Calculation

$(T + F)/(T - F)$ = iodine/chlorine ratio

where T = ml. $Na_2S_2O_3 \times N$ required for total halogen

F = ml. $KIO_3 \times N$ required for free iodine

Derivation

$(T - F)$ = ml of N $Na_2S_2O_3$ required for the ICl

$(T - F)/2$ = ml of $Na_2S_2O_3$ required for the Cl or the I in the ICl

$$\frac{(T - F)/2 + F}{(T - F)/2} = (T + F)/(T - F)$$

Determination of Halogen Ratio of Iodine Monochloride

It is necessary first to prepare a Wijs solution from the iodine monochloride and then determine the halogen ratio by the foregoing procedure. The iodine monochloride must contain a slight excess of free iodine so that its I/Cl ratio is about 1.1.

Procedure

Pipet 5 ml of reagent grade iodine monochloride into a liter of glacial acetic acid, and mix to form Wijs solution.

Determine the free iodine and the total halogen, using 25.00-ml portions by the foregoing procedure described under Halogen Ratio of Wijs Solution, and calculate the iodine/chlorine ratio.

REFERENCES

1. Lopes, H. D., JAOCS September, 1951, p 390.
2. Kolthoff, I. M., and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, 1957, p 451–53.

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Analysis of Alpha Olefins Using a Gas Chromatograph-Mass Spectrometer Combination[1]

R. M. TEETER, C. F. SPENCER, J. W. GREEN and L. H. SMITHSON,
Chevron Research Company, Richmond, California

Abstract

The gas chromatograph-mass spectrometer (GCMS) combination with and without catalytic hydrogenation is the most effective way to obtain detailed analysis of commercial alpha olefin mixtures. Previous descriptions of this technique presented examples only up to C_{10} alpha olefins. We have extended this technique to include alpha olefins up to C_{20}. The complete analysis of a C_{11}–C_{14} alpha olefin mixture is given as an example.

Introduction

THE COMPLETE ANALYSIS of a mixture of olefins is complicated by the large number of possible isomers. Commercial alpha olefins contain between 85 and 95% straight chain alpha olefins and varying amounts of internal, branched, and cyclic olefins; normal, branched, and cyclic paraffins; and diolefins.

Gas chromatography is a useful tool for analyzing alpha olefins, and several techniques have been reported (1,2). However, a more detailed analysis of the minor components can be obtained by using the gas chromatograph-mass spectrometer combination (GCMS).

Gohlke (3) used a gas chromatograph connected to a time-of-flight mass spectrometer for the characterization of complex mixtures. Lindeman and Annis (4) of this laboratory used a gas chromatograph with a magnetic deflection mass spectrometer to analyze the C_5–C_8 hydrocarbons in a California naphtha. Lindeman (5) subsequently analyzed an olefin fraction from a light catalytic cracked gasoline using the GCMS with catalytic hydrogenation before and after the gas chromatograph.

In this paper we present an analysis of a commercial C_{11}–C_{14} alpha olefin mixture using the GCMS with catalytic hydrogenation. The experimental technique involves separating the olefin mixture by gas chromatography and passing the eluted components into the mass spectrometer directly from either the chromatograph or the catalytic hydrogenator. The mass spectral records are then interpreted and the components determined. The amounts of the components are calculated from the gas chromatograph record. In cases of multicomponent peaks, the distribution of the components is estimated from the mass spectral records.

[1] Presented at the AOCS Meeting, Houston, April 1965.

Experimental

Instrumentation

The gas chromatograph is a specially built dual-column chromatograph with two temperature program modes, 1C and 0.5C per minute. The thermal conductivity detectors are coupled to a 1-mv recorder modified to print time marks.

The gas chromatograph columns used in these experiments are 50-ft by ¼-in. bifilar-wound copper tubes packed with 15% Ucon LB 550X, 0.2% Alkaterge T, and 0.2% Span 80 on 60–80 mesh firebrick.

