Infrared Spectrophotometric Procedure for Determining Azelaaldehydic Acid Derivatives

D. E. ANDERS and E. H. PRYDE, Northern Regional Research Laboratory,[1] Peoria, Illinois

Abstract

A convenient and accurate infrared procedure was developed for determining the conversion of azelaaldehydic esters to acetals by measuring disappearance of the aldehydic C–H stretching vibration at 2720 cm^{-1} (3.68 μ).

Introduction

Aldehyde oils are potentially valuable aldehydic triglyceride products. They are conveniently prepared by reductively decomposing partially or completely ozonized glycerides such as soybean, linseed, *Crambe abyssinica* or margarine oils (8–10). These aldehyde oils are highly reactive chemical intermediates and undergo a variety of reactions including condensation with urea, amines, diamines, diols, polyols and phenols (9). However, the aldehyde oils, particularly unsaturated ones, exhibit a relatively short shelf life compared to some of their derivatives. When contemplating the use or storage of an aldehyde oil for more than a few days, our research group has found it advisable to remove all acidic or basic catalysts and to store the oil under refrigeration and an inert atmosphere. Alternatively, the aldehyde oil can be converted to a useful and stable derivative like the dimethyl acetal. This acetal easily undergoes alcoholysis and can be used to form other acetals such as the heat-stable, cyclic, ethylene glycol acetal. In preparing acetal oil derivatives, it became evident that a procedure for determining the extent of conversion was lacking. Employment of the conventional methods of analyses used for aldehydes, such as gas-liquid chromatography (GLC), molecular weight combined with wet analyses before and after conversion or observation of the decreasing infrared carbonyl band at 1740 to 1720 cm^{-1}, could not be conveniently applied to the oils.

Although there is much spectral data on aldehydes, little has been done to establish infrared as an accurate analytical tool for determining the extent of aldehyde conversion to acetals. Melchior (4) employed ultraviolet absorption to observe the differences in the spectra of certain ortho-substituted aldehydes in neutral methanol as compared to the same aldehydes in acidified methanol. Emphasis was placed on establishing equilibrium constants for these mixtures both at 2 and 25C. Crowell et al. (3) took advantage of the ultraviolet spectral changes resulting from acetal formation to determine the extent to which several *n*-aliphatic, unsaturated aliphatic and aromatic aldehydes reacted with acidified methanol. Acetal formation was measured by percent reduction in absorbance of the carbonyl maxima. Ashdown and Kletz (1) observed the infrared spectra of various aldehydes and alcohols in tandem pairs as well as in mixtures. They observed severel new bands in the fingerprint region, due to neither reagent but to hemiacetal formation, as well as a decrease in intensity at 2720 cm^{-1} (C–H stretching) and 1730 cm^{-1} (C = O vibration). Pinchas (6,7) studied the shift in the aldehydic C–H band of several ortho-substituted benzaldehydes in the 3000–2600 cm^{-1} region, but only to elucidate their structure. Brugel and Ostor (2) found a sharp, but not strong, characteristic infrared band of acetals at 2820–2830 cm^{-1}. Unfortunately, the band could not be used to determine acetal concentration because of its nearness to the 2850 cm^{-1} C–H vibration and because a suitable concentration of the acetal must be presented before the band is detectable.

We have developed a convenient and accurate procedure for ascertaining the extent of aldehyde oil conversion to acetal oil by measuring absorbance of the aldehydic C–H group appearing near 2720 cm^{-1} (3.68 μ).

Apparatus and Reagents

Infrared spectra were obtained in potassium bromide cells with a Perkin-Elmer grating spectrophotometer, model 337, with slit width programmed mechanically at position "N" (normal). Methyl azelaaldehydate (MAZ), 99.8% pure by GLC, was obtained by fractionally distilling the bisulfite-purified ozonolysis products of soybean oil methyl esters (5). Methyl azelaaldehydate dimethyl acetal (MAZDMA), 100% pure by GLC, was prepared by refluxing MAZ for 4 hr in the presence of excess methanol and 2,2-dimethoxypropane, with $KHSO_4$ as the catalyst. Aldehyde oil was obtained from catalytically reduced, completely ozonized, soybean oil. The dimethyl acetal was prepared by refluxing the aldehyde oil in excess methanol for 16 hr with Dowex 50W-X8 used as the catalyst.

Procedure

Except for the relative intensity of the aldehydic C–H group, spectra for azelaaldehydic esters and aldehyde oils are nearly identical in the 1200–4000 cm^{-1} range. MAZ and MAZDMA were chosen to demonstrate the effectiveness of this new infrared procedure because the exact concentration of each component could be determined more readily than for their triglyceride counterparts. A series of samples of different concentration was prepared by weighing and mixing a known amount of each ingredient. Absorbance at 2720 cm^{-1} (3.68 μ) was measured experimentally for each sample, and the absorptivity for each was calculated according to the equation $A = abc$, where A is the absorbance; a, the absorptivity; b, the cell width; and c, the concentration (the Beer-Lambert law) (Table I). Measurements were made in a 0.023 mm KBr cell for MAZ and MAZDMA and in a 0.05 mm KBr cell for the aldehyde-acetal oil samples. (The KBr cell was not necessary in preference to a NaCl cell for the work reported herein.)

The mean absorptivity for the entire range was 2.47 ± 0.07 g/(mm × meq). The decrease in absorbance at 2720 cm^{-1} as the acetalization of an aldehyde oil proceeds is shown in Table II.

---

[1] No. Utiliz. Res. Dev. Div., ARS, USDA.

