Characteristic Absorption Bands of Vinyl Ethers

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The infrared spectra of vinyl ethers was investigated by G. D. Meakins[1], and by W. H. T. Davison and G. R. Baets[2], but the feature of the spectra associated with the presence of —$COCH=CH_2$ was not yet clear. In the present paper the infrared spectral data of a considerable number of vinyl ethers and ethyl vinylthioether are given, and the characteristic frequencies of vinyl ethers are discussed.

Experimental

a) Measurement.—A Perkin-Elmer Model 21 infrared spectrometer, with a rocksalt prism, was used. The spectrum of methyl vinyl ether is measured in its gaseous state, the others in liquid state or 10% solution of carbon tetrachloride or of carbon disulfide. In the case of solutions no bands-shift owing to solvent effect is observed.

b) Materials.—All of vinyl ethers and vinyl thioether are prepared in our Research Laboratories by applying the technique developed by W. Reppe and his co-workers. The purity of samples cannot be proved exactly, but distillations were repeated many times until all the impurity bands which had existed in the raw materials completely disappeared. The boiling point of each sample is as follows: methyl vinyl ether 5.5°C, ethyl vinyl ether 36.2°C, *n*-propyl vinyl ether 63.8°C isopropyl vinyl ether 55.0°C, *n*-butyl vinyl ether 93.8–94.1°C, 2-ethylhexyl vinyl ether 53.8–54.2°C/7 mmHg, benzyl vinyl ether 187.5–188.0°C, phenyl vinyl ether 49.5–50.0°C/13 mmHg, ethyl vinyl thioether 91.5–92°C.

Experimental Results

The observed spectra are shown in Fig. 1 and the wave-numbers of the observed absorption maxima of methyl vinyl ether are listed in Table I.

TABLE I
THE FREQUENCIES OF THE ABSORPTION BANDS OF METHYL VINYL ETHER

Frequencies	Intensity	Type of vibration	Species
3125	M	CH str. of vinyl	
3065	M	CH str. of vinyl	
3000	M	CH str. of vinyl	
2951	M	CH str. of methyl	
2842	M	CH str. of methyl	
1655	Sh	2×817	A′
1630 P	VS	CC str. of vinyl	A′
1618 Q	Sh		
1610 R	VS		
1481	Sh	$=CH_2$ def.	A′
1462 Q	M	CH_3 def. (assym.)	A″
1390	W	CH_3 def. (sym.)	A′
1335 P	M	$-CH=$in-plane def. of vinyl	A′
1325 Q	M		
1312 R	M		
1235 P	VS	CO str.	A′
1225 Q	Sh		
1212 R	VS		
1149 P, Q ?	M	$=CH_2$ rock.	A′
1130 R	M		
1085	VW	CH_3 def.	A′
1025 P, Q	M	$-CH_2$ rocking	A″
1015 Q	W	CO str.	A′
1003 R	M		

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[1] G.D. Meakins, *J. Chem. Soc.*, **1953**, 4170.

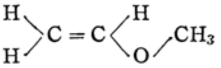
[2] W.H.T. Davison and G.R. Baets, *J. Chem. Soc.*, **1953**, 2607.

Frequencies	Iitensity	Type of vibration	Species
965 Q	M	$-CH=$out-of-plane def.	A″
945	Sh		
902 P	M		
880 R	M		
817 Q	S	$=CH_2$ out-of-plane def.	A″

Interpretation

a) Methyl Vinyl Ether

Methyl vinyl ether has axes of internal rotation. Therefore, the determination of special configuration of this molecule is a very difficult problem. But the assumption that the molecule takes such molecular configuration as



makes it possible to have a reasonable interpretation of the absorption bands.

In order to calculate the moment of inertia, further assumptions with regard to interatomic distances and bond angles are made. The CH, CO and CC distances for the molecule are assumed to be 1.07Å, 1.42Å and 1.34Å, respectively. The HCH and COC angles are taken to be 116° and 110°, respectively. The principal moments of inertia are, then, 18, 196 and 209×10^{-40} g. cm^2.

