IR Spectra of Long Chain Vinyl Derivatives[1]

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Abstract

Differences in their IR spectra are used to identify and analyze compounds containing a monosubstituted ethylenic (vinyl) group. Variations in location, shape and intensity of the various bands due to this structure were studied. Although previous work was briefly reviewed, emphasis was on new information obtained from IR spectra of long chain vinyl compounds related to vegetable oils, including 1-alkenes, acrylic esters, allyl esters and ethers, vinyl esters, vinyl ethers and vinyl ketones. In IR spectra of long chain (C_{10}–C_{18}) vinyl compounds bands caused by the vinyl structure show clearly and, usually, without interference. These bands consist of stretching vibrations of the vinyl olefinic bond and the three vinylic C–H bonds, and of in-plane and out-of-plane deformations of the C–H linkages. Since the vinyl group and neighboring groups influence one another, the interactions of vinyl groups with carbonyl groups and single C–O bonds, as in esters and ethers, were investigated.

Introduction

Many chemical compounds containing a monosubstituted ethylenic (vinyl) structure are commercially important in the preparation of polymers and adducts. These compounds offer a prime example of how IR spectroscopy can differentiate between compounds with overall structural differences by identifying absorption bands due to a common functional group. IR spectroscopy is useful in the identification and analysis of vinyl compounds whether they are the product, byproduct, an impurity or the reactant in a polymerization. Fundamental and overtone vibrations of the vinyl group provide a series of identifying absorption bands throughout the IR region of the spectrum. This paper reports IR data on a variety of vinyl compounds either from commercial sources or prepared from vegetable oils at the Northern Laboratory (Table I), it relates this information to that obtained by others on short chain vinyl compounds. All the information on long chain vinyl compounds is new and may be helpful to others.

Methods

The IR spectra from 4000 to 625 cm^{-1} were obtained with a Beckman model IR-8 spectrophotometer. The instrumental parameters were chosen for optimal signal noise level and resolution for this instrument. The normal settings were: slow scan speed (25 min), balance 0, gain 6, slit width programmed, slit control setting 0. With certain compounds the spectra from 650 to 200 cm^{-1} were obtained with a Perkin-Elmer model 621 spectrophotometer.

The grating monochrometer in these instruments permits a resolution of 2 cm^{-1}, a critical factor in the study of the carbon-hydrogen (C–H) stretching region. Normally, the C–H stretching modes are not resolved in spectra run upon instruments with prism monochromators.

TABLE I

Vinyl Compounds Examined

Compound type	Number
n-1-Alkenes	13
3-Substituted-1-alkenes	10
1,3-Alkadienes	14
Styrenes	14
Vinyl ketones	5
Alkyl acrylates	21
Allyl esters	11
Allyl ethers	9
Vinyl esters	42
Vinyl ethers	40

Spectra suitable for qualitative analysis were obtained on thin films and mulls of the vinyl compounds. Mulling agents were mineral oil and Fluorolube. Quantitative analyses of spectra from 4000 to 625 cm^{-1} were run in CS_2 and CCl_4 and below 625 cm^{-1} in *n*-hexane. Intensities of the absorption bands were calculated by a baseline technique and are expressed as 1 mole^{-1} cm^{-1}.

Results

Because all the vinyl compounds studied in this series contain other functional groups, their spectra are discussed by specific IR active vibrations.

Vinyl C=C Stretching Vibration

The absorption band caused by this vibration is reported to be at 1639–1645 cm^{-1} for 1-alkenes (1,2). Spectra obtained on a series of normal 1-alkenes from 1-hexene to 1-eicosene exhibited this band over a narrow frequency range (Table II) as a sharp, fairly strong singlet near 1638 cm^{-1} (Fig. 1) with an average intensity of 32 1 mole^{-1} cm^{-1} in CCl_4. Chain length had little influence on either the location or intensity of this band. Branching of the alkyl chain either α or β to the vinyl group caused a slight shift in wave number. With an aromatic, carbonyl or another olefinic group β to the vinyl group, no significant shift in location was noted. When these groups were α to, and conjugated with, the vinyl group, this band was split and the location shifted. If the vinyl group was conjugated with a second olefinic group, as in a Δ1,3-diene configuration,

