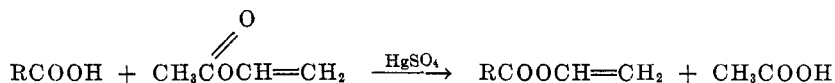


## THE INTERCHANGE REACTION OF VINYL ACETATE WITH ORGANIC ACIDS

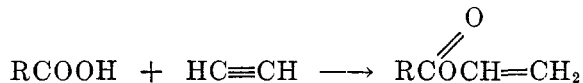
ROBERT L. ADELMAN

*Received May 4, 1949*

The reaction of vinyl acetate with carboxylic acids in the presence of mercuric salts of strong acids as catalysts to form the vinyl ester of the acid was first reported by Hermann and Haehnel (1) and Toussaint and MacDowell (2).



This reaction, which we will call the "Vinyl Interchange" Reaction, to differentiate it from typical ester interchange and ester-acid interchange reactions, is a well-known and useful method for the laboratory preparation of many of the simpler vinyl esters. The very mild reaction conditions and the low yields of by-products lead to high yields of monomers of greater purity and activity than those prepared by the reaction of acetylene with acids.

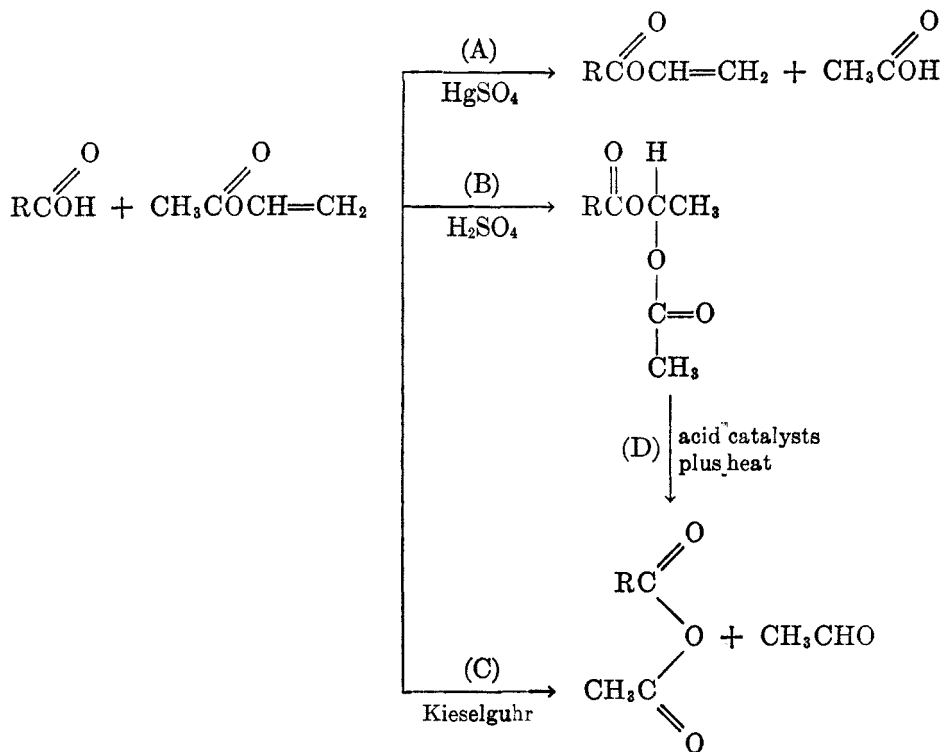


Furthermore, vinyl esters of dibasic acids are prepared much more easily by vinyl interchange than through the acetylene route, and recent work in this laboratory has shown that the reaction of vinyl acetate catalyzed with mercuric salts is not restricted to carboxylic acids, but will occur with other compounds containing active hydrogen, such as acetoacetic ester and glycolic esters.

There are three major reactions of vinyl acetate with carboxylic acids: (A) the vinyl interchange reaction, which occurs at low temperatures (20–80°) in the liquid phase, (B) the formation of ethylidene diesters at somewhat higher temperatures, generally in the liquid phase with acid catalysts, (3, 4) and (C) the formation of anhydrides of the acids present, in the vapor phase with acid and dehydrating catalysts (5).

Reaction (A), the vinyl interchange reaction, is usually run as described by Toussaint and MacDowell (2). At the same time, ethylidene diester formation (reaction B) occurs significantly under vigorous conditions (75°), especially after long reaction periods. When the formation of the latter occurs, in order to obtain good yields of the vinyl esters, another step is required, the decomposition of the ethylidene diesters to recover the free acids (reaction D) (6). If the reaction temperature is kept at 30° or below, however, the formation of ethylidene diester by-products is generally negligible and high yields of vinyl esters are obtained. This is illustrated in Tables I and II. It is true, however,

that an interchange that proceeds to a final equilibrium value in 1-6 hours at 75° may require 72 hours at 30°.



The reaction is reversible. The higher vinyl esters with acetic acid will all form vinyl acetate under the same experimental conditions as the forward reaction.

In this paper will be presented evidence that the vinyl interchange reaction proceeds through the dissociation of the vinyl acetate, in the presence of mercuric sulfate catalyst, into an acetylene-mercury complex and acetic acid. The acetylene-mercury complex is then capable of reacting with the various acids present to form the vinyl derivatives:

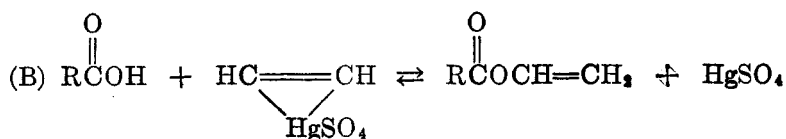
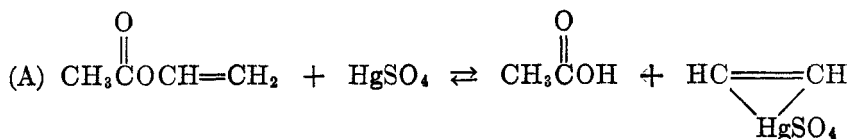


TABLE I  
 PREPARATION OF VINYL ESTERS BY VINYL INTERCHANGE

VINYL ESTER	REACTION TEMP., °C.	CONVERSION, % <sup>d</sup>	YIELD, % <sup>e</sup>	B.P., °C/MM.	$n_D^t$	$d^{tb}$
Stearate	30 <sup>a</sup>	62.5	88	169-178/3 <sup>c</sup>	1.4423 <sup>33</sup>	0.8517 <sup>40</sup>
	75	49	74	187-188/4.3 (24)	(24)	(24)
Laurate	75	73	93	105/3 <sup>f</sup> (23)	1.4386 <sup>21.5</sup>	.8770 <sup>28</sup>
				142/10 (24)	1.4368 <sup>30</sup>	.8639 <sup>30</sup>
Oleate	75	39	82	184-186/3.5	1.4533 <sup>30</sup>	.869 <sup>30</sup>
				178/2.8 (22)	(22)	(22)
Benzoate	75	71		72-74/3	1.5259 <sup>21.5</sup>	1.0706 <sup>28</sup>
				100-101/25 (12, 14)		1.0686 <sup>28</sup>
Trimethyl acetate	30	54	98	110-112	1.4068 <sup>20</sup>	0.873 <sup>28</sup>
	30	80	98			
	75	50	70			
Caprylate	30	72.5	95	65-68/3	1.4271 <sup>22.5</sup>	.8898 <sup>29</sup>
	75	52	83	135/100 (24)	1.4256 <sup>30</sup>	.8719 <sup>30</sup>
3,5,5-Trimethylhexanoate	75	67	89	85-95/20-26	1.4226 <sup>21.5</sup>	(24)
Octyl phthalate	30	71	82	138-142/0.01	1.4979 <sup>21</sup>	1.01 <sup>20</sup>
	75	65	90			
Adipate	75	24	65	102-118/2-3		

<sup>a</sup> 75° for 15 min., followed by 30° for 60 hours. <sup>b</sup> Many of the density measurements were taken by V. Aungier of this laboratory. <sup>c</sup> M.p. 30-32° [lit. (24) 35-36°]; anal. 95% vinyl stearate by titration with bromine in acetic acid. <sup>d</sup> Conversion is defined as  $(100 \times \frac{\text{moles product}}{\text{moles original acid}})$ . <sup>e</sup> Yield is defined as  $100 \times \frac{\text{moles product}}{\text{moles original acid} - \text{moles recovered acid}}$ .