As a preliminary guide to the interpretation of the infrared spectra it is useful to consider what information may be expected from the band envelopes. The twenty-four normal vibrations of methyl vinyl ether are divided on the basis of symmetry C_s into two classes: sixteen modes in species A′ and eight modes in A″. Five CH stretching, five skeletal and six CH deformation freqencies belong to the former class and one CH stretching, one skeletal and six CH deformation frequencies belong to the latter class. Five of them (three A′ and two A″) are unlikely to be observed in the rock salt region. The envelopes of the A′ bands may be expected to have a hybrid character, each partaking in some degree of the conventional type A and type B contours. The A″ bands have type C envelopes, and Badger tell and Zumwalt's curves[3] show that the contours are characterized by very prominent Q branches. As a matter of fact, strong and clearly resolved A″ bands can be identified without hesitation. An excellent example of the type C envelope is given in 817 cm^{-1} band. This easy and definite identification of A″ bands in the spectra is a valuable aid in the subsequent vibrational analysis.

The envelopes of the bands at 1462, 965 and 817 cm^{-1} clearly indicate that their type is C. The bands at 1149 and 1025 cm^{-1} may also represent C type bands, although these overlap to the P branches of the other bands.

It is helpful to consider the spectral regions in which the fundamentals may be expected to occur. The modes associated with the CH stretching vibrations appear in the vicinity of 3000 cm^{-1}. Moreover, the bands due to $=CH_2$ or $=CRH$ group which have wave numbers higher than 3000 cm^{-1} are distinguishable from the CH_3 frequencies which appear in a longer wave-length region. The $C=C$ and C—O frequencies occur around 1650–1600 cm^{-1} and 1250–1000 cm^{-1} respectively. The CH out-of-plane deformation frequencies of mono-substituted ethylenes are assigned by several investigators[4] to two bands near 990 and 910 cm^{-1}. In the present case, however, the corresponding bands are found in a somewhat longer wave-length. The reliability of these interpretations will be shown later.

On taking into account the preceding discussion and on comparing the spectral data on a series of other vinyl ethers and a vinyl thioether investigated in the present study, the tentative vibrational assignments are made and are given in the third column of Table I. (Weak absorptions in the overtone region are omitted from this table).

b) Other Vinyl Ether and Ethyl Vinyl-thioether

i) 3150–2800 cm^{-1} Region.—In this region there exist the CH stretching frequencies. The bands arising from the vinyl group should appear in 3200–3000 cm^{-1} and in the case of methyl vinyl ether the three bands at 3125, 3065 and 3000 cm^{-1} were assigned to them. In the case of other vinyl ethers, nearly all compounds, except phenyl and benzyl vinyl ether, have three absorption maxima above 3000 cm^{-1} (shown in Table II), which are very similar to each other. This fact shows that the CH stretching vibrations of the vinyl group remain almost constant and are not remarkably affected by the other parts of the molecule. In the case of phenyl and benzyl vinyl ether, these bands overlap CH bands arising from phenyl group. It is of interest to note the fact that phenyl vinyl ether shows no band below 3000 cm^{-1} in this region because of the absence of saturated —CH_2— or —CH_3 group.

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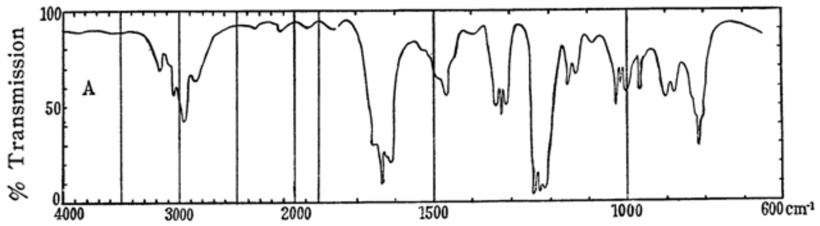
[3] Badger and Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