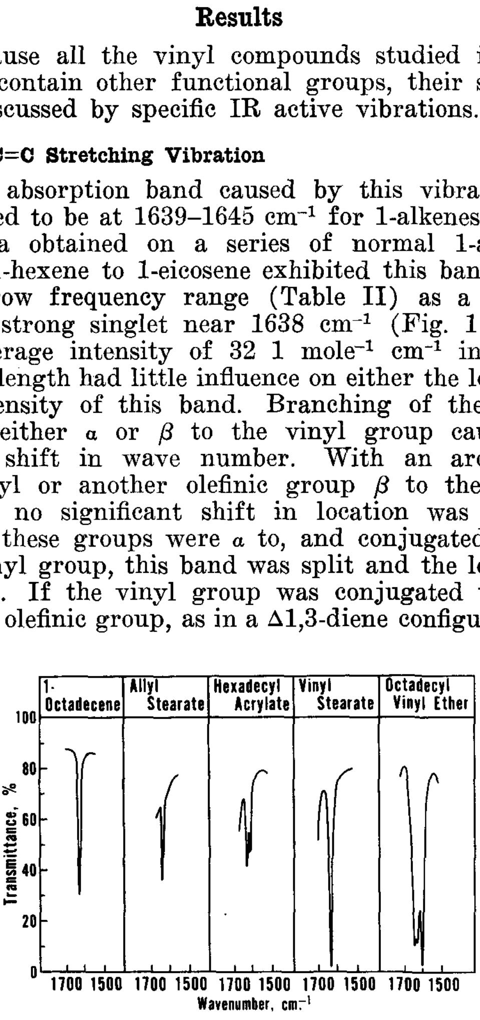

FIG. 1. Vinyl C=C stretching region (pure compound vs. air, 0.015 mm path length).

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[1] Presented at the AOCS Meeting, New York, October 1968.
[2] No. Market. Nutr. Res. Div., ARS, USDA.

TABLE II

Vinyl C = C Stretching Vibration

Compound		ν Range[a]	ν Normal
n-1-Alkenes		1634–1642	1638
Branched-chain 1-alkenes		1638–1645	1642
1,3-Alkadienes	all	1650–1669	1653
	1,3-*trans*	1616–1629	1622
	1,3-*cis*	1600–1608	1604
Styrenes		1625–1635	1631
		1597–1605	1601
Vinyl ketones		1650–1653	1653
		1616–1620	1616
Alkyl acrylates		1625–1640	1631
		1610–1625	1614
Allyl esters		1639–1642	1640
Allyl ethers		1640–1648	1644
Vinyl esters		1638–1642	1640
Vinyl ethers		1637–1653	1644
		1625–1640	1631
		1600–1620	1605

[a] ν, Wave number.

one of the bands appeared near 1653 cm^{-1} while the second depended upon configuration of the Δ3 bond and was near 1622 cm^{-1} with a *trans* olefin and near 1604 cm^{-1} with a *cis* olefin. Conjugation with an aromatic ring system, as in styrenes, shiffted these bands to 1601 and 1631 cm^{-1}.

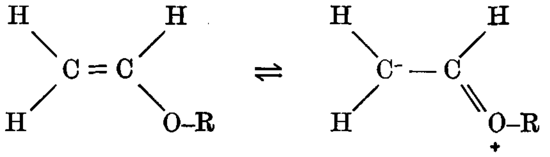
Two types of compounds were studied in which the vinyl group was conjugated with a carbonyl group: vinyl ketones and acrylates. For vinyl ketones a band due to the s-*cis* conformation has been reported in the 1610–1625 cm^{-1} region (3–5) and at 1615–1646 cm^{-1} (3,4) for the s-*trans* conformation. The vinyl ketones examined exhibited bands near 1616 and 1653 cm^{-1}.

The same isomerically influenced C = C stretching bands are found in the spectra of long chain alkyl acrylates (Fig. 1) near 1631 and 1614 cm^{-1} with intensities of 39 and 23 1 $mole^{-1}$ cm^{-1}, respectively. Earlier literature (2) reported these bands at 1638 ± 2 cm^{-1} and 1622 ± 2 cm^{-1} with intensities of 38–55 and 30–50, respectively. Acrylic acid shows much stronger bands at 1631 and 1611 cm^{-1} with intensities of 90 and 70, respectively.

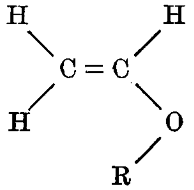
Long chain allyl esters exhibit a single peak for the C = C stretching mode near 1640 cm^{-1} with an intensity of near 20 1 $mole^{-1}$ cm^{-1}. Allyl acrylate exhibits bands at 1634 and 1613 cm^{-1} with respective intensities of 30 and 20. Allyl ethers show an average wave number of 1644 cm^{-1} with an average intensity of 16.

Compared to 1-alkenes, the spectra of most vinyl esters of carboxylic acids show no significant shift with the band at 1640 ± 2 cm^{-1}, but a significant increase in intensity to 160 1 $mole^{-1}$ cm^{-1} in CCl_4 is noted (6). Shifts from this narrow region are observed only with vinyl esters of formate, acetate and polyhydroxystearate and with those esters that have unsaturation or substitution α to the carbonyl unit.