<sup>f</sup> Anal. 96% vinyl laurate.

Possible intermediate steps include:

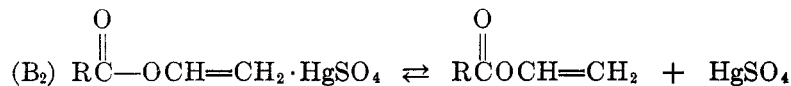
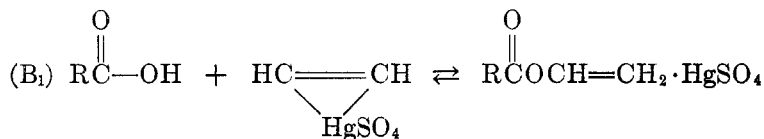
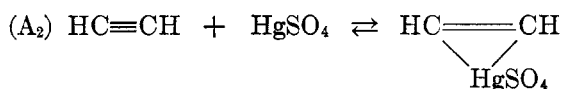
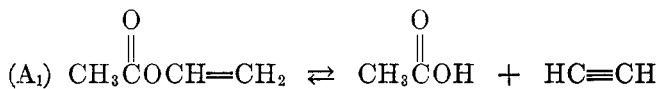
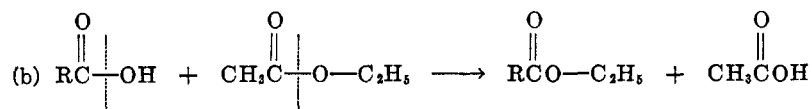
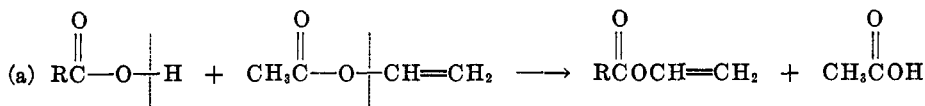


TABLE II  
EFFECT OF TEMPERATURE ON BY-PRODUCT FORMATION IN VINYL INTERCHANGE

ACID USED	REACTION TEMP./TIME	CONVERSION TO VINYL ESTER, %	YIELD OF VINYL ESTER, %	CONVERSION TO ETHYLIDENE DIESTER, %
Trimethylacetic acid	75°/6-12 hrs.	50	70	25
	30°/36 hrs.	54	98	<2
Stearic acid	75°/8 hrs.	50	65	26
	75°/15 min. + 30°/60 hrs.	62.5	88	<14

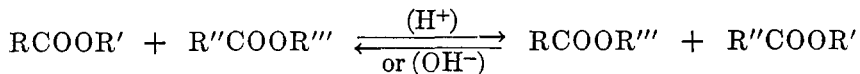
Thus, the reaction must proceed with a breaking of the oxygen-hydrogen bond in the acid,  $\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$  and a breaking of the oxygen-vinyl carbon bond in the vinyl ester  $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}=\text{CH}_2$  [Equation (a) below]. This is contrary to the mechanism of typical ester-acid interchanges [Equation (b)] in which



the carbonyl carbon-to-oxygen bond is broken in the ester, and the carbon-oxygen bond is broken in the acid (7).

Support for this mechanism is found in the following evidence:

(A) *There are marked differences in vinyl interchange reactions as compared to ester interchanges or acid-ester interchanges.* Thus, ester-acid or ester-ester interchanges are catalyzed by acids or bases (although different mechanisms are postulated for the two cases) (7), whereas the vinyl interchange is not catalyzed by either acids or bases (see Table III).<sup>1</sup> Furthermore, the well-known interchange between two different carboxylic acid esters, such as



has not been successfully carried out when one of the esters is a vinyl ester.

<sup>1</sup> It is advantageous to use mercuric acetate and sulfuric acid to prepare mercuric sulfate *in situ*, rather than add already prepared mercuric sulfate, as the former leads to a considerably more soluble catalyst.

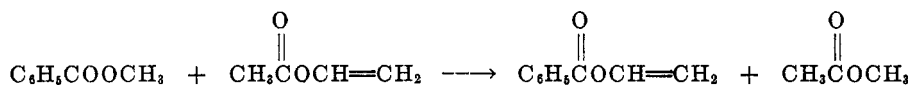
TABLE III  
EFFECT OF VARIOUS CATALYSTS ON THE RATE OF VINYL INTERCHANGE (30°)

CATALYST (0.02 MOLE)	CATALYST SOLUBILITY	EXTENT OF REACTION*, %			REMARKS
		6 Hr.	24 Hr.	104 Hr.	
(a) H <sub>2</sub> SO <sub>4</sub> .....	Sol.	0	0	0.2	
" HgAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	Sol.	96	91	72	
" PbAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	Insol.		0	0.4	
" Pb .....	Insol.		0	0	The lead turned white-flaky
" HgAc <sub>2</sub> + AgNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> .....	Partially Sol.	>96	83	73	
" Dimethylaniline .....	Sol.		0	0	
" Tetramethylammonium iodide .....	Insol.		0	0	
" Cuprous chloride (green) hydrate (?) + H <sub>2</sub> SO <sub>4</sub> ..	Insol.		0	0.8	
" FeCl <sub>3</sub> .....	Sol.		0	0	The high H <sub>2</sub> O-sol. acid content due to FeCl <sub>3</sub> neutralization alone.
" MnAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	Insol.		0	0.2	
(b) CdAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	"	17	21	27	
" SnAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	"	19		50	
" HgAc <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> .....	Sol.	75	90		
" BF <sub>3</sub> ·Etherate .....	Sol.			<6	An exothermic reaction does occur at reflux temp. with the formation of ethylidene diesters.

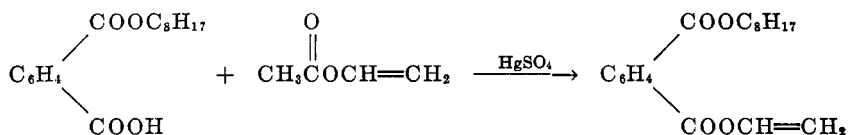
\* Extent of reaction measured by total amount of water-soluble acid formed in reaction mixture.

(a) Capric acid (1 mole), vinyl acetate (6 moles), and copper resinate (0.001 mole) made up the reaction mixture. (b) The same as (a), but caprylic acid rather than capric acid was used.

Thus, the attempt to react methyl benzoate and vinyl acetate was unsuccessful,



using sulfuric acid, dimethylaniline or mercuric sulfate as catalysts. Further examples of unsuccessful ester-ester interchange with vinyl acetate were with mono-octyl phthalate, in which only the free carboxyl group reacted, and the



ester group was unchanged, and with methyl lactate (8), in which acylation of hydroxyl group occurs with no interchange in basic media, ethyl formate, propyl formate, and acetoacetic ester, although another reaction occurred with the latter which will be discussed more fully in another connection. Many other examples could be mentioned. This can be readily explained by the fact that as ordinary carboxylic acid esters tend to undergo fission at the carbonyl

carbon-to-oxygen bond ( $\text{RC} \begin{array}{c} \text{O} \\ \parallel \\ \text{---} \end{array} \text{OR}$ ), with very little tendency to split at the

oxygen-to-alcohol-carbon linkage ( $\text{RC} \begin{array}{c} \text{O} \\ \parallel \\ \text{---} \end{array} \text{O---R}$ ), an interchange with vinyl ace-

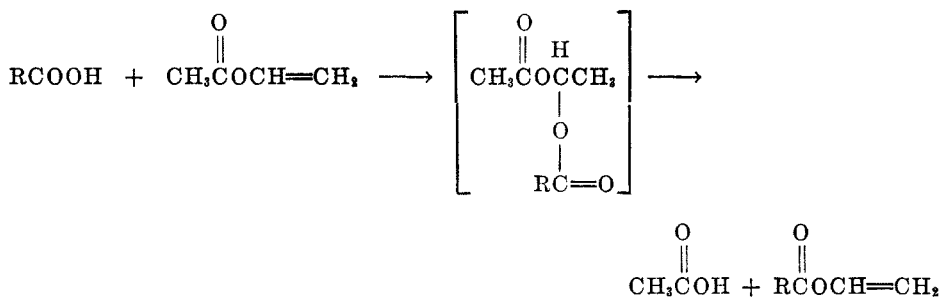
tate (a reaction of an ester with acetylene-mercury complex) proceeds with great difficulty. On the other hand, the oxygen-to-hydrogen bond in carboxylic

acids ( $\text{RC} \begin{array}{c} \text{O} \\ \parallel \\ \text{---} \end{array} \text{O---H}$ ) is easily broken and so vinyl interchange occurs with the

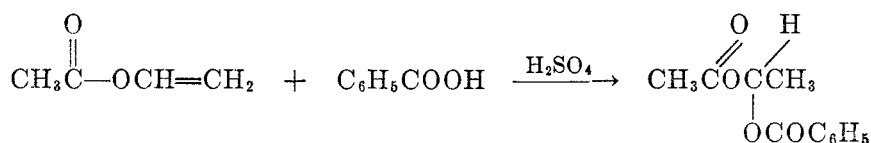
free acids (furthermore, no reaction occurs between acetylene and esters of carboxylic acids under these conditions).

