• **TECHNICAL**

The Acetolysis of Glycerides. I. Preliminary Investigation and Approximate Kinetics

EDWIN M. MEADE, Department of Food Chemistry, University of Toronto; DILYS M. WALDER, Canada Packers Ltd., Toronto, Canada

Below 120°C., direct acidolysis of fats by acetic acid is vanishingly slow, the observed reaction being a slow hydrolytic fat splitting to partial glycerides followed by a rapid acetylation. Water is an essential reactant, and strong acid catalysis of the reaction is effective only in its presence. The reaction is unimolecular with respect to the acid catalyst, and probably also to the ester linkages, but molecularity falls below unity with respect to water, which has strong effects on acid strengths in an acetic acid medium. The reaction velocity has a temperature coefficient of 1.6 per 10°C. over the range 77–118°C.

Using a three-fold weight of 98% acetic acid, 1% of catalyst, and 12–24 hours' reaction at 100–118°C., fat splits of around 90% can be attained.

THE ACETIC ACID esters of glycerol, the "acetins," are manufactured by the acetylation of refined glycerol. It would be advantageous to avoid the intermediate isolation of glycerol, by producing acetins direct from glyceride oils; this has been done by Schwartz (1) using the sulphuric acid catalyzed acetolysis of coconut oil, and by Meade (2) using sodium butoxide catalyzed ester interchange between castor oil and butyl acetate. The present work was undertaken as a study of the potentialities of the Schwartz method.

Acidolysis, the general interchange which takes place when an ester is reacted with an acid, is fairly well known outside the field of glyceride chemistry; its equilibria seem to be largely statistical, with little selectivity being shown between long and short chain acids, provided that volatility differences are not allowed to disturb the system. The reaction would be expected to occur step-wise in the case of glycerides, e.g., $GSat_3 \rightarrow GSat_2Ac \rightarrow GSatAc_2 \rightarrow GAc_3$, and the final stage and overall reaction could be studied under conditions of high acetic acid excess. Assuming a purely statistical equilibrium, and that the final acetolysis stage is the only one to make a major contribution, the possible yields of triacetin and fatty acids can be calculated as a function of the acetic acid used, as in Table I, where each molecule of $GSat_3$ is assumed to have already yielded two molecules of HSat, and the equilibrium constant for the $GSatAc_2$ to GAc_3 reaction is taken as being unity. See Table I.

At first sight the 95% yield of fatty acids for the lowest acetic acid usage seems very attractive, but the other 5% is a diacetoglyceride of high saponification value, which would give the crude fatty acids an ester value of nearly 20, and which would tend to co-distil with them. It is seldom economically practicable to approach closely the equilibrium position of a slow reaction, owing to the severe drop in unit plant capacity as it is approached. Economic operating conditions would therefore be expected to lie in the range of higher acetic acid usage, 200–300% w/w on fat, with a progress of some 90–95% towards equilibrium. A medium degree of fatty acid fractional distillation would be needed to keep down the ester value, together with a reworking of the still bottoms, their amount having been increased by stopping short of equilibrium. These leads were well borne out by later work, but initial experiments on the acid-catalyzed acetolysis of tallow gave widely varying and non-reproducible results, so the system was simplified to the acetolysis of methyl stearate under rigorously anhydrous conditions.

TABLE I

Equilibrium Yields from Hydrogenated Tallow

Acetic acid used		Calculated Yields Obtainable			
		Triacetin		Fatty acids	
Moles per $GSat_3$	% w/w on Tallow	% Molar	% w/w on tallow	% Molar	Ester [a] value
14.3	100	86.0	21.7	95.3	18
21.5	150	90.7	22.9	96.9	12
28.7	200	93.0	23.5	97.7	9
43.0	300	95.3	24.1	98.5	6
100.0	700	98.0	24.8	99.3	2
Infinite		100.0	25.3	100.0	0

[a] From calculated Ac_2MG content.

Effect of Water on Acetolysis

The use of anhydrous conditions gave the immediate and unexpected result of a complete lack of reaction. This was checked by demonstrating that successfully reacting tallow or methyl stearate acetolysis could be stopped by the addition of enough acetic anhydride to ensure anhydrous conditions, and then be restarted by the addition of water. See Table II.

High temperature alcoholysis is used technically, particularly in the surface coatings field, but it seems clear from these results that direct true acidolysis must be slower than hydrolysis plus re-esterification by a very wide margin, and that for lower temperature reactions water is not just an alternative catalyst but an essential reactant. Similar effects have been noted before, thus Eckey (3) has recommended the use of water as a catalyst for fat acidolysis at 200°C., and Cohen (4) has shown that methyl benzoate fails to undergo acid catalyzed acetolysis when 6% of acetic anhydride is present, though isopropyl benzoate continues to react slowly.

