Methanolysis of Triglycerides

L. HARTMAN, Fats Research Laboratory, Department of Scientific and Industrial Research, Wellington, New Zealand

THE EXTENSIVE use of methyl esters of fatty acids in fat analysis has created a need for rapid and economical methods for their preparation. The usual method of saponifying fats with alcoholic alkali hydroxides, decomposing the soaps and esterifying fatty acids with methanol, is time-consuming and requires comparatively large amounts of solvents. Conversion of the soaps directly into methyl esters by double exchange with dimethyl sulphate has been suggested (1), but alkali catalyzed methanolysis of triglycerides on the lines suggested by Bradshaw and Meuly (2) seems to be more convenient, particularly in the case of large samples. According to Bradshaw and Meuly's original method, about 0.5% of alkali hydroxide and 1.2–1.75 equivalents of methanol are employed, but since the catalyst is gradually used up with the simultaneous formation of soap, the yield of esters usually does not exceed 98%. The efficiency of several other catalysts, beside sodium hydroxide, was therefore determined from the amount of glycerol set free and the degree of soap formation. Sodium methoxide was found to ensure a practically complete alcoholysis, but since it is known to promote a migration of double bonds and other secondary reactions, its use is not always advisable. Contrary to expectations magnesium and aluminum alkoxides were without effect whereas the oxides of calcium, strontium, and barium were moderately effective. Apart from sodium methoxide the best results were obtained with ignited potassium carbonate, especially when used in quantities of about 10% of the fat. Sodium carbonate and weak organic bases, such as triethanolamine, had very little effect. It might be mentioned that Purdie, who discovered the catalytic effect of sodium methoxide in the interaction of ethyl fumarate and methanol (3), was also first to stress the usefulness of potassium carbonate for this purpose.

> The addition of ignited potassic carbonate produces the same effect as sodic methoxide; the carbonate of sodium and lithium, or ignited borax act in the same manner, but more slowly. The effect of these reagents is probably due to the presence of small quantities of caustic alkali (4).

These remarks seem to apply likewise to the present work on the methanolysis of triglycerides.

Experimental

Samples of ox fat, coconut oil, and linseed oil were neutralized with sodium hydroxide, washed, and dried *in vacuo*. Their glycerol contents, determined by Malaprade's periodate method (5) slightly modified, were as follows: ox fat, 10.73%; coconut oil, 14.17%; and linseed oil, 10.46%. One hundred-gram samples of the above fats were heated with 25 g. of methanol and various catalysts at 60° or under reflux conditions.

The reaction mixtures were acidified with acetic acid, and the esters were extracted with ethyl ether and thoroughly washed with water. The degree of alcoholysis was computed from the amount of glycerol determined in the aqueous extract by the periodate method. The degree of soap formation was found by estimating the acid value of the esters recovered from the ethereal solution and dividing it by their saponification number. Results are shown in Table I. It will be seen that the amount of glycerol set free, when using sodium methoxide and potassium carbonate, was 99–99.5% of the total glycerol. The residual glycerol was most likely combined as monoglyceride. Other catalysts appear less useful for analytical purposes.

In actual practice the reaction mixture is not acidified but washed free of soap with water. When preparing large samples, the use of ethyl ether for the extraction of methyl esters can be omitted. The method is obviously applicable only to fats with low acid values.

Summary

Alkali-catalyzed methanolysis of fats as a means of preparing methyl esters for analytical purposes has been investigated. Of the various catalysts employed sodium methoxide and ignited potassium carbonate have been found to set free 99–99.5% of total glycerol and to cause the least degree of saponification.

REFERENCES

1. Youngs, C. G., and Craig, B. M., J. Am. Oil Chemists' Soc., *28*, 521–2 (1951).
2. Bradshaw, G. B., and Meuly, W. C., U. S. Pat. 2,271,619 (1942).
3. Purdie, T., J. Chem. Soc. (London), *49*, 855–78 (1885).
4. Purdie, T., J. Chem. Soc. (London), *51*, 627–34 (1887).
5. Malaprade, L., Bull. Soc. Chim. France, *43*, 683–96 (1928).

[Received October 10, 1955]

TABLE I

Degree of Methanolysis and Saponification When Using Various Catalysts

Catalyst, type	%	Conditions		Ox Fat		Coconut Oil		Linseed Oil	
		Time	Temperature	Glycerol set free	Saponification	Glycerol set free	Saponification	Glycerol set free	Saponification
		hours	°*C.*	%	%	%	%	%	%
$NaOCH_3$	0.5	2	60	99.39	0.55	99.41	0.63	99.24	1.63
K_2CO_3	10.0	2	reflux	99.35	0.50	98.92	0.96	99.32	1.44
$NaOH$	0.5	4	60	97.84	1.11	98.02	0.92	98.11	1.23
CaO	1.5	8	reflux	97.25	2.85	96.50	2.28	96.87	2.33
BaO	1.5	8	reflux	82.94	3.12	89.26	2.98	89.93	3.67
SrO	1.5	8	reflux	70.30	3.42	78.41	3.17	75.54	3.56