Also, those acids which would undergo acid-catalyzed esterifications or ester interchanges much more slowly than straight chain acids because of steric hinderance, such as trimethylacetic acid and *ortho*-substituted benzoic acids, have no difficulty in undergoing the vinyl interchange because the actual locus of reaction occurs farther away from the interfering groups, being more distant by one oxygen atom. Thus, trimethylacetic acid (pivalic acid), caprylic acid, benzoic acid, and monoethyl phthalate react with vinyl acetate at similar rates under nearly identical conditions.

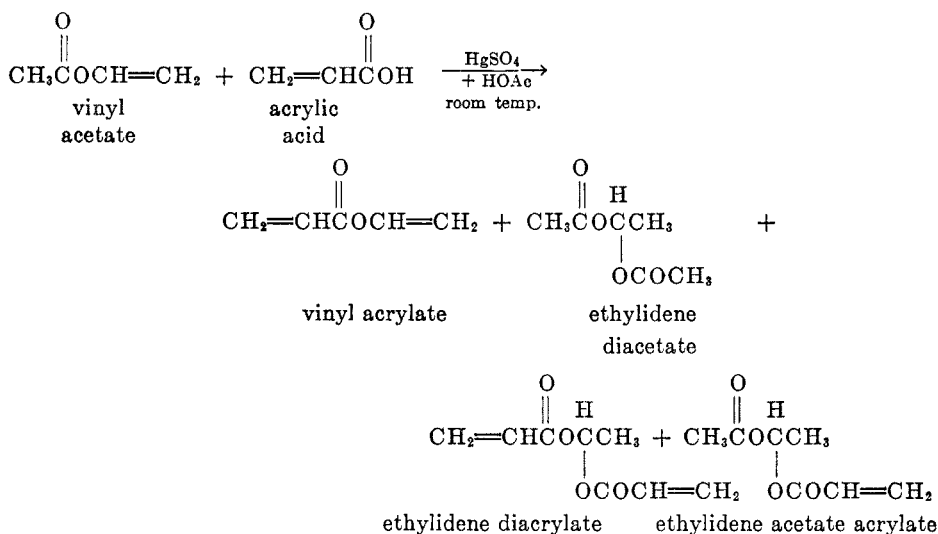
(B) A potential mechanism involving the ethylidene diester as an intermediate followed by decomposition to the vinyl ester is unacceptable, as (a) the vinyl ester



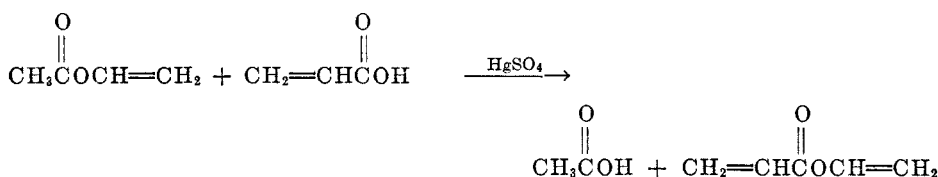
interchange reaction is not catalyzed by acids, whereas, the formation of ethylidene diesters is subject to general acid catalysis. An illustration of this point is found in the yields of ethylidene acetobenzoate from equimolar quantities of vinyl acetate and benzoic acid, which are claimed to be quantitative (9).



If the sulfuric acid acted as a vinyl interchange catalyst, some vinyl benzoate, or at least some ethylidene diacetate, should have been found, due to acetic acid formation; whereas, in the presence of *mercuric sulfate* + acetic acid, vinyl acetate and acrylic acid form mixtures of vinyl esters and ethylidene diesters (10):

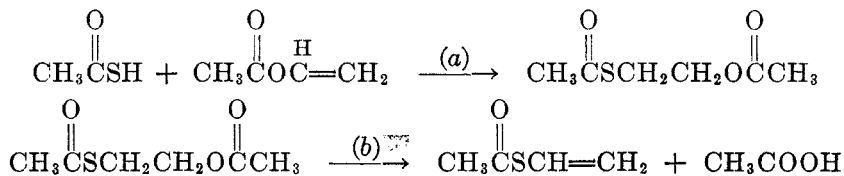


Here are found all the products expected from the initial formation of vinyl acrylate and acetic acid, due to mercuric sulfate acting as a vinyl interchange



catalyst followed by the reaction of carboxylic acids with the vinyl esters present. The acidic substances present act as catalysts to give the observed ethylidene diesters.

(b) The reaction of thioacetic acid with vinyl acetate proceeds as follows:



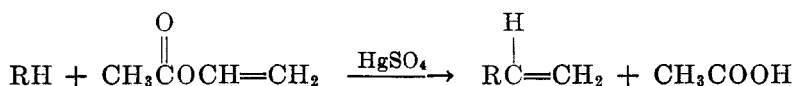
but step (a) requires oxygen or peroxides, which are not necessary (or desirable) for the vinyl interchange reaction (which suggests a different mechanism for this step), and step (b) occurs only by pyrolysis in the vapor phase at high temperatures (11).

(c) The formation of ethylidene diesters must require a greater energy of activation than the formation of vinyl esters, and so could not possibly act as an intermediate in the vinyl interchange reaction. This is evidenced in the reaction of vinyl acetate with acrylic acid, mentioned above, in which some vinyl acrylate was isolated. This suggests that vinyl acrylate is the intermediate for the ethylidene diester reaction. Furthermore, the conversions to ethylidene diester increase as compared to vinyl ester conversions, at higher temperatures, showing a greater activation energy for the ethylidene diester reaction (See Table II).

(C) *Acetylene plus various hydrogen-active compounds leads to identical products under similar conditions as from vinyl acetate plus these compounds.* Thus, for example, the catalysts for the vinyl interchange reaction are the same as those used for the production of vinyl esters from acetylene and carboxylic acids. Coes first called attention to this fact (10). It should be noted that the proposed mechanism offers the explanation that an acetylene-catalyst complex is the intermediate in both types of reaction. Furthermore, these catalysts, such as mercuric salts of strong acids, will catalyze both types of reactions under similar experimental conditions. Thus, for the reaction of acetylene with trichloroacetic acid in the liquid phase at 50–57° with mercuric phosphate as catalyst, a 25–65% conversion to vinyl trichloroacetate was obtained. Similar results were obtained with chloroisobutyric acid and acetylene. The use of zinc or cadmium salts of the carboxylic acids as catalysts for the acetylene reaction (following the patent of Reppe for stearic or lauric acid), requires higher temperatures (140–190°) (12), and this may correspond to the decreased rate of vinyl interchange when using cadmium or zinc salts as catalysts at 30° (See Table III). Acids and bases are not catalysts for the vinyl interchange reaction any more than they are for the reaction of carboxylic acids with acetylene at low temperatures. Apparently a certain type of coordinate complex of acetylene with mercury is as necessary for vinyl acetate to undergo reactions of this type with carboxylic acids as it is for acetylene itself (13).

Table III indicates that the same catalysts that are active for the production of vinyl esters from carboxylic acids and acetylene are also active for the production of vinyl esters from carboxylic acids and vinyl acetate, that is, mercury, zinc, and cadmium salts.

