Conformations of Some αβ-Unsaturated Carbonyl Compounds. Part V.[1] Assignments of Raman and Infrared Spectra of Methyl and [$^2H_3$]Methyl Acrylates and *trans*-Crotonates

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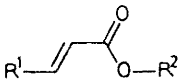
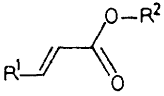
Raman and i.r. spectra of methyl and [$^2H_3$]methyl acrylates and *trans*-crotonates in the liquid state at room temperature and as frozen solids are presented together with vibrational assignments for particular conformers. Intensities of selected Raman bands at different temperatures lead to enthalpy differences (ΔH^0 ± standard deviation) of 377 ± 56 cal mol^{-1} between the high and low energy forms of methyl *trans*-crotonate, in very good agreement with a previous result based on i.r. measurements.

VARIABLE-TEMPERATURE i.r. studies[2] of methyl, [$^2H_3$]-methyl, ethyl, and [$^2H_5$]ethyl acrylates and *trans*-crotonates enabled bands to be assigned to low (I) and high (II) energy conformers. On this basis enthalpy and entropy differences were calculated for the system



(I)



(II)

R^1 = H or Me
R^2 = Me, [$^2H_3$]Me, Et, or [$^2H_5$]Et

(I) $\rightleftharpoons$ (II). However, Williams, Owen, and Sheridan[3] detect only (II) in the microwave spectrum of methyl acrylate. In order to resolve this apparent contradiction, measurement by an independent method was desirable. In the present work conformer bands are identified in the Raman spectra. Although Raman and i.r. spectra are both a consequence of molecular vibrations, the selection rules and the experimental techniques differ considerably and studies of different bands by each method can be regarded as independent in terms of assessing the validity of the conclusions of quantitative measurements. A ΔH^0 value for the equilibrium (I) $\rightleftharpoons$ (II) is, therefore, presented for methyl *trans*-crotonate for comparison with results of previous studies. The present studies enable previous[4-6] vibrational assignments for unsaturated esters to be revised and extended, with inclusion of information on assignments obtained by a recent study[7] of various deuteriated methyl acetates.

EXPERIMENTAL

Samples were obtained or prepared and purified by methods described previously.[2]

I.r. spectra of films and frozen solids were recorded on a Perkin-Elmer 457 instrument by using Beckman–R.I.I.C. variable-temperature equipment.

Raman spectra of liquids and annealed frozen solids were recorded with a JEOL JRS-SI Raman spectrophotometer fitted with a V.T. 3B variable-temperature accessory; the blue and green lines of the Coherent Radiation 52G Argon ion laser were used for excitation of the sample. Standard calibrations were employed; wavenumber scales for i.r. and Raman are expected to be within 1—3 cm^{-1} and the temperature scales for variable temperature measurements within 1—2 °C.

RESULTS AND DISCUSSION

The fundamental modes of vibration of methyl and [$^2H_3$]methyl acrylate and *trans*-crotonate are included in Tables 1 and 2, in terms of vibrations within or between CH_2:CH, CH_3·CH:CH, CO_2, and CH_3 groups. This description is only approximate since there will be considerable interaction in the case of many fundamentals. However, in a number of cases this approximate description has merit over others. Assignments are made on the basis of temperature dependence (bands which are associated with high and low energy conformers designated $\downarrow$ and $\uparrow$, respectively), comparison between CH_3 and $C(^2H)_3$ compounds, and comparison of the spectra of related families of compounds. Methyl acrylate and *trans*-crotonate have at best a plane of symmetry corresponding to the C_s point group leading to $20a' + 10a''$ fundamental modes in methyl acrylate and $25a' + 14a''$ fundamental modes in methyl *trans*-crotonate. The in-plane (a') and out-of-plane (a'') modes are both i.r. and Raman active, but should be polarized and depolarized respectively in the Raman. The observed vibrational spectra of the acrylates and *trans*-crotonates are presented in Tables 1 and 2 together with the assignments. These assignments are briefly discussed for particular spectral regions.