With alkyl vinyl ethers a triplet is normally observed in the olefinic double bond stretching region. These bands are considered by some to result from rotational isomerism (7–9). Others (10,11) believe that the rotational isomer's C = C stretching mode is influenced by a Fermi-type resonance with an overtone of a C–H out-of-plane deformation (2 × 810 cm^{-1}). The strongest band ($\epsilon \sim 120$ 1 $mole^{-1}$ cm^{-1}) of the triplet is found near 1605 cm^{-1}. This band is attributed to a resonance-stabilized planar s-*trans* conformation.



This system causes a weakened double bond character and a shift in location, as well as an increase in intensity compared with 1-alkenes. With most vinyl ethers this peak is uniformly located. Only those with electron withdrawing groups, which tend to reduce this resonance, increase the wave number of the band. The solvent influences intensity greatly. Average values of 122, 134 and 194 1 $mole^{-1}$ cm^{-1} were obtained for long chain alkyl vinyl ethers in CCl_4, CS_2 and *n*-hexane, respectively. *n*-Alkyl vinyl ethers show a second, somewhat weaker (70 1 $mole^{-1}$ cm^{-1}) band near 1631 cm^{-1}. Based upon steric studies and comparisons with other vinylic C = C stretching vibrations, this band is attributed to a *cis* planar conformation



A third band occurred in this region near 1644 cm^{-1}. This band is normally weaker than the other two, often appearing as a shoulder or weak blip on the side of the 1631 cm^{-1} band.

In spectra of vinyl compounds at longer path lengths (⩾0.025 mm) or with more concentrated solutions, the first overtone of the C = C stretching mode is observed in the 3260–3360 cm^{-1} region. It is normally found near 3300 cm^{-1} with an intensity of 0.7 1 $mole^{-1}$ cm^{-1} in 1-alkenes and near 3330 and 3360 cm^{-1} in allylic and acrylic compounds. Alkyl vinyl ethers have two bands at 3260 and 3370 cm^{-1} with respective intensities of 1.0 and 0.5. The overtone is near 3314 cm^{-1} in the spectra of vinyl esters with an intensity of 2 1 $mole^{-1}$ cm^{-1}.

C-H Stretching Vibration

There are three possible C–H stretching vibrations attributable to the vinyl group: the asymmetric and symmetric stretchings of the terminal methylene and the stretching of the C–H bond of the olefinic methine. The asymmetric stretching mode is reported (1) at 3095–3075 cm^{-1}, the symmetric mode at 2980–3010 cm^{-1} (12) and the methine stretching mode at 3040–3010 cm^{-1} (1). In the IR spectra (Fig. 2) of long chain

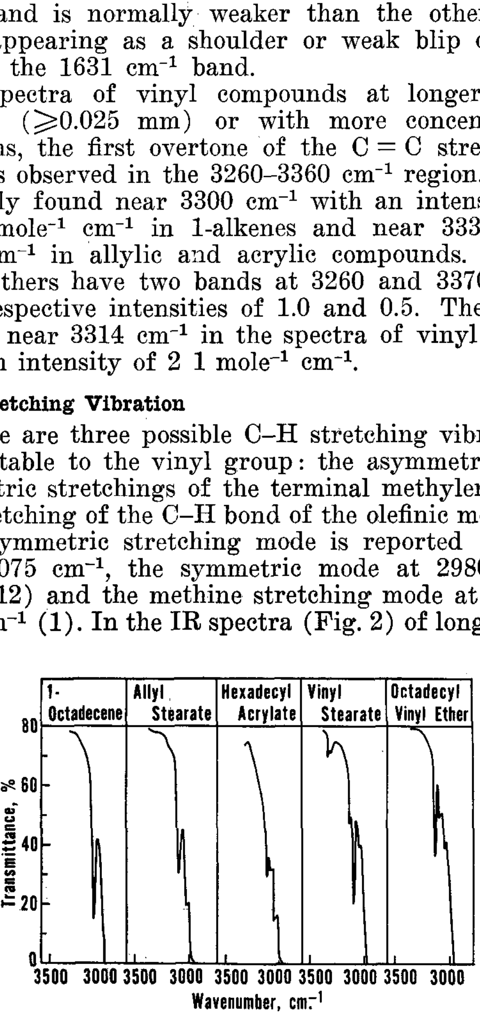


FIG. 2. Vinyl C–H stretching region (pure compound vs. air, 0.10 mm path length).

