TABLE IV

Fatty Acid Composition of Fat Extracted from Potatoes after Frying

Fatty acids (%)	Oil (5 hr)	Oil (10 hr)	Lard (5 hr)	Lard (10 hr)
Myristic	.7	.8	1.4	1.6
Palmitic	23.8	31.2	26.1	30.0
Palmitoleic	.8	1.8	1.8	2.6
Stearic	2.9	3.6	17.2	18.9
Oleic	17.8	21.0	44.7	42.6
Linoleic	54.0	41.2	6.8	4.8

chicken is reported in Table V. Also, in the table is reported the fatty acid composition of a chicken obtained from the same source which had been fed the same ration. The raw chicken was ground and dried at 100C for six hr. Fat extracted from the dry material was used for fatty acid analyses.

These data show that while the fatty acid content of the fat extracted from the chicken reflects the fat it was cooked in, the fatty acid composition also depends quite a bit on the chicken itself. There appears to be little difference in the fatty acid components of chicken cooked in cottonseed oil whether the fat was used for five or ten hr. The same is true of chicken fried in lard. Thus, there is evidence that any catalytic activity of hematin compounds in the chicken was offset by the deterrent effect of fat, amino acids or some unidentified protective agent in the meat.

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TABLE V

Fatty Acid Composition of Fat Extracted from Chicken Before and after Frying

Fatty acids (%)	Oil (5 hr)	Oil (10 hr)	Lard (5 hr)	Lard (10 hr)	Raw
Myristic	.9	.7	1.0	.8	.9
Palmitic	26.0	25.4	25.2	25.8	25.4
Palmitoleic	2.7	2.0	2.7	4.9	5.8
Stearic	5.6	5.0	15.1	12.2	8.8
Oleic	28.2	27.4	38.4	39.8	41.9
Linoleic	36.0	38.7	16.6	15.4	17.3

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[Received July 19, 1963—Accepted March 3, 1964]

Hydroxyl Group Determination in High Molecular Weight Alcohols and Complex Organic Mixtures

D. E. JORDAN, Continental Oil Company, Research and Development Department, Ponca City, Oklahoma

Abstract

Acetylation of complex organic mixtures and high mol wt alcohols is inconsistent by existing procedures because of sample insolubility. By choosing a suitable mixed paraffin-ethyl acetate solvent to bring about nearly instantaneous solution, and utilizing the known catalysis property of perchloric acid, acetylation is quantitative in 10 min or less at room temp. The effect of perchloric acid concn on these high mol wt systems was studied, and from 0.05–0.45M consistent results were obtained without difficulty.

Acetylation of polyethylene oxide (P.E.O.) adducts of straight chain monohydric alcohols proceeds normally and without degradation by the prescribed procedure. Extended reaction time results in partial degradation of the polyether linkages and amounts to nearly 8% after 30 min.

Introduction

THE PUBLISHED CLASSICAL base catalyzed acetylation and phthalation procedures, including the AOCS procedure (1), for determining organic hydroxyl groups in alcohols are time consuming, oftentimes inconsistent, and not applicable to high mol wt alcohols, alcohol-P.E.O. adducts and complex mixtures. Increased interest in high mol wt and complex organic systems has necessitated development of a rapid and quantitative procedure applicable to these systems.

Mehlenbacher (7) presents an excellent review of the pertinent literature through 1952. Siggia et al. (8) use pyromellitic dianhydride to esterify alcohols, while Sully (11) employs stearic anhydride and elevated temp. Burton and Praill (2,3) described a reaction mechanism for perchloric acid catalyzed acetylation which was later used by Fritz and Schenk (6), who extended it to include the pyridinium acetylinium ion suggested by Gold and Jefferson (5). Fritz and Schenk (6) also mention p-toluene sulfonic acid as a mild catalyst for acetylation. Stetzler and Smullin (10) use it and elevated temp to acetylate polypropylene oxide adducts of Sorbitol. They, Fritz and Schenk (6) and Critchfield (4), observed that perchloric acid degrades propylene oxide linkages on polyhydric alcohols. Work in this laboratory shows that degradation of alcohol-propylene oxide adducts does indeed occur as described, but for straight chain aliphatic alcohol-P.E.O. products no degradation occurs in the recommended reaction time. In fact, significant degradation occurs only after three times the prescribed reaction time.

