Gas Density Balance versus Flame Ionization Detector

ABSTRACT

Comments are made on a paper by Lanser, et al., comparing the flame ionization detector with the gas density balance for quantitative gas liquid chromatography (GLC) analysis of a mixture of aldehydes and aldehydic esters. The suggestion that a gas density balance should be preferred to a flame ionization detector, according to our experience, is not very convincing and requires more supporting evidence.

INTRODUCTION

Recently, Lanser, et al., (1) published a paper in which the gas density balance (GDB), used as a detector for the quantitative gas chromatographic analysis of lipids, was compared with a flame ionization detector (FID). They concluded that the FID gave larger deviations, even after correction for ionizable carbon atoms, than the GDB, with respect to the molar ratios between aldehydes (A) and their corresponding aldehydic esters (AE) obtained from positionally isomeric methyl octadecenoates after oxidative degradation. They also applied the correction method developed by us (2). Although a certain improvement was obtained, they found systematic deviations, viz. molar ratios of $A/AE > 1$ originating from degradation products of isomers with the double bond in the 5-8 position and ratios of $A/AE < 1$, when the double bond was in the 10-13 range. These findings are not clear to us.

DISCUSSION

Let us consider the FID data given by Lanser, et al., (Table I), which related to a sample obtained by reductive ozonolysis of monoenes isolated from partially hydrogenated methyl linolenate. We introduced K'' for the molar ratio A/AE, calculated from peak areas after correction for ionizable carbon atoms. Depending on the origin of the sample, the values obtained usually diverged to some extent. For example, traces of polyenes, possibly still present in an isolated monoene fraction of partially hydrogenated polyenoic fatty acid esters, gave aldehydes and aldehydic esters which could affect considerably some K'' values. Nevertheless, we derived the most probable value of K'' as follows (2): a) Investigation of chromatogram and observation of well resolved peak areas of corresponding degradation products. b) Determination of the K'' values in question. c) Several of these K'' values were almost equal, whereas, some deviated to some extent. We rejected the latter values and determined the mean value of the first ones. This value was defined as the most probable K'' value.

TABLE I

Corrected Peak Area Values of Aldehydes (A) and Aldehydic Esters (AE) Obtained From Uncorrected FID Data[a]

Double bond position	Uncorrected relative peak areas					Corrected relative peak areas	
	A	AE	R_n[b]	K''[c]	R'_n[d]	A	AE
5	2.09	0.32	6.53	2.18	3.18	1.02	0.32
6	3.37	1.00	3.37	1.53	2.33	2.33	1.00
7	3.07	1.85	1.66	0.99	1.77	3.07	1.73
8	3.84	2.81	1.37	1.06	1.37	3.84	2.81
9	5.05	4.67	1.08	1.08	1.06	5.05	4.67
10	5.52	6.75	0.82	1.05	0.83	5.52	6.75
11	5.84	7.88	0.74	1.23	0.64	5.04	7.88
12	4.91	7.25	0.68	1.51	0.48	3.48	7.25
13	3.17	9.16	0.35	1.05	0.35	3.17	9.16

[a] Obtained from Table III, Lanser, et al. (1).

[b] R_n = uncorrected peak area ratio A/AE.

[c] K'' = molar ratio A/AE calculated from the peak areas after correction for ionizable carbon atoms.

[d] R'_n = adjusted peak area ratio A/AE based on $K'' = 1.06$ (mean K'' value of Δ_8, Δ_9, Δ_{10}, Δ_{13}).

TABLE II

Double Bond Distribution Based on Amounts of Aldehydes (A) and Aldehydic Esters (AE) Calculated from Flame Ionization Detector Data (After Correction) and Gas Density Balance Data[a]

Double bond position	Double bond distribution (%) in partially hydrogenated linolenate			
	FID[b]		GDB[b]	
	A	AE	A	AE
5	1.78	1.75	2.74	3.07
6	4.42	4.43	4.13	4.13
7	6.43	6.39	5.79	4.83
8	8.88	8.91	7.87	6.70
9	13.20	12.94	10.95	11.21
10	16.50	16.54	15.70	14.45
11	17.58	17.52	18.27	18.05
12	14.61	14.58	17.67	20.53
13	16.58	17.00	15.99	17.93

[a] Obtained from Table III, Lanser, et al. (1).

[b] FID = Flame ionization detector; GDB = gas density balance.

Lanser, et al., have not published the chromatograms of their data. Nevertheless, we assume that the peak areas of the degradation products of Δ_8, Δ_9, Δ_{10}, and Δ_{13} (Table I) satisfy our conditions. From the K'' values belonging to the degradation products in question, we derived the most probable K'' value of 1.06. K'' values which deviated from 1.06 are ascribed to too large peak areas of one of the corresponding degradation products, due to overlap or to the contribution of degradation products of compounds other than monenes. This implied that K'' values > 1.06 originated from too large peak areas of aldehydes, and K'' values < 1.06 from too large peak areas of aldehydic esters. These peak areas were corrected in such a way that after correction $K'' = 1.06$.

The results (Table II) showed that: a) No such systematic deviations were found for the FID as suggested by Lanser, et al. b) The average double bond distribution obtained via the FID agreed fairly well with that obtained via the GDB, except for Δ_{12}. However, it may be that the aldoester peak in question needed correction instead of the aldehyde peak. In that case, 19.4% of Δ_{12} (on the basis of A and AE) was found, which made the agreement even better.