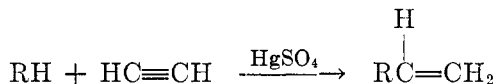
Furthermore, if this mechanism is correct, it should be possible to react compounds of the general type R—H with vinyl acetate as follows:



provided the R—H bond is sufficiently labile. Or, looking at the problem from

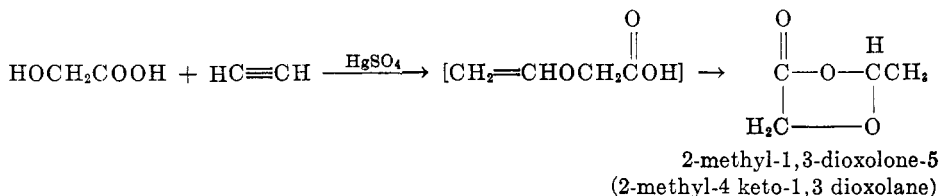


another point of view, if the R—H bond is sufficiently labile to allow addition of R—H to acetylene under mild conditions, with mercuric sulfate as catalyst,

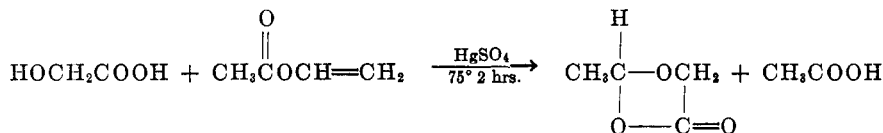


it should be able to undergo the vinyl interchange reaction.

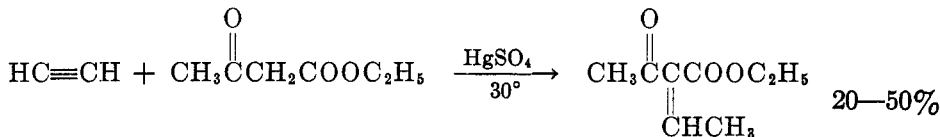
Thus, a cyclic lactide was prepared by Conaway (14) by the addition of glycolic acid to acetylene, probably through the vinyl ether.<sup>2</sup> The catalyst used was mercuric sulfate plus acetic anhydride.



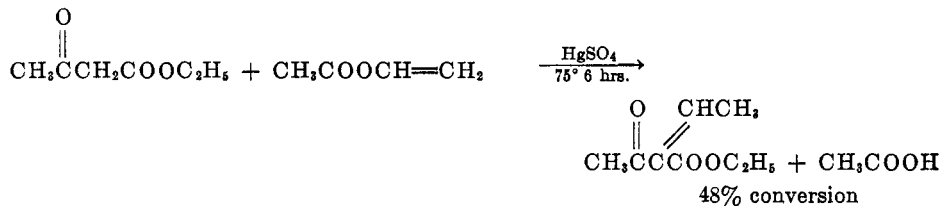
This compound was also obtained with glycolic acid and vinyl acetate in over 60% yield.



Ethylidene acetoacetic ester has been prepared by the reaction of acetylene with acetoacetic ester.



The same product was obtained by the reaction of the methylene group of acetoacetic ester with vinyl acetate to form the ethylidene derivative.



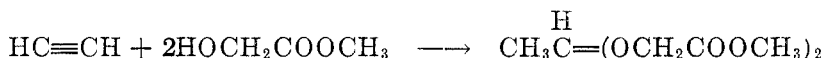
A considerable amount of ethylidene diacetate was also formed due to the vigorous conditions used in this experiment, and this may have helped the reaction proceed by removing one of the products of the primary reaction, that is,

<sup>2</sup> The reactions of alcohols in general with vinyl acetate may be adequately explained by this mechanism, and will be presented in a forthcoming paper.

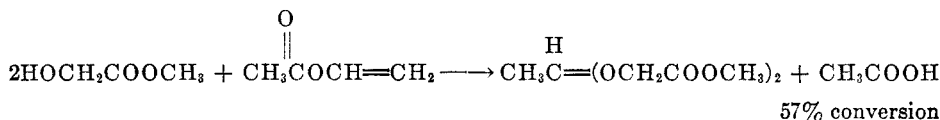
acetic acid [See reaction (B), described previously]. This is also proof that a carboxyl group is not essential to the mechanism.

The same product is also obtained from the reaction of acetaldehyde and acetoacetic ester. However, the acetylene or vinyl acetate reactions with acetoacetic ester were performed in anhydrous systems, at relatively low temperatures. Very little acetaldehyde forms under these conditions, and hence could not play a major role in the mechanism of the reaction.

Acetaldehyde *bis*-carbomethoxymethyl acetal has been prepared from acetylene and glycolic ester at 25–35° with boron trifluoride-methanol complex as catalyst in 81% yield (15).



And in similar fashion to the other examples, vinyl acetate and glycolic ester, at 35° formed acetaldehyde *bis*-carbomethoxymethylacetal in 57% conversion.



It has been recently shown that vinyl acetate plus alcohols, in the presence of a mercuric oxide-boron fluoride catalyst, forms acetals (16), and these products and conditions are precisely the same as for acetal formation from acetylene and alcohols (17).<sup>2</sup>

The reaction of another active RH-type compound with vinyl acetate was investigated, namely 1-chloro-1-nitroethane. This compound has a strongly acidic hydrogen, but no vinyl derivative was obtained, and only 2% of polymeric material was isolated.

It has been suggested that the failure of this compound to react in actuality supports the postulated vinyl interchange mechanism, as the hydrogen atom in this nitro compound is labilized only under alkaline conditions.

Similar experiments with propyl formate and ethyl formate indicate that if a vinyl derivative is formed, it is unstable under these conditions, as about 15–20% of a hard, black, brittle polymer was formed.

This mechanism may help to explain the surprisingly small amount of polymer formation during the vinyl interchange reaction, even when run at reflux for many hours with no inhibitor present, for it is known that small amounts of acetylene tend to inhibit vinyl polymerizations.

Attempts to get a chemical test for the presence of free acetylene in solution or vapor phase by precipitating cuprous or silver acetylide have given negative results.

(D) *Substantiation for intermediate steps A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>, is considerably more difficult.* However, physical evidence for the existence of an acetylene-catalyst complex, and possibly for step A<sub>1</sub>, was suggested from infrared absorption spectra studies.

To summarize our observations of the infrared spectra: (a) weak absorption bands are found in vinyl esters which are near to well-known absorption bands of acetylene; (b) the presence of vinyl interchange catalysts tends to increase the intensity of these acetylene-equivalent absorption bands; (c) vinyl interchange catalysts have effects on the absorption spectra of vinyl esters which are very similar to the action of dissolved acetylene on the absorption spectra.

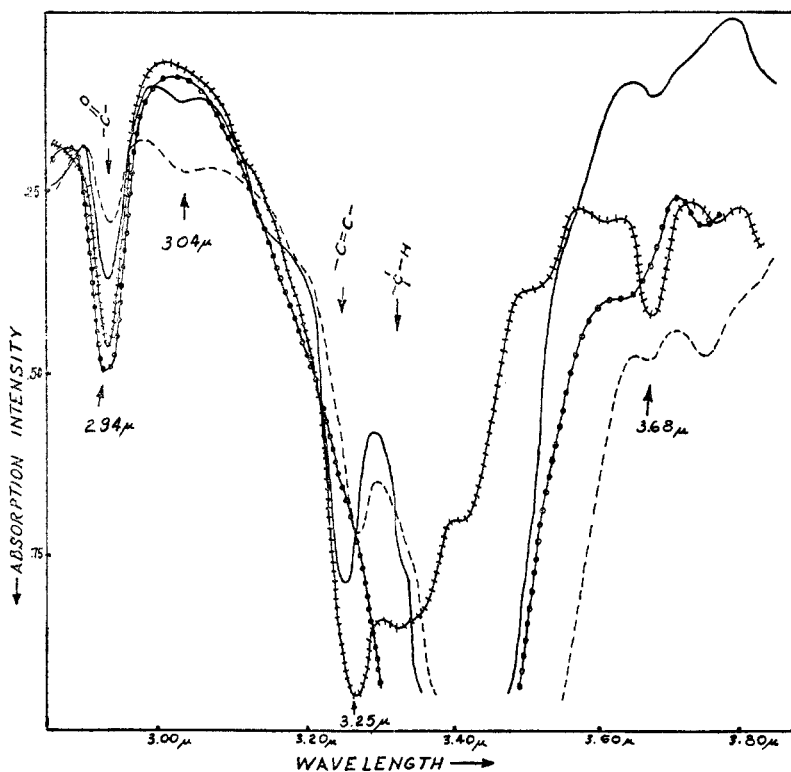


FIG. 1

+++++	Vinyl acetate
-O-O-O-O-	Ethyl acetate
—————	Vinyl laurate
-----	Vinyl trimethylacetate

It thus appears that the infrared absorption spectra evidence supports the idea that *small amounts of acetylene may be present in all vinyl esters, and that the concentration of the acetylene is increased in the presence of a vinyl interchange catalyst, such as mercuric sulfate* (possibly by acetylene-mercury complex formation).