TABLE III

Vinyl C–H Stretching Vibrations

Compound	$\nu \overset{a}{=} CH_2$[a]		$\nu = CH-$[b]		$\nu \overset{s}{=} CH_2$[c]	
	Range	Normal	Range	Normal	Range	Normal
1-Alkenes	3077–3086	3077	3030–3040	3035	2985–3003	2996
3-Substituted-1-alkenes	3077–3106	3096	3010–3040	3020	2980–3005	2990
3,3-Disubstituted-1-alkenes	3095–3125	3113	3010–3049	3030	2980–3010	3000
Allyl ethers	3067–3077	3077	3012–3021	3012	2980–3000	2985
Allyl esters	3067–3096	3086	3012–3040	3012	2985–3003	2985
Acrylic esters	3096–3125	3104	3067–3077	3072	3030–3050	3036
Vinyl ethers	3098–3125	3116	3060–3078	3073	3000–3050	3049
Vinyl esters	3106–3125	3117	3086–3106	3096	3030–3049	3035

[a] $\nu \overset{a}{=} CH_2$, asymmetric C–H stretching of $=CH_2$.
[b] $\nu = CH-$, C–H stretching of $=CH-$.
[c] $\nu \overset{s}{=} CH_2$, symmetric C–H stretching of $=CH_2$.

normal 1-alkenes the asymmetric $=CH_2$ stretching mode (Table III) predominates in this region with an average intensity of 28 1 mole^{-1} cm^{-1}. The absorptions of $=CH-$ and $=CH_2$ symmetric C–H stretching at 3035 and 2996 cm^{-1} are weak peaks between the $=CH_2$ asymmetric peak and the long chain methyl and methylene's C–H stretching peaks. Substitution *a* to the vinyl group has an effect on the vinyl's C–H stretching bands. This effect is more pronounced in the asymmetric $=CH_2$ stretching mode, where an average shift of 19 cm^{-1} occurs for a single alkyl substituent on the 3 position and 36 cm^{-1} for a disubstituted compound. A single methylene unit between the branching and the vinyl group, 4-substituted-1-alkenes, provides sufficient isolation to bring the band locations back to normal.

No shift is observed in the $=CH_2$ asymmetric stretching band's location of allyl ethers; however, the other two modes decrease slightly in wave number. Slight shifts in wavelength and intensity are noted for these bands in the spectra of allyl esters of long chain acids. The intensity of the asymmetric $=CH_2$ mode is approximately half that for a comparable chain length 1-alkene.

Location of the C–H stretching modes shifts significantly in long chain alkyl acrylates. A similar shift is reported for methyl acrylate (13). While there is a noticeable decrease in the intensity of these bands, they are more pronounced in the spectra of the acrylates than they are in that of similar chain length 1-alkenes (Fig. 2). The C–H stretching modes of vinyl ketones occur in the same range.

The three bands are quite distinct in the spectra of alkyl vinyl ethers. The asymmetric $=CH_2$ stretching mode at 3116 cm^{-1} has an average intensity of 13 1 mole^{-1} cm^{-1}; the symmetric mode, 12 1 mole^{-1} cm^{-1} while the intensity of the $=CH-$ stretching mode is 8 1 mole^{-1} cm^{-1}.

Vinyl esters of carboxylic acids have a distinctive C–H stretching region because the $=CH-$ peak near 3096 cm^{-1} predominates the region (6) with an intensity of 15 1 mole^{-1} cm^{-1} and is flanked by the asymmetric and symmetric stretching modes of the $=CH_2$ at 3117 and 3035 cm^{-1} with average intensities of 5 and 8 1 mole^{-1} cm^{-1}, respectively.

Compounds containing two different types of vinyl groups, such as vinyl acrylate, have the distinctive C–H stretching peaks of both vinyl groups.

C-H In-Plane Deformations

Three different in-plane deformations are observed in the IR region due to the vinyl group: a scissors-type deformation of the terminal methylene, a rocking type of motion about the internal olefinic methine and a rocking motion of the terminal methylene (Table IV).

The first band is usually seen near 1411 cm^{-1} in the spectra of 1-alkenes as a sharp, rather weak (about 12 1 mole^{-1} cm^{-1}) peak on the side of the band due to methylene in-plane deformation and methyl asymmetric in-plane deformation. Allyl esters and ethers shift slightly in wave number but increase markedly in intensity, to an average of 29 and 20 1 mole^{-1} cm^{-1}, respectively. Alkyl acrylates show a small negative shift in wave number but a marked increase in intensity (126–150 1 mole^{-1} cm^{-1}). A negative shift in wave number to 1401–1406 cm^{-1} is noted in the spectra of vinyl ketones. The vinyl esters and alkyl vinyl ethers absorb close to the normal 1-alkenes (near 1413 cm^{-1}) with intensities of 19 (6) and 4 1 mole^{-1} cm^{-1}, respectively.