The mass spectrometer is a Consolidated Electrodynamics Corporation Model 21-103C equipped with an Applied Physics Model 36 vibrating reed amplifier and modified for fast, repetitive scanning. The time constant in the scan circuit of the mass spectrometer has been decreased to allow a mass range of 50 to 200 to be scanned in 40 sec. A resetting interval timer is used to constantly repeat the scan. Valve V-6 (Fig. 1) is a Nuclear Products all-metal bellows valve added to the instrument to isolate the spectrometer from the chromatograph when necessary.

The output from the mass spectrometer is fed to an Adage Mass Spectrum Digitizer (6), which prints mass numbers and peak heights and supplies the timing signal to the chromatograph recorder. The conventional light beam galvanometer mass spectrum

recorder is also used, but the mass marker light is now manually controlled so that coded information can be put on the record.

Procedure

The apparatus is arranged as shown in Figure 1. However, the hydrogenator is bypassed and helium is used in place of hydrogen as carrier gas.

The helium flow rate is adjusted to 60 ml/min, and the chromatograph column oven temperature is set at 100C. The chromatograph injector block, detector oven, and all interconnecting lines between the chromatograph and spectrometer are set at 250C. Valve V-6 is opened and Valve V-5 throttled down to yield a reading of 7×10^{-6} torr on the mass spectrometer exhaust vacuum gage (VG-1A). The magnetic field is adjusted to about 3400 gauss; the scan rate, initial accelerating voltage, and scan time are adjusted to give a scan of m/e 39 to ~120 in about 30 sec. A 150-μl sample is injected into the chromatograph; upon emergence of the air peak, the temperature programmer is started at a rate of 1C/min. The galvanometer recorder on the mass spectrometer is left off; but the digitizer monitors the output, recording mass spectrometer background and printing the elapsed time in minutes on both the digitizer output tape and the chromatograph record.

When the chromatograph column temperature reaches 185C, the temperature program rate is reduced to 0.5C/min and an isothermal limit of 225C set.

As the molecular weights increase, it is necessary to increase the scanned mass range. After emergence of the 1-octene peak (approximately 60 min after the air peak), the initial mass spectrometer settings are changed to give a 30-sec m/e 50–160 scan. The settings are changed again after about 130 min to extend the scan range to m/e 190 and after about 150 min to scan to m/e 215. The latter scans require about 45 sec.

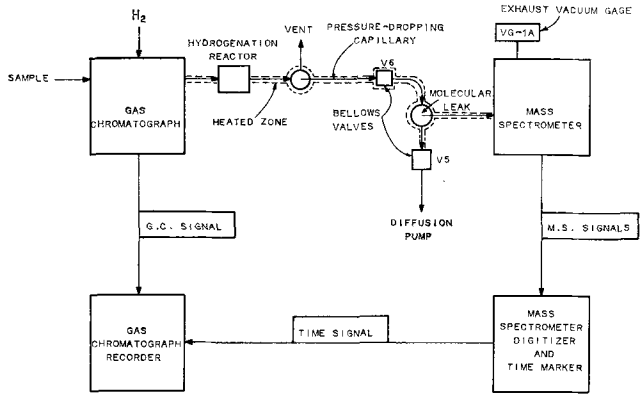

FIG. 1. Chromatograph hydrogenator-spectrometer schematic.

Gas Chromatograph-Hydrogenation-Mass Spectrometer Procedure

In order to establish the amount of unsaturation responsible for the varying degrees of hydrogen deficiency revealed by the first GCMS run, it is necessary to hydrogenate each component upon elution from the chromatograph before passing it into the mass spectrometer. This is done by the apparatus arranged as shown in Figure 1.

The hydrogenation reactor is a 15-in. by 1/8-in. stainless steel tube packed with 0.7% platinum on silica gel. It is heated to between 245C and 260C throughout the run by means of a tube furnace.

After the equipment has reached flow and temperature equilibrium, 100 μl of dimethyl disulfide is injected into the reactor through a septum at the reactor inlet. This deactivates sites on the catalyst which otherwise would cause thermal cracking. A 150-μl sample is then injected into the chromatograph. The operation is identical with the first part of the procedure, except that Valve V-5 is throttled to give a reading of 2×10^{-5} torr on the exhaust vacuum gage (VG-1A).

