hydrogenation, the caloric value of unsaturated fat might be increased by selectively eliminating the protozoa from the rumen.

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Quantitative Analysis of 1-Olefins by Programmed Temperature Gas Chromatography

R. W. POE and E. F. KAELBLE, Inorganic Chemicals Division, Research Department, Monsanto Chemical Co., St. Louis, Missouri

Abstract

Gas chromatography has been extremely valuable for the analysis of materials used in the manufacture of surfactants. Temperature programming, which makes possible the efficient separation of wide boiling range mixtures, has extended the usefulness of the technique.

In the work described, mixtures of 1-olefins from C_8–C_{18} in chain length were completely separated on a silicone rubber column in 17 min. The peaks were sharp, symmetrical and almost evenly spaced. A flame ionization detector was used.

Using synthetic mixtures, it was found that over the C_8–C_{18} range, peak area percent agrees very closely with weight percent. On a large number of measurements, the average deviation between area percent and weight percent was 0.5% absolute, with a range of ± 2%. No bias in instrument response was observed with respect to chain length. Average carbon numbers calculated from chromatographic data were accurate to within ± 0.2 units.

Chromatographic results were compared with mass spectrometer data and were found to be significantly more precise and accurate. Furthermore, olefins could be detected in concentrations low enough that they were missed by the mass spectrometer (0.1%).

Introduction

BRANCHED-CHAIN OLEFINS, particularly tetrapropylene, have long been used as intermediates in the manufacture of detergents. With improved technology, straight-chain 1-olefins are expected to become available soon in large volume and at commercial prices. As such, they are regarded as basic raw materials and valuable intermediates for the detergents of the future. The need arises, therefore, for a rapid, reliable method for analyzing commercial mixtures of 1-olefins in the C_8–C_{18} range. Gas chromatography has proved useful for analyzing detergent intermediates and related materials in the past (1–4), and we have found this technique, with the addition of programmed column temperature, to be useful also for 1-olefins.

Experimental

An F&M Model 609 gas chromatograph was used in this work. The instrument was equipped with a flame ionization detector and a Disc integrator. Silicone gum rubber (SE-30) was found to be a very efficient stationary phase for separating 1-olefins in the C_8–C_{18} range. The column used was 2 ft long, ¼ in. O.D. stainless steel packed with 20% SE-30 on 60–80 mesh Chromosorb P.

Separation was best when the column temperature was programmed upward from 75C at a linear rate of 9C per minute. Flow rate of the helium carrier gas was 30–35 cc per minute. Injection port and detector temperatures were 270C and 325C, respectively. Sample size was varied between 0.1 and 1.0 μl. To check quantitative response, a series of nine synthetic mixtures was prepared from pure, even-numbered 1-olefins in the C_8–C_{18} range. The mixtures contained from two to six components ranging in concentration from 5–95%.

Results and Discussion

A typical programmed temperature chromatogram of an experimental olefin mixture is shown in Figure 1. Figure 2 shows the chromatogram of the same sample run under isothermal conditions. The increased efficiency of programmed temperature operation in separating mixtures spanning a wide boiling-point range is strikingly demonstrated. Not only is resolution improved by temperature programming, but higher boiling components (i.e., C_{16}, C_{17}, and C_{18} olefins), so diffused in isothermal operation as to be