It was realized that attempted identification of absorption bands in vinyl esters specifically due to acetylene would be very difficult because of the significant displacement of a gaseous  $\text{H}-\text{C}\equiv\text{CH}$  absorption band when in a polar solvent. An example of that can be seen in Figure 2, where a sample of vinyl

acetate containing dissolved acetylene gave an absorption (plotted as the reciprocal of the absorption intensity, arbitrary scale, *vs* wave length) specifically due to the addition of acetylene, at 3.14–3.17 $\mu$ , but which corresponds to the 3.047 $\mu$  acetylene absorption in the vapor phase. Furthermore, the acetylene-mercury complex may be even more displaced. Nevertheless, certain conclusions are obtainable if these possible displacements are kept in mind.

When infrared spectra of various aliphatic vinyl esters were compared, it was found that they were, of course, quite similar in gross structure, with very

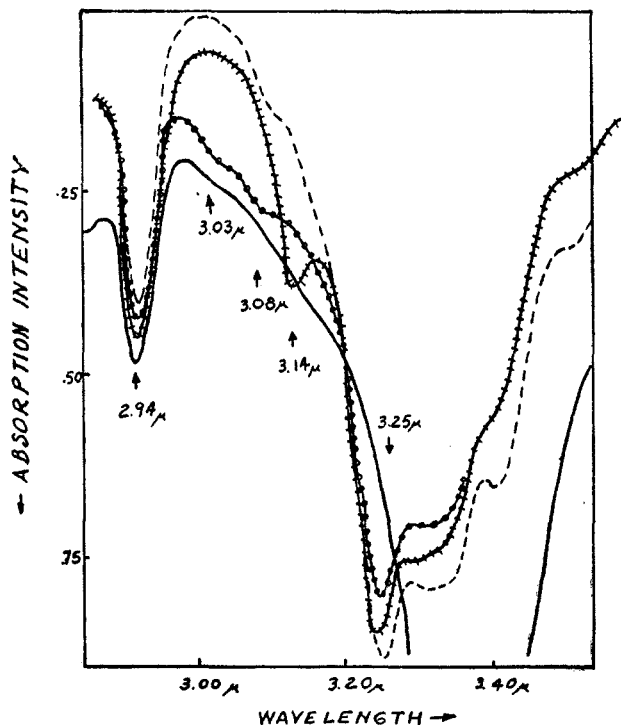


FIG. 2

- - - - - Vinyl acetate (pure)  
 + + + + + Vinyl acetate + acetylene  
 o - o - o - o - o Vinyl acetate + catalyst  
 ————— Ethyl acetate + catalyst + .5% acetic acid

large absorptions near 7.8 $\mu$  due to the C—O—C linkage in the ester group, 5.8 $\mu$  due to the carbonyl groups, etc. Similarly, when looking at the smaller absorption bands, one, at  $2.93 \pm 0.02\mu$ , was found to be present in all esters.<sup>3</sup> The magnitude of absorption was found to be proportional to the magnitude of the ester groups as compared to the total molecular weight. For comparison of the spectra of different vinyl esters, the 2.93 $\mu$  band was superimposed.

<sup>3</sup> This band may be the first harmonic of the carbonyl-in-ester absorption appearing at 5.8 $\mu$ , and is not to be confused with the band due to hydroxyl groups which may appear in undried or enolizable esters at  $2.78 \pm 0.04\mu$ .

Figure 1 shows a comparison of three vinyl esters. At  $3.25\mu$  is observed the strong absorption maximum of all vinyl esters, while the very large unresolved absorption near  $3.4\mu$  is due to carbon-hydrogen bonds. Other weak absorption bands found only in vinyl esters (as compared to saturated esters) are at  $3.70\mu$ ,  $4.40\mu$ ,  $5.42\mu$ ,  $6.15\mu$ ,  $6.78\mu$ ,  $7.09\mu$ ,  $7.70\mu$ , and  $13.2\mu$ . (Figures 1, 5 and 6). Also small indications of absorption near  $3.04\text{--}3.10\mu$  are found in all vinyl esters, with the exception of vinyl acetate (Figure 1), but it was also found in the latter upon the addition of mercuric sulfate (Figure 2).

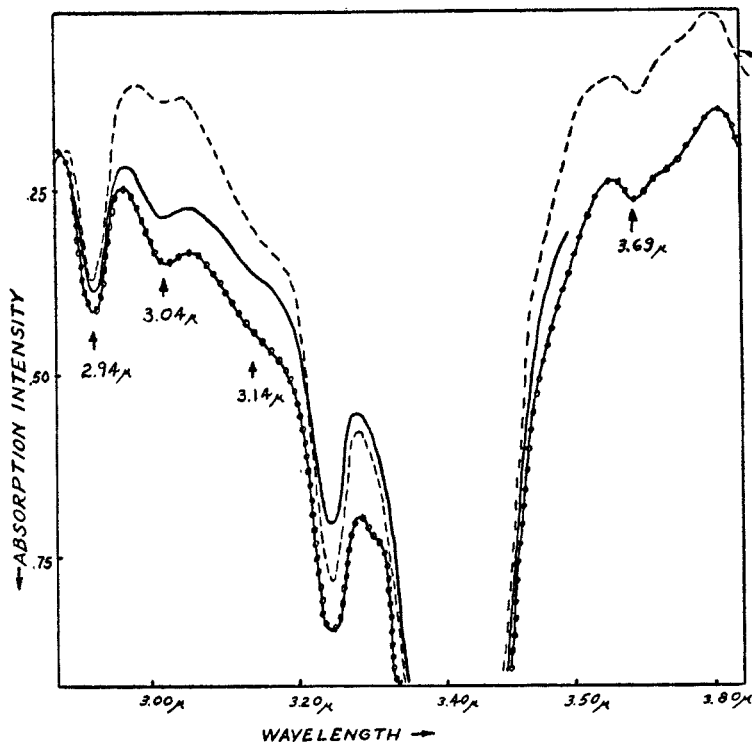


FIG. 3

- - - - - Vinyl trimethylacetate (pure)  
 ○-○-○-○-○ Vinyl trimethylacetate + catalyst  
 ————— Vinyl trimethylacetate + 1% trimethylacetic acid

The above specific absorptions for all vinyl esters are made significant for the present investigation by a comparison with the known absorption maxima for gaseous acetylene. The literature gives values of  $2.56\mu$  (weak), (18);  $3.047\mu$  (strong), (16);  $3.70\mu$  (medium) (16);  $4.40\mu$  (medium) (17);  $5.11\mu$  (weak) (16);  $7.67\mu^4$  (strong) (19); and  $13.7\mu$  (strong) (16), for acetylene gas. An interesting correlation is found in that bands closely situated to *all the significant acetylene absorption bands are weakly present in the vinyl ester spectrum*, except those that are masked by other absorptions of similar wave length. Thus, the carbon

<sup>4</sup> Actually found a doublet at  $7.31\mu$ ,  $7.62\mu$  for acetylene gas.

dioxide-water triplet would mask the  $2.56\mu$  band, and possibly the  $7.53\mu$  band is masked by the methyl group absorption. This suggests the presence of small amounts of acetylene in vinyl esters (at least in the presence of catalyst).