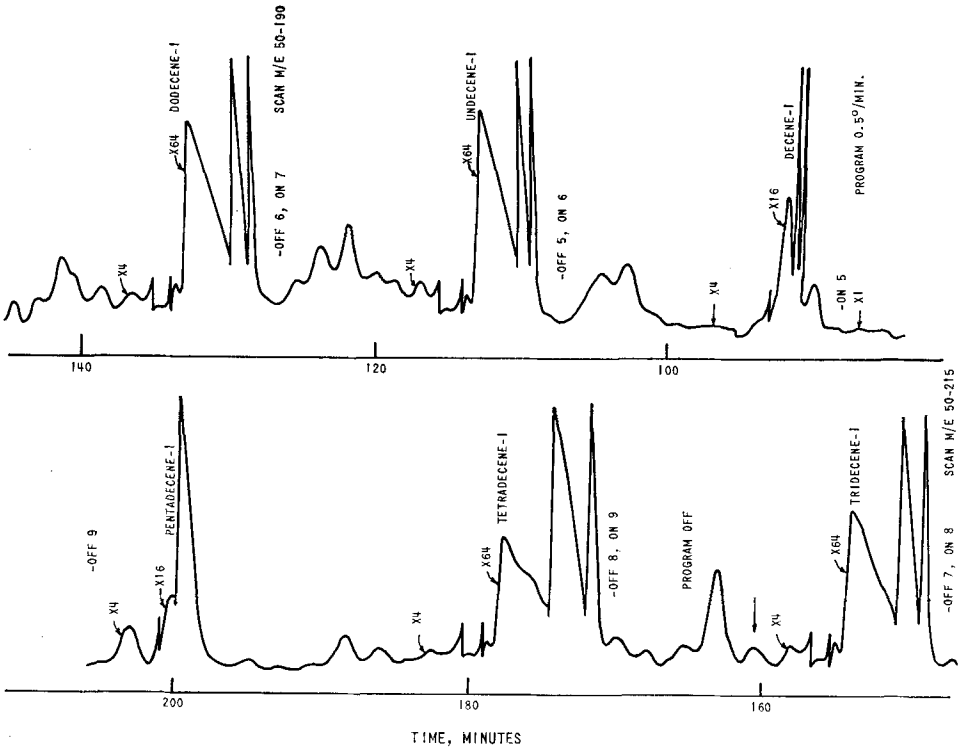

FIG. 2. Gas chromatogram of C_{11}–C_{14} Chevron Alpha Olefin.

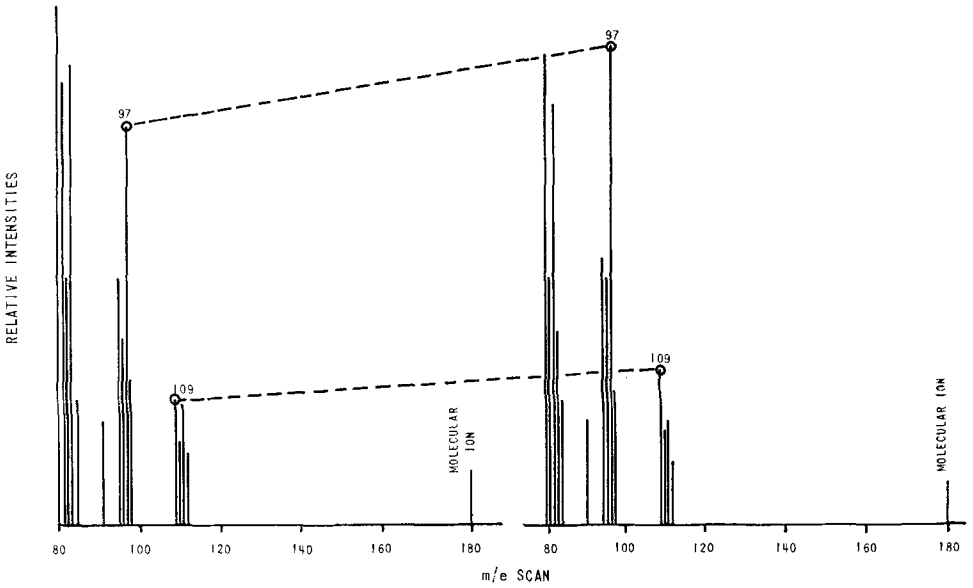

FIG. 3. Mass spectra, helium carrier.

