Analysis. Calc. for $C_{20}H_{17}O_3N$: C, 75.1; H, 5.3. Found: C, 74.9; H, 5.6.

When the ester is heated with conc. aqueous potassium hydroxide it is converted into a mixture of the corresponding acid and the hydroxy-pyridine. The acid readily loses carbon dioxide at 250° and passes quantitatively into the same hydroxy-pyridine.

Summary.

1. Under the influence of sodium alcoholate, benzoyl-phenylacetylene rapidly condenses with malonic esters to form pyrone esters that have an ester group in the 3 position.

2. Pyrone esters which have the ester group in the 3 position are readily distinguished from those which have this group in the 5 position by their behavior towards alkalies.

3. By opening the ring of an α-pyrone which has phenyl groups in the 3 and 6 positions it is possible to get unsaturated δ-ketonic acids which have the carbon chain that is responsible for the peculiar isomerism of the glutaconic acids.
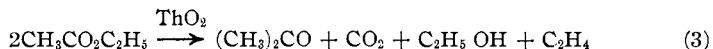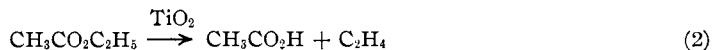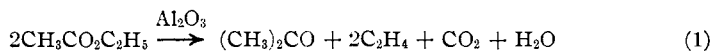
CAMBRIDGE 38, MASSACHUSETTS.

THE ACTION OF ALUMINA, TITANIA AND THORIA UPON ETHYL AND ISOPROPYL ACETATES.

BY HOMER ADKINS AND A. C. KRAUSE.

It has seemed that a more intensive, quantitative study of some of the gas-phase reactions of organic compounds induced by catalysts might shed some light upon the mechanism of catalysis. In view of the widely different decompositions which, according to Sabatier, are induced in esters by alumina, titania and thoria, it was suggested by Dr. Wilder D. Bancroft that these reactions offered a fruitful field for study. Sabatier[1] reports that alumina induces Reaction 1; titania, 2; and thoria, 3.

$$2CH_3CO_2C_2H_5 \xrightarrow{Al_2O_3} (CH_3)_2CO + 2C_2H_4 + CO_2 + H_2O \qquad (1)$$

$$CH_3CO_2C_2H_5 \xrightarrow{TiO_2} CH_3CO_2H + C_2H_4 \qquad (2)$$

$$2CH_3CO_2C_2H_5 \xrightarrow{ThO_2} (CH_3)_2CO + CO_2 + C_2H_5 OH + C_2H_4 \qquad (3)$$

If these equations accurately represent the decompositions, we have a very specific reaction for each catalyst, and it was hoped that it would be possible to find some connection between the properties of the catalyst and the reaction induced. Our results do not indicate that the catalysts are highly specific, but we have found that the decomposition of the esters offers the possibility of a comparative study of the same catalyst upon

[1] Sabatier "La Catalyse en Chemie Organique," Van Nostrand Co., 1920, p. 341.

two distinct reactions; that of decarboxylation and of dehydration, under conditions which are automatically identical for such variables as "space-time-velocity" and concentration.

Experimental Part.

The apparatus and method of procedure were similar to those used by Engelder.[2]   A sketch of the apparatus is shown in Fig. 1.

The ester was introduced from the buret A into the reservoir B, the outlet from which led through a boiling water-bath into the catalyst tube E.   This latter consisted of a Pyrex glass tube 2×42 cm. constricted to a diameter of 5 mm. at its outlet end.
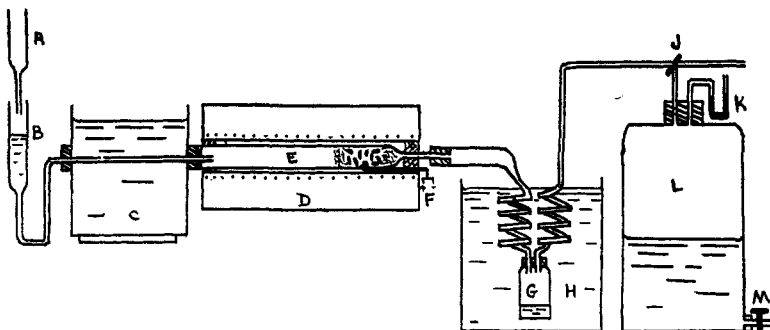
The tube contained an indentation for the head of the thermocouple F at a point 2 cm. from the constriction and 4 cm. from the outlet end of the electrically-heated furnace D. The catalyst in the form of pills was placed around the indentation and held in place by glass beads and glass wool.   Asbestos paper was wrapped around the tube and thermocouple.   The products of the reaction passed through the spiral condenser into the receiver G in which the liquid products were collected.   The receiver G and the condensers were immersed in an ice-bath.   The gaseous products passed out through the second condenser and were collected over a saturated salt solution in the 7.5-liter bottle L, which was provided with a manometer K.