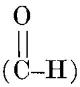
TABLE I

Absorbance of Methyl Azelaaldehydate (MAZ)-methyl Azelaalehydate Dimethyl Acetal (MAZDMA) Mixtures at 2720 cm^{-1}

Number	Sample composition		Aldehyde content, meq/g	MAZ, mole %	Absorbance	Absorptivity, g/mm/meq
	MAZ, g	MAZDMA, g				
1	0.0114	0.0932	0.586	13.2	0.032	2.37
2	0.0149	0.1173	0.605	13.7	0.036	2.59
3	0.0192	0.0930	0.919	20.5	0.052	2.46
4	0.0265	0.0898	1.22	26.9	0.070	2.49
5	0.0493	0.1345	1.97	41.9	0.118	2.60
6	0.0202	0.0267	2.31	48.5	0.136	2.56
7	0.0725	0.0589	2.96	60.5	0.170	2.49
8	0.0832	0.0452	3.48	69.7	0.201	2.51
9	0.0929	0.0308	4.03	78.9	0.223	2.41
10	0.1171	0.0229	4.49	86.4	0.254	2.46
11	0.1194	0.0093	4.99	94.1	0.265	2.31
12	....	0.0000	5.37	100.0	0.295	2.39

Mean absorptivity = 2.47.
Average difference = 0.07.
Standard deviation = 0.09.

Results and Discussion

The appearance of a (C–H) stretching vibration in aldehydes  $(\overset{\overset{\textstyle O}{\|}}{C}\text{–}H)$ near 2720 cm^{-1} accompanied by the carbonyl stretching absorption band at 1740–1720 cm^{-1} is excellent evidence for the presence of an aldehyde group. Ordinarily, aldehyde conversion to acetal can be followed by disappearance of the stronger of the two bands at 1740–1720 cm^{-1}. However, in the azelaaldehydic ester and aldehyde oil samples we have prepared, disappearance of this band is masked by the ester carbonyl (C = O) stretching vibrations. Therefore, the aldehyde-to-acetal reaction was followed by the fading of the medium (C–H) band appearing at 2720 cm^{-1} (3.68 μ).

For any given cell thickness, absorption in the aldehydic C–H region (2720 cm^{-1}) was stronger for MAZ than it was for aldehyde oil because of the higher concentration of aldehydic C–H in the former compound. Because saturated fatty esters are present in the original oil, aldehyde oils seldom contain more than 3.25 to 3.50 meq carbonyl/g compared to 5.37 meq C= O/g for MAZ. Accordingly, considerable variation in cell thickness was necessary. Absorbance resulting from the aldehydic C–H stretching in MAZ and aldehyde oil were measured in 0.023 mm and 0.05 mm KBr cells, respectively.

From absorbance values found for each MAZ/MAZDMA mixture an average absorptivity for the entire range was calculated. Mean absorptivity was 2.47 ± 0.07 g/(mm × meq). This value was used to calculate the percent conversion of an aldehyde oil to an acetal oil (Table II).

TABLE II

Conversion of an Aldehyde Oil to its Dimethyl Acetal

Number	Absorbance [a]	Aldehyde content, meq/g	Conversion, mole %
1	0.291	2.36	0.0
2	0.221	1.79	24
3	0.165	1.34	43
4	0.103	0.83	65
5	0.050	0.40	83
6	0.040	0.32	86
7	0.032	0.26	88
8	0.022	0.18	92.4

[a] Absorbance at 2720 cm^{-1} with a 0.05 mm KBr cell.

Alcohols must be absent in samples used for carbonyl determinations because of formation of hemiacetals, which do not show the C–H stretching vibration at 2720 cm^{-1}. Hemiacetal formation was demonstrated for a number of pelargonaldehyde-*n*-butyl alcohol solutions of different concentrations by spectrophotometric determination of the residual aldehyde. The amount of hemiacetal formed depended upon the amount of alcohol present (alcohol/aldehyde mole ratio—hemiacetal, per cent conversion): 0.146–14.3; 0.66–44.1; 1.04–54.3; 1.36–65.3; 2.64–74.6; 8.0-*ca.* 100. The aldehyde concentration as determined spectrophotometrically remained constant over a 3-day period. Initial readings were made at least 20 min after the alcohol and aldehyde had been mixed. Analyses by GLC of certain of the samples showed that aldehyde disappearance resulted from hemiacetal rather than acetal formation, since peaks for butanol and pelargonaldehyde were the only major ones detected. A minor peak for pelargonaldehyde dibutyl acetal indicated that the acetal was present only in trace amounts.

ACKNOWLEDGMENT

Analyses of the pelargonaldehyde-butanol solutions performed by D. J. Massa; samples of aldehyde and acetal oils from R. E. Beal; helpful discussions on the spectrophotometric analyses by D. J. Moore.

REFERENCES

1. Ashdown, A., and T. A. Kletz, J. Chem. Soc. — 1454–1456 (1948).
2. Brugel, W., and R. Oster, Angew. Chem. *68,* 441 (1956).
3. Crowell, E. P., W. A. Powell and C. Varsel, Anal. Chem. *35,* 184–189 (1963).
4. Melchior, N. C., J. Am. Chem. Soc. *71,* 3651–3654 (1949).
5. Miller, W. R., D. J. Moore and J. G. Fullington, JAOCS *40,* 720–721 (1963).
6. Pinchas, S., Anal. Chem. *27,* 2–6 (1955).
7. Pinchas, S., Ibid. *29,* 334–339 (1957).
8. Pryde, E. H., and D. E. Anders, U.S. 3,112,329 (1963).
9. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, JAOCS *38,* 375–379 (1961).
10. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, Ibid. *40,* 497–499 (1963).

[Received September 16, 1965]