The presence of large amounts of hydrogen or helium in the ion chamber changes the mass spectrometer fragmentation patterns. Fragment peaks at lower masses are magnified, while the molecular ion peaks are attenuated. The effect resembles that of an increase in temperature of the hydrocarbon during ionization. The fragmentation patterns are, however, still readily recognizable.

Interpretation

Mass numbers are assigned to the prominent peaks in the galvanometer spectrum by comparison with the digitizer record. Particular attention is given to those peaks, no matter how small, which are, or could be, due to molecular ions. Since the major components of the mixture, the straight chain 1-olefins, are easily identified, the region in any given section where molecular ion peaks are expected is well defined. Observation of the spectra in blocks of three to five scans generally reveals that certain molecular ion and fragment ion peaks rise and fall together, indicating a common source. In cases where some rise and others fall, the presence of two or more parent compounds in a chromatograph peak is suggested. Techniques for handling such cases have been previously discussed (4).

Once molecular weights and fragmentation patterns have been determined, the components of the mixture are identified by comparison with standard spectra from the Catalogue of Mass Spectral Data of API Project 44 or any other source of reference spectra. Since very few of the compounds of interest above C_9 are represented in collections of spectra, it is necessary in most cases to restrict indentification to compound type and molecular weight rather than to attempt a complete explication.

Assuming there are only hydrocarbons present, all compounds in the sample may be described by the general formula C_nH_{2n+Z}. Molecular weights may be calculated for paraffins knowing that they belong to the $Z = +2$ series. With the gas chromatographic column and conditions used in this analysis, the paraffins emerge just prior to the alpha olefins with the same carbon number. In the mass spectrometer record there may be overlap between the n-paraffin and alpha olefin at high carbon numbers.

Monoolefins and cycloparaffins are in the series $Z = 0$. The fragmentation patterns of the normal 1-olefins are characteristic enough for identification, but internal or branched olefins are difficult to differentiate from cycloparaffins. Any material whose spectrum shows no change in Z-series on hydrogena-

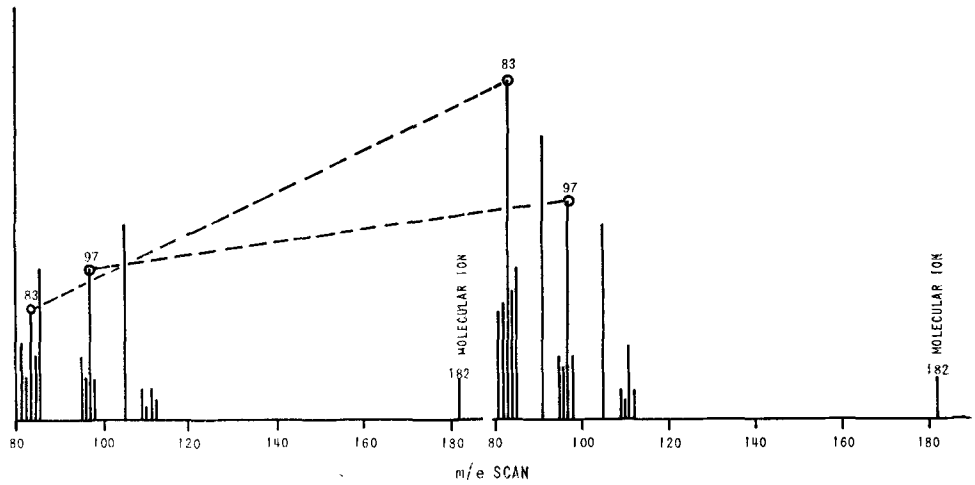

FIG. 4. Mass spectra, hydrogen carrier.