Furthermore, on the addition of mercuric sulfate catalyst to vinyl acetate, there are some indications of new absorption bands at  $3.03\mu$  and  $3.10\mu$ , very near to the band of gaseous acetylene ( $3.047\mu$ ), and to the band of acetylene dissolved in vinyl acetate ( $3.14\mu$ ) (Figure 2). That these absorptions of vinyl

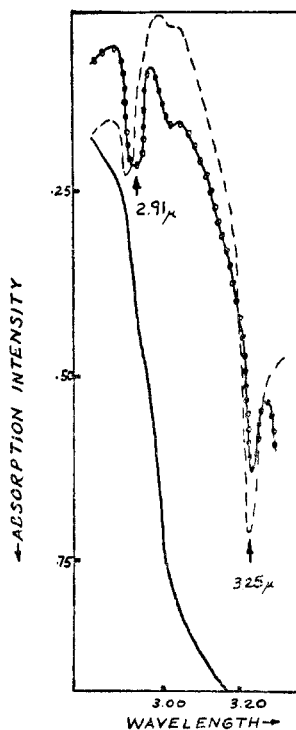


FIG. 4

- - - - - Vinyl trimethylacetate vapor (over catalyst liquid phase)  
 ○-○-○-○ 99% vinyl trimethylacetate + 1% trimethyl acetic acid  
 ————— 80% vinyl trimethylacetate + 20% trimethylacetic acid

esters in the  $3.03$ – $3.10\mu$  range are specific for *vinyl* esters only is also seen on Figure 2, where the spectrum for ethyl acetate plus mercuric sulfate plus acetic acid is shown.<sup>5</sup> The absorption at  $3.09\mu$  also increases for vinyl trimethylacetate on the addition of catalyst (Figure 3). It should be noted that this entire region of the spectrum is extensively depressed after catalyst addition to the vinyl ester (and after standing at room temperature for several hours) (Figures 2 and 3). This general depression of the spectrum from approximately  $2.95$ – $3.25\mu$  is due to the formation of free carboxyl groups as the catalyzed decomposition

<sup>5</sup> The solutions were filtered clear before spectra were taken.

of the vinyl ester proceeds. This can be seen in a comparison of the pure ethyl acetate spectrum in Figure 1, with the ethyl acetate + catalyst + 0.5% acetic acid spectrum in Figure 2. Also Figures 3 and 4 illustrate the depression of the vinyl trimethylacetate spectrum on the addition of 1% and 20% trimethylacetic acid. The spectrum of ethyl acetate, catalyst, and acetic acid, (Figure 2), shows, however, that the acid formed does not cause the observable absorption in the 3.03–3.10 $\mu$  region, but in large amounts actually obliterates any indication of minute absorption bands in this region (Figure 4).

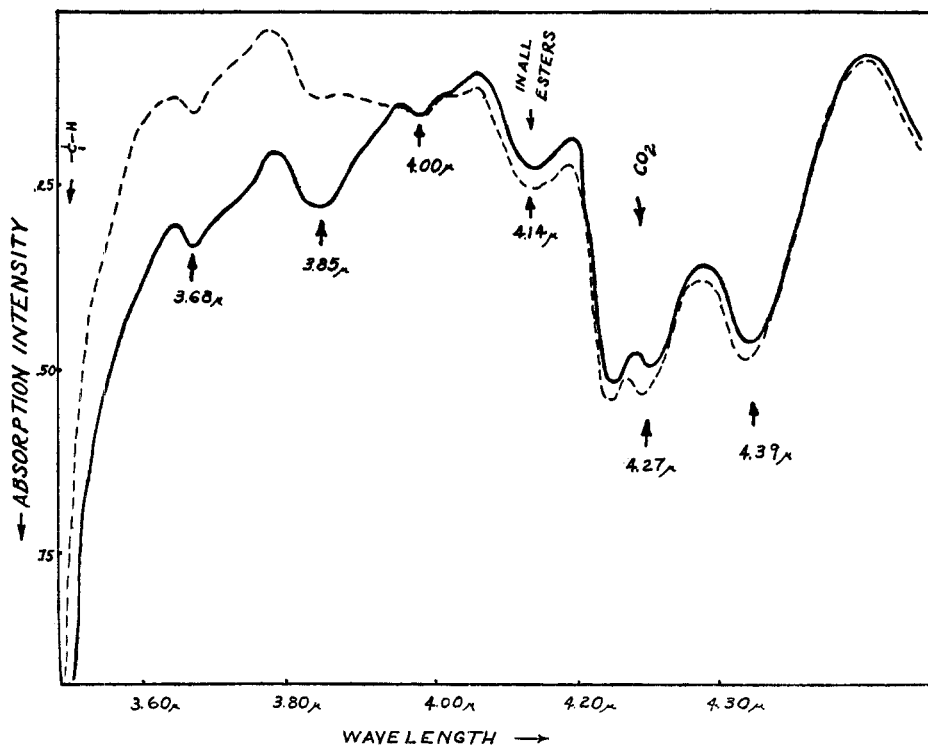


FIG. 5

----- Vinyl trimethylacetate pure, liquid phase  
 ————— Vinyl trimethylacetate + catalyst

Similar results are obtained in other parts of the spectrum. Thus, the solution of acetylene in vinyl acetate resulted in a general increase of absorption of the vinyl acetate spectrum from approximately 3.6 $\mu$  to 4.05 $\mu$ , with maxima at 3.70 $\mu$  and 3.87 $\mu$  (Figure 6). On the other hand, the addition of vinyl interchange catalyst (mercuric sulfate) to vinyl trimethylacetate led to almost precisely the same result (Figure 5).

Studies were also made in the vapor phase, in which the spectra of pure vinyl trimethylacetate vapor were compared with the spectra of the gases collected over liquid vinyl trimethylacetate plus mercuric sulfate catalyst (Figure 7).

The catalyzed liquid had been placed in a sealed chamber for 3 weeks, after which time the gas in the chamber was pulled into a 1-meter cell and the spectrum taken. Although the concentrations of the two samples are not exactly equivalent, yet it is clear that a much greater absorption at  $3.70\mu$  has developed in the vapor standing over the catalyzed liquid. As this corresponds to the  $3.70\mu$  acetylene absorption band, and a titration of the residual liquid indicated a large increase in acid content (18% based on trimethylacetic acid), intermediate steps  $A_1$  and  $A_2$  may be added to our postulated mechanism of the reac-

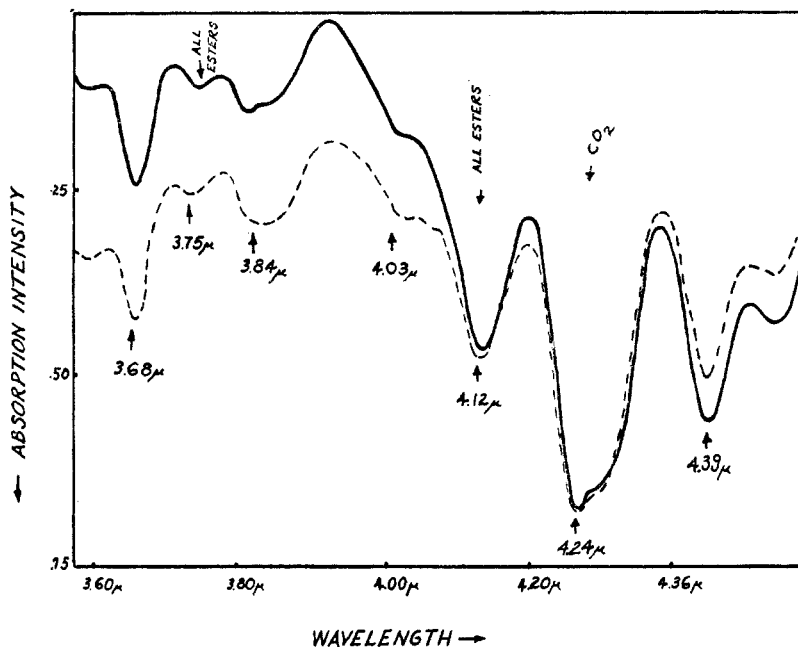


FIG. 6

————— Vinyl acetate (pure)  
 - - - - - Vinyl acetate + acetylene

tion. However, the fact that no correspondingly significant increase in absorption occurred at  $3.04\text{--}3.19\mu$  (the largest known acetylene absorption), and that acetaldehyde vapor also has a strong absorption at  $3.67\text{--}3.70\mu$  makes these final observations rather tentative.

It is very desirable that other types of investigation be carried out, such as

the use of the heavy oxygen isotope in the carboxylic acid ( $\text{RC}=\overset{\text{O}}{\parallel}\text{O}^{18}\text{H}$ ) to further prove the permanency of the  $\text{C}\text{--}\text{O}^{18}$  bond in the acid during the vinyl interchange. However, it is believed that the evidence thus far collected furnishes strong support for the mechanism of the reaction as described.



*Acknowledgement.* The author wishes to express his appreciation to Drs. O. W. Cass and H. W. Bryant of the Electrochemicals Department, the du Pont Co., for their suggestions and encouragement toward the presentation of this work, and to John Anderson and Harlan Colburn of the Analytical Laboratory for their cooperation in the infrared absorption measurements.