The thermocouple was connected to a Leeds and Northrup potentiometer, recorder and controller[3] which automatically regulated the temperature of the furnace to ±2°.

The gas formed by the decomposition of ethyl acetate was analyzed according to the usual methods.   (1) The *carbon dioxide* was absorbed in (1:1) potassium hydroxide contained in a Hempel single pipet.   (2) *Ethylene* was absorbed in a water solution of bromine contained in a Hempel double pipet.   The bromine fumes were removed with potassium hydroxide.   (3) *Carbon monoxide* was absorbed in an acid solution of cuprous chloride.[4]

The distillate was analyzed by the standard methods.   (1) *Acetic acid:* about 2 g. of weighed distillate was mixed with about 100 cc. of water and titrated at once with a standard 0.5 N solution of sodium hydroxide.   (2) *Ethyl acetate:* a weighed sample was saponified in a standard (0.5 N) alcoholic solution of potassium hydroxide, contained in a pressure bottle, held in a boiling water-bath for 45 minutes.   The excess of alkali was

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[2] Engelder, *J. Phys. Chem.*, **21**, 679 (1917).

[3] Funds for the purchase of this apparatus were allotted by the Research Committee of the University of Wisconsin upon the recommendation of Dean C. S. Slichter and Dr. J. H. Mathews.

[4] Krauskopf and Purdy, *J. Ind. Eng. Chem.*, **12**, 158 (1920).

titrated with a 0.5 N sodium hydroxide solution using phenolphthalein as indicator.
(3) *Acetone:* about 0.4 g. of weighed distillate was dissolved in 100 cc. of water to which
had been added 50 cc. of a 0.5 N solution of sodium hydroxide. After standing for 10
minutes, a 0.4 N solution of iodine in potassium iodide solution was added drop by drop
until at least a 25% excess had been added. After standing for 10 minutes, the acid
equivalent of the alkali solution was added and the excess iodine titrated with a 0.5 N
solution of sodium thiosulfate using starch as an indicator.

The Preparation of the Catalysts.

Three hundred g. of hydrated aluminum nitrate, $Al(NO_3)_3.9H_2O$, was dissolved
in 2 liters of distilled water. The solution was heated to boiling and conc. ammonium
hydroxide added until precipitation was complete. The solution was diluted to 8 times
its original volume, heated to boiling for 15 minutes and allowed to cool. The pre-
cipitate was then washed with distilled water by decantation until free from ammonium
nitrate. It was filtered off and dried in a hot-air oven at 165°. Catalysts were also
prepared from the sulfate in the same general way.

Thoria was prepared by ignition of the nitrate and also by the precipitation of tho-
rium hydroxide as indicated for alumina.

Titania was prepared by dissolving the oxide in hot conc. sulfuric acid, diluting
with 10 volumes of water and precipitating as with alumina. This catalyst was also
made by precipitating blue titanous hydroxide from a solution of titanic chloride and
allowing it to oxidize, in the solution, to the white hydroxide.

The catalysts were made into pellets with a pill machine. These were of such a
size that 20 of them (the unit charge) weighed about 2.5 g. We believe that by the use
of the catalyst in this form it may be placed in the tube to better advantage than when
used as a powder. Its catalytic activity is not impaired by this treatment. It was
interesting to note that apparently as much reaction took place in the center of the pel-
lets as at the surface. This was evidenced by the equal deposition of carbon throughout
the pellet.

Notes on Catalysts Used.

Runs 1-5. An alumina catalyst prepared from the sulfate. The sulfur compounds
had been removed by passage of a few cubic centimeters of ester over the heated catalyst.
The catalyst had been dried for 24 hours at the temperature of the reaction. In all
the runs in which alumina (or ignited titania) was used there was 3-4% of hydrogen
and saturated hydrocarbons in the gaseous products.