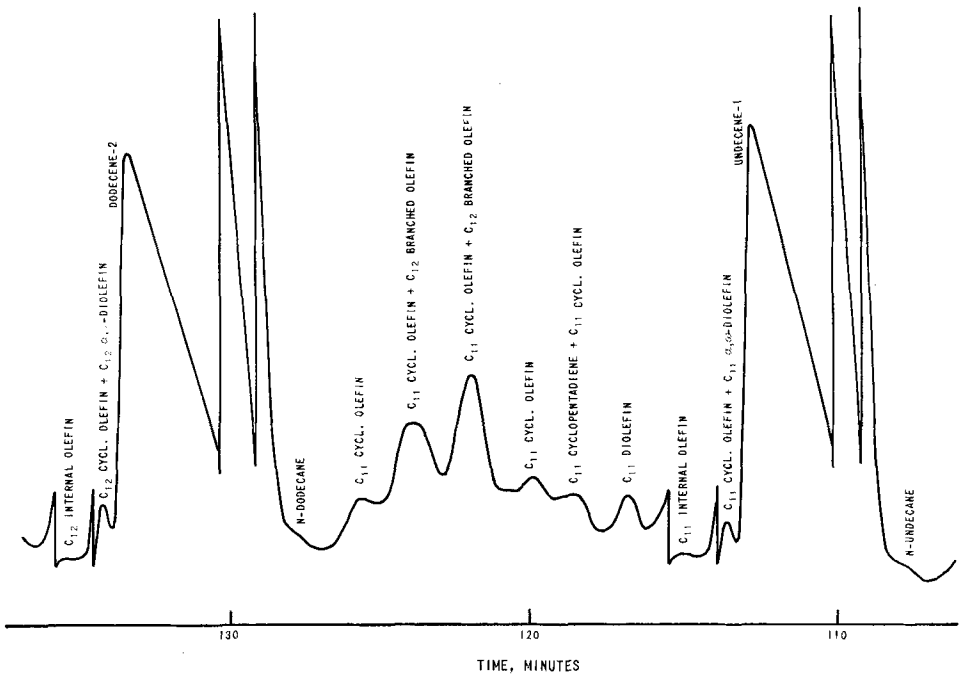

FIG. 5. C_{11}–C_{12} Segment from the gas chromatogram of C_{11}–C_{14} Chevron Alpha Olefin.

tion must be a cycloparaffin. Hydrogenatable materials in the series $Z = 0$ are olefins. Internal straight chain olefins show very little loss of CH_3 groups in the fragmentation pattern, while branched olefins, internal, and terminal do show loss of CH_3 groups.

Diolefins, cyclic monoolefins, and bicyclic saturated hydrocarbons belong to the series $Z = -2$; and these, upon hydrogenation, increase in molecular weight by 4, 2, and 0, respectively.

Molecular ions are not the only mass spectrometric features of interest in the identification of compounds as they are eluted from the chromatograph. Fragment ions are very important; and in some cases, where the molecular ion is very small or absent, they must be used for compound identification. To the first approximation, fragments in the series $Z = +1$ (m/e 57, 71, 85, 99, 113) are characteristic of the $Z = +2$ series; $Z = -1$ (m/e 55, 69, 83, 97, 111) represent the $Z = 0$ series; and $Z = -3$ (m/e 67, 81, 95, 109) indicate the $Z = -2$ series. Some specific compounds will give extra fragments that are usually in addition to those expected.

Calculations

The amount of each species present is calculated from the area under its peak in the chromatogram, assuming unit response factors for each component. When the mass spectral data indicate that there is more than one component in a chromatographic peak, the relative amount for each component is estimated from the mass spectrometer data and normalized to the weight per cent of the chromatograph peak. A table is then prepared showing the amounts, by carbon number, for each compound type present. The types are summed to give the composition of the sample.

Discussion

A sample of C_{11}–C_{14} Chevron Alpha Olefin was analyzed by GCMS alone and by GCMS with hydrogenation. Figure 2 shows the chromatographic record for the GCMS without hydrogenation. The overloading of the major components, the alpha olefins, is necessary in order to obtain useful mass spectra of the minor components. The chromatogram is labeled with the operating conditions and schedules. The peak areas were measured using a Gilliland Automatic Integrator that has been previously described (7). Unresolved peaks were separated using the minimum between them as the dividing line between the peaks; and in cases where this is not possible, the dividing line was obtained by dropping a perpendicular line from the intersection of the tangents to the inside of the slopes of the overlapping peaks (8).

