disabling the pen drive during the interanalysis intervals, and by reversing the recorder to make zero the circumference of the chart.

The analyzer should be applicable on many organic liquid and gas streams. The principal requirements are that the sample have adequate transmission at 3.05 microns and not contain components, other than water, which will react with calcium carbide.

ACKNOWLEDGMENT

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Determination of Aliphatic Formates by Near Infrared Spectrophotometry

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▶The near infrared spectra of aliphatic formates have a well defined band at 2.15 microns. Comparisons of spectra of formates and deuterated formates indicate that the band is a combination of formyl C—H and C═O stretching vibrations. The feasibility of utilizing the 2.15-micron band for determining aliphatic formates is described.

NEAR INFRARED SPECTROPHOTOMETRY is usually concerned with overtones of C—H, N—H, and O—H fundamentals. Frequently combination bands are of sufficient intensity to be of analytical value. The authors recently have reported (*3*) that the combination band at 2.21 microns of formyl C—H and C═O vibrations in aromatic aldehydes may be used for quantitative analysis. Other classes of compounds that might be expected to show similar combination bands are aliphatic aldehydes, formamides, and formate esters. This work continues the study of combination bands in the near infrared region with the determination of aliphatic formate esters.

Goddu (*1*, *2*) reported that the presence of absorption bands in the 2.1- to 2.2-micron region is due to the formate structure. In the present work several aliphatic formate esters were examined and two bands at 2.15 and 2.07 microns were found to be characteristic of formates. Since esters of higher acids show weak absorption in this region, it is possible to utilize these two bands for quantitative determinations. Several mixtures of formate and acetate esters were analyzed with the result that the 2.15-micron band gave more precise values than the 2.07-micron band.

EXPERIMENTAL

Spectrophotometer. A Beckman Model DK-2 recording spectrophotometer was used for near infrared measurements. For quantitative work the instrument was set at scanning speed 20, period 0.2, with sensitivity adjusted to maintain a slit width of 0.029 mm. at 2.15 microns. Quartz cells of 1-cm. cell path were used.

Infrared measurements for Table I were made with a Beckman infrared spectrophotometer Model IR-4 with sodium chloride optics. The instrument settings were: gain, 6%; period, 8 seconds; scanning speed, 0.04 micron per minute (Auto In); slit schedule, selective (50 microns at 3.5 microns). The samples were run as 5% (weight volume) carbon tetrachloride solutions, using sodium chloride cells of 0.1 mm. thickness.

Solvent. Baker "analyzed" carbon tetrachloride was used without further purification.

Formate Esters. All esters were commercially available. The purity was checked by gas chromatography. Methyl formate-*d* was obtained from Merck and Co. Ltd. Montreal, Canada. Its isotopic purity was verified by nuclear magnetic resonance (NMR) spectroscopy.

Preparation of *n*-propyl formate-*d*. *n*-Propyl formate-*d* was prepared by ester interchange of methyl formate-*d* and *n*-propyl alcohol in the presence of titanium isopropoxide, and then isolated by preparative gas chromatography. The purity was confirmed by NMR spectroscopy.

The 2.15-Micron Combination Band. Aliphatic formates exhibited a strong, well defined band at 2.15 microns. With the formyl C—H frequency of formate at about 3.41 microns (2933 cm.$^{-1}$) and the C═O frequency at about 5.78 microns (1730 cm.$^{-1}$), this band was expected to be a combination of C—H and C═O vibrations. When the formyl hydrogen was replaced by deuterium, the shift of the 2.15-micron (4651 cm.$^{-1}$) band to about 2.58 microns (3876 cm.$^{-1}$) could empirically confirm the assignment. The spectra of methyl and *n*-propyl formate and their deuterated formates are shown in Figures 1 and 2. Good agreement was found between the calculated and observed absorption maxima for several representative formates (Table I). The data for methyl, ethyl, and *n*-propyl formate agree with those reported by Goddu (*1*). It was also observed that the infrared spectra of