Runs 6-10. An alumina catalyst prepared as for Runs 1-5. 45 cc. of ethyl
acetate was passed over the catalyst between Runs 8 and 9.

Runs 11-12. The catalyst was a sample of titania obtained from the Will Cor-
poration.

Runs 13-14. An alumina catalyst prepared from the nitrate. It was dried at the
temperature of the reaction for 12 hours.

Run 15. Same as for Runs 13-14.

Runs 16-17. Same as Runs 1-5, 6-10. *Iso*propyl acetate used instead of ethyl
acetate.

Runs 18-19. An ignited thoria catalyst. It was dried overnight at the tempera-
ture of reaction. The catalyst was heated at 455° for 6 hours between Runs 18 and 19.
There was 9-12% hydrogen and saturated hydrocarbons in the gaseous products.

Run 20. Catalyst prepared as for Runs 18-19. *Iso*propyl acetate was used.
There was no hydrogen in the gaseous products.

Runs 21-22. Titania prepared from sulfate. Ethyl acetate used in 21 and *iso*-
propyl acetate in 22. Gas showed 17% ethane and 6% hydrogen in 21.

Run 23.   Titania from the same sample as that used for Runs 21–22 but which had been ignited for an hour at red heat.   There was 14% ethane in the gas.

Runs 24–25.   The catalyst was that used in Runs 1–5 and later ignited at red heat for 2 hours.

Runs 26–27.   Titania prepared from titanium trichloride.   Gas contained 13% hydrocarbons in Run 26 when ethyl acetate was used.   *Iso*propyl acetate was used in Run 27.

Run 28.   Thoria prepared from nitrate by solution and precipitation as hydroxide with subsequent drying at the temperature of reaction.   There was 5–6% of hydrogen and hydrocarbons in the gaseous products.   After ignition of this catalyst its ethylene efficiency had been reduced with a consequent rise in the amounts of saturated hydrocarbons formed.

Run 29.   An alumina catalyst dried overnight at the temperature of reaction.   A molecular mixture of 45 g. of alcohol and acetic acid was substituted for the ethyl acetate.

Run 30.   An alumina catalyst dried for 24 hours at the temperature of reaction.

Run 31.   An alumina catalyst, not previously dried at the temperature of reaction.

Explanation of Table.

In calculating the equivalents of the products of the reaction, it is assumed that 2 molecules of ethyl acetate are equivalent to 2 molecules of ethylene, 1 of acetone, 2 of acetic acid, and 1 of carbon dioxide.   (See Equations 1 and 2).   Col. 15 of the table gives in percentages the amounts of acetone found in the distillate as compared with the amount that should have been there if one molecule of carbon dioxide is formed for each molecule of acetone.

Col. 17 gives in percentages the degrees to which the relative production of carbon dioxide and ethylene satisfy the requirements of Equation 1. The percentage of the total number of molecules decomposed that produce carbon dioxide (and acetone) is given in Col. 20 of the table.   The same information in regard to ethylene is given in Col. 21.   These figures may be taken as representing the efficiency of the catalyst in these two phases of the reaction.

Discussion.

The question arises as to the extent to which the results here recorded agree with the general statements of Sabatier[1] as to the specificity of the catalysts for inducing decompositions.   If the alumina induces Reaction 1, then the volume of ethylene should be twice that of the carbon dioxide. Analyses of the effluent gas made within a few minutes of the beginning of a run indicated that such a ratio was approximated.   However, the percentage of carbon dioxide in the gas rapidly decreased to an amount which was rather characteristic of the method of preparation of the catalyst and its subsequent treatment.   The figures in Col. 20 of the table indicate that upon use the efficiency of an alumina catalyst for the production of carbon dioxide (and of acetone) decreases while the efficiency of the catalyst for the production of ethylene is not much changed (Col. 21).   A fresh

