Near IR Spectra of Long Chain Vinyl Derivatives[1]

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ABSTRACT

The near IR spectra of a series of compounds derived from long chain fatty acids and containing the vinyl structure were examined. These included 1-alkenes; acrylic, allyl and vinyl esters; and allyl and vinyl ethers. The bands caused by the vinyl structure were observed clearly and usually without interference. These bands consist of overtones of the fundamental C-H stretching vitrations found in the normal IR region and of combination bands. Interactions between the vinyl group and the rest of the molecule were observed by changes in location, shape and intensity of the near IR bands. Quantitative analysis for vinyl derivatives based on near IR bands is usually convenient.

INTRODUCTION

Organic compounds that contain a vinyl group are used in the preparation of polymers and adducts of commercial importance. Near IR spectroscopy is an excellent technique for identification and analysis of these organic chemicals. Analysis by near IR spectrophotometric methods is useful whether the compound is the product of a desired reaction, a byproduct, an impurity or the reactant in a polymerization.

In a study of the near IR spectra of a series of fatty acids and other compounds, Holman and Edmondson (1) reported absorption bands at 1.65, 2.12, 2.17 and 2.23 μm in compounds containing the vinyl group. The band at 1.65 μm is attributed to the first overtone of the asymmetrical C-H stretching vibration of the terminal methylene (1,2). The other three absorption bands are the result of a combination of more than one mode of vibration occurring simultaneously and are commonly referred to as combination bands.

In a study of compounds containing internal or terminal unsaturation, Goddu (3) showed that double bonds of two types could be readily detected and determined by near IR spectroscopy. Terminal methylene groups were analyzed quantitatively at 1.6 or 2.1 μm with a sensitivity of as low as 0.01% C=CH2 and a precision and accuracy of ±2%. Also, *cis* double bonds were determined at 2.14 μm with a sensitivity of about 1% -CH=CH-. In the analysis for terminal methylene or *cis* unsaturation, *trans* double bonds and saturated hydrocarbons gave no interference.

A fourth combination band at 1.3 μm and the second overtone of the C-H stretching mode at 1.11 μm have been attributed to the terminal methylene unit (4,5).

EXPERIMENTAL PROCEDURES

The vinyl compounds included in this study were either research products of this Laboratory or commercial chemicals. These compounds included 1-alkenes; acrylic, allyl and vinyl esters; and allyl and vinyl ethers. All spectra are the result of several research programs at this Laboratory.

The near IR spectra of these compounds were obtained with a Cary Model 14 spectrophotometer. The instrument parameters were: chart speed 2 in. min^{-1}, scan speed 5.0 nm sec^{-1}, slit control setting 25, slit height out, normal range limit settings 800-2400 nm. The spectra of CCl_4 solutions of these compounds were obtained in 50 and 100 mm cells; the reference beam was compensated with an equivalent cell containing CCl_4.

The intensities of the various absorption bands were calculated as molar absorptivities by standard baseline techniques. The units of intensity were expressed as liter mole^{-1} cm^{-1}.

RESULTS

The near IR region of the spectrum is primarily made up of overtones of fundamental stretching vibrations and combinations of fundamental vibrations. With long chain vinyl compounds the absorption bands of interest are overtones of the C-H stretching mode of the terminal methylene and C-H combination bands. Discussion of bands due to other parts of the molecule is limited to the influence of the vinyl group on these bands.

Vinyl C-H Combination Bands

Four C-H combination bands are observed in the near IR spectra of long chain vinyl compounds (Table I). One band is found at 2.217-2.233 μm on the side of other strong combination bands caused by the methyl and methylene units of the alkyl chain. For a series of normal 1-alkenes ranging in size from 1-hexene to 1-eicosene, this band occurs at 2.231 ± 0.002 μm (Fig. 1). With a baseline drawn between the absorption minima at 2.188 and 2.250 μm the intensity of this band is 0.83-0.93 liter mole^{-1} cm^{-1}, with an average intensity of 0.87 liter mole^{-1} cm^{-1}.

A slight shift is noted in the location and intensity of this band in allyl esters and ethers, to 2.224 μm and 0.735 liter mole^{-1} cm^{-1}. With a carbonyl group adjacent to the vinyl group, two bands are observed in this region. Long chain fatty acrylates have bands at 2.229 and 2.221 μm. Variation in intensities is considerable, the range being 0.52-1.03 liter mole^{-1} cm^{-1} for the band at 2.221 μm and 0.62-1.22 liter mole^{-1} cm^{-1} for the band at 2.229 μm.