3500—2000 cm^{-1}.—The six CH stretching modes of methyl acrylate are assigned to bands between 2950 and 3110 cm^{-1}. Three bands occur in the i.r. and Raman spectra of methyl and [$^2H_3$]methyl acrylate in the 3030—3110 cm^{-1} region. We consider the most likely assignment to be that in which the highest and lowest wavenumber bands are assigned to the antisymmetric and symmetric CH_2 stretching modes, respectively. The relative weakness of the band near 3070 cm^{-1} in the Raman spectra would suggest a combination assignment, possibly 1633 + 1436 cm^{-1}. The symmetric CH_3O stretching mode is assigned at 2955 cm^{-1} and the corresponding antisymmetric mode is considered to

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[1] Part IV, W. O. George, and A. J. Porter, *J.C.S. Perkin II*, 1973, 954.

[2] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

[3] G. Williams, N. L. Owen, and J. Sheridan, *Trans. Faraday Soc.*, 1971, **67**, 922.

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[5] W. R. Feairheller and J. E. Katon, *J. Mol. Structure*, 1967, **1**, 239.

[6] F. Dalton, P. S. Ellington, and G. D. Meakins, *J. Chem. Soc.*, 1960, 3181.

coincide with the =CH stretching mode near 2994 cm^{-1}. CH_3O stretching modes of similar wavenumber values are assigned in methyl *trans*-crotonate; additional bands in this region of the spectrum of methyl and [$^2H_3$]methyl *trans*-crotonate are associated with corresponding modes of the CH_3C group. There appears to be considerable band overlap in this region.

TABLE 1

Vibrational spectra of methyl and [$^2H_3$]methyl acrylate (ν/cm^{-1})

Methyl acrylate			[$^2H_3$]Methyl acrylate			
I.r. (liquid)	Raman (liquid)	p †	I.r. (liquid)	Raman (liquid)	p †	Assignment
3106vw	3110w	dp	3106vw	3109m	dp	CH_2 as. str., a'
3074vw, sh	3068w, sh	?	3074vw	3077w	?	1633 + 1436 = 3609
3036w, sh	3038vs	sp	3040vw	3041vs	sp	CH_2 s. str., a'
3020vw, sh						
2994w, sh	2994vs	sp	2993vw	2995vs	sp	CH str. a', CH_3O as str., a' CH_3O as. str., a''
2955m	2955vs	sp				CH_3O s. str., a'
			2925vw	2930vw		
2905w	2911vw	sp				
	2892vw, sh					
2850w, sh	2857w	sp				
2837w, sh	2837w	sp				
	2804vw, sh	sp				
			2280w, sh	2280w	dp	
			2257w	2260w, sh	dp	$C(^2H)_3O$ as. str., a''
			2197w	2196m	sp	1725 + 455 = 2180, 1407 + 781 = 2188
			2129vw	2127s	sp	$C(^2H)_3O$ as. str., a'
			2083w	2082s	sp	$C(^2H)_3O$ s. str., a'
			2015vw			
1725vs	1726s	sp	1725vs	1722s	sp	C=O str., a'
			1655vw, sh	1655vw, sh	sp	
1633m	1634vs	sp	1633m	1635vs	sp	C=C str., a'
1620m			1618m			1277 + 351 = 1628, 2 × 810 = 1620
	1519vw	sp				
1460m, sh	1458w, sh	dp				CH_3 as. bend, a'
1450m, sh	1450w, sh	dp				CH_3 as. bend, a''
			1445vw, sh			
1436s	1440w	?				CH_3 s. bend, a'
1400vs	1404vs	sp	1407vs	1407vs	sp	CH_2 scissor, a'
	1310vw, sh	sp				
1293m, sh↑	1297m, sh	sp	1307vs↑	1308w, sh	sp	CH bend a'(I), CH_3O rock, a'(I)
1277vs↓	1282m	sp	1290vs, sh↓	1283m	sp	CH bend a'(II), CH_3O rock a'(II)
1206vs↑	1210w	sp	1220vs	1219w	sp	C–O str., a'(I), CH_3O rock, a''(I)
1184vs, sh↓	1184vw	dp				C–O str., a'(II), CH_3O rock, a''(II)
			1092vs	1088w, sh	sp	$C(^2H)_3O$ s. bend, a', $C(^2H)_3O$ rock, a'
1068vs↓	1067w	?	1073m↓	1072w	?	CH_2 rock, a'(II)
			1057w, sh	1059vw, sh	dp	$C(^2H)_3O$ as. bend, a''
1003w, sh	996w	?	1003vw, sh	1002w	sp	CH_2 rock, a'(I)
984vs			984vs	976vw, sh	mp	CH=CH def., a''
972s, sh	970w	mp	960m, sh	956m	mp	CH_2 def., a''
			947w, sh	944w, sh	?	
			902w	920vw, sh	dp	$C(^2H)_3O$ rock, a''
855m	856vs	sp				CH_3–O str., a'
812vs	813w	?	811s	802vs	sp	C–C str., a'
				781s, sh	sp	$C(^2H_3)O$ rock, a'', $C(^2H)_3O$ str., a', O–C=O bend, a'
677vw, sh			675vw, sh			O–C=O bend, a' and a''
663m↑	663vw↑	dp	647w↑	645vw	dp	CH_2=CH def., a''(I)
626vw↓	625w↓	sp	611vw↓	607vw	?	CH_2=CH def., a''(II)
522vw	523w, sh	sp	520vw	522vw, b, sh	?	C–C–O bend, a'(II) ?
476vw, sh	470m	sp	456vw, sh	454m	sp	C–C–O bend, a'(I)
	351m	sp				CH_3–O bend, a'
				330m	sp	$C(^2H)_3O$ bend, a'
	235m	sp		220m	?	C–OCH_3 bend, a'
	198w, sh	dp		185w, sh	dp	O–CH_3 torsion, a'', –OCH_3 torsion, a'', C–C torsion, a''