TABLE I.—ANALYTICAL DATA

Run	Ester introduced G.	Ester recovered G.	Ester decomposed G.	Distillate G.	AcOH G.	Me_2CO G.	CO_2 G.	CH_4 G.	CO G.	Ester $= CO_2$ G.	Ester $=$ AcOH G.	Ester $= CO_2$ + AcOH G.	MeCO recovered G.	MeCO recovered %	Ester $= H_2$ G.	Reaction A %	Duration of run Min.	Temp. °C	CO_2 efficiency %	C_2H_4 efficiency %
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
1	38.7	3.0	35.7	18	3.8	5.2	7.6	11.4	0.10	30.4	5.5	35.9	15.8	52	35.8	80	141	455	80	100
2	42.7	4.9	37.7	21	5.56	5.7	7.3	11.7	0.20	29.2	8.1	37.3	17.3	59	36.7	80	123	457	78	97
3	42.3	7.2	35.1	24	6.25	5.3	6.6	11.0	0.22	26.4	9.1	35.5	16.1	61	34.5	77	135	454	75	97
4	42.3	6.6	35.7	24	8.40	5.3	6.1	11.1	0.20	24.4	12 9	37.3	16.1	66	34.9	72	138	454	69	97
5	45.0	6.9	38.1	25.5	7.65	5.0	6.4	11.7	0.20	25.6	11.2	36.8	15.2	60	36.7	71	130	455	67	96
6	33.3	5.6	27.7	18.5	5.10	3.8	5.35	8.40	0.10	21.6	7.5	29.1	11.5	53	26.4	82	130	417	78	95
7	42.3	15.7	26.6	31	7.60	3.7	4.6	7.9	0.15	18.4	11.1	29.5	11.2	67	24.8	74	100	417	69	93
8	40.0	9.6	30.4	25.5	8.30	3.7	4.6	9.7	0.15	18.4	12.1	30.5	11.2	67	30.4	60	128	417	60	100
9	42.3	8.2	34.1	28	14.10	3.7	3.5	10.5	0.25	15.0	20.6	35.6	11.2	75	33.0	45	120	455	44	97
10	44.5	8.7	35.8	29	15.8	2.4	2.7	11.4	0.25	10.8	23.1	33.9	7.3	68	35.8	30	113	455	30	100
11	41.4	10.7	30.7	29	13.3	1.9	2.4	9.5	0.25	9.6	19.4	29.0	5.8	60	29.8	32	105	455	31	97
12	39.6	...	...	...	16.9	0.3	[Ratio 1:14]		..	..	..	24.7	...	0.9	..	...	..	120	455	..	..
13	36.5	2.5	34.0	17	5.0	4.1	6.9	11.1	0.10	27.6	7.4	35.0	12.3	45	34.9	81	120	455	81	100
14	42.0	5.5	36.5	25	12.9	3.9	3.7	10.9	0.35	14.8	19.0	33.8	11.7	80	34.2	45	139	455	41	90
15	44.0	11.1	32.9	27	6.9	4.5	6.0	10.1	0.10	24.0	10.1	34.1	13.5	56	31.7	76	120	455	73	96
16	43.0	1.5	41.5	19	8.7	4.6	6.4	16.1	..	29.6	14.8	44.4	16.2	55	39.1	75	120	455	71	94
17	45.0	2.0	43.0	20	9.7	4.6	5.6	16.8	..	25.9	16.5	42.4	16.2	63	40.8	63	102	455	60	94
18	41.0	9.0	32.0	30	0.3	6.0	7.8	2.4	0.55	31.2	0.45	31.7	18.2	58	7.5	..	105	455	97	23
19	42.0	7.9	34.1	31	0.2	7.9	8.0	2.6	0.40	32.0	0.3	32.3	24.0	75	8.2	..	103	455	92	24
20	40.0	3.1	36.9	20.0	0.35	7.8	7.4	11.6	0.20	34.3	0.6	34.9	27.4	76	28.2	..	105	455	93	76
21	46.0	30.0	16.0	39.0	2.6	1.6	2.4	2.3	0.20	9.6	3.8	13.4	4.8	50	7.2	..	95	455	60	45
22	44.0	20.0	24.0	35.0	11.7	0.7	1.2	8.4	..	5.5	19.9	24.4	2.5	45	20.5	..	90	455	23	85
23	43.0	38.0	5.0	41.0	1.6	0.2	0.5	1.0	0.04	2.0	2.3	4.3	0.7	35	3.1	..	80	455	40	62
24	38.5	17.4	21.1	29.0	4.6	3.5	3.4	5.7	..	13.6	6.8	20.4	10.5	80	17.9	67	140	455	64	85
25	35.5	14.7	20.8	26.0	5.2	3.3	3.4	5.8	..	13.6	7.6	21.2	9.9	73	18.2	63	129	455	65	87
26	43.0	16.8	26.2	930.5	5.0	3.7	4.4	7.1	0.10	17.6	7.4	25.0	11.3	74	22.4	74	133	455	67	90
27	44.0	1.4	42.6	18.5	5.4	5.2	6.9	17.1	..	31.9	9.2	41.1	19.3	60	40.6	79	100	455	75	95
28	87.0	14.6	72.4	49.0	5.3	12.0	17.0	18.0	0.50	68.0	7.8	75.8	36.5	51	56.5	..	340	455	94	78
29	37.3	9.4	27.9	40.0	14.7	2.0	2.8	5.5	..	11.3	21.5	32.8	6.1	53	17.3	..	105	455	..	..
30	270.0	106.4	163.6	190.0	46.4	12.9	23.7	50.4	..	94.8	68.2	163.0	39.0	41	158.3	59	991	455	58	96
31	127.0	32.3	94.7	81.2	21.3	6.5	13.2	25.4	..	52.8	30.7	83.5	19.8	37	79.8	70	434	455	65	96