TABLE II

Effect of Water on Acetolysis at 100°C.

Ester	Conditions [a]	Acid Value of Product [c]			
		2	4	8	24 hrs.
Me stearate	No addn.	7	9	13 [d]	37
	+2% Ac_2O	2	1	2	2
	+2% H_2O	72	115	140 [d]	187
	+4% H_2O	110	153	180	187
Hydrog. tallow [b]	+0.5% Ac_2O	100	100	101	103
	+2% H_2O	124	140	161	170
	+4% H_2O	130	150	170	181

[a] Three volumes of technical anhydrous acetic acid, approximately 0.045 N. w.r.t. $ArSO_3H$ catalyst, additions w/w on acetic acid.

[b] Tallow first reacted with 1% water present until homogeneous and product A.V. 101, reaction mass then rendered anhydrous by calculated amount of Ac_2O.

[c] Product isolated by addition to water, filtration, and air drying below m.p. until odorless.

[d] Calculated by interpolation from 7.5-hour runs.

The initial water content, not being in equilibrium, is reduced in operation by an early excess of hydrolysis over esterification. The lower steady state levels of water were not determined, but observed drops in the S.V. of the isolated triacetin fractions, increasing with increasing initial water content, were evidence of the hydrolytic loss of water to form diacetin at the end of the reaction series. Initial water contents of from 0.5 to 8% were used in other experiments, with the general evidence that reaction velocities increased in a slow and nonlinear manner with increasing water content. Two per cent of water was a near optimal quantity, giving 75% of the maximum attainable velocity, without excessive initial immiscibility or undue later loss in degree of acetylation. Thus with three volumes of 98% acetic acid and the later discussed range of catalysts, tallow became miscible after 2–3 hours, and hydrogenated tallow after about 4 hours of refluxing, and the acetins obtained contained about 2.8 acetyl groups per glycerol.

Effect of Catalysts

Since the "acetolysis" is in fact a hydrolysis followed by re-esterification, any substance showing strong acidity in an acetic acid medium should be an effective catalyst, provided that its acid strength persists in the presence of a few per cent of water. Also, since the bulk of the reactions occurs in the acetic acid phase, oil solubility of the catalyst is unlikely to be important. Preliminary results on tallow methyl esters confirmed this. See Table III. These results show the superiority of perchloric acid as a catalyst, but also its ability to cause degradation of the fatty matter, leading to a lower free fatty acid content at 24 hr. than at 6 hr., accompanied by obvious carbonization. These adverse effects disappeared when methyl stearate, or low I.V. hardened tallow, but not tallow itself, replaced tallow methyl esters.

Lower catalyst concentrations were then used with hydrogenated tallow, together with an increase of the water content to 2.0%. See Table IV. The successful experiments are also presented graphically in Fig. 1. These curves were extrapolated to give the approximate time at which A.V. 60 and complete miscibility had occurred, and the results were then replotted using this point as the origin, in order to obtain a better basis for comparison. See Figure 2. Perchloric acid was again the most powerful catalyst and this time there was no sign of over-reaction.

The Effect of Temperature

The effect of temperature on reaction velocity, without interference from partial miscibility, was investigated by reacting with agitation until miscibility occurred, and then comparing reaction speeds over the ensuing middle third of the reaction progress. See Table V. Comparing the results within the interpolated median A.V. range of 82 to 121, gross coefficients are obtained of 3.0 for 77–100°C. and 2.3 for 100–118°C. Reduced to the standard 10°C. temperature range, both these figures yield the same result of 1.6 as the standard temperature coefficient. A figure of 1.7 per 10°C. was obtained for methyl stearate under similar acetolysis conditions.

TABLE III

The Effect of Catalysts on the Acetolysis[a] of Tallow Methyl Esters

Catalyst[b]	Acid Value of Product	
	6 hr.	24 hr.
None	0.5	0.9
2% $HClO_4$	181	174
4% p-toluent sulphonic acid	162	186
2% mixed alkane sulphonic acids	148	183
1.6% HCl[c]	107	181
2%H_2SO_4	85	178
10% Amberlite I.R. 120 acid form	70	162

[a] Esters reacted with 3 volumes of acetic acid containing 1% water and indicated catalyst in closed unstirred containers at 100°C.
[b] Catalyst w/w on fat.
[c] Added as 35% HCl aqueous + calculated Ac_2O.