Figures 3 and 4 show spectra from the GCMS without hydrogenation and with hydrogenation, respectively. The spectra were taken of a peak, indicated by an arrow in Figure 2, that emerges 160 min after the air peak. The m/e 180 peak is due to the compound under examination and corresponds to a compound in the $Z = -2$ series in the C_{13} molecular weight region (i.e., $C_{13}H_{24}$). The compound must contain either two saturated rings, one ring and one double bond, two double bonds, or one triple bond. Since there is no generalization that can be made about these spectra to differentiate the above four classes, it is necessary to examine the spectra after hydrogenation. The mass spectra taken after hydrogenation (Fig. 4) show that the molecular ion peak's mass has increased by two units to 182. Thus, the original compound must have contained only one double bond and a ring; and consequently it is identified as a C_{13} cyclic olefin.

Figure 5 shows the 1-undecene to 1-dodecene region of the above chromatogram with all of the peaks labeled. The general feature of this segment and all similar portions of the chromatogram is that many of the minor peaks in the chromatogram contain two or more unresolved components. In some cases, for example, in the unresolved α,ω-diolefin and cyclic olefin peak, the compounds can be distinguished only by hydrogenation.

Where pure compounds are available, spiking experiments are used to assist mass spectral identification. In the case of the α,ω-diolefins, the mass spectral data were supported by retention volume data ob-

TABLE I
GCMS Analysis of C_{11}–C_{14} Chevron Alpha Olefins

Compound	Per cent	Compound	Per cent
1-Hexene	Trace	n-Dodecene (internal)	0.3
		n-Dodecadiene (internal)	0.1
1-Heptene	Trace	C_{12} Cyclopentadiene / C_{12} Cyclic olefin	0.2
1-Octene	Trace	C_{13} Branched olefin	0.3
		C_{12} Cyclic olefin	0.1
1-Nonene	Trace	C_{12} Cyclic olefin	0.2
		C_{12} Cyclic olefin	0.2
n-Decane	Trace		
1-Decene	1.6	n-Tridecane	0.1
C_{10} Cyclic olefin	Trace	1-Tridecene	22.4
C_{10} Cyclic olefin	Trace	1,12-Tridecadiene / C_{13}-Cyclic olefin	0.8
C_{10} Cyclic olefin / C_{11} Branched olefin	0.2	n-Tridecene (internal)	0.2
C_{10} Cyclic olefin / C_{11} Branched olefin	0.3	C_{13}-Cyclic olefin / C_{13}-Cyclic Paraffin	0.1
		C_{13} Cyclic olefin	0.1
n-Undecane	0.1	C_{13} Cyclic olefin	0.5
1-Undecene	19.7	C_{14} Branched olefin	0.1
1,10-Undecadiene / C_{11}-Cyclic olefin	0.8	C_{13} Cyclic olefin	0.1
		C_{13} Cyclic olefin	0.1
n-Undecene (internal)	0.2		
n-Undecadiene (internal)	0.1	n-Tetradecane	0.1
C_{11} Cyclopentadiene / C_{11} Cyclic olefin	0.2	1-Tetradecene	22.4
C_{11} Cyclic olefin	0.2	1,13-Tetradecadiene / C_{14} Cyclic olefin	0.8
C_{11} Cyclic olefin / C_{12} Branched olefin	0.4	n-Tetradecene (internal)	0.2
		C_{14} Cyclic olefin	0.1
C_{11} Cyclic olefin / C_{12} Branched olefin	0.4	C_{14} Cyclic olefin	0.1
		C_{14} Cyclic paraffin	0.2
C_{11} Cyclic olefin	0.2	C_{14} Cyclic olefin	Trace
		C_{14} Cyclic olefin	Trace
n-Dodecane	0.1	C_{14} Cyclic olefin	Trace
1-Dodecene	23.1	n-Pentadecane	Trace
1,11-Dodecadiene / C_{12} Cyclic olefin	0.9	1-Pentadecene	1.5
		n-Pentadecene	0.2

tained by spiking the lower molecular weight fractions with pure α,ω-diolefins.