The spectra of alkyl vinyl ethers have a smaller intensity range (0.45-0.80 liter mole^{-1} cm^{-1}). Their range in wavelength is also small, this band being found at 2.221 ± 0.004 μm. The spectra of vinyl esters of carboxylic acids also exhibit a band at 2.228 ± 0.004 μm. While the average intensity is 1.26 liter mole^{-1} cm^{-1}, the range is large (0.87-1.40 liter mole^{-1} cm^{-1}).

A second C-H combination band is reported at 2.17 μm in 1-alkenes (1). This band was observed at 2.162-2.179 μm in all the vinyl compounds except vinyl esters. In the series of *n*-1-alkenes this band was observed at 2.172 ± 0.002 μm (Table I). The absorption minima determining the baseline are 2.150 and 2.188 μm. This absorption band is weaker than the band at 2.23 μm, having an intensity of 0.14-0.23 liter mole^{-1} cm^{-1}.

While the spectrum of allyl stearate shows a slight shift in wavelength to 2.162 μm, no significant change in intensity is seen. In the long chain alkyl acrylates a weak (0.06 liter mole^{-1} cm^{-1}) band is observed at 2.168 μm. Because of its intensity, averaging 0.57 liter mole^{-1} cm^{-1}, this band is of more value in the analysis of alkyl vinyl ethers.

No band is observed at 2.17 μm in the spectra of vinyl esters of saturated carboxylic acids and saturated derivatives of oilseed fatty acids, such as vinyl 9,10-dichlorostearate. In such esters a band at 2.125-2.147 μm has a wide

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TABLE I

Combination Bands of Long Chain Vinyl Derivatives

	Normal Wavelength							
	2.22		2.17		2.11		1.34	
Compound type	λ^a	ϵ^b	λ	ϵ	λ	ϵ	λ	ϵ
1-Alkenes	2.231	0.87	2.172	0.17	2.116	0.46	1.332	0.008
Allyl esters and ethers	2.224	0.74	2.162	0.14	2.110	0.42	1.324	0.003
Acrylates	2.229 2.221	0.77 0.69	2.168	0.06	2.108	0.22	1.327	0.011
Vinyl ethers	2.221	0.67	2.173	0.57	2.099	0.15	1.324	0.009
Vinyl esters	2.228	1.26	2.138	0.16	2.097	0.13	1.324	0.006

[a] Wavelength, μm, average.
[b] Molar absorptivity, liter mole^{-1} cm^{-1}, average.

intensity range, 0.068-0.309 liter mole^{-1} cm^{-1}. However, this absorption band does not appear in the spectra of vinyl esters of polyunsaturated or oilseed fatty acids. Instead, there is a band at 2.179 ± 0.003 μm with an intensity of 0.030 ± 0.010 liter mole^{-1} cm^{-1}.

A third C-H combination band has been reported in the same region of the spectrum (1,3,5). It is found at 2.09-2.14 μm with an intensity of 0.1-0.6 liter mole^{-1} cm^{-1} (5). With normal 1-octene this band appears at 2.116 μm with an intensity of 0.5 liter mole^{-1} cm^{-1} (4). With the series of alkenes (1-hexene-1-eicosene), this band at 2.116 ± 0.003 μm is seen to be extremely uniform in intensity, with a range of 0.45-0.48 liter mole^{-1} cm^{-1} (Table I).

Apparently chain length has little effect on the combination band of allyl esters. It is found at 2.105 μm with an intensity of 0.43 liter mole^{-1} cm^{-1} in allyl acetate and at 2.110 μm with an intensity of 0.420 liter mole^{-1} cm^{-1} in allyl stearate. Ethyl acrylate reportedly exhibits this band at 2.103 μm (3) or 2.107 μm (4) with an intensity of 0.63 liter mole^{-1} cm^{-1} (3). With long chain alkyl acrylates this band is at 2.108-2.109 μm with an intensity of 0.54 ± 0.03 liter mole^{-1} cm^{-1}. A shift is reported for vinyloxy compounds (5), with this band being found at 2.08-2.12 μm with a decreased intensity to 0.2 liter mole^{-1} cm^{-1}. Our work on alkyl vinyl ethers and oilseed fatty vinyl ethers has shown this band at 2.094-2.106 μm. The average wavelength, based on 22 vinyl ethers, is 2.099 μm. The intensity of this band is 0.08-0.29 liter mole^{-1} cm^{-1}. The shift in wavelength and intensity is also reflected in the spectra of vinyl esters of carboxylic acids where this band occurs at 2.090-2.100 μm with an intensity range of 0.09-0.31 liter mole^{-1} cm^{-1}.