The $=CH-$ rocking mode is normally observed near 1297 cm^{-1} with an intensity of only 6 1 mole^{-1} cm^{-1} for 1-alkenes. This band shifts slightly in allyl esters and ethers with varied intensities. The band shifts little (Table IV) in alkyl acrylates, but intensity increases markedly to 110–120 1 mole^{-1} cm^{-1}. Vinyl ketones also have a moderately strong band near 1294 cm^{-1} for this mode.

Vinyl esters shift in wave number like acrylates but decrease in intensity, to an average of 23 1 mole^{-1} cm^{-1} (6). A marked shift in location of this band occurs in alkyl vinyl ethers where a sharp, strong band appears near 1318 cm^{-1} (intensity near 109 1 mole^{-1} cm^{-1}). The location and intensity of this $=CH-$ rocking mode depends upon the structure attached to the vinyl group.

The third C–H in-plane deformation band is attributed to a rocking type of motion of the terminal $=CH_2$. Other bands in this region reduce its use-

TABLE IV

C–H In-Plane Deformations of the Vinyl Group

Compound	$\delta = CH_2$[a]		$\rho = CH-$		$\rho = CH_2$	
	Range	Normal	Range	Normal	Range	Normal
Ethylene		1444				1286
1-Alkenes	1408–1416	1411	1296–1299	1297	1053–1075	1070
Allyl ethers	1418–1425	1420	1282–1295	1289	1072–1090	1082
Allyl esters	1408–1425	1410	1299–1316	1308	1091–1111	1099
Acrylates	1400–1410	1405	1290–1299	1292	1050–1070	1061
Vinyl esters	1406–1429	1413	1285–1298	1291	1087–1099	1092
Vinyl ethers	1406–1425	1413	1314–1323	1318	1072–1075	1074

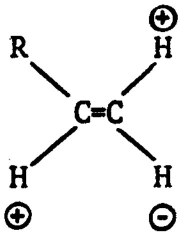
[a] δ, In-plane deformation; ρ = rocking deformation.

fulness as a good definitive band for vinyl compounds. In 1-alkenes, the in-plane deformation band is observed as a weak band (2 1 mole^{-1} cm^{-1}) near 1070 cm^{-1}. In allyl esters, acrylates, vinyl esters and vinyl ethers it is near 1099, 1061, 1092 and 1074 cm^{-1} with average intensities of 42, 77, 48 and 31 1 mole^{-1} cm^{-1}, respectively. This band is greatly influenced by neighboring bands from the (C–O–C) stretching mode.

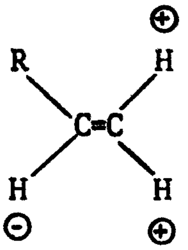
A series of weak bands appears at a shorter wave number than the C–H stretching bands of the alkyl chain's methyl and methylene units. These bands are due to a series of overtones and combinations of various C–H in-plane deformations. For most long chain vinyl derivatives the location (and assigned cause) of the bands are: 2825 ± 5 cm^{-1} ($2 \times \delta{=}CH_2$), 2778 ± 8 cm^{-1} ($\delta{=}CH_2 + \overset{s}{\delta}\text{-}CH_3$ or $\delta\text{-}CH_2\text{-} + \rho{=}CH\text{-}$), 2732 ± 8 cm^{-1} ($\delta{=}CH_2 + \rho{=}CH\text{-}$), 2674 ± 5 cm^{-1} ($\overset{s}{\delta}\text{-}CH_3 + \rho{=}CH\text{-}$), 2622 ± 10 cm^{-1} ($2 \times \rho{=}CH\text{-}$). Their intensities are all less than 5 1 mole^{-1} cm^{-1}.

C-H Out-of-Plane Deformations

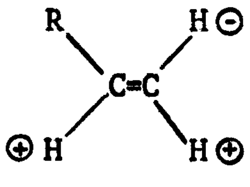
No element of symmetry exists within the vinyl group except the plane of the five atoms comprising the group. These atoms give rise to three separate IR active C–H out-of-plane deformations. Certain characteristics of two of the three out-of-plane deformations are discussed by Potts and Nyquist (14) and Cunliffe-Jones (15). Normally these are located near 990 cm^{-1}, in a band attributed to a twisting about the vinyl double bond:



(where ⊕ indicates motion forward from the plane of the paper and ⊖ backward through the plane of the paper), and near 910 cm^{-1} in a band attributed to a CH$_2$ wagging motion:



The third out-of-plane deformation is referred to as occurring at 580 cm^{-1} (14) but it not discussed by Potts and Nyquist. We actually observed this mode near 630 cm^{-1} in the spectra of 1-alkenes and attribute it to a quasi-rotational type of motion:



Overtones of both twisting and wagging-type vibrations are observed in the IR spectra. The first overtone of the twisting mode occurs at a wave number lower than the calculated wave number while the wagging mode's overtone is found near the calculated wave number.

