some isopropyl alcohol and the benzol-alcohol phase which is returned to the esterification.

2. Carbon Dioxide

In an esterification containing no volatile matter carbon dioxide gas may be introduced beneath the surface of the mixture. Gas bubbles then carry off water as a vapor.

E. Testing Esters

1. Tests by plant personnel

Two tests are carried out by non laboratory personnel. These are the specific gravity and the acid value or acid number (which is a measure of the free or unreacted acid remaining in an ester). After several years of such tests we have accumulated enough results to predict with reasonable accuracy from these data the assay of an ester.

2. Laboratory Tests

Frequent checks are made on the tests made by plant personnel. In addition a true assay is taken on shipments of ester. The method used is the one approved by the Association of Official Agricultural Chemists and consists of igniting a sample of ester in a Parr bomb using sodium peroxide and boric anhydride. The resulting mixture is then tested for chlorides.

F. Specifications of Esters

1. Technical Ester: Normally sold as 99% ester for volatile esters and 97% for low volatile.
2. Formulation Grade Ester: Ester assays from 97-99% ester for formulations.

DS 00011726

G. Corrosion

1. The most resistant materials we use are:

- a. Glass and glass-linings
- b. Porcelain
- c. Teflon
- d. Tantalum
- e. Gold
- f. Havg
- g. Karbate (carbon)

2. Less resistant but still usable are:

- a. Monel (corrodes under acid conditions)
- b. #316 stainless steel (corrodes under acid conditions)

3. Non-resistant materials are:

- a. Iron (non-resistant to acid conditions only)
- b. Rubber (non-resistant to solvent action)
- c. Saran, and most plastics (non-resistant to solvent action)

H. Hydrolysis of Ester: The isopropyl ester hydrolysis, or reverts back to acid and alcohol under certain conditions, namely, presence of sulfuric acid and at a high temperature.

II. YIELDS:

Our standard production cost figures are based upon the following percentages:

Type of Ester	% Acid Converted	% Excess Alcohol Used	Allowable Consumption of Benzol, gals./lb. of Ester
Butyl-D	90.5	33	0
Butyl-T	86.3	40	0.05
Iso-D	91.4	55	0.035
Iso-T	85	62	0.04
HBP-D	94.2	1	0.01
HBP-T	95.3	1	0.015
PEG200-D	94.7	10	0.01

↑
Charge 2 mols alcohol per mol acid
except on low Volatiles

DS00011727

III. History of Process Development:

Process development in 2,4-D and 2,4,5-T esters has been aimed at either:

A. Lowering costs by:

1. Decreasing reaction time
2. Manufacturing esters by different methods
3. Decreasing losses, or
4. Decreasing the amount of processing required or

B. Producing a more acceptable ester (customer acceptable)

A. Decreasing reaction time:

1. **Catalysis:** Although several catalysts have been tried in an effort to speed up esterifications and/or decrease decomposition of the alcohols used, sulfuric acid remains the optimum catalyst. Among catalysts tried have been: benzene sulfonic acid, alkane sulfonic acid, phosphoric acid, and zinc chloride.
2. **Flash Vaporization:** An article in Industrial and Engineering Chemistry outlined a method for more rapid removal of water of reaction. This was accomplished by pumping the reaction mixture through a heat exchanger, heated with steam, and allowing the hot mixture to emerge suddenly into a relatively large vessel which caused the azeotrope mixture to flash off from the ester. The ester is then returned to the esterifier. Several batches were tried in the plant with varying results. For example, one batch esterified in 9 hours as against 18 hours normally; however, other batches took nearly twice as long as normally. Need for the equipment employed elsewhere forced postponement of this experiment.
3. **Benzol Sparging:** The alcohol-benzol mixture from the separator normally is returned to the esterifier into the top. Since the system the alcohol-benzol mixture returns to is very hot we believe that some of the mixture may be flashing off and not doing its full share of removing water. Accordingly, we tried to introduce the refluxing benzol under the surface of the liquid in the esterifier. Mechanical difficulties caused us to abandon this on one esterifier and we are at present in the process of installing the system on another esterifier.

*2.7% H₂SO₄ is
white ester;
1st in BPP
added water
Laf*

DS 00011728

4. Drying Reflux: In order to attempt to drive off the last traces of water at the end of an esterification, thus producing a greater conversion of acid to ester, we installed a simple calcium chloride dryer in the line carrying the refluxing alcohol-benzol mixture. No change in completeness of esterification was noticed in the several batches tried.

B. Alternate Methods of Manufacture:

1. Chlor acetate: Dr. Ira Weil investigated the possibility of manufacturing esters by a "reverse" method. In this method monochloroacetic acid is esterified with the desired alcohol and the resulting chloracetate ester condensed with 2,4-dichlorophenol. The method worked; greatest disadvantage is that the intermediate chloracetate ester is a powerful lacrymator causing severe handling problems.