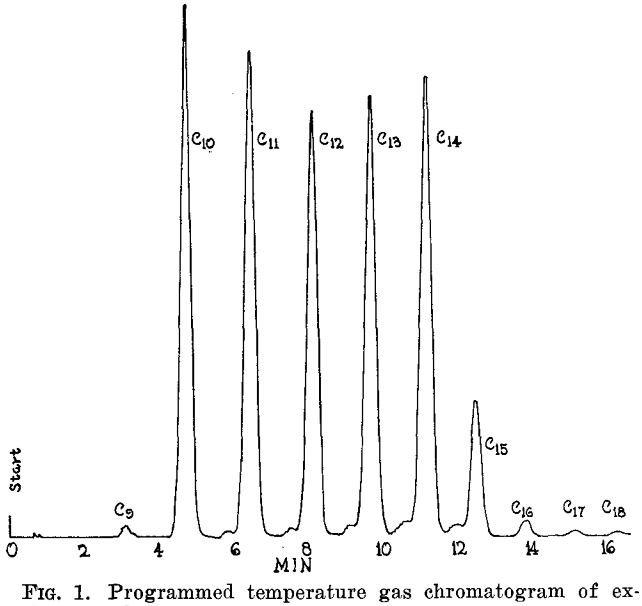

FIG. 1. Programmed temperature gas chromatogram of experimental olefin.

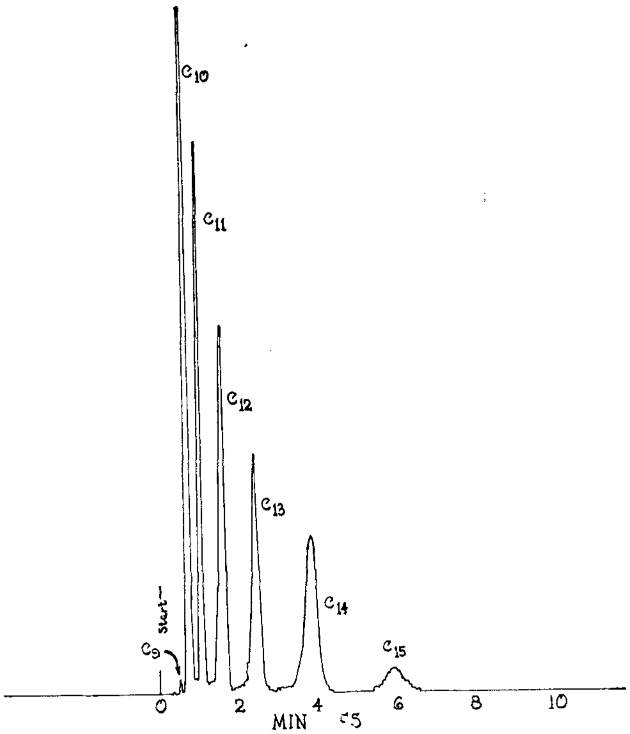

FIG. 2. Gas chromatogram of same experimental olefin run isothermally at a column temperature of 125C.

unseen on the chromatogram, can be readily detected. The identity of the small shoulders associated with the major peaks is uncertain and was not investigated in this work. They are thought to be due either to diolefins or to positional isomers.

With the synthetic mixtures described previously, it was found that the relative peak areas agree very closely with weight percents. For 43 measurements, the average deviation between area percent and weight percent was 0.5% absolute, with a range of ± 2%. Average carbon number values calculated from chromatographic data were accurate to within ± 0.2 units. For purposes of comparison, mass spectrometric data were also obtained on some of the synthetic and experimental olefin mixtures. Results are summarized in Tables I and II.

TABLE I

Gas Chromatographic and Mass Spectrometric Data on Synthetic Mixtures of 1-Olefins