Classical base catalyzed acetylation or phthalation of high mol wt and complex organic systems often requires four or more hr. A reaction time longer than six hr was necessary for many P.E.O. alcohol adducts, and in several cases acetylation was still incomplete.

The present work demonstrates that choosing a suitable paraffin-ethyl acetate solvent to ensure rapid sample solution of the complex systems studied and utilizing the known catalysis property of perchloric acid, acetylation proceeds at room temp normally and without degradation in 10 min or less. By extending the acetylation reaction time to 15 min, degradation of ether linkages of aliphatic P.E.O. alcoholates begins and after 30 min still is only 5–8%.

Reagents and Solutions

2M Acetic Anhydride in Ethyl Acetate. Add 5.2 g (3.0 ml) 72% perchloric acid to 150 ml ACS grade ethyl acetate in a clean 250-ml glass-stoppered flask. Pipet 8 ml ACS grade acetic anhydride into the flask and allow it to stand at room temp for at least 30 min. Cool the contents of the flask to 5C and add 42 ml cold acetic anhydride. Keep the flask at 5C for an hour, then allow the reagent to come to room temp. Some yellow color will develop, but the color and anhydride content of the reagent remain at satisfactory levels for at least two weeks at room temp.

Acetylating Reagent. Mix 4 parts perchloric acid catalyzed 2M acetic anhydride in ethyl acetate with 1 part *n*-hexane.

0.05M Sodium Hydroxide. To 364 g aqueous 50% (W/W) sodium hydroxide (Carbonate free) add 75 ml distilled water and dilute to 9 liters with Formula 30 alcohol. Standardize against potassium acid phthalate.

Mixed Indicator. Mix one part 0.1% aqueous ortho cresol red with 3 parts 0.1% aqueous thymol blue, each neutralized with sodium hydroxide.

Ethyl Acetate. ACS grade or better.

Potassium Acid Phthalate. Primary standard grade.

n-Hexane. 95 mole per cent minimum.

Formula 30 Alcohol. 95% ethanol, 5% methanol.

Pyridine. ACS grade or better.

Alcohol Samples. All pure alcohol samples used in this work were prepared in our Distillation Laboratory, further purified by our Separations Analysis Group, and are ±99.9% pure, as determined by GLC.

Polyethylene Oxide-Alcohol Adducts. These samples were prepared and purified in our Petrochemical Research Laboratory.

Recommended Procedure

Accurately weigh 0.2–0.5 g of sample into a 250-ml glass-stoppered flask containing exactly 5.0 ml acetylating reagent. Solid samples are melted and weighed rapidly by difference. Allow the reaction to proceed at room temp for 5 min for alcohols up to eicosanol including P.E.O.-alcohol adducts, and 10 min for alcohols above eicosanol and complex mixtures. Add 2 ml water, swirl the mixture, and let stand 2 min, then add 10 ml 3:1 pyridine-water solution and allow the flask to stand for 5 min. Titrate with 0.50M sodium hydroxide using the mixed indicator. The end point is a matter of choice as long as the same end point is taken for both the blank and the sample titrations. A reproducible end point occurs when the color change is from yellow to violet or when the color changes to a deep pure blue. The titrations also can be done potentiometrically with a recorder readout or plotted or the end point taken at an apparent pH of 9.8. Run a reagent blank in the same manner as described for a sample using 5.0 ml acetylating reagent but none of the sample. The difference between the blank and sample titrations is used to calculate the percentage of organic hydroxyl groups in the sample.

CAUTION—Organic solvents containing perchloric acid have been widely used. No hazard exists under the conditions described in the above procedure. Solutions containing perchloric acid should not be heated, however, and should be disposed of immediately after the determination is completed.

Discussion

Preparation of 2M acetic anhydride in ethyl acetate occasionally resulted in a temporarily dark brown solution. Upon standing for ca. 12 hr it turned a light lemon yellow and was stable. The reason for the dark color is not known but it is probably due to an intermediate formation of some quinoidal type colored molecules which, upon standing, form a more stable configuration.