C. Decreasing Losses: Losses in any process can occur in several ways. This outline neglects the obvious one such as leaky valves, broken lines, etc.

1. Vacuum Distillation: Until about a year ago isopropyl esters, at the completion of esterification, were distilled at atmospheric pressure to recover the unused solvents. Since that time, using a method developed by Mr. S. Falcone by neutralizing the crude ester first to prevent decomposition we have been able to distill under vacuum. By actual checks on each batch run we now know that no alcohol or benzol is left in to be lost.
2. Other losses have been checked by catch tanks in the line before entering the sewer, more accurate checks on quantity of acid charged and better acidification for recovery of the acid.

D. Decrease in Processing: Unwashed ester: By neutralizing the excess acid in a crude ester it was felt that an ester good enough for formulating would be obtained. Darker color and excessive free acid in the ester caused us to abandon this.

E. Other Esters:

1. Low volatile esters: Previously made were polyethylene glycol esters of 2,4-D and 2,4,5-T. These have been replaced because of their poor fuel oil solubility, with butoxy ethoxy propanol esters.
2. Secondary butyl: This ester has been replaced by the normal butyl as previously mentioned.

DS 00011729

F. Emulsions in Washing Esters: A problem that gives occasional trouble in 2,4-D esters and more frequent trouble in 2,4,5-T esters is the formation of emulsions during the washing procedure, especially caustic washes. Remedies tried are:

1. Greater water to ester ratio in washing has been the greatest help.
2. Sulfuric acid added to an emulsion frequently "breaks" it.
3. Increased agitation sometimes helps.
4. Use of a surface active agent to change surface (interface) tension has been of help frequently. No one method works all the time and we usually discover the best for that batch by trial and error.

IV. FUTURE POSSIBILITIES FOR PROCESS DEVELOPMENT

- A. Esterify low volatiles at a higher temperature: Suggested by Mr. G. Barker from his experience at Glyco Products. Higher temperatures would mean faster reactions.
- B. Revive Chloracetate Method: The disadvantage of this method could be overcome by better design, i.e., a totally enclosed system to keep the lacrymator out of the air.
- C. A different azeotrope agent: Use of a higher boiling azeotrope could mean higher reaction temperatures and hence faster reactions. Tolpol has had some laboratory work done on it and appears to be one possibility. In addition to a higher boiling point Tolpol is somewhat cheaper, will not solidify during cold spells, and is somewhat more tolerable in the atmosphere than benzol..
- D. Catalysts: Although some work has been done, the field of catalysts for esterification has by no means been exhausted.
- E. Continuous Esterification: No extensive work has been done on this subject anywhere but several esters other than 2,4-D have been prepared continuously. With a low boiling ester the problem is simply one of continuous distillation, with high boiler such as 2,4-D esters the situation changes.

One method of preparation used was passing a mixture of the alcohol and the acid down a packed column while injecting carbon dioxide gas through the bottom. Water vapor was carried out the top and ester removed through the bottom.

DS 00011730

A possibility exists for adjusting the flash vaporization method previously mentioned to continuous esterification. Instead of returning the ester separated in the flash chamber it, being presumably purer than the mixture in the esterifier, would be passed to another esterifier where the flashing would continue. This process might take 2,3 or more esterifiers in a line, the exact number would have to be determined by experimental methods.

- F. Different Method of Esterification: There is a possibility of producing the isopropyl esters by reacting isopropyl chloride with the sodium salt of 2,4-D. Other esters have been prepared in this manner; the biggest disadvantage is the necessity of a high temperature which would probably mean using an autoclave.
- G. Unwashed Esters: Although we had poor results using isopropyl and butyl esters without washing, the fact that low volatile esters are used this way would seem to indicate that all possibilities have not been exhausted.

V. PRODUCT DEVELOPMENT

A. Low Volatile

1. The following esters of 2,4-D and 2,4,5-T have been made and because of ease of esterification and lighter color seem to hold promise: 2-ethyl hexanol, capryl alcohol and iso-octyl alcohol. Samples of these esters have been sent out for field tests.
2. Negative results have been obtained with the following:
 - a. Polypropylene glycol 150 - poor fuel oil solubility.
 - b. Ethoxy ethoxy propanol - difficult to esterify.
 - c. Ethylene glycol, di-ethylene glycol-these are solids and hence difficult to formulate.
 - d. Butyl cellosolve-patented.
 - e. Butyl carbitol-patented.

B. Volatile

A mixed ester consisting of iso butanol and normal butanol esters of 2,4-D has been prepared and is of interest because of its low freezing point. Similar esters have been patented for use in Canada.

KAspinwall:jp
9/16/54

DS 00011731