Table I presents the results of the GCMS analysis of C_{11}–C_{14} Chevron Alpha Olefins. Table II shows the carbon number and group-type breakdown of these GCMS data. This is a complete analysis of the C_{11}–C_{14} Chevron Alpha Olefins utilizing the identifying powers of the mass spectrometer.

TABLE II
Carbon Number Breakdown of GCMS Data from the Analysis of C_{11}–C_{14} Chevron Alpha Olefin

	C_{11}	C_{10}	C_{12}	C_{13}	C_{14}	C_{15}	Totals
1-Olefins							
Straight	1.6	19.7	23.1	22.4	22.4	1.5	90.8[a]
Branched		0.3	0.4	0.3	0.1		1.1
Internal monoolefins							
Straight		0.2	0.3	0.2	0.2	0.1	1.0
Naphthenic	0.3	1.2	0.9	1.2	0.6		4.2
Diolefins							
Alpha, Omega		0.4	0.5	0.5	0.5		1.9
Others		0.2	0.2				0.4
Saturates							
Paraffins	Trace	0.1	0.1	0.1	0.1	Trace	0.4
Cycloparaffins				Trace	0.2		0.2
Totals	1.9	22.1	25.5	24.7	24.1	1.6	

[a] C_9–C_9 1-olefins amounted to about 0.1% in this sample and are included in this total but not in the body of the table.

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REFERENCES

1. Poe, R. W., E. F. Kaelble, JAOCS *40*, 347 (1963).
2. Hachenberg, Von H., J. Gutberlet, Brenn. Chemie *5*, 133 (1964).
3. Gohlke, R. S., Anal. Chem. *31*, 535 (1959).
4. Lindeman, L. P., J. L. Annis, Anal. Chem. *32*, 1742 (1960).
5. Lindeman, L. P., Preprints of the Division of Petroleum Chemistry, American Chemical Society, Atlantic City, Sept. 9–14, 1962.
6. Klaver, R. F., and R. M. Teeter, ASTM Committee E-14 in San Francisco, May 19–24, 1964.
7. Gas Chromatograph (Ed. Nathaniel Brunner and Others), Academic Press, New York, 1962, p. 349.
8. Pecsok, R. L., in "Principles and Practice of Gas Chromatography" R. L. Pecsok, Ed., John Wiley and Sons, New York, 1959, p. 145 ff.

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Selective Hydrogenation of Soybean Oil with Sodium Borohydride-Reduced Catalysts[1]

SAMBASIVARAO KORITALA and H. J. DUTTON, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

The reaction of metallic salts in aqueous solution with sodium borohydride produces finely divided metals that are catalytically active for hydrogenation. Salts of nickel, cobalt, palladium and platinum give active catalysts for the selective hydrogenation of soybean oil. Iron and silver salts, when reduced with sodium borohydride, show no activity at 200C and atmospheric hydrogen pressure. The cobalt catalyst produces the least amount of stearate. Incorporation of palladium, platinum, copper or chromium up to 2% enhance the activity of the nickel catalyst. Copper and chromium salts, when reduced together, form catalysts that hydrogenate linolenyl groups in soybean oil seven times more rapidly than linoleyl groups. No stearate formation is observed with these binary catalysts.

[1] Presented at the AOCS Meeting, Houston, April 1965.
[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

Introduction

THE REDUCTION OF NICKEL salts from aqueous or alcoholic solutions with alkali metal borohydrides produces finely divided metal that possesses catalytic activity for hydrogenation reactions (2,15,16). A sodium borohydride-reduced nickel had excellent "reuse properties" for the hydrogenation of safrole (16). This catalyst contained boron in addition to nickel (15,16). It was suggested that the catalyst corresponds to Ni_2B; later studies indicated the presence of Ni_3B (10). Other catalysts prepared with sodium borohydride included cobalt, copper, platinum, palladium, rhodium, ruthenium, osmium and irridium (3,15). The first 5 of these catalysts also contained varying amounts of boron (15–17).

The simplicity and rapidity with which catalysts can be produced with borohydride have encouraged us to prepare several catalysts and to evaluate their selective hydrogenation characteristics for the linolenyl ester groups in soybean oil. Also included were binary copper-chromium oxide catalysts, which are extremely selective for linolenate hydrogenation in soybean oil.