[4] Sheppard and Sutherland, *Proc. Roy. Soc.*, A **196**, 195 (1949). Anderson and Seyfried, *Anal. Chem.*, **20**, 998 (1948).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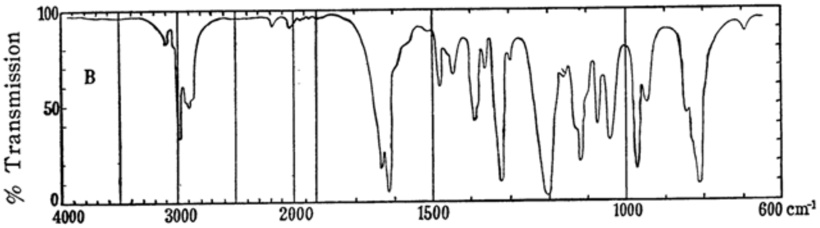
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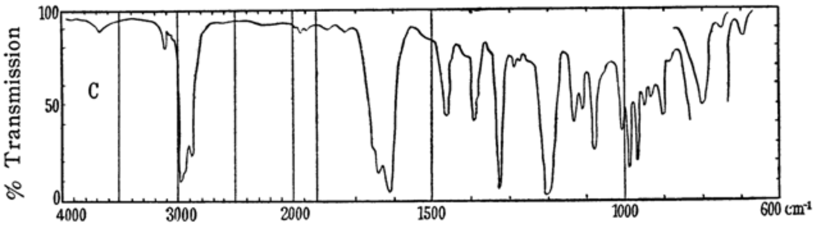
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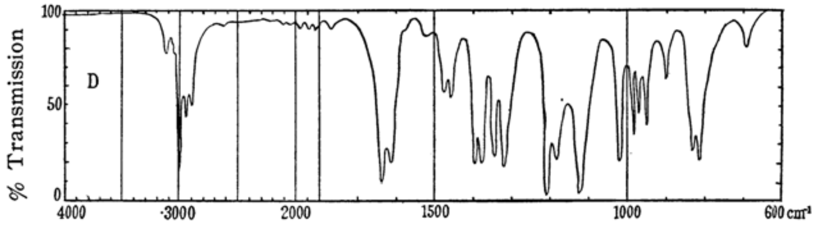
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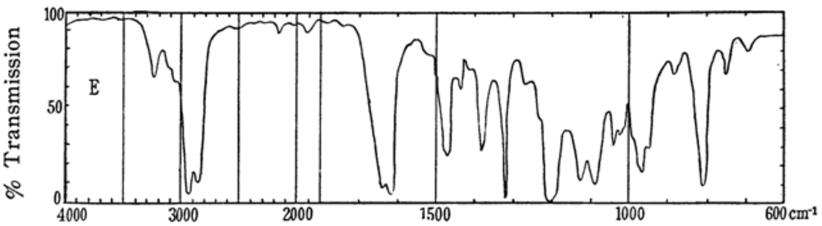
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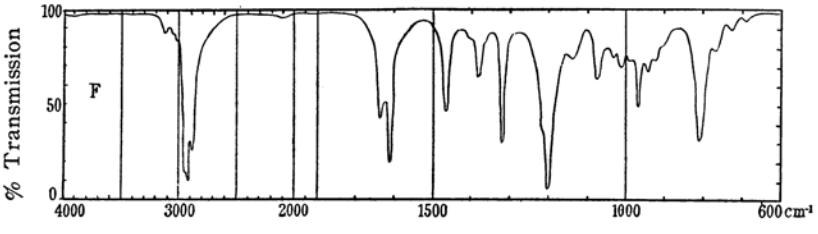
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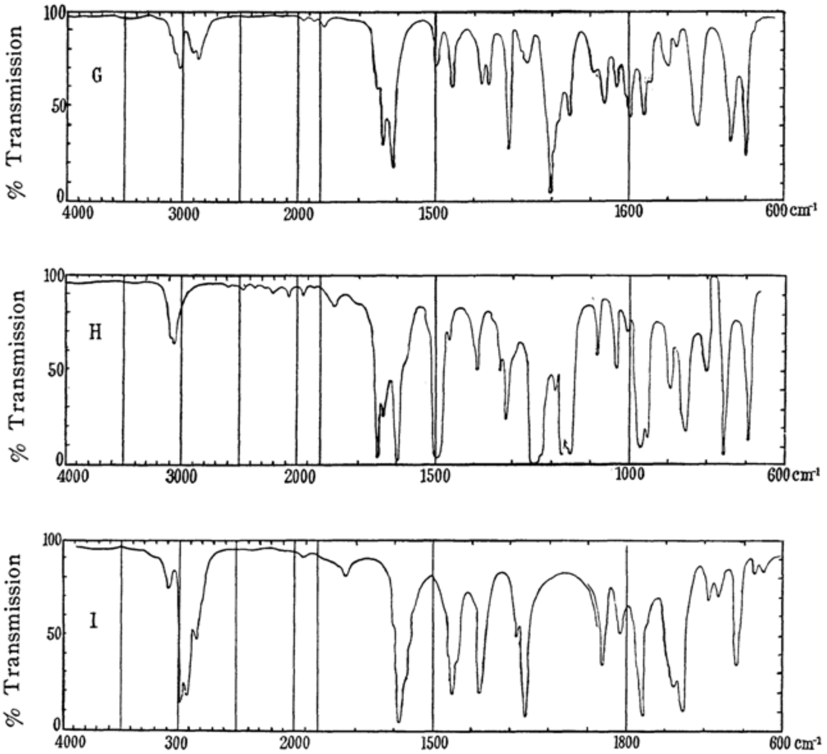

Fig. 1. Infrared spectra of vinyl ethers and ethyl vinyl thioether.