TABLE IV

The Effect of Catalysts on the Acetolysis[a] of Hydrogenated Tallow

Catalyst	% w/w on fat	Acid Value of Product			
		4 hr.	6 hr.	8 hr.	24 hr.
$HClO_4$	0.5	90	120	144	184
Alkane SO_3H	1.0	72	95	113	179
Toluene SO_3H	1.0	67	81	96[b]	165
Toluene SO_3H	2.0	90[b]	115	138	184
H_2SO_4	1.0	59	85	110	172
HCl[c]	1.6	The reaction mixtures never became homogeneous			
Amberlite 120	10				
$C_7F_{15}COOH$	6				
BF_3	2				

[a] Fat reacted with 3 volumes of acetic acid containing 2% water and catalyst at 100°C., with agitation until homogeneous.
[b] These results referred to in discussion on kinetics.
[c] HCl added as 35% HCl aqueous + calculated Ac_2O. Much HCl escaped at reaction temperature, via the agitator seal.

Miscibility

Most fats are only partially miscible with acetic acid, and both temperature and water content affect the degree of miscibility, which increases rapidly as the reaction proceeds. Miscibility in the absence of reaction was investigated, using a sealed tube technique, and working fast enough to avoid appreciable reaction when catalyst was present. See Table VI. Temperatures sufficient to give immediate and complete miscibility in the presence of some 1–2% each of water and catalyst are thus low enough to involve only low-gauge pressures in totally enclosed conditions.

Approximate Kinetics

The results for toluene sulphonic acid in Table IV, and other results for sulphuric and perchloric acids, show the reaction to be substantially unimolecular with respect to each of these catalysts. The order of

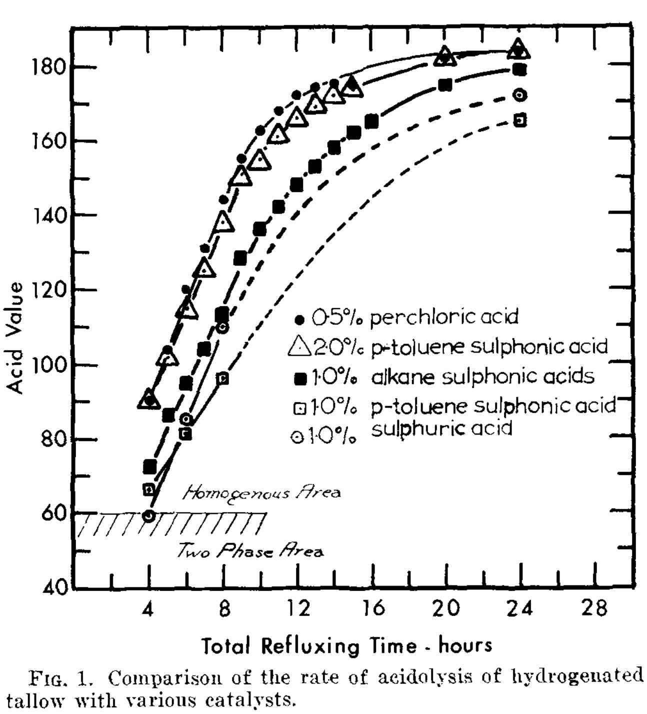

FIG. 1. Comparison of the rate of acidolysis of hydrogenated tallow with various catalysts.

TABLE V
The Effect of Temperature on the Acetolysis[a] of Tallow

Time, hr.	Acid Value of Product		
	77°C.	100°C.	118°C.
2	......	......	94[d]
4	......	61[c]	146
6	......	93	164
8	20[b]	121	......
24	82	163	......
32	119	......	......
40	140	......	......
64	170	......	......

[a] Tallow reacted with 3 volumes of acetic acid containing 1% water. and 1% w/w on fat $HClO_4$, in double wall flask, with refluxing solvent in annulus for thermostat.
[b] Not homogeneous.
[c] Miscible just before 4 hrs.
[d] Some initial exotherm noticed, due to double bond reactivity.