In normal long chain 1-alkenes the three C–H out-of-plane deformation bands are clearly (Fig. 3) at 990, 908 and 631 cm^{-1} with average intensities of 38, 123 and 8 1 mole^{-1} cm^{-1}, respectively. The first overtones of the twisting and waggering modes, at 1969 and 1815 cm^{-1}, have respective average intensities of 0.4 and 4 1 mole^{-1} cm^{-1} (Table V). Branching of the alkyl chain on the carbon atom adjacent to the vinyl group (C$_3$) results in the location of the twisting mode being slightly shifted with no significant change in intensity. The wagging mode absorption band is unaffected by monosubstitution on C$_3$ but shifts when this carbon atom is disubstituted. Marked shifts are noted in the third out-of-plane deformation band with the C$_3$ branched chain 1-alkenes. When the adjacent carbon atom is olefinic in nature as in 1,3-dienes, wave number shifts are similar to those in compounds with branching at the adjacent carbon atom. Conjugation of the vinyl group with an aromatic ring, as in styrenes, normally results in bands at 989, 907 and 696 cm^{-1}. Substitution on the ring system affects the location of these bands. The twisting type of vibration is found at 995 cm^{-1} when the branched-chain, additional olefinic group or aromatic group is separated from the vinyl group by one methylene unit. Their wagging mode is observed at 910 cm^{-1}.

Allyl ethers and esters exhibit the twisting mode at a normal wavelength, 990 and 986 cm^{-1}, respectively, with average intensities of 68 and 92 1 mole^{-1} cm^{-1}, respectively, for long chain allyl ethers and esters.

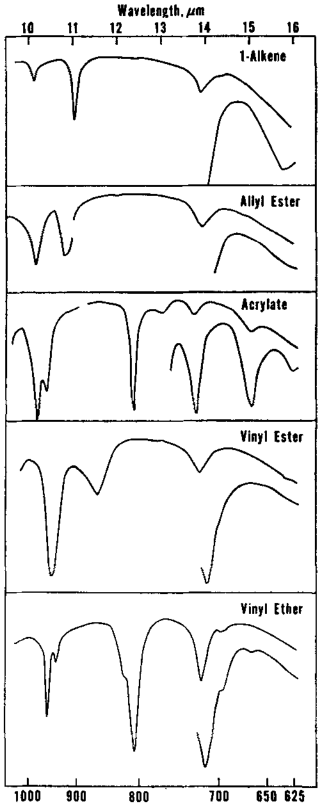


FIG. 3. C–H out-of-plane deformation region (pure compound vs. air, 0.015 and 0.10 mm path lengths).

TABLE V

C–H Out-of-Plane Deformations of the Vinyl Group

	γC–H twisting		γC–H wagging		γC–H rotational		2 × γC–H twisting		2 × γC–H wagging	
Compound	Range	Normal	Range	Normal	Range	Normal	Range	Normal	Range	Normal
n-1-Alkenes	988–992	990	907–910	908	629–633	631	1965–1972	1969	1812–1820	1815
3-Substituted-1-alkenes	985–999	992	900–912	908	650–678	668	1969–2000	1987	1818–1845	1825
3,3-Disubstituted-1-alkenes	988–1000	994	911–922	918	684–690	686	1957–1983	1970	1825–1850	1838
1,3-Alkadienes	982–1012	992	900–910	905	667–690	682	1953–2000	1984	1812–1825	1817
Allyl ethers	985–991	990	920–927	922	625–647	637	1930–2000	1940	1845–1869	1857
Allyl esters	983–997	986	924–932	929	625–633	631	1969–1984	1976	1852–1853	1852
Acrylate esters	980–989	984	806–811	809	662–668	664	2033–2058	2041	1610–1629	1621
	960–970	964			626–630	628	1923–1961	1935		
Vinyl ketones	992–997	992	953–958	954	603–605	603				
	982–987	983								
Alkyl vinyl ethers	958–967	961	821–831	823	692–699	696	1905–1920	1905		
	939–945	943	806–811	809	603–606	606	1866–1884	1869		
Vinyl esters	943–957	947	860–873	868	600–606	603	1869–1894	1885	1706–1728	1712

There is a notable shift in the location of the $=CH_2$ wagging mode in allyl ethers and esters, to 922 and 929 cm^{-1} normally, with intensities averaging 95 and 99 1 mole^{-1} cm^{-1}, respectively.

