

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.

[CONTRIBUTION FROM THE LABORATORIES OF THE TEXAS COMPANY.]

A SIMPLER METHOD OF DETERMINING ACETYL VALUES.

BY LEON W. COOK.

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Lewkowitsch¹ 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.

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

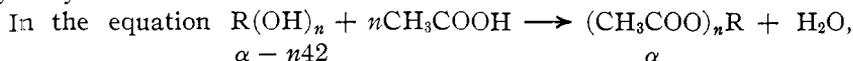
This method was first suggested by M. Émile André.² He gives the following formula,

$$A = S' - S \left(1 + \frac{\lambda S}{1 - \lambda S} \right)$$

where A is the acetyl value; S the saponification value before acetylation; S' the value after acetylation, and λ is $42/56 = 0.75$.

To use this formula, we must define both acetyl and saponification values as g. instead of mg. of potassium hydroxide per g. of material. The latter (mg.) is the correct definition and the one given by André himself. It will be seen upon inspection that if $S > 4/3$, his acetyl value is negative. In order to use the values as correctly defined, we must give λ the value of $0.042/56$ or 0.00075 . André's derivation of his formula is rather involved, employing the limit of a geometric series, and is confined to monohydric alcohols. Such a formula will be derived by simple algebra and the derivation will be extended to include polyhydric alcohols. By alcohol is meant any organic hydroxy compound which can be acetylated.

Let A be the acetyl value; S , the neutral saponification value before acetylation; S' , the value after acetylation; α , the mol. wt. of acetate; x , the mg. of acetate in 1 gram of acetylated oil, and n the number of hydroxyl radicals in the alcohol.



the difference between the molecular weight of an alcohol and its corresponding acetate is $n42$. Every α mg. of acetate corresponds to $\alpha - n42$ mg. of alcohol in the oil, and every x mg. of acetate to $x - \frac{n42x}{\alpha}$

mg. of alcohol; for $\alpha : \alpha - n42 :: x : \text{mg. of alcohol}$; and therefore $\text{mg. alcohol} = \frac{\alpha x - n42x}{\alpha} = x - \frac{n42x}{\alpha}$. x Mg. of acetate represents a gain in weight in

acetylation of $\frac{n42x}{\alpha}$ mg. Thus 1000 mg. of acetylated material containing

x mg. of acetate was obtained from $1000 - \frac{n42x}{\alpha}$ mg. of original oil. So

if it takes S mg. of potassium hydroxide to saponify 1000 mg. of oil, it

will take $S \left(\frac{1000 - \frac{n42x}{\alpha}}{1000} \right)$ mg. to saponify $1000 - \frac{n42x}{\alpha}$ mg. or the

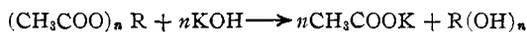
amount of original oil in 1000 mg. of acetylated material. The difference

$S' - S \left(1 - \frac{n0.042x}{\alpha} \right)$ represents the difference between the alkali necessary

² André, *Compt. rend.*, 172, 984 (1921); *Bull. soc. chim.*, [4] 29, 745 (1921).

to saponify 1 g. of acetylated material and the alkali necessary to saponify the original oil contained in that amount. This difference is therefore the alkali necessary to neutralize the acetic acid obtained from 1 g. of acetylated oil or is the acetyl value.

$$A = S' - S \left(1 - \frac{n0.042x}{\alpha} \right)$$



$$\begin{array}{ccc} \alpha & n56 & \\ x & A & \\ x: A = \alpha: n56 & & \text{and } x = \frac{A\alpha}{n56} \end{array}$$

Substituting

$$A = S' - S \left(1 - \frac{n0.042 \frac{A\alpha}{n56}}{\alpha} \right) = S' - S \left(1 - \frac{0.042}{56} A \right) = S' - S + \frac{0.042S}{56} A$$

$$A - \frac{0.042S}{56} A = S' - S, \quad A \left(1 - \frac{0.042S}{56} \right) = S' - S$$

$$A = \frac{S' - S}{1 - 0.00075S}$$

By a similar derivation which I shall not give in detail the percentage of alcohol in the original sample may be found providing the molecular weight (M) of the alcohol is known;

$$\% \text{ alcohol} = \frac{M(S' - S)}{560 - 0.42S'}$$

Summary.

A formula has been derived by which the acetyl value of an oil may be calculated from the saponification value before and after acetylation. This method is quicker and more accurate than the one given in Lewkowitsch, commonly used. This formula has been used extensively in this laboratory with very satisfactory results.

BAYONNE, NEW JERSEY.