TABLE VI
Miscibility Temperatures[a]

Fat	Water content[b]	Catalyst content[c]	Misc. temp. °C.
Tallow	0	0	93
Tallow	1.5	0	126
Tallow	3.0	0	154
Tallow	0	2.0	95–6
Tallow	0.7	2.0	106
Hydrogenated tallow	0	0	93
Hydrogenated tallow	0.7	0	112
Hydrogenated tallow	0.7	2.0	113

[a] In 3 ml. acetic acid per 1 g. of fat.
[b] % w/w on acetic acid.
[c] % p-Tol. SO_3H, w/w on fat.

reaction against glyceride linkages is more difficult to deduce, owing to the series of reactions and to the blurring of the equilibrium position by side reactions, but the general shape of the curves in Figures 1 and 2, supported by detailed work on methyl stearate, again indicates a pseudo-unimolecular reaction. The high excess of acetic acid used masks the order against this component.

The case of water is more complicated because its concentration cannot be varied without simultaneously affecting the strength of the acid catalyst. Perchloric acid is an exceptionally strong acid in completely anhydrous acetic acid, but its strength is very sensitive to water, causing an apparently very low order for the total reaction in respect to water, an acceleration of only 25% accompanying the doubling of low water contents in presence of perchloric acid catalysis. Sulphuric acid (known to be monobasic in acetic acid) and the sulphonic acids are less sensitive to water and give apparent reaction orders against water of about 0.5. These orders would be still lower if properly referred to the standing state instead of the initial water concentrations, as increasing initial water additions will undergo decreasing hydrolytic loss.

Hydrolysis is the rate determining step, the re-esterification being relatively fast and not limiting. The low temperature coefficient of 1.6 per 10°C. confirms this to some extent, since fat splitting is known to have a low coefficient. The consequent low activation energy is also in accord with the largely statistical nature of the equilibria, and their comparative immobility with respect to temperature. In contrast to this, the side reaction involving the addition of acetic acid to the double bond is highly temperature-dependent with a coefficient of around 4; it is exothermic, and its equilibrium point is markedly sensitive to temperature.

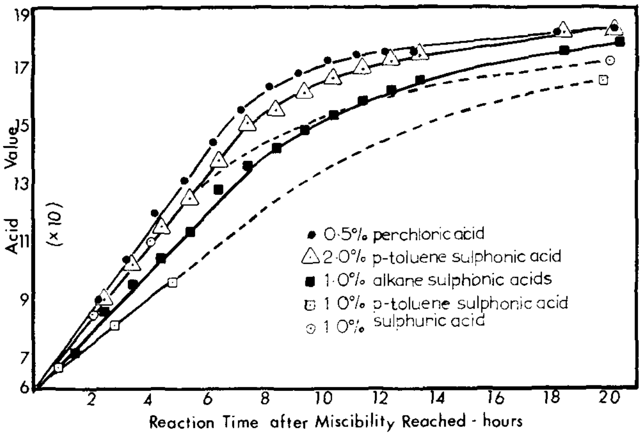

FIG. 2. Comparison of the rate of acidolysis of hydrogenated tallow with various catalysts after the reaction has become miscible at A.V. 60.

Relative catalyst activity is in line with equivalent conductivities in the reaction medium of acetic acid, rather than with aqueous pK values, perfluorcarboxylic acids thus being weak catalysts. The relative strengths of acids in anhydrous acetic acid, derived by Haszeldine (8) from conductance figures ($HClO_4$ 40 : H_2SO_4 3.5 : HCl 1) are leveled down in 95–98% acetic acid by the specific effect of water on perchloric acid and to a lesser extent on sulphuric acid, leading to the relative molar catalytic activities for the acetolysis reaction of the following very approximate list: $HClO_4$ 4 : $ArSO_3H$, $AlkSO_3H$, H_2SO_4 1.3 : HCl 1.

Side Reactions

The necessary presence of water leads to hydrolytic by-products. A further side reaction (which we found to be partially inhibited by water) occurs with unsaturated fats, as acetic acid adds to double bonds (5,6,7,): G Unsat. + HAc $\longrightarrow$ G (Acetoxysat). This leads to acetoxy bearing glycerides in the early stages, which explains the quicker onset of miscibility with unsaturated fats, and to acetoxy fatty acids later on. These acids codistil to a considerable extent with the unsubstituted acids, causing increased ester value and decreased unsaturation in the distillate.

Prolonged reaction times lead to a more deep seated reaction, particularly when polyunsaturation is present, as shown by an increasing amount of pitchy material low in both ester and iodine values; this is most marked with perchloric acid catalysis. Hydrochloric acid catalysis is accompanied by catalyst consumption to form glycerol chlorhydrin acetates. Acetic acid breaks up the HCl/H_2O system, giving increased HCl partial pressures, but does not similarly affect the $HClO_4/H_2O$ system as 70% $HClO_4$ was found to be nonvolatile in acetic acid vapor.

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