531. *Infra-red Absorptions of Vinyl and* iso*Propenyl Groups in Polar Compounds.*

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The characteristic olefinic absorptions of a number of polar allyl, vinyl, and *iso*propenyl compounds have been measured in solution, and new correlations established for the esters, ketones, and ethers. The correlations for acrylates and methacrylates include absorptions associated with the ester group.

Conjugation explains some of the shifts of $\nu_{C:C}$, but is not responsible for those of δ_{CH}, for which no suitable models exist. An additivity rule is suggested and tested.

Characteristic infra-red absorptions for vinyl and *iso*propenyl groups in hydrocarbon environment are well established (Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915; McMurray and Thornton, *Analyt. Chem.*, 1952, **24**, 318; Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1) but little has been reported on the effect of polar substituents upon these absorptions apart from the vinyl halides (Thompson and Torkington, *J.*, 1944, 597) and allyl halides (*idem*, *Trans. Faraday Soc.*, 1946, **42**, 432).

The vibrational modes of the characteristic absorptions (Sheppard and Simpson, *loc. cit.*, give an excellent review of the nature of these absorptions) are $\nu_{C:C}$ (C:C stretching at *ca.* 1650 cm.$^{-1}$) and δ_{CH} (hydrogen deformation vibrations at *ca.* 1400 and 850—1000 cm.$^{-1}$). $\nu_{C:C}$ is primarily dependent upon the C:C stretching force constant and is therefore lowered by conjugation; its intensity (group molar absorptivity) should be increased by adjacent polar groups. The assignments of the δ_{CH} vibrations are fairly definite, but there is no suitable model which relates their frequencies to the conventional structural representation of the molecule.

Experimental and Results

The materials used were mainly made and supplied by Dr. W. Cooper and Mr. E. Catterall. Spectra were all measured in "AnalaR" carbon tetrachloride (usually as 0·5M-solutions

Table 1. *Vinyl compounds*, $CH_2{:}CH{\cdot}X$.

	$\nu_{C.C}$,		δ_{CH},		δ_{CH},		δ_{CH},	
Compound	cm.$^{-1}$	ε	cm.$^{-1}$	ε	cm.$^{-1}$	ε	cm.$^{-1}$	ε
Allyl ethers (X = $CH_2{\cdot}OR$) *and acetals* [$(CH_2{:}CH{\cdot}CH_2{\cdot}O)_2CHR$]								
Diallyl ether	1648	6	988	36	925	98	N.I.	—
Diallyl formal	1645	17	989	75	923	100	1420	20
							1404	18
1 : 1-Diallyloxybutane	1644	20	991	90	921	97	1425	28
							1410	22
1 : 1 : 3-Triallyloxypropane	1644	~15	989	~70	923	~85	1420	~25
Summary	1645 ± 2	6—20	989 ± 1	36—90	923 ± 2	85—100	1422 ± 3	20—28

TABLE 1.—*Continued.*

Compound	$\nu_{C:C}$, cm.$^{-1}$	ε	δ_{CH}, cm.$^{-1}$	ε	δ_{CH}, cm.$^{-1}$	ε	δ_{CH}, cm.$^{-1}$	ε
Allyl esters (X = $CH_2{\cdot}O{\cdot}CO{\cdot}R$)								
Adipate	1650	27	986	100	932 923 (sh)	100 84	1420	48
Sebacate	1654	27	988	95	932 920 (sh)	100 72	1423	45
Acrylate	(i)	—	983 (i)	135 (i)	932 921	90 75	(i)	—
Methacrylate	(i)	—	984	90	939 (i) 922	140 (i) 75	1420	45
Summary	1652 ± 3	~27	985 ± 3	90—100	932 922 ± 1	90—100 72—84	1421 ± 2	45—48
Vinyl ethers (X = OR)								
Ethyl	1634 1608	72 112	964	80	943	28	N.I.	—
n-Butyl	1632 1610	65 110	960	55	942	33	N.I.	—
*iso*Butyl	1632 1608	65 110	962	60	941	37	N.I.	—
2-Ethylhexyl	1632 1610	74 122	963	75	944	35	N.I.	—
2-Chloroethyl	1640 1617	65 120	960	80	941	40	N.I.	—
Summary	1634 ± 3 1611 ± 4	65—74 110—120	962 ± 2	55—80	942 ± 1	28—40	N.I.	—
Vinyl esters (X = $O{\cdot}CO{\cdot}R$)								
Acetate	1647	90	948	90	872	110	N.I.	—
Benzoate	1647	100	948	105	871	130	N.I.	—
Crotonate	1647	120	949	100	868	120	N.I.	—
Summary	1647	90—120	948 ± 1	90—105	870 ± 2	110—130	N.I.	—
Vinyl ketones (X = $CO{\cdot}R$)								
Methyl	1618	~90	983	~100	953	~120	N.I.	—
Ethyl	1619	48	984	68	955	85	N.I.	—
Propyl	1620	~55	982	~75	954	~65	N.I.	—
Summary	1619 ± 1	48—90	983 ± 1	68—100	954 ± 1	65—120	N.I.	—
Conjugated diolefins (X = $CR{:}CR'R''$) [a]								
$CH_2{:}CH{\cdot}CH{:}CMe_2$ (API 453)	—	—	994	—	893	—	—	—
$CH_2{:}CH{\cdot}CMe{:}CH_2$ (API 278)	—	—	990	—	~910	—	—	—
cis-$CH_2{:}CH{\cdot}CH{:}CHMe$ (API 496)	—	—	998	—	908	—	—	—
trans-$CH_2{:}CH{\cdot}CH{:}CHMe$ (API 497)	—	—	1002	—	900	—	—	—
$CH_2{:}CH{\cdot}CH{:}CH_2$ (API 919)	—	—	1014	—	909	—	—	—
Summary	—	—	1000 ± 9	—	904 ± 7	—	—	—
Miscellaneous								
X = $CH_2{\cdot}CN$	1645	26	984	57	928	68	1420	48
X = CN	1612 1645	3·5 2·5	960 [b]	78	[b]	—	1413	26
X = $CO{\cdot}H$	1618	—	985	—	971 913	—	N.I.	—
X = CO_2H	1635 1615	90 70	981	110	973 930 [c]	120 80	N.I.	—
X = $CH(OEt)_2$	1647	~5	986	125	935	96	1413	46
X = $CH(CN){\cdot}O{\cdot}CO{\cdot}Me$	1649	—	978	—	946	—	1418	—