The C–H twisting mode is reported at 984 ± 1 cm^{-1} in acrylates (2) and at 989 cm^{-1} in methyl acrylate (13). The wagging mode is reported at 965 ± 1 cm^{-1} (2) and 970 (13). Feairheller and Katon (13) also report a third γC–H band at 811 cm^{-1} and overtones at 1622 cm^{-1} (2 × 811) and 1930 cm^{-1} (2 × 970). Rotational isomerism in alkyl acrylates is responsible for two strong γC–H twisting bands at 984 and 964 cm^{-1} (average intensities of 103 and 79 1 mole^{-1} cm^{-1}). The $=CH_2$ wagging mode occurs near 809 cm^{-1} with an intensity of 75 1 mole^{-1} cm^{-1}. Two bands are also noted in the rotational γC–H region. Rotational isomerism effects are found in the spectra of long chain vinyl ketones where bands appear at 992 cm^{-1} for the s-*trans* and 983 cm^{-1} for the s-*cis* conformational isomer. The conformations and band locations agree with literature values (2,12,16).

Presumably the out-of-plane C–H deformation bands of vinyl ethers occur at 962 ± 2 and 942 ± 1 cm^{-1} (2,12) or at 965 ± 5 and 815 ± 5 cm^{-1} (11,17). A more detailed study on the location of these bands (14) indicated considerable variance with alcohol type. Primary alkyl vinyl ethers, including those with internal unsaturation, have a major peak at 961 cm^{-1}, with an average intensity of 71 1 mole^{-1} cm^{-1} and a shoulder at 943 cm^{-1} due to the twisting mode. Secondary alkyl vinyl ethers normally exhibit bands of equal intensity at 966 and 944 cm^{-1}. Tertiary alkyl vinyl ethers exhibit only one band, near 945 cm^{-1}. Aryl vinyl ethers reverse the twisting mode seen in primary alkyl ethers, with a shoulder at 962 cm^{-1} and the major peak at 944 cm^{-1}.

The methylene wagging mode of primary alkyl vinyl ethers is a strong band (154 1 mole^{-1} cm^{-1}) at 809 cm^{-1} with a shoulder at 823 cm-1, while secondary alkyl vinyl ethers show two peaks of equal intensity at 824 and 812 cm^{-1}. Tertiary alkyl vinyl ethers and aryl vinyl ethers exhibit single bands due to the wagging mode at 824 and 851 cm^{-1}, respectively. Only weak bands appear in the spectrum for the third out-of-plane deformation. In long chain alkyl vinyl ethers, bands with an average intensity of 2 1 mole^{-1} cm^{-1} are found near 696 and 606 cm^{-1}. Overtones of the twisting type of motion are found near 1905 and 1869 cm^{-1} with respective intensities of 2 and 1 1 mole^{-1} cm^{-1}. Overtones of the wagging motions are probably involved in the triplet within the C=C stretching region.

The vinyl esters of carboxylic acids have a strong (110 1 mole^{-1} cm^{-1}) twisting mode at 947 ± 1 cm^{-1} (6). The wagging mode is also strong (100 1 mole^{-1} cm^{-1}) at 868 cm^{-1}. The rotational type of motion occurs at 603 cm^{-1} as a weak band (2.6 1 mole^{-1} cm^{-1}). Overtones of the twisting and wagging modes of the vinyl esters are found at 1885 cm^{-1} with an average intensity of 1.3, and at 1712 cm^{-1} as a weak peak on the side of the ester carbonyl-stretching peak.

C-O Stretching Vibrations

Absorption bands caused by C–O stretching vibrations are found at 1300–1000 cm^{-1}. Alkyl ethers and polymerized vinyl ethers normally have a strong band (156 1 mole^{-1} cm^{-1}) at 1100 cm^{-1}. Allyl ethers exhibit a strong, broad peak at 1090–1140 cm^{-1} with a norm of 1114 cm^{-1} (Fig. 4). Vinyl ethers exhibit two C–O stretching bands; a strong band at 1200 cm^{-1} (331 1 mole^{-1} cm^{-1}) and a band at 1136 cm^{-1} (19 1 mole^{-1} cm^{-1}). The third band observed in Fig. 4 at 1074 cm^{-1} is the C–H in-plane deformation. Vinyl ethers deviate little in wave number, 1200–1225 and 1132–1138 cm^{-1}.