The fourth vinyl C-H combination band is reported (5) to be at 1.325-1.350 μm in compounds containing a terminal methylene unit and at 1.315-1.333 μm in vinyloxy compounds with an intensity of 0.02 liter mole^{-1} cm^{-1}. Our work shows that this band is found at 1.329-1.335 μm in the spectra of 1-alkenes with intensities normally less than 0.01 liter mole^{-1} cm^{-1} (Table I). Long chain alkyl acrylates exhibit a difference, having two bands in this region at 1.327 and 1.350 μm.

The decrease in wavelength with vinyloxy compounds is reflected in the spectra of alkyl vinyl ethers where this combination band appears at 1.316-1.340 μm. The lowered intensity is also observed, being 0.001-0.018 liter mole^{-1} cm^{-1}. This change is not so great with vinyl esters, the band being at 1.321-1.334 μm. The intensity is lowered to 0.002-0.008 liter mole^{-1} cm^{-1}. However, the average wavelength (1.324 μm) is common to both vinyl esters and vinyl ethers.

Vinyl C-H Stretching Overtone Bands

The asymmetric C-H stretching vibration of the terminal methylene unit results in an absorption band at 3077 cm^{-1} in 1-alkenes (6). Thus the first overtone of this band would be expected near 1.625 μm. This overtone is reported at 1.620-1.650 μ with an intensity of 0.3 liter mole^{-1} cm^{-1} (5). For the series of 1-alkenes ranging in size from 1-hexene to 1-eicosene this band is found at 1.631-1.637 μm, with an average location of 1.635 μm (Table II). The absorption band caused by this overtone is sufficiently separated from the bands due to the first overtones of the alkyl methyl and methylene units to allow its use for quantitative analysis (Fig. 1). The intensity of this band for these 1-alkenes is 0.327 ± 0.010 liter mole^{-1} cm^{-1}.

Allyl alkyl ethers have this overtone band at 1.630 μm with an average intensity of 0.25 liter mole^{-1} cm^{-1}. Allyl esters of long chain fatty acids normally have this band at

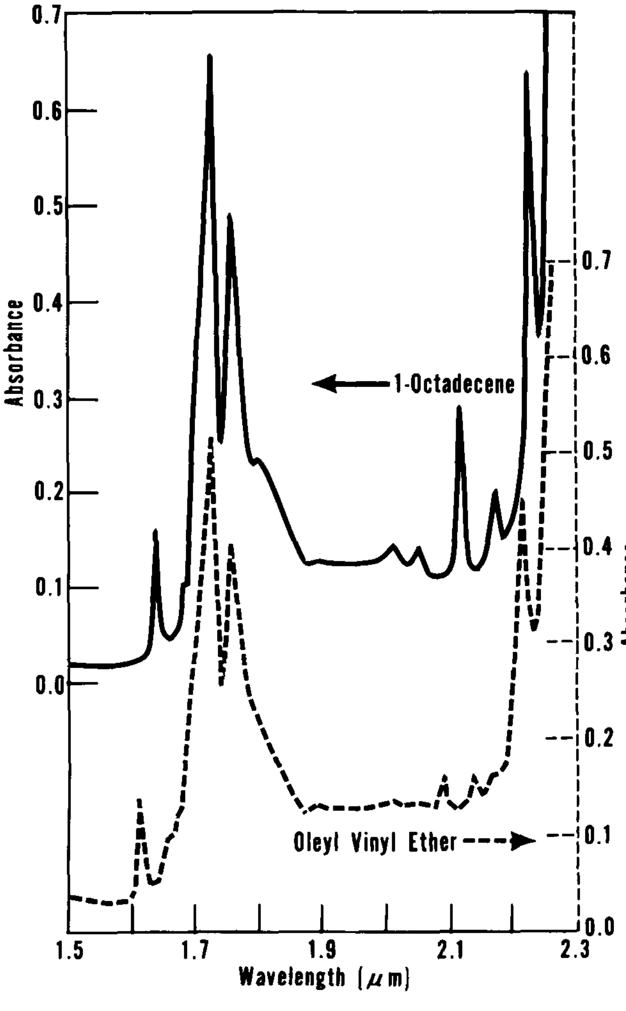

FIG. 1. Near IR spectra of 1-octadecene (0.0803 mole liter^{-1}) and oleyl vinyl ether (0.1355 mole liter^{-1}) (CCl_4 solution, 50 mm).