Notes to Tables 1—3.

N.I. Not investigated. (sh) Shoulder. (i) Interference from other olefinic groups.

[a] Published spectra; not in CCl_4. [b] Unresolved doublet (Thompson and Torkington, *J.*, 1944, 597). [c] Possibly the ~900-cm.$^{-1}$ acid band (Flett, *J.*, 1951, 962). [d] Insufficient data for correlation. [e] The mean frequency of the doublets is used to calculate the summary mean. [f] Methyl excepted.

TABLE 2. iso*Propenyl compounds*, $CH_2{:}CMeX$.

Compound	$\nu_{C:C}$, cm.$^{-1}$	ε	δ_{CH}, cm.$^{-1}$	ε
Esters (X = O·CO·R)				
Acetate	1673	80	869 (899)	110 (60)
Benzoate	1676	~70	877	~75
Summary	1674 ± 2	~80	873 ± 6	~100
iso*Propenyl ketones* (X = CO·R)				
Methyl	1632	39	930	110
2-Chloroethyl	1654	—	931	~50
Summary	[d]	—	930 ± 1	50—110
Conjugated diolefins (X = CR:CR′R″) [a]				
$CH_2{:}CMe{\cdot}CH{:}CHMe$ (API 452)	—	—	883	—
$CH_2{:}CMe{\cdot}CMe{:}CH_2$ (API 451)	—	—	890	—
$CH_2{:}CMe{\cdot}CH{:}CH_2$ (API 278)	—	—	~895	—
Summary	—	—	889 ± 5	—
Miscellaneous				
X = CO_2H	1632	~100	947	100
X = CN	1620	22	929	110

TABLE 3. *Acrylates and methacrylates.*

	$\nu_{C:O}$	$\nu_{C:C}$	δ_{CH}	A	B	C	D	δ_{CH}	δ_{CH}
Acrylates									
*cyclo*Hexyl	1725 (120)	1640 (40) 1622 (42)	1407 (100)	1298 (130)	1272 (150)	1192 (140)	1050 (115)	983 (100)	964 (100)
2-Ethyl-hexyl	1723 (140)	1637 (40) 1625 (38)	1407 (100)	1295 (120)	1270 (140)	1180 (160)	1054 (100)	983 (100)	964 (85)
*iso*Propyl	1717 (140)	1640 (55) 1619 (50)	1407 (95)	1295 (130)	1274 (140)	1196 (130) 1182 (120)	1047 (95)	984 (100)	965 (85)
Methyl	1735 (140)	1637 (45) 1625 (35)	1404 (90)	1290 (90)	1273 (150)	1197 (150) 1179 (150)	1068 (110)	984 (105)	965 (80)
Ethyl	1726 (120)	1637 (38) 1622 (30)	1406 (110)	1285 (130)	1271 (150)	1187 (160)	1060 (110)	984 (95)	965 (75)
Allyl	1723 (130)	1635 (47) 1620 (43)	1405 (97)	1296 (120)	1271 (140)	1184 (90)	1049 (90)	983 (i) (135)	966 (110)
Summary	1723 ± 4 [f] (120—140)	1638 ± 2 (38—55) 1622 ± 2 (30—50)	1406 ± 1 (90—110)	1293 ± 5 (90—130)	1272 ± 2 (140—150)	1187 ± 4 [e] (90—160)	1055 ± 8 (90—115)	984 ± 1 (95—105)	965 ± 1 75—110
Methacrylates									
n-Butyl	1717 (140)	1640 (65)	1404 (47)	1318 (140)	1297 (140)	1156 (160)	1011 (50)	— —	938 (120)
2-Ethyl-hexyl	1717 (130)	1635 (67)	1404 (52)	1321 (130)	1296 (140)	1163 (160)	1013 (70)	— —	939 (120)
Allyl	1714 (140)	1635 (70)	1404 (38)	1314 (130)	1295 (130)	1156 (160)	1012 (70)	— —	939 (140)
Summary	1716 ± 2 (130—140)	1637 ± 3 (65—70)	1404 (38—52)	1318 ± 5 (130—140)	1296 ± 1 (130—140)	1158 ± 4 (160)	1012 ± 1 (50—70)	— —	939 ± 1 (120—140)