The spectra of allyl esters of long chain carboxylic acids exhibit four absorption bands in the C–O stretching region: a weak (36 1 mole^{-1} cm^{-1}) band at 1258–1266 cm^{-1}, normally at 1266 cm^{-1}; a second band at 1220–1238 cm^{-1} with an average wave number of 1230 cm^{-1} and intensity of 56 1 mole^{-1} cm^{-1} and a third band at 1093–1114 cm^{-1}, usually at 1100 cm^{-1} with an intensity of 32 1 mole^{-1} cm^{-1}. These three bands (Fig. 4) flank the major C–O stretching peak at 1161–1169 cm^{-1}. Generally this strong band appears at 1167 cm^{-1} with an average intensity of 169 1 mole^{-1} cm^{-1}. Vinyl esters of carboxylic acids have

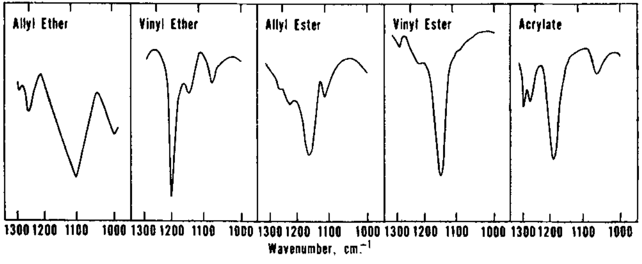


FIG. 4. C–O stretching region (pure compound vs. air, thin film between NaCl plates).

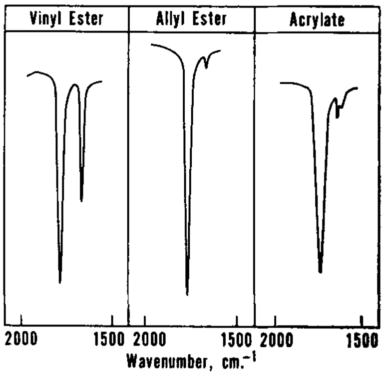


FIG. 5. C=O stretching region (pure compound vs. air, thin film between NaCl plates).

a strong (508 1 mole^{-1} cm^{-1}) band at 1142 cm^{-1} (range 1136–1147 cm^{-1}) (6). A secondary peak is observed at 1220 cm^{-1}. The principal C–O stretching band in alkyl acrylates is located near 1183 cm^{-1} with an intensity near 500 1 mole^{-1} cm^{-1} and a range of 1170–1189 cm^{-1}. A doublet is observed at 1293 ± 3 cm^{-1} and 1271 ± 2 cm^{-1} with average intensities of 120 and 140 1 mole^{-1} cm^{-1}. The $=CH_2$ rocking mode is observed (Fig. 4) at 1061 cm^{-1}.

Normal alkyl alkanoates exhibit a carbonyl-stretching band near 1735 cm^{-1}. In vinyl esters of carboxylic acids the vinyloxy resonance interferes with the normal ester carbonyl resonance system and shifts the carbonyl stretching mode to 1756 ± 5 cm^{-1} with an average intensity of 520 1 mole^{-1} cm^{-1} (Fig. 5)(6). In long chain allyl esters (e.g., hexadecanoates), the carbonyl stretching mode returns to 1632 ± 2 cm^{-1} with an intensity about 500 1 mole^{-1} cm^{-1}.

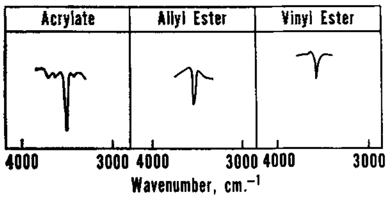


FIG. 6. First overtone of carbonyl stretching vibration (pure compound vs. air, 0.05 mm path length).

When the vinyl group and a carbonyl group are conjugated as in acrylates, an ene-one resonance system competes with the ester carbonyl resonance and results in a carbonyl-stretching peak at 1724 ± 3 cm^{-1} with an average intensity of 400 1 mole^{-1} cm^{-1}. If the vinyl group is conjugated with a ketone carbonyl, as in vinyl alkyl ketones, the carbonyl stretching modes depend on the rotational isomerism. The s-*cis* conformational isomer absorbs at 1692 ± 12 cm^{-1} with an intensity near 390 1 mole^{-1} cm^{-1}, whereas the s-*trans* conformer absorbs at 1670 ± 10 cm^{-1} with an average intensity of 320 1 mole^{-1} cm^{-1}. The first overtone of the carbonyl stretching vibration is observed as a fairly weak, sharp peak in the 3450–3550 cm^{-1} region (Fig. 6). Vinyl esters usually exhibit this overtone near 3493 cm^{-1} with an average intensity of 4 1 mole^{-1} cm^{-1}. Alkyl acrylates and allyl esters of long chain acids exhibit this overtone near 3448 cm^{-1} with an intensity of 2–3 1 mole^{-1} cm^{-1}.

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