We always obtained good agreement between the experimental and real composition of mixtures of positional isomers (2). Table III shows some experimental data on Δ_6, Δ_9, and Δ_{12} isomers. In contrast with the findings of Lanser, et al., we did not observe a shortage of degradation products with a short chain for the positional isomers mentioned. K″, derived from well resolved and reliable peaks, was independent of the position of the double bond, but it truly depended on GLC conditions, for unknown reasons (2). When, for instance, a column was replaced by another with the same immobile phase and support, the K″ values changed under the same operational conditions. We also observed a change in K″ values during the lifetime of a column. It may be that the differences between the FID and GDB data reported by Lanser, et al., also were due to differences in GLC conditions and types of column.

Our conclusion is that for a good evaluation of differences between these detection systems on the basis of the degradation products mentioned, application of the same GLC conditions/columns may play a major role.

P. VAN DER PLANK
Unilever Research
Vlaardingen,
The Netherlands

TABLE III

Measured Peak Areas of Aldehydes (A), Aldehydic Esters (AE), and Their Molar Ratios (K″) After Correction for Ionizable Carbon Atoms

Sample		Double bond position	Measured peak areas A	Measured peak areas AE	K″
1[a]	cis	6	1571	589	1.21
	cis	9	1158	982	1.18
2[b]	cis	9	250	231	1.08
	cis	12	117	239	1.09
	trans	9	76	67	1.13
	trans	12	46	96	1.07
3[b]	cis	9	116	103	1.13
	cis	12	54	108	1.11
	trans	9	255	237	1.08
	trans	12	152	296	1.13

[a] Sample 1 is a 50:50 mixture of methyl oleate and methyl petroselinate.

[b] Isolated fractions from partially hydrogenated methyl linoleate.

REFERENCES

1. Lanser, A.C., A.E. Johnston, and H.J. Dutton, JAOCS 51:274 (1974).
2. van der Plank, P., Ibid. 49:489 (1972).

[Received February 10, 1975]

Net Hydrogenation Activity: A Rational Index

ABSTRACT

In a fixed regime of temperature, agitation, and hydrogen pressure, regression analysis yields a rational technique for indexing the activity of hydrogenation catalysts. Refractive index measurements as a function of time were analyzed to produce a family of rate constants. These, in turn, were analyzed via polynomial regression to yield a quantitative activity index.

INTRODUCTION

In a nickel hydrogenation catalyst development program, the quickest methods of activity comparison, dead end, fixed time hydrogenation, produced highly scattered data despite relative stability of raw stock, in this case refined soybean oil. A quantitative method for comparing the activities of nonselectively used catalysts was required. The character of the refractive index versus log time relationship suggested that a regression analysis correlation would yield an efficient means for quantifying activities.

EXPERIMENTAL PROCEDURES

All hydrogenations were conducted in a Parr Equipment Company 2-liter converter with internal cooling loop and catalyst dropping device. All conversions were done at 40 psig hydrogen pressure using 640 rpm agitation and temperature stabilization at 210 ± 2 C. Vacuum purge was used throughout the heating process, and hydrogen at the reaction pressure was purged through the charge for 1-2 min at an intermediate temperature (∿110 C). Vacuum purging was re-established, and conversion began 5 min after stabilization of the temperature at 210 C.

A specific catalyst was chosen to be a standard of comparison. In this case, a commercially available material, Girdler G-53, was selected. Hydrogenation experiments were done, at least in duplicate, at a series of nickel concentrations varying from 0.0104% Ni to ∿0.176% Ni. Refractive index [N_D(70 C)] measurements were made as a function of hydrogenation time. This hydrogenation regime yielded an extensive region of linearity when N_D(70 C) was plotted as a function of log time. Typical data for 3 different hydrogenation reactions are shown in Figure 1. The linear regions of each are indicated. Conversions initially were measured by iodine value methods (1). A large number of these analyses, ranging in iodine value (IV) from

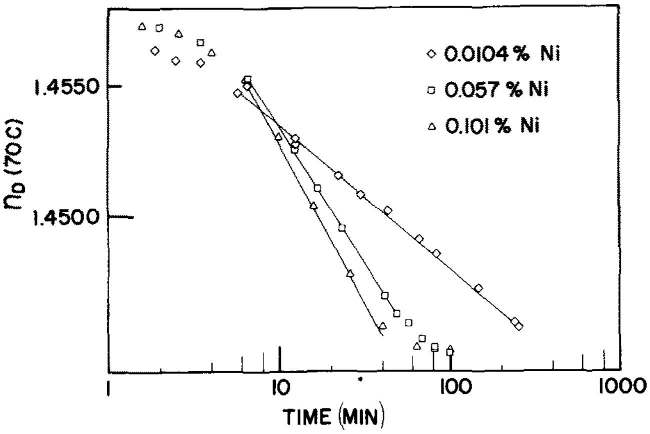

FIG. 1. Typical hydrogenation data for standard catalyst. All experiments were conducted at hydrogen pressure = 40 psig, agitation 640 rpm, and temperature = 210 ± 2 C.