Note.—Unbracketted figures are frequencies (cm.$^{-1}$), bracketted figures are absorptivities (ε).

in a 0·2-mm. cell) with a Grubb–Parsons single-beam spectrometer and rock-salt prism. Frequencies are within 3 cm^{-1}. in the 1600-cm.$^{-1}$ region, and 1 cm.$^{-1}$ in the 900-cm.$^{-1}$ region.

Intensities are expressed as group molar absorptivities (ε) given by absorbance ($\log_{10} I_0/I$) divided by the product of optical path in cm. and concentration in g.-equiv./l.

The results are tabulated for vinyl (Table 1) and *iso*propenyl groups (Table 2). Acrylates and methacrylates (Table 3) are given separately and include absorptions not associated with the olefinic groups. Frequencies are summarised by the mean and standard deviation, and the correlations are given in Table 4. The 1400-cm.$^{-1}$ band was not investigated in many cases (marked N.I.).

TABLE 4. *Olefinic group correlations.*

Group	No. of cpds.	$\nu_{C:C}$	$\Delta\nu$ [h]	ε	δ_{CH}	$\Delta\nu$ [h]	ε	δ_{CH}	$\Delta\nu$ [h]	ε
Type CH_2:CH.										
CH_2:CHR [g]	—	1642 ± 3	0	28—44	997 ± 6	0	33—57	912 ± 4	0	110—150
CH_2:CH·CR:CR′R″	5	N.I.	—	—	1000 ± 9	+ 3	—	904 ± 7	− 8	—
CH_2:CH·CH_2·OR ...	4	1645 ± 2	+ 3	6—20	989 ± 1	− 8	36—90	923 ± 2	+11	85—100
CH_2:CH·CH_2·O·CO·R	4	1652 ± 3	+10	~27	985 ± 3	−12	90—100	932	+20	90—100
								922 ± 1	+10	72—84
CH_2:CH·OR	5	1634 ± 3	− 8	65—74	962 ± 2	−35	55—80	942 ± 1	+30	28—40
		1611 ± 4	−31	110—120						
CH_2:CH·O·CO·R	3	1647	+ 5	90—120	948 ± 1	−49	90—105	870 ± 2	−42	110—130
CH_2:CH·CO_2R	6	1638 ± 2	− 4	38—55	984 ± 1	−13	95—100	965 ± 1	+53	75—100
		1622 ± 2	−20	30—50						
CH_2:CH·CO·R	3	1619 ± 1	−23	48—90	983 ± 1	−14	68—100	954 ± 1	+42	65—120
Type CH_2:CMe.										
CH_2:CRR′ [g]	—	1650 ± 11	0	20—42	—	—	—	889 ± 6	0	120—200
CH_2:CMe·CR:CR′R″	3	N.I.	—	—	—	—	—	889 ± 5	0	—
CH_2:CMe·O·CO·R ...	2	1674 ± 2	+24	~80	—	—	—	873 ± 6	−16	~100
CH_2:CMe·CO_2R	3	1637 ± 3	−13	65—70	—	—	—	939 ± 1	+50	~125
CH_2:CMe·CO·R	2	[d]	—	—	—	—	—	930 ± 1	+41	50—110

[g] Based on data of McMurray and Thornton, *loc. cit.*
[h] Frequency shift from unconjugated hydrocarbon value.

DISCUSSION

All the characteristic absorptions for classes of polar-substituted vinyl and *iso*propenyl groups have standard deviations of within 4 cm.$^{-1}$, and this, together with the large shifts observed between the classes of compounds, indicates that the correlations are reliable, even when only a small number of compounds has been examined for a given class.