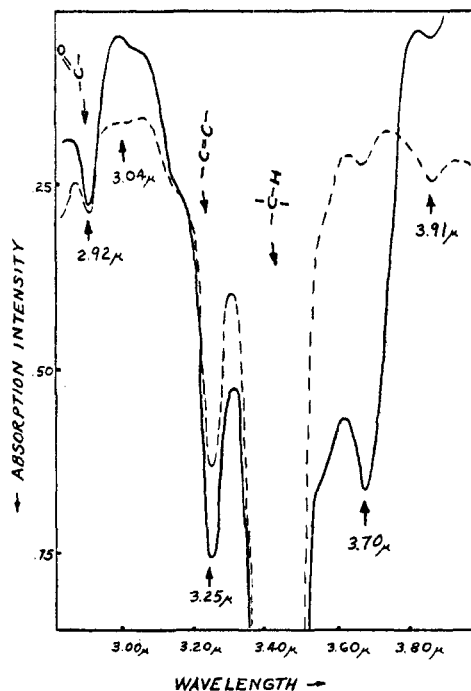


FIG. 7

----- Vinyl trimethylacetate vapor phase  
 \_\_\_\_\_ Vinyl trimethylacetate, vapor phase, over catalyst in liquid phase for three weeks

## EXPERIMENTAL

*Starting materials.* The starting materials were distilled through a three-foot column packed with a glass helices, with the exception of the lauric and stearic acids. These were commercial Armour "Neo Fats" (No. 11, 1-65) and were used directly.

## THE VINYL INTERCHANGE REACTION

The vinyl interchange reaction is the procedure similar to that described by Toussaint and McDowell (2) with the following additional observations:

- For yields of vinyl esters, it is essential to keep the temperature low (20-30°). This eliminates the formation of ethylidene diesters.
- When the reaction is run at low temperatures, a sufficient reaction time must be permitted to allow good conversions (see Table II).
- The extent of reaction was followed by removing a small aliquot, extracting it well with ice-water, and titrating the water extracts with standard alkali for acetic acid. As

the extent of by-product formation is small, the determination of acetic acid concentration is a good measure of the conversion to vinyl ester.

(d) The addition of sodium acetate completely stops the reaction. Thus, in a typical reaction mixture of vinyl acetate, trimethylacetic acid, mercuric acetate, and sulfuric acid, a batch that had reached 67% of the final acetic acid concentration was treated with 3% (by weight of acid) sodium acetate. No further change in acetic acid concentration occurred.

(e) The mercuric salt of a strong acid is essential for high catalyst activity. Thus, on mixing trimethylacetic acid and a 6-fold molar excess of vinyl acetate at room temperature, the reaction proceeded at a rate of 3% conversion in the first five minutes with mercuric acetate alone. On addition of 3% mercuric acetate and sulfuric acid (based on trimethylacetic acid) to an identical mixture as above, the salt dissolved, and the reaction proceeded at a rate of 15% conversion in the first five minutes (Table III also demonstrates that sulfuric acid without any mercuric acetate has no catalytic activity whatsoever).

An illustration of the technique to be used in running a low-temperature vinyl interchange reaction is demonstrated for vinyl caprylate. The reagents are added to a 5-liter glass balloon flask in the following order: caprylic acid (b.p. 108–109°/0.5 mm.; 5 moles, 720 g.), vinyl acetate (30 moles, 2580 g.), copper resinate (0.5 g.), mercuric acetate (2% of carboxylic acid, 14 g.), and sulfuric acid (0.5% of acid, 3.6 g.). The mixture was vigorously stirred before and after the addition of the sulfuric acid, and after a homogeneous solution resulted, the solution was allowed to stand at room temperature (30°). Five-ml. samples were withdrawn at intervals to see the extent of reaction.

The analyses were run as follows: a 5-ml. sample was shaken with 50 cc. of ice-water. Then 20 ml. of vinyl acetate was added and the mixture was shaken again. The mixture was allowed to stand for 10 minutes until the layers were well separated and clear. The water layer was run off, ice was added, and the cold aqueous layer titrated to the phenolphthalein end point with standard NaOH solution.

After 1.5 hours, the reaction had gone 57% to completion; after 72 hours, the reaction had reached a steady state (calculated over 90% conversion). Ten grams of sodium acetate was added, with good stirring, and the mixture was then heated to 40–45° under water-pump vacuum to remove most of the excess vinyl acetate and the acetic acid that was formed. When the pressure in the system had dropped to about 20 mm., the residue was distilled rapidly under more reduced pressures through a small 1-ft. packed column. The fractions were as follows:

- (a) 20 g., b.p. 45–65°/3 mm.
- (b) 710 g., b.p. 65–75°/3–5 mm.
- (c) 40 g., b.p. 76–105°/3 mm.
- (d) 80 g., b.p. 105–112°/3–4 mm.
- (e) 40 g., holdup and residue.

Analyses of (e) indicated 20% holdup, 25% water-soluble salts, 55% higher ethylidene diesters, and polymer. Analysis of (d) indicated 86% caprylic acid (by NaOH titration in methanol-water mixtures) and 15% vinyl caprylate (by Br<sub>2</sub> titration in glacial acetic acid-methanol mixtures). Fraction (b) was redistilled. The fractions obtained were:

- (b<sub>1</sub>) 10 g., b.p. 55–65°/3 mm.
- (b<sub>2</sub>) 630 g., b.p. 65–68°/3 mm.
- (b<sub>3</sub>) 15 g., b.p. 68–105°/3 mm.
- (b<sub>4</sub>) 45 g., b.p. 106°/3 mm.
- (b<sub>5</sub>) 10 g., holdup and residue.

Fraction (b<sub>2</sub>) was pure vinyl caprylate; (b<sub>3</sub>) and (b<sub>4</sub>) had increasingly larger percentages of caprylic acid over vinyl caprylate.

The conversion to actually obtained pure product, even with a very inefficient column, was 72.5%. At any rate, only 40 g. of material was lost, resulting in a yield of 95% based on recoverable materials.

*Reaction of vinyl acetate with glycolic acid.* One mole (76 g.) of glycolic acid, 6 moles

(516 g.) of vinyl acetate, and 0.9 g. of sulfuric acid were mixed together at 30°; a homogeneous solution resulted. The solution was heated to reflux (75°) with stirring for two hours, cooled to 30°, and 5 g. of sodium acetate added, with stirring. The mixture was distilled directly and 65 g. (64% conversion) of 2-methyl-1,3-dioxolone-5 (2-methyl-4-keto-1,3-dioxolane) was obtained. B.p., 78–83°/45–54 mm., neutral equiv., 104 (theory, 101);  $d^{20}$  1.11, decomposes in water after a few seconds. Tests for unsaturation were negative. These physical constants compare well with the product obtained from acetylene and glycolic acid (14).

*Reaction of vinyl acetate with acetoacetic ester.* Two moles (260 g.) of ethyl acetoacetate (b.p. 57°/3 mm.,  $n_D^{25}$  1.4200), 12 moles (1032 g.) of vinyl acetate (b.p. 72°), copper resinate (0.1 g.), 5.2 g. (2%) of mercuric acetate, and 2.6 g. (1%) of sulfuric acid were mixed in the above order and the reaction solution was heated to reflux with stirring for 22 hours. Sodium acetate (6 g.) was added with stirring, and the excess vinyl acetate and acetic acid were removed by a water pump. The liquid residue was fractionated under reduced pressure, and the following fractions were obtained:

- (a) 153 g., b.p. 45–60°/4 mm.  $n_D^{23}$  1.4082
- (b) 104 g., b.p. 60–73°/4–3 mm.  $n_D^{23}$  1.4302
- (c) 148 g., b.p. 74–76°/3 mm.  $n_D^{27}$  1.4482,  $d^{20}$  1.0272
- (d) 78 g., residue and holdup.

Fraction (a) was a mixture of ethyl acetoacetate and ethylidene diacetate. Fraction (c) was ethylidene acetoacetic ester (48% conversion), which gave positive tests for unsaturation with bromine in carbon tetrachloride, and compared well with the product prepared from acetylene and acetoacetic ester (see below).

The product prepared from acetaldehyde and acetoacetic ester had the following physical constants: b.p. 101°/15 mm.,  $n_D^{17}$  1.4526,  $d_4^{17}$  1.026. (21) *Anal.* C, 61.20; H, 7.79 (21).

*Reaction of acetylene and acetoacetic ester* (previously carried out by Conaway). Acetylene (1 mole) was added to 1 mole of the ester in the presence of 2% mercuric sulfate. The reaction temperature was kept below 40° to prevent considerable resinification. The products were filtered and distilled at 2 mm. Yield, 37 grams (20%) of ethyl  $\alpha$ -ethylideneacetoacetate; a colorless liquid, with a sharp pungent odor, b.p. 90°/10 mm.,  $d_4^{25}$  1.0158,  $n_D^{25}$  1.4510, *Anal.* Calc'd: C, 61.54; H, 7.69.