A) Methyl vinyl ether	D) iso-Propyl vinyl ether	G) Benzyl vinyl ether
B) Ethyl vinyl ether	E) *n*-Butyl vinyl ether	H) Phenyl vinyl ether
C) *n*-Propyl vinyl ether	F) 2-Ethylhexyl vinyl ether	I) Ethyl vinyl thioether

TABLE II

CHARACTERISTIC FREQUENCIES OF VINYL ETHERS $CH_2=CH-O-R$

R		(CH)		(C=C)	(CH)	(CO)	(CH)	(=CH_2)
CH_3—	3125,	3065,	3000	1620	1323	1223	965	817
C_2H_5—	3110,	3065,	3035	1610	1320	1205	967	810
n-C_3H_7—	3120,	3070,	3046	1615	1323	1203	968	811
iso—C_3H_7	3125,	3078,	3050	1614	1322	1203	969	812
C_4H_9—	3100,	3060,	3023	1613	1323	1200	962	810
C_8H_{17}—	3098,	—,	3015	1610	1320	1205	963	810
$C_6H_5CH_2$—		a)		1611	1320	1200	960	820
C_6H_5—		a)		1644	1313	1235	965	806
$CH_2=CH-S-Et$	3080,	—,	—	1585	1260	719b)	960	860

a) The CH stretching frequencies of vinyl group overlap with those of phenyl group.

b) This is associated with the C—S stretching mode.

ii) 1600 cm^{-1} Region.—In this region every vinyl ether shows two absorption maxima. The stronger one is assigned to the C=C stretching frequency, and the other to the overtone of a CH out-of-plane deformation frequency arising from the $=CH_2$ group. The intensity of these two bands may be explained as the Fermi resonance between the C=C stretching frequency and the overtone of 810 cm^{-1} band, because the intensities of these two bands are not greatly different from each other. In the case of ethyl vinyl thioether, however, the overtone of the CH deformation frequency appears in the vicinity of 1720 cm^{-1} and its intensity is far weaker than the C=C bands at 1585 cm^{-1}, and the Fermi resonance is excluded. In the case of ethyl β-chlorovinyl ether(5) which has no $=CH_2$ group, only one band appears in this region.

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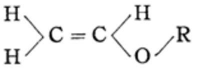
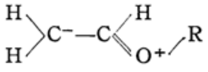
5) Cis- and trans-ethyl-β-chlorovinylether absorbed at 1649 and 1620 cm^{-1}, respectively, according to the unpublished data in our laboratories.

The frequencies assigned to C=C stretching vibration are listed in Table II. One of the characteristic frequencies of alkyl vinyl ether is 1615 ± 5 cm^{-1}. This frequency is rather low, as compared with the corresponding frequencies of mono-substituted ethylenes which are about 1650 cm^{-1}. For explaining the shift from 1650 to 1615 cm^{-1}, the resonance between two mesomeric forms



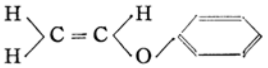
(I)



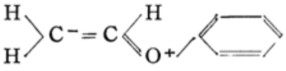
(II)

is taken into consideration. The contribution of the ionic form (II) makes the double bond character weak, and the band shift to somewhat lower position may be expected. In the case of ethyl vinyl thioether the C=C stretching frequency has a frequency as low as 1585 cm^{-1}, which is explained in a similar way. In this case S atom has lower electronegativity than O atom of vinyl ethers, and the ionic structure which is similar to (II) referred to above becomes more stable.

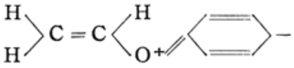
In phenyl vinyl ether three bands occur in the vicinity of 1600 cm^{-1}; the first band at 1653 cm^{-1} is assigned to the C=C vibration of vinyl group, the second at 1635 cm^{-1} to the overtone mentioned before, and the last at 1600 cm^{-1} to the ring vibration of the phenyl group. In this case the status concerning the resonance form is somewhat different and the following five mesomeric forms are possible:



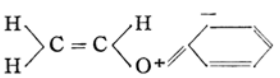
(III)



(IV)



(V)



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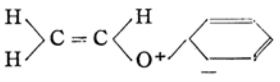

(VII)

The difference from the case of alkyl vinyl ether is that the three ionic forms (V), (VI) and (VII) in addition to (IV) contribute to the normal state.