Table I. Absorption Data of Aliphatic Formates

	(A), Formyl C—H, Cm.$^{-1}$	(B), C═O, Cm.$^{-1}$	Sum of (A) and (B), Cm.$^{-1}$	Observed Maximum		Absorptivity, Liter/Mole-Cm.
				Cm.$^{-1}$	μ	
Methyl formate	2939	1736	4675	4662	2.145	0.86
Ethyl formate	2934	1730	4664	4655	2.148	1.04
n-Propyl formate	2933	1730	4663	4653	2.149	1.01
Isobutyl formate	2937	1730	4667	4655	2.148	0.93
n-Hexyl formate	2933	1730	4663	4653	2.149	0.94

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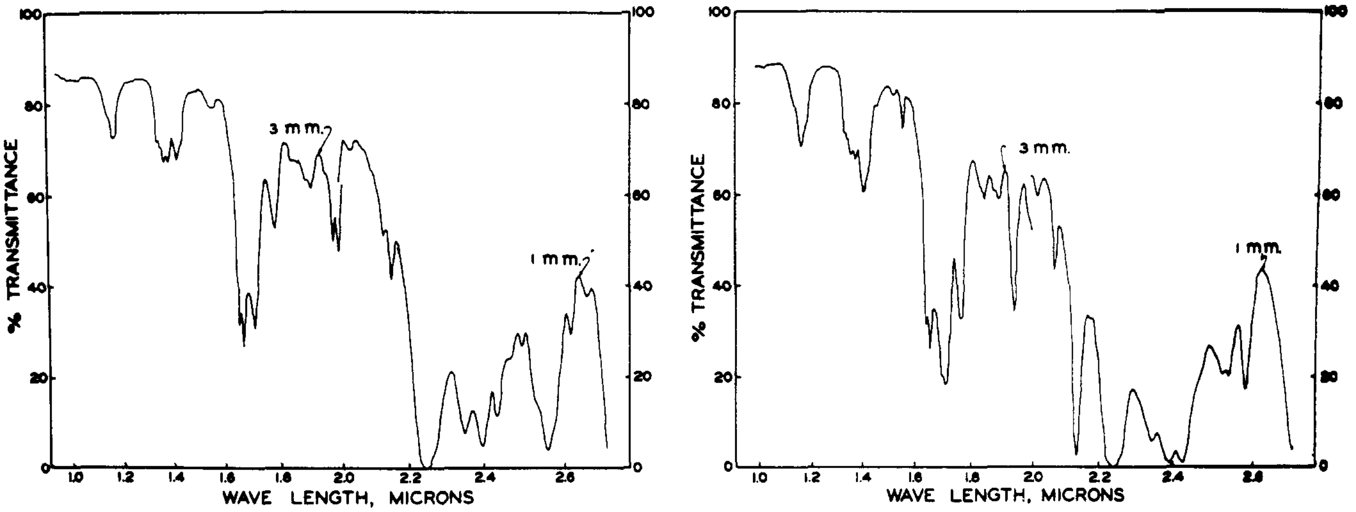

Figure 1. Left, methyl formate-*d*; right, methyl formate

Samples were run "as is" vs. air; cell paths are shown as indicated

methyl and *n*-propyl formate-*d* showed a split of C═O band at 1735 cm.$^{-1}$ and 1700 cm.$^{-1}$ while formate had only one well defined band with a peak at 1730 cm.$^{-1}$

Carbon tetrachloride solutions ranging from 0.06 mole per liter to 0.72 mole per liter were measured for the Beer's law test of the 2.15-micron band. A linear relationship between absorbance and concentration was obtained.

Determination of Formates. Synthetic mixtures of several formates and their corresponding acetates were measured to test the analytical feasibility of the 2.15-micron band. Carbon tetrachloride solutions were prepared by mixing a definite amount of formate with variable amounts of acetate and diluting to 25 ml. The absorbances were compared with the values obtained from the solution containing only formate. The baseline technique was applied for the measurements, the line being drawn across the band approximately between 2.20 and 2.09 microns.

Three formate-acetate pairs—ethyl, isobutyl, and *n*-hexyl—were investigated. Each result listed in Table II is the average of three individual determinations. The relative errors of the absorbance were about 1.2%. Above a 1:1 weight ratio of acetate to formate the deviation exceeded 2%. The data indicated that the determination of formate could be made in the presence of 50% of its corresponding acetate.