Solutions of acetic anhydride are much less stable in the 4:1 ethyl acetate-hexane solvent than in pure ethyl acetate. The mixed reagent is stable only 2 or 3 days compared to 2–3 weeks for pure ethyl acetate reagent. To simplify manipulation as much as possible, a stock solution of perchloric acid and acetic anhydride added to ethyl acetate was prepared as described above and the mixed acetylating reagent was then prepared as needed. In this manner the stability was not impaired and the perchloric acid concn could be changed to any desired level.

Addition of *n*-hexane to ethyl acetate mixture lowers the perchloric acid concn. Since various ratios of hexane-ethyl acetate were investigated to establish a general solvent system, it became desirable in view of other work (6) to see if different perchloric acid concn also affected these high mol wt systems. The work done in this laboratory shows that for these systems perchloric acid concn up to 0.45M has no discernible effect on acetylation results.

Several additional solvents have been described as siutable for acetylation of hydroxyl groups (6) but none of these were as applicable to our complex systems or as stable as the mixed solvent described above. Pyridine has been used extensively for base catalyzed and moderately used for acid catalyzed acetylation. It offered no advantage over the mixed solvent used and, in fact, was much less stable.

Solution of the solid samples used in this work was quite slow, thus necessitating a longer acetylation time. Nearly instantaneous solution and rapid acetylation are attained, however, by inverse addition of the

TABLE I

Sample	Number of replicate determinations	Per cent hydroxyl			Relative standard deviation per cent
		Range	Avg	Theory	
Octanol	7	12.97–13.21	13.07	13.06	±0.31
Decanol	4	10.67–10.84	10.75	10.75	±0.38
Tridecanol	2	8.55– 8.61	8.58	8.53	....
Hexadecanol	7	7.00– 7.10	7.06	7.02	±0.21
Eicosanol	3	5.69– 5.75	5.72	5.70	....
Polyethoxylate-A [a]	2	6.13– 6.15	6.14	......	....
Polyethoxylate-B [a]	2	5.46– 5.54	5.50	......	....
Polyethoxylate-C [a]	2	6.91– 6.95	6.93	......	....
Polyethoxylate-D [a]	2	6.46– 6.53	6.50	......	....
Polyethoxylate-E [a]	2	5.87– 5.93	5.90	......	....
Complex mixture-1 [b]	2	5.73– 5.78	5.76	......	....
Complex mixture-2 [b]	3	4.84– 5.06	4.98	......	....
Complex mixture-3 [b]	2	3.83– 3.86	3.85	......	....
Complex mixture-4 [b]	2	5.02– 5.09	5.05	......	....

[a] Dodecanol-tetradecanol adducted with various molar quantities of ethylene oxide.

[b] Complex mixtures 1,2 and 4, approx composition includes 65–75% alcohols ranging from C_{20} through $C_{40}OH$, 25–35% paraffin, olefin, ester, acid, ether and carbonyl compounds. Complex mixture 3, similar to above except it also contains 3% sodium borohydride.

TABLE II

Acetylation at Room Temperature of Complex Distillation Residues by Classical and 0.15M Perchloric Acid Catalyzed Procedures

Sample	Reaction time min	Acid catalysis		Base catalysis
		Ethyl-acetate solvent[a]	Mixed solvent	Classical[b]
Complex mixture-3	5	68.2	98.9	......
	10	80.5	99.9	......
	60	......	......	72.4
	240	......	......	87.3
	360	......	......	91.6
Complex mixture-1	5	84.6	99.7	......
	10	93.6	100.2	......
	60	......	......	83.7
	240	......	......	98.7
	360	......	......	99.8

Mixture 1 and 3 correspond to the samples described in Table I.

[a] Incomplete acetylation is due primarily to slow and incomplete solubility of the complex mixture.

[b] Reference 8 in bibliography.

melted sample onto the acetylating reagent. All other samples can be treated as desired since solution by either technique poses no problem.

Nearly all the complex systems studied have quantitatively acetylated in 5 min. Occasionally, a sample containing organic hydroxyl groups included impurities that seemed to retard acetylation. However, these completely reacted in 10 min or less which is the suggested time outlined in the procedure for all of the complex systems.