32 29 g. of acetone over alumina at 455° in 1 hour. 65% of the acetone was recovered in the distillate. Negligible amount of gas.

33 40 0. of "commercial acetone" containing 24 g. of $(CH_3)_2$ CO passed over alumina at 455° during 3 hours.
62% of $(CH_3)_2CO$ was recovered as such in the distillate.

alumina catalyst in a 2-hour run split carbon dioxide out of 80% (Run 1) or 78% (Run 6) of the molecules decomposed. In the case of a catalyst (Run 10) which had previously been used 6 times, the efficiency for the production of carbon dioxide had fallen to 30% while the efficiency as an ethylene producer was still in the vicinity of 100%. The degree to which Reaction 1 was induced (Col. 17 of the table) was 80% to 82% (Runs 1 and 6) in the first run and then fell off until in Run 10 only 30% of the activity of the catalyst was manifested in the production of this reaction. Ignition of such a catalyst restored to it the property of producing carbon dioxide and ethylene in the former ratio, but the catalyst decomposed only $1/2$ to $2/3$ as much ester in a given length of time as did a fresh catalyst (Runs 24 and 25).

A titania catalyst (Run 11) showed itself to be 31% efficient in the production of carbon dioxide and 97% efficient in producing ethylene. This result is almost identical with that obtained by the use of a used alumina catalyst in Run 10. On the other hand, a titania catalyst (Run 26) prepared from titanous chloride ($TiCl_3$) by precipitation of the blue titanous hydroxide, and then oxidizing this to the titanic hydroxide gave a result which is very similar to that obtained with a fresh alumina catalyst; that is, the catalyst was 67% efficient in producing carbon dioxide and 90% efficient in producing ethylene. In Run 27, in which isopropyl acetate was the ester used, the efficiency was 75% for carbon dioxide and 95% for propylene, the reaction going according to Equation 1 to the extent of 79%, a value which is very nearly the same as that obtained with a fresh alumina catalyst.

A thoria catalyst (Run 18) prepared by the ignition of the nitrate gave a result similar to the one obtained by Sabatier. It showed a 97% efficiency in the production of carbon dioxide and 23% for ethylene.

A thoria catalyst (Run 28) which had been prepared by precipitation of the hydroxide was approximately as efficient as a carbon dioxide-acetone producer as was the ignited thoria (Run 18) catalyst, but it was much more effective in the production of ethylene. It showed an efficiency of 94% as a carbon dioxide producer and 78% for ethylene, the latter figure being more than three times as large as that for the ignited catalyst and approaching in magnitude that obtained for alumina.