Aromatic absorptions caused appreciable interference. The authors tried to analyze benzyl formate-benzyl acetate mixture and found that simple measurements were not satisfactory. Although aromatic formates showed an absorption peak at 2.15 microns, contributions due to the overlapped aromatic C—H absorptions must be considered to obtain reliable analytical results. Terminal methylene groups

Table II. Determinations of Formate in Formate-Acetate Mixtures

Concentration, G./25 Ml. of CCl_4		Absorbance at 2.15 μ	Deviation of Absorbance, %
Formate	Acetate		
A. Methyl Ester			
0.8820	0	0.506	...
0.8820	0.0927	0.513	1.38
0.8820	0.4635	0.499	1.38
0.8820	0.9274	0.506	0
B. Isobutyl Ester			
0.8750	0	0.307	...
0.8750	0.0865	0.304	0.98
0.8750	0.4325	0.304	0.98
0.8750	0.8650	0.303	1.30
C. *N*-Hexyl Ester			
0.8940	0	0.254	...
0.8940	0.0809	0.251	1.18
0.8940	0.4045	0.249	1.97
0.8940	0.8092	0.248	2.36

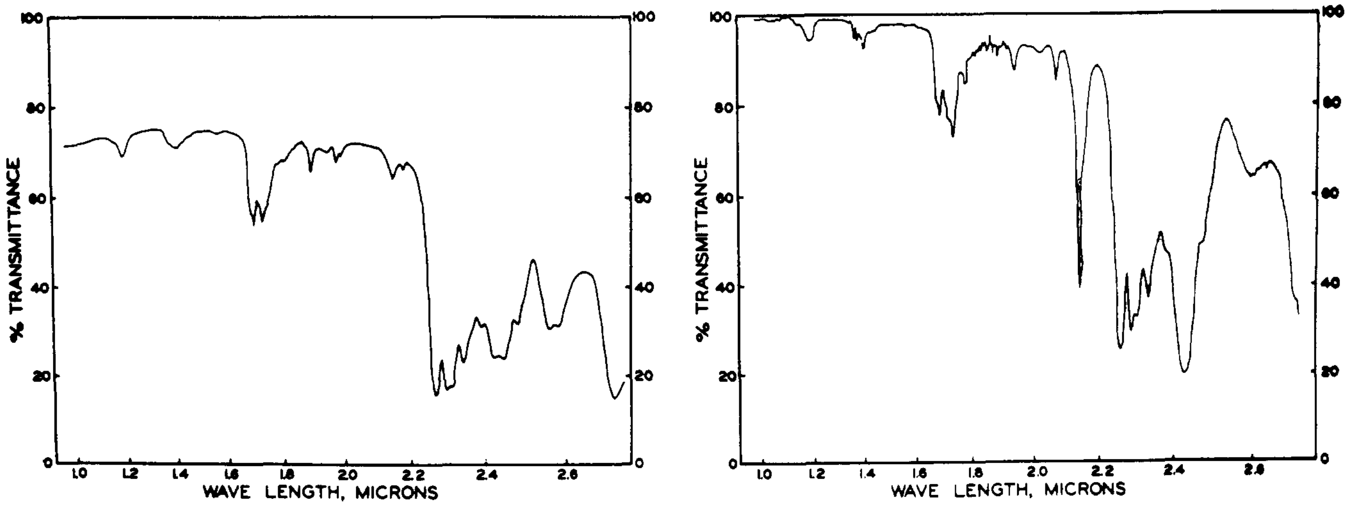

Figure 2. Left, *n*-propyl formate-*d*; right, *n*-propyl formate

Samples were run as 0.35*M* CCl_4 solution vs. CCl_4, cell paths 1 cm.

and aldehydes also interfered, and, to a lesser extent, alcohols.

The band at 2.07 microns was also characteristic of aliphatic formates. For ethyl formate, absorbance of this band followed Beer's law. The concentration range studied was 0.12 mole per liter to 0.72 mole per liter, with an absorptivity of 0.10 liter per mole-cm. This is a rather weak band, and much larger relative errors were observed—e.g., 2.47% for a mixture of 1 gram of ethyl formate and 0.5 gram of ethyl acetate in 25 ml. of carbon tetrachloride.