Results

Data in Table I represent the results obtained for pure alcohols, various complex mixtures and P.E.O.-alcohol adducts. The method is a general one and the data show that with pure alcohols it is accurate to better than ±1.0% of the true value and with a relative standard deviation of less than ±0.5%. Although the absolute purity of the P.E.O.-alcoholates and complex mixtures is not known, the precision and accuracy for them should also be ±1.0%. The results summarized here for pure alcohols were obtained over a period of several weeks using several preparations of acetylating reagent and are, insofar as is possible, representative of actual practical laboratory conditions.

Table II compares the similarities and differences in acetylation of organic hydroxyl groups in complex systems by the perchloric acid catalyzed and classical (9) procedures. It shows that while ethyl acetate is an acceptable solvent for some systems (6), it is totally unsuitable for the type of samples analyzed in our work. It is quite likely, however, that quantitative results would be obtained in ethyl acetate solvent after an extended reaction time provided the sample was evenly dispersed during the acetylation reaction. The classical base catalyzed procedure is unsuitable in some cases even after an extended reaction time of 6 hr. The mixed solvent acetylating reagent was chosen for the 100% reaction based on data in Table I. It readily dissolves complex mixtures as well as P.E.O. adducts and simple alcohols with quantitative acetylation in less than 10 minutes without difficulty.

TABLE III

Effect of 0.15M Perchloric Acid on Acetylation Time of Ethylene Oxide Adduction Products of *N*-Aliphatic Alcohols

Sample	Per cent reaction[a] after			
	5 Min	10 Min	15 Min	30 Min
A	99.7	99.9	100.4	107.6
B	99.2	100.1	102.1	107.3
C	99.0	99.7	101.2	104.1
D	99.7	99.7	100.4	105.2
E	99.6	99.8	100.1	107.4
F	99.3	99.7	100.3	106.6

[a] Based on results obtained using *p*-toluene sulfonic acid procedure (10).

TABLE IV

Effect of Perchloric Acid Concentration on Acetylation of Hydroxyl Groups at Room Temperature for 10 Minutes Using Mixed Ethyl Acetate and Hexane Solvent

Perchloric acid concn	Per cent reacted			
	Complex mixture-3[a]	Complex mixture-1[a]	Poly-ethoxy-late A[a]	Eicosanol
0.0 M	25.1	24.8	49.5	75.8
0.05M	99.7	100.2	99.8	99.9
0.15M	99.8	99.7	100.9	99.9
0.30M	100.1	99.9	99.8	100.0
0.45M	100.2	101.1	100.4	100.2

[a] Approx composition corresponds to samples described in Table I.

Data in Table III show the effect of reaction time of perchloric acid catalysis on the acetylation of P.E.O. adducts of *n*-aliphatic alcohols. The results for each sample show a definite degradation trend near a 15-min reaction time. After 30 min the degradation becomes quite significant and it is reasonable to assume that degradation would continue with an extended reaction. Since a normal reaction time in this work is 10 min or less, little or no interference will occur with these types of polyoxyethylates. However, results by previous workers (10), and confirmed in this laboratory, show that significant degradation does indeed occur in P.E.O. or P.P.O. adducts of polyhydric alcohols. The method then is not a general procedure but is fully applicable to the various P.E.O. adducts of aliphatic monohydric alcohols, and is probably also applicable to the dihydric alcohol analogs.

The results in Table IV describe the effect of perchloric acid concn on the acetylation of organic hydroxyl groups. There is little to choose from above 0.05M acid concn. Even for the P.E.O. sample, there was no significant effect. Eicosanol was used as a control sample since the purity of the other samples was unkown. This sample was extensively analyzed prior to the other samples shown in Table IV, and no significant effect due to perchloric acid, including erratic results and low anhydride concn, was observed. Since it is known (6) that erratic results and low anhydride level result with a perchloric acid concentration above ca. 0.25M, it can only be assumed that with high mol wt samples the factors causing erratic results are no longer significant. Another point worth consideration is that in the present work, there was no excess water in the acetylating reagent at high concn of perchloric acid (0.15M and higher), thus the anhydride level was essentially the same for all the described work.

Samples on which the described procedure has been used with excellent results, but which are not described in detail here, include hydrolysis products from trialkyl aluminum and dialkyl alkoxy aluminum mixtures, distillation overhead and residue samples, trace alcohol in non-alcoholic mixtures, paraffins and olefins, organic esters and acids, and dimerized, branched and tertiary alcohols.

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[Received January 20, 1964—Accepted April 17, 1964]