The comparisons just made of the various catalysts have not involved any consideration of the amounts of acetic acid and acetone produced. In Col. 13 of the table is given the sum of the amounts of the ester equivalent to the carbon dioxide and acetic acid found. This amount is in most runs approximately equal to the amounts of ethyl acetate decomposed (Col. 4). This indicates that a decrease in carbon dioxide production is accompanied by an equivalent increase in the amount of acetic acid. Col. 15 of the table gives in percentages the amount of acetone found in the

distillate as compared to the amount that should have been there if the weight of carbon dioxide obtained had been taken as the basis of the calcula- ation.   It may be seen that the recovery in the case of a fresh alumina cata- lyst prepared from the sulfate is 52% or 53% (Runs 1 and 6) and 45% in the catalyst prepared from the nitrate (Run 13).   Upon continued use of the catalyst, the acetone recovery increases in several cases to over 70%. The distillate becomes lighter in color and supposedly the condensing power of the alumina for the acetone becomes less.   That alumina does have a condensing action upon acetone is shown by Runs 32 and 33.   Only 62 to 65% of the acetone passed over the catalyst was recovered unchanged. That the action was a condensing one is indicated by the facts that with the pure acetone (Run 32), (1) only a small amount of gas was formed, (2) the weight of the distillate was only one gram less than the weight of the acetone introduced, and (3) the distillate showed no acidity and con- tained products boiling from 150° to 275°.

Runs 30 and 31 were made with the object of determining the effect on the efficiency of the catalyst of long continued runs and of previous drying of the catalyst at the temperature at which it was later to be used as a catalyst.   During the period of the runs there was no marked change in the ratio of the gases produced by the decomposition.   The results given below are the averages of the observations made during 7-hour periods.

Run 30 (dried catalyst): gas per cc. AcOEt, 199 cc. (42 cc. of CO_2, 148 cc. of C_2H_4); ratio 1:3.5.

Run 31 (undried catalyst): gas per cc. AcOEt, 245 cc. (58 cc. of CO_2, 175 cc. of C_2H_4); 1:3.0.

These results show that the undried catalyst is more active in the pro- duction of both gases but much more so with respect to carbon dioxide (26%) than with respect to ethylene (11%).

In all of the work discussed the production of the unsaturated hydro- carbon seems to vary independently of the production of acetone, acetic acid, or carbon dioxide.   This indicates that the decomposition studied is that of the acid (or acid residue) and of the alcohol (or alcohol residue) rather than that of the ester.   It seems that saponification of the ester precedes decomposition.   A further study of the saponification of esters in the gas phase is anticipated.

Sabatier[5] explains that the difference in the decomposition of esters by various catalysts is due to the relative stabilities of the intermediate com- pounds formed between the catalyst and the acid and the catalyst and the alcohol.   For example, if the instability of the two temporary compounds is of the same order, then the reaction goes according to Equation 1. If the salt of the alcohol is more rapidly decomposed than that of the acid,

    [5] Ref. 1, *Compt. rend.*, **152**, 669 (1911).

the water so formed reacts with the salt of the acid, liberating the acid, and the reaction goes according to Equation 2. It is difficult for us to believe that thorium ethoxide is more unstable when the catalyst is prepared from the nitrate by precipitation than it is when the catalyst is prepared from the nitrate by ignition, or that titanium acetate is more unstable when the catalyst is prepared in solution than when it is prepared in some other way. Yet it would seem necessary to make this assumption in order to explain our experimental results according to Sabatier's theory.

Summary.

1. Experimental confirmation of the statement that alumina, titania and thoria catalyze specific decompositions of ethyl acetate, has not been obtained. The results obtained by us indicate that in determining the order of efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of equal if not of greater importance than the particular metallic element present in the catalyst.

2. Evidence is presented indicating that the course of the decomposition is not determined by the relative instability of the salts of the acid and of the alcohol.

3. The probabilities are that saponification of the ester precedes decomposition.

4. An unignited alumina catalyst prepared from the hydroxide exerts a strong condensing action upon acetone at 455°.

MADISON, WISCONSIN.

A SIMPLER METHOD OF DETERMINING ACETYL VALUES.

By LEON W. COOK.

Lewkowitsch[1] defines the acetyl value as "the number of milligrams of potassium hydrate required for the neutralization of the acetic acid obtained on saponifying one gram of an acetylated fat or wax." The method for determining the acetyl value as outlined by Lewkowitsch has been adopted as the standard method of analysis. This method of obtaining the acetyl value by actual titration of the acetic acid used in acetylation, involving as it does the separation of this acetic acid by somewhat laborious means can be considerably improved. This value may be obtained more quickly and with greater accuracy by a knowledge of the saponification values of the oil before and after acetylation. This involves only an operation that is being continually performed in an oil laboratory.

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[1] Lewkowitsch: "Chemical Analysis of Oils, Fats, and Waxes," Macmillan and Co., 5th ed., vol. 1, p. 428.