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Nuclear Magnetic Resonance Study of Butadiene-Isoprene Copolymers

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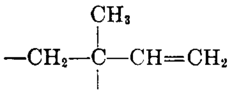
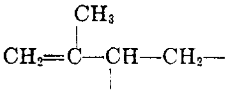
▶ Butadiene-isoprene copolymers in the molecular weight range of 100,000 to 200,000 with varying ratios of butadiene to isoprene were studied by high resolution nuclear magnetic resonance techniques. Well resolved spectra of these copolymers were obtained in carbon tetrachloride solution at room temperature, despite the high molecular weight and the high viscosities of the solutions. Absorption peak assignments were made on the basis of recorded chemical shifts. By measuring the area under each individual peak, the relative concentration of the protons in different molecular environments may be determined. The relative concentrations of the various units (with about 2 to 3% maximum error) for an experimental 1 to 1 butadiene-isoprene copolymer are presented. The method described is also applicable to polyisoprene and polybutadiene.

Since its discovery, high resolution nuclear magnetic resonance has proved to be an important tool in determining the chemical structure of molecules. However, up to the present time, relatively few articles have appeared in the literature on the application of high resolution NMR to the study of polymers. This situation may stem from the fact that very few polymers have a high enough solubility and at the same time exhibit narrow enough line width to permit a detailed analysis of their spectra. A general discussion of the application of high-resolution nuclear magnetic resonance to polymers has been given by Bovey, Tiers, and Filipovich (*1*).

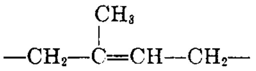
In butadiene-isoprene copolymers, butadiene and isoprene units are found in the following forms:



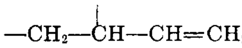
$$\text{—}CH_2\text{—}\underset{|}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{—}CH{=}CH_2 \qquad (A)$$



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{—}\underset{|}{CH}\text{—}CH_2\text{—} \qquad (B)$$



$$\text{—}CH_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH\text{—}CH_2\text{—}\ \text{(cis and trans)} \qquad (C)$$



$$\text{—}CH_2\text{—}\overset{|}{CH}\text{—}CH{=}CH_2 \qquad (D)$$

$$\text{—}CH_2\text{—}CH{=}CH\text{—}CH_2\text{—}\ \text{(cis and trans)} \qquad (E)$$

The assumption is made that secondary polymerization through double bonds in the polymer is negligible. Because of the type of polymerization used, it is unlikely that this reaction takes place to any appreciable extent.

A slight change in the relative concentrations of these units in a copolymer affects its physical properties. Hence, a reliable method of determining these relative concentrations is highly desirable for quality control of the polymer. In this work, a rapid method for the analysis of our experimental butadiene-isoprene copolymers by high resolution nuclear magnetic resonance is described. After solution, 2 to 3 hours are required for the analysis of a group of six samples.

EXPERIMENTAL

Spectra were obtained at a frequency of 60 megacycles per second with a Varian V-4302 DP-60 NMR spectrometer equipped with a 12-inch electromagnet and magnetic flux stabilizer. The temperature of the probe was maintained at 25° ± 1° C. Polymer solutions were prepared by dissolving about 5% by weight of the sample in reagent grade carbon tetrachloride. The solutions were sealed in a standard 5-mm. tube for the spectrometer with tetramethylsilane as internal standard. The frequency of the audio-oscillator employed was first calibrated at intervals of 60 cycles per second against the 60-c.p.s. power line frequency. The area under each peak may be measured either by a Varian V-3521 NMR integrator or by cutting out peak areas from the chart and weighing with an analytical balance to the nearest 0.1 mg. Peak shifts with respect to the reference peak were measured by the usual side band technique. Because of some overlapping in the peaks, the weight method was used for most of the polymers under study for best accuracy. Although the spectrometer was adjusted to avoid radio-frequency (rf) field saturation or reduce it to a minimum, the signal strength for the peaks was still great enough for accurate area measurements.

Commercial grades of synthetic polybutadienes and polyisoprenes were used as reference compounds without further purification. The natural rubber reference was purified by solution in carbon tetrachloride and centrifuging for one-half hour at 2500 r.p.m. to separate the clear solution from the undissolved gel. The pure rubber was then precipitated by adding a large volume of acetone to the clear solution. The precipitated white gum was collected and dried under vacuum. Other pure hydrocarbons used as references are listed in Table I.

RESULTS AND DISCUSSION

The spectra of butadiene-isoprene copolymers with a butadiene-isoprene ratio of 10 to 1, 4 to 1, and 1 to 1 are