Found: C, 61.36; H, 7.91.

*Reaction of vinyl acetate with methyl glycolate.* One mole (90 g.) of methyl glycolate (b.p. 71°/41 mm.,  $n_D^{20}$  1.4147), 6 moles (516 g.) of vinyl acetate, 0.001 g. of copper resinate, and 1.8 g. of reagent-grade mercuric sulfate were added in the above order to a 3-necked flask with good stirring at 35°. An exothermic reaction occurred, which raised the internal temperature to 39° (bath temp. 36°) over a period of 30 min. When the heat evolution ceased the reaction solution was stirred at 40° for 2 hours, at which time the solution analyzed 0.6 mole of acetic acid. Five grams of sodium acetate were added, stirring was continued for 5 minutes, and the mixture then was distilled at reduced pressure through a 1-foot packed column.

- (a) cold trap, 503 g., b.p. less than 45°/4 mm.
- (b) 16 g., b.p. 45–55°/4 mm. (methyl glycolate)
- (c) 10 g., b.p. 56–109°/2 mm.
- (d) 67 g., b.p. 109–112°/2 mm.,  $n_D^{22}$  1.4297.

57% conversion, at least 70% yield of acetaldehyde *bis*-methylglycolate acetal.

- (e) 5 grams, residue and holdup.

*The reaction of acetylene with methyl glycolate* is described by Coffman (15).

*The reaction of vinyl acetate with 1-chloro-1-nitroethane.* One-half mole (55 g.) of 1-chloro-1-nitroethane (b.p. 125–126° neutral equivalent 113), 3 moles (258 g.) of vinyl acetate, 2.2 g. of mercuric acetate, 0.1 g. of copper resinate, and 1.1 g. of sulfuric acid were added in the above order. The solution was heated to reflux with stirring for 7 hours. Five g. of sodium acetate was added, and the mixture distilled at atmospheric pressure through a 3-foot packed column. After the vinyl acetate was removed, the temperature rose imme-

diately to 120–128°, and 57 g. of chloronitroethane was recovered. A residue of 7 g., which was hard, black, and brittle, remained in the distilling flask.

*The reaction of vinyl acetate with n-propyl formate.* Two moles (176 g.) of *n*-propyl formate (bp. 78–80°), 12 moles (1032 g.) of vinyl acetate, 0.2 g. of copper resinate, 5.2 g. of mercuric acetate, and 2 g. of sulfuric acid were mixed with stirring. The solution was then heated to reflux with stirring for 7 hours, 6 g. of sodium acetate was added, and the mixture distilled at 750 mm.

(a) b.p. 70–75°, 1074 g. (mainly vinyl acetate)

(b) b.p. 75–85°, 26 g.

(c) b.p. 85–128°, 3 g.

(d) b.p. 128–131°, 16 g., low unsaturation test, slowly decomposes in water, turned black on standing. After an attempted water wash the product boiled over a 100–135° range.

(e) 37 g., black brittle residue.

*Chemical tests for the presence of free acetylene in solution.* Negative results were obtained with the following procedures: A very slow stream of nitrogen was passed through a catalyzed sample of vinyl caprylate at room temperature and the issuing stream passed through a solution of the Ilosvay and Schultz reagent for acetylene (20) ( $\text{CuSO}_4 + \text{NH}_3 + \text{NH}_2\text{OH} \cdot \text{HCl} + \text{gelatin}$ , which gives a reddish-brown dispersion with acetylene). This sensitive but unstable reagent tended to break down after several days, and a blue-green precipitate of copper hydroxide was observed. Negative results were also obtained with a test solution of silver nitrate in ethanol or ethylene glycol. At higher temperatures (60°), a small amount of acetaldehyde (1 g.) was evolved from 220 g. of vinyl caprylate over 36 hours, and also an increase in the acid content of the residues occurred. This suggests that a reaction similar to (C) is occurring under these conditions to a small extent.

*Infrared spectra measurements.* The vinyl esters were all redistilled for this work.

The instrument was a Perkin-Elmer Infrared Spectrometer, Model 12B, containing a sodium chloride prism. In general, a 0.05 mm. slit and sealed cells 5 mils thick were used in order to study the liquid samples. Room temperature was not controlled, and so slight variations (0.02  $\mu$ ) in displacement of spectra were observed from time to time. Thus, for purposes of comparison in this work, the spectra were superimposed on reference bands, rather than compared on a basis of instrument calibration of drum reading *vs.* wave length.

To calibrate the instrument in the region under investigation, reference points used were the 2.67 $\mu$  and 2.76 $\mu$  water vapor bands, the 3.05 $\mu$  of acetylene, the 4.23 $\mu$  and 4.28 doublet for carbon dioxide, and 5.76 $\mu$  and 7.042 $\mu$  of water vapor.

The instrument is sensitive enough to determine quantitatively acetylene in the gas phase at a concentration of 0.1% (10 cm. cell).

#### SUMMARY

1. In the interchange reaction of vinyl acetate with carboxylic acids to form the vinyl ester of the carboxylic acids, (called the vinyl interchange reaction) it is found that at lower temperatures (30°) the formation of the major by-products, ethylidene diesters, is almost completely eliminated.

2. A mechanism for the vinyl interchange reaction is presented, which accounts satisfactorily for all of the characteristics of the reaction. The mechanism involves the dissociation of the vinyl ester, in the presence of catalyst, into the free carboxylic acid and an acetylene-catalyst complex. Considerable chemical and physical evidence is presented in support of the mechanism.

3. The above chemical evidence includes several new reactions of vinyl acetate. The new reactions of vinyl acetate are with glycolic acid, methyl glycolate,

and acetoacetic ester. Two new vinyl esters, vinyl 3,5,5-trimethylhexanoate and vinyl octylphthalate, were also prepared.

NIAGARA FALLS, NEW YORK

BIBLIOGRAPHY

- (1) HERRMANN AND HAEHNEL, U. S. Patent 2,245,131.
- (2) TOUSSAINT AND MACDOWELL, U. S. Patent 2,299,862.
- (3) U. S. Patent 1,449,918.
- (4) U. S. Patent 1,856,215; German Patent 503,131; German Patent 537,363.
- (5) U. S. Patent 2,116,657.
- (6) German Patent 346,236.
- (7) POLANYI AND SZABO, *Trans. Faraday Soc.*, **30**, 508 (1934); ROBERTS AND UREY, *J. Am. Chem. Soc.*, **60**, 2391 (1938); *J. Am. Chem. Soc.*, **61**, 2584 (1939).
- (8) HANSLEY, U. S. Patent 2,342,612.
- (9) German Patent 313,696.
- (10) COES, U. S. Patent 2,296,837.
- (11) ELLINGBOE, U. S. Patent 2,423,641.
- (12) REPPE, U. S. Patent 2,066,075.
- (13) HENNION, *J. Org. Chem.*, **1**, 159 (1936).
- (14) CONAWAY, U. S. Patent 2,370,779.
- (15) COFFMAN, U. S. Patent 2,387,495; See also *J. Org. Chem.*, **13**, 223 (1948).
- (16) CROXALL, GLAVIS, AND NEHER, *J. Am. Chem. Soc.*, **70**, 2805 (1948); See also MOWRY, YANKO, AND RINGWALD, *J. Am. Chem. Soc.*, **69**, 2358 (1947).
- (17) NIEUWLAND, *et al.*, *J. Am. Chem. Soc.*, **52**, 1018, 2892 (1930).
- (18) Values obtained from HERZBERG, *Infra-Red and Raman Spectra*, D. Van Nostrand Co., 1945, p. 290. Also values of 4.51  $\mu$  (weak) and 7.530  $\mu$  (medium) are given.
- (19) Values obtained from WEISSBERGER, *Physical Methods of Organic Chemistry*, II, Interscience Publishers, 1946, p. 805.
- (20) *Chem. Abstr.*, **30**, 6309<sup>s</sup> (1936).
- (21) CLAISEN AND MATTHEWS, *Ann.*, **218**, 172 (1883).
- (22) SWERN, BILLEN, AND KNIGHT, *J. Am. Chem. Soc.*, **69**, 2441 (1947).
- (23) LANGE, U. S. Patent, 2,156,093.
- (24) SWERN AND JORDAN, *J. Am. Chem. Soc.*, **70**, 2334 (1948).