TABLE II

Overtones of Vinyl C-H Stretching Vibrations

	νCH[a]	2 x νCH		3 x νCH		4 x νCH	
Compound type	λ	λ[b]	ϵ[b]	λ[b]	ϵ[b]	λ[b]	ϵ[b]
1-Alkenes	3.25	1.635	0.33	1.120	0.01	0.875	0.002
Allyl esters and ethers	3.25	1.628	0.23	1.109	0.003	---	---
Acrylates	3.22	1.621	0.34	1.110	0.02	0.80	---
	3.30	1.650	0.04	1.138	0.04	0.84	---
Vinyl esters	3.24	1.615	0.43	1.105	0.01	0.921	0.008
Vinyl ethers	3.21	1.614	0.38	1.110	0.02	0.922	0.011

[a] C-H stretching vibration.
[b] Average values.

1.628 μm with an intensity of 0.227 liter mole^{-1} cm^{-1}.

Long chain fatty acrylates exhibit two bands in the first overtone region of the spectrum. These are near 1.621 and 1.650 μm with intensities of 0.34 and 0.04 liter mole^{-1} cm^{-1} on the average. These are probably caused by first overtones of asymmetric and symmetric C-H stretching vibrations of the terminal methylene. These modes would be calculated to occur near 1.608 and 1.647 μm, respectively.

The fundamental asymmetric stretching of the terminal methylene of alkyl vinyl ethers appers at 3114 cm^{-1} and its first overtone would be expected near 1.606 μm. This overtone is observed at 1.609-1.621 μm in the spectra of alkyl vinyl ethers with the average wavelength being 1.614 μm. Unsaturated fatty vinyl ethers show no shift in wavelength. With normal alkyl vinyl ethers the intensity of this band is 0.381 ± 0.02 liter mole^{-1} cm^{-1}. Vinyl esters of carboxylic acids exhibit the first overtone band at 1.610-1.618 μm with an intensity of 0.300-0.491 liter mole^{-1} cm^{-1}. It is a good band for analysis appearing at 1.615 μm for the normal vinyl ester with an average intensity of 0.429 liter mole^{-1} cm^{-1}. No significant shift is observed in either wavelength or intensity when unsaturation is present as in fatty acids.

A second overtone of the asymmetric C-H stretching of the terminal methylene would be expected near 1.08 μm. In 1-alkenes (C_6H_{12} to $C_{20}H_{40}$) this band is observed at 1.118-1.124 μm as a very weak band (ϵ = 0.004-0.018 liter mole^{-1} cm^{-1}). Allyl stearate has this band at 1.109 μm with an intensity of 0.003 liter mole^{-1} cm^{-1}. As noted in the first overtone region, two weak bands are observed in the spectra of alkyl acrylates at 1.110 and 1.138 μm.

Alkyl vinyl ethers exhibit this band at 1.1000-1.1324 μm with an intensity of 0.014-0.025 liter mole^{-1} cm^{-1}. The normal wavelength is 1.1099 μm and the normal intensity 0.018 liter mole^{-1} cm^{-1}. No significant difference was noted between long chain saturated and unsaturated vinyl ethers. The second overtone band is seen at 1.1029-1.1059 μm in the spectra of vinyl esters. Its intensity is 0.0045-0.0081 liter mole^{-1} cm^{-1}. The average location and intensity are 1.1046 μm and 0.0058 liter mole^{-1} cm^{-1}.

The third overtone of the C-H stretching vibration has been reported at 0.878 μm in the spectra of 1-hexene and 1-dodocene (2). In the near IR spectra of 1-alkenes ranging from 1-hexene to 1-eicosene the location of this band is 0.875-0.900 μm. This band is very weak, having an intensity of only 0.002 liter mole^{-1} cm^{-1}. Very weak absorptions at 0.80 and 0.84 μm are also found in the alkyl acrylate spectra.