The presence of these forms makes the contribution of structure (IV) smaller and the frequency of the C=C vibration of phenyl vinyl ether remains almost unshifted from those of usual mono-substituted ethylenes.

iii) 1320 cm^{-1} Region.—The band around 1320 cm^{-1} is the most important characteristic band to the vinyl ether, for every vinyl ether examined shows a very strong band at 1321 ± 2 cm^{-1}. This band may be assigned to the CH in-plane frequency for several reasons. Stamn[6] carried out the vibrational analysis of vinyl acetylene and assigned the band at 1288 cm^{-1} to the CH in-plane rocking vibration of vinyl group. Torkington and Thompson[7] investigated a series of vinyl halides and showed that the frequencies concerned are assigned to 1306, 1280, 1262 and 1229 cm^{-1} for fluoride, chloride, bromide and iodide, respectively. It seems reasonable that the bands at 1321 ± 2 cm^{-1} of vinyl ethers should be assigned to CH in-plane rocking frequencies. This conclusion is compatible with the assignment in the gaseous methyl vinyl ether from the consideration of band contours. Isopropyl vinyl ether has two bands at 1322 and 1340 cm^{-1}, which may be associated with the two CH groups contained in the molecule, the one in the isopropyl group and the other in the vinyl group. In the other vinyl ethers examined, no other band is observed around 1340 cm^{-1}.

Ethyl vinyl thioether shows a fairly strong absorption at 1260 cm^{-1} instead of 1340 cm^{-1}. This band is probably interpreted to the CH in-plane rocking frequency, although the reason for the band shift is uncertain. This rocking vibration may have considerable coupling effect with the C—S streching vibration.

iv) 1200 cm^{-1} Region.—In general alkyl ethers, the C–O stretching frequencies are found around 1100 cm^{-1}. In the present case, however, almost every vinyl ether shows a strong absorption at 1203 ± 2 cm^{-1}, which is assigned to the C–O stretching frequency. The C–O bond adjacent to vinyl group has a somewhat double bond character as a result of the resonance effect referred to before. This is the reason why the frequency rises to a higher position.

The C–S stretching frequencies in mercaptans and sulphides are found in the range 700–600 cm^{-1} [8]. The corresponding frequency of ethyl vinyl thioether may be assigned to the fairly strong band at 719 cm^{-1}.

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[6] Stamn; *J. Chem. Phys.*, **17**, 104 (1949).

[7] Torkington and Thompson, *J. Chem. Soc.*, **1944**, 303.

v) Bands around 965 and 810 cm^{-1}.—The bands around 965 and 810 cm^{-1} are also found in all vinyl ether and are useful characteristic frequencies. The vinyl type double bond gives rise to two strong bands at 995–985 cm^{-1} and 915–905 cm^{-1} [8], these being concerned with the CH out-of-plane vibration of the $-CH=CR-$ and $=CH_2$ group, respectively. The bands of vinyl ethers around 965 and 810 cm^{-1} may be assigned to the corresponding frequencies, because these two bands are similar to the two bands referred to above in their intensity and constancy in frequency, and because the contours of bands at 965 and 810 cm^{-1} in methyl vinyl ether show the C type. Both bands appear in considerably lower frequencies, as compared with the other mono-substituted ethylenes. Bellamy's suggestion that the "overtone" bands afford a useful confirmation of the presence of the $=CH_2$ groupings,[8] may give another proof for the assignment of the bands around 810 cm^{-1}.

Summary

The infrared spectra of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, 2-ethylhexyl, benzyl and phenyl vinyl ether and also ethyl vinyl thioether were investigated over the region of 4000–650 cm^{-1}. The assignment of the spectrum of methyl vinyl ether has been made by the aid of the bands contours. The absorption bands of the other were discussed and the characteristic frequencies of vinyl ethers are concluded as follows.

(1) three bands near 3100 cm^{-1}......
CH stretching of vinyl group
(2) 1615±5 cm^{-1}......C=C stretching
(3) 1321±2 cm^{-1}......
CH in-plane deformation
(4) 1203±2 cm^{-1}......C-O stretching
(5) 965±5 cm^{-1}......
$=CH-$ out-of-plane deformation
(6) 815±5 cm^{-1}......
$=CH_2$ out-of-plane deformation

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[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London (1954).