Even when purely empirical, such correlations are of value for identification and structural determinations, but an understanding of the reasons for the frequency shifts would greatly assist in extending the results to new compounds.

The effect most readily interpreted is that of conjugation which lowers $\nu_{C:C}$. In the diolefins the interpretation is complicated by the effects of mechanical coupling and the selection rules, and for this reason values of $\nu_{C:C}$ are omitted from the Tables. Butadiene, for example, has an infra-red band at 1592 cm.$^{-1}$, and a Raman shift at *ca.* 1653 cm.$^{-1}$, the result of coupling. The mean value of *ca.* 1614 is lower than normal, presumably owing to conjugation (Sheppard and Simpson, *loc. cit.*, p. 32).

Where coupling does not occur, the observed value of $\nu_{C:C}$ is approximately related to the strength of the bond. Thus conjugation accounts for the lowering of $\nu_{C:C}$ in conjugated nitriles (ν_{CN} is also lowered; Sheppard and Sutherland, *J.*, 1947, 453; Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334) and in conjugated ketones and esters of α-unsaturated acids ($\nu_{C:O}$ is also lowered; Hartwell, Richards, and Thompson, *J.*, 1948, 1436). For the esters of unsaturated alcohols, however, $\nu_{C:C}$ is raised (as is $\nu_{C:O}$; *idem, ibid.*).

The doubling of $\nu_{C:C}$ for the vinyl ethers and the acrylates is probably due to rotational isomerism rather than Fermi degeneracy, but in the absence of low-temperature spectra of the crystals a decision cannot be made. It seems unlikely that such consistent splitting is due to degeneracy, since this would require a further characteristic absorption (below

650 cm.$^{-1}$) to give a second overtone or a combination degenerate with $\nu_{C:C}$. The doubling of $\nu_{C:O}$ in vinyl ketones also suggests rotational isomerism.

In consideration of the effect of polar groups upon the δ_{CH} absorptions at 850—1000 cm.$^{-1}$, conjugation is obviously unimportant (from the negligible shifts for the diolefins). Furthermore, an examination of the vinyl correlations shows that no single parameter can explain the shifts of the two bands. For example, in general the absorptions move in opposite directions, but for the vinyl esters both absorptions move to lower frequencies. However, the vinyl ester 870-cm.$^{-1}$ absorption may be wrongly assigned, and the two δ_{CH} absorptions may be superimposed at 948 cm.$^{-1}$ (cf. acrylonitrile, Table 1). There is a general qualitative parallelism between the shifts for vinyl and *iso*propenyl compounds similar to that reported for vinyl and vinylidene halides (Sheppard, Thesis, Cambridge, 1947, pp. 109 *et seq.*).

The large frequency shifts arising from polar substituents, and the constancy of the correlations, suggest that polar and electron-displacement effects, rather than mass effects, are responsible. In such a case, one might expect that the shifts would be algebraically additive when more than one substituent is present; unfortunately, only two suitable compounds were available to test this suggestion.

For 3 : 3-diethoxyprop-1-ene, $CH_2{:}CH{\cdot}CH(OEt)_2$, the shifts may be regarded as twice those for an allyl ether, *viz.*, $997 - 2 \times 8 = 981$ (obs. 986 cm.$^{-1}$) and $912 + 2 \times 11 = 934$ (obs. 935 cm.$^{-1}$). 3-Acetoxy-3-cyanoprop-1-ene may be regarded as having the shifts of an allyl ester imposed upon the frequencies for allyl cyanide, *viz.*, $984 - 12 = 972$ (obs. 978 cm.$^{-1}$) and $928 + 20 = 948$ (obs. 946 cm.$^{-1}$); although the agreement is quite good, further reference compounds would be needed to test the suggested additivity.

The possible use of the 1400-cm.$^{-1}$ absorption was not realised until much of the experimental work was completed, and the results are therefore incomplete with respect to this band. The relatively small range of frequencies observed (1404—1425 cm.$^{-1}$) suggests that, although the band might be useful for confirming the presence of the olefinic group, it would be of little value for deciding the nature of the substitution.

In addition to the olefinic absorptions, acrylates and methacrylates (Table 3) have five strong characteristic absorptions; those designated C and D are probably associated with the C–O vibrations observed in other esters (Thompson and Torkington, *J.*, 1945, 640). The A and B bands may be δ_{CH} (in plane) modes (Sheppard and Simpson, *loc. cit.*, Tables 4 and 7).

The authors are greatly indebted to Dr. W. Cooper and Mr. E. Catterall for supplying most of the compounds examined. They also thank the Dunlop Rubber Company for permission to publish this work.

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[*Received, March* 16*th*, 1953.]