This overtone band appears at 0.880-0.928 μm in alkyl vinyl ethers. Vinyl esters of carboxylic acids show a band at 0.9147-0.9265 μm. The average wavelengths are 0.9219 and 0.9206 μm for vinyl ethers and vinyl esters. While still very weak, this band is stronger than that of 1-alkenes being 0.011 liter mole^{-1} cm^{-1} in vinyl ethers and 0.008 liter mole^{-1} cm^{-1} in vinyl esters.

Influences of Other Functional Groups

The principal absorption bands in the near IR spectra of any long chain compound result from the methyl and methylene units of the alkyl chain. The first overtones of the C-H stretching vibration of the methyl group are at 1.658 and 1.706 μm, but are not noticed as distinct peaks in alkyl chains of great length. The methylene unit's overtones at 1.724 and 1.763 μm are noteworthy in long chain compounds. These overtones are sufficiently separated from the corresponding overtone of the vinyl group to permit quantitative analysis (Fig. 1).

The vinyl C-H combination band at 2.23 μm is not suitable for quantitative analysis because of combination bands of the methyl (2.260 μm) and methylene (2.304 and 2.347 μm) group. The strength of these bands in long chain vinyl compounds decreases sensitivity of the 2.23 μm band and makes its use as a quantitative band unsatisfactory. The influence of these bands is shown in alkyl vinyl ethers, for example, in which the C-H combination band at 2.22 μm has a baseline corrected intensity of 0.67 liter mole^{-1} cm^{-1} but an intensity of 1.345 liter mole^{-1} cm^{-1} when only corrected for the solvent absorption.

The vinyl C-H combination bands at 2.11 and 217 μm remain significantly unaffected by these combination bands of the alkyl chain (Fig. 1).

Internal unsaturation in the long chain vinyl compound does not interfere with any of the bands due to the vinyl group. *Trans* unsaturation has no significant absorption band in the near IR. At 2.14 μm *cis* unsaturation does exhibit a combination band (Fig. 1). This band is observed at a point in between the vinyl C-H combination bands at 2.11 and 2.17 μm. Quantitative analysis for *cis* unsaturation in vinyl derivatives may be performed on the basis of this band. The first overtone of the *cis* C-H stretching mode is observed at 1.677 μm as a weak band, which also does not interfere with the vinyl C-H stretching overtone band.

In the near IR spectra of the vinyl compounds containing a carbonyl group, overtones of the carbonyl-stretching mode are observed. The first overtone of this mode is near 2.9 μm, outside the near IR region. The second overtone of the carbonyl-stretching vibration of esters results in bands at 1.90 and 1.95 μm (1). Allyl stearate exhibits these bands at 1.890 and 1.935 μm with intensities of 0.054 and 0.032 liter mole^{-1} cm^{-1}, respectively. In alkyl acrylates these bands are at 1.894 and 1.950 μm with average intensities of 0.098 and 0.050 liter mole^{-1} cm^{-1}.

Vinyl esters exhibit one of these bands at 1.950-1.960 μm and the second at 1.913-1.924 μm. The average locations are 1.954 and 1.918 μm with intensities of 0.006 and 0.036 liter mole^{-1} cm^{-1}, respectively.

The third overtone of the carbonyl-stretching mode is observed as a weak band at 1.432, 1.417 and 1.324 μm, respectively, for acrylates, vinyl esters and allyl esters. Fourth overtones of this mode occur at 1.167, 1.109 and 1.105 μm in the spectra of acrylates, allyl esters and vinyl esters.

Analysis of alkyl vinyl ethers for the amount of alcohol is easily accomplished by the first overtone of the O-H stretching mode at 1.407 μm with an average intensity of 1.86 liter mole^{-1} cm^{-1}. Neither it not the other alcohol bands at 2.050 and 0.970 μm interfere with vinyl bands.

The first overtone of the C-H stretching mode of the methylene in epoxy compounds, such as vinyl epoxystearate, is at 1.656 μm, with an average intensity of 0.16 liter mole^{-1} cm^{-1}, between the C-H overtones of the vinyl group and those of the alkyl chain. Its combination band is at 2.138 μm with no interference with the vinyl bands at 2.11 and 2.17 μm.

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