Constituent	Actual % by weight	Gas chromatography		Mass spectrometry	
		%	Diff.	%	Diff.
Mixture 1					
1-Octene	5.0	5.3	+0.3	5.0	0.0
1-Decene	10.0	10.4	+0.4	7.4	—2.6
1-Dodecene	15.0	15.2	+0.2	13.2	—1.8
1-Tetradecene	20.0	20.4	+0.4	17.4	—2.6
1-Hexadecene	24.9	23.7	—1.2	26.5	+1.6
1-Octadecene	25.1	25.0	—0.1	30.5	+5.4
Average carbon no.	14.5	14.4	—0.1	14.9	+0.4
Mixture 2					
1-Octene	24.9	23.2	—1.7	19.4	—5.5
1 Decene	24.9	25.1	+0.2	19.1	—5.8
1-Dodecene	20.0	20.1	+0.1	21.3	+1.3
1-Tetradecene	15.0	15.5	+0.5	15.9	+0.9
1-Hexadecene	10.1	10.2	+0.1	16.3	+6.2
1-Octadecene	5.1	5.7	+0.6	8.1	+3.0
Average carbon no.	11.5	11.6	+0.1	12.3	+0.8
Mixture 3					
1-Octene	5.0	5.1	+0.1	6.7	+1.7
1-Decene	10.0	10.5	+0.5	10.4	+0.4
1-Dodecene	20.1	20.7	+0.6	23.4	+3.3
1-Tetradecene	49.8	47.8	—2.0	38.1	—11.7
1-Hexadecene	10.0	10.3	+0.3	13.0	+3.0
1-Octadecene	5.1	5.7	+0.6	8.4	+3.3
Average carbon no.	13.3	13.3	0.0	13.3	0.0
Mixture 4					
1-Decene	5.0	6.1	+1.1	......	......
1-Hexadecene	95.0	93.9	—1.1	......	......
Mixture 5					
1-Decene	25.1	26.4	+1.3	......	......
1-Hexadecene	74.9	73.6	—1.3	......	......
Mixture 6					
1-Decene	49.9	48.3	—1.6	......	......
1-Hexadecene	50.1	51.7	+1.6	......	......
Mixture 7					
1-Decene	74.8	74.3	—0.5	......	......
1-Hexadecene	25.2	25.7	+0.5	......	......
Mixture 8					
1-Decene	95.0	94.9	—0.1	......	......
1-Hexadecene	5.0	5.1	+0.1	......	......

TABLE II

Gas Chromatographic and Mass Spectrometric Data on an Experimental Olefin

Chain length	Mass spec. data		Gas chromatography (%)
	% Monoolefin	% Diolefin	
C_9	......	......	0.5
C_{10}	22.5	1.9	19.2
iso-C_{11}	......	......	0.3
C_{11}	19.6	1.6	18.9
iso-C_{12}	......	......	0.3
C_{12}	16.4	1.2	16.8
iso-C_{13}	......	......	0.3
C_{13}	14.2	1.2	17.3
iso-C_{14}	......	......	0.8
C_{14}	16.2	0.8	18.4
iso-C_{15}	......	......	0.6
C_{15}	4.4	......	5.3
C_{16}	......	......	0.9
C_{17}	......	......	0.3
C_{18}	......	......	0.1
Total	93.3	6.7	100.0
Average carbon no.	11.9		12.2

No bias in chromatographic response was observed with respect to chain length in the C_8–C_{18} range. It was noted that, in general, deviations were positive at low concentrations and negative at high concentrations, indicating some deviation from linearity with respect to concentration. Deviations, however, were within the range given above.

Precision at 95% confidence was found to be ± 2% of the amount present over the 5–95% concentration range investigated. Precision data were obtained over a two-week period during which such activities as turning the instrument on and off repeatedly, removing and reinstalling the column, and cleaning the detector were performed.

It is apparent from Table I that the chromatographic results on the synthetic mixtures are superior to mass spectrometric data. It must be pointed out, however, that the mass spectrometric data presented here were obtained on an instrument which was not specifically calibrated for 1-olefins. Therefore, they do not represent the highest accuracy attainable. Average deviation of mass values is 3.3% absolute.

A further comparison of chromatographic and mass spectrometric results is found in Table II, which shows data for an experimental olefin sample. The mass spectrometer is superior in its ability to distinguish diolefins. The identity of small chromatographic peaks is uncertain, and they are reported simply as isomeric structures. The gas chromatograph showed the presence of small amounts of C_9, C_{16}, C_{17}, and C_{18} olefins not detected by mass spectrometry. The two techniques require about the same time, 20–25 min per sample, including calculations. Gas chromatography has the important advantage of requiring far less expensive equipment than does mass spectrometry.

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