† Polarizations: sp = strongly polarized; mp = moderately polarized; dp = depolarized.

The i.r. spectra of [$^2H_3$]methyl acrylate and *trans*-crotonate show five bands of similar intensity between 2070 and 2280 cm^{-1}, but in the Raman spectra the three lowest wavenumber bands are more intense than the two highest wavenumber bands. The assignments shown in the Tables are in accordance with polarization measurements.

TABLE 2

Vibrational spectra of methyl and [$^2H_3$]methyl *trans*-crotonates (ν/cm^{-1})

Methyl *trans*-crotonate			[$^2H_3$]Methyl *trans*-crotonate			
I.r. (liquid)	Raman (liquid)	p †	I.r. (liquid)	Raman (liquid)	p †	Assignment
3050vw, sh	3055w, sh	?	3058vs, sh	3055w, sh	?	CH=CH as. str., a'
3030w, sh	3034m	sp	3030vw, sh	3033m	sp	CH=CH s. str., a'
2995w, sh	2990w, sh	?				CH_3O as. str., a'
2975w, sh	2978w, sh	?	2977w	2976w, sh	dp	CH_3C as. str., a', CH_3O as. str., a''
2950m	2953vs	sp	2945w	2943m ,sh	?	CH_3C as. str. a'', CH_3O s. str. a'
2920w, sh	2917vs	sp	2918w	2919vs	sp	CH_3C s. str., a'
	2885w, sh	sp	2877vw	2877w, sh	sp	
2850w, sh	2850m	sp	2853vw	2853m	sp	
				2734vw	sp	
			2273w, sh	2274vw	dp	1321 + 968 = 2289, 1198 + 1092 = 2290
			2252w	2252vw	dp	$C(^2H)_3O$ as. str., a''
			2200w	2194m	sp	2 × 1105 = 2210, 1321 + 903 = 2124
			2130vw	2125m	sp	$C(^2H_3)O$ as. str., a'
			2078w	2077s	sp	$C(^2H)_3O$ s. str., a'
1720vs	1719vs	sp	1720vs	1714vs	sp	C=O str., a'
1680w, sh	1680vw, sh	?	1675vw, sh	1676vs, sh	?	2 × 840 = 1680
1661s	1663vs	sp	1660m	1652vs		C=C str., a'
1653m, sh			1657w, sh			
	1637vw, sh	sp		1630vw, sh	sp	
1448w, sh	1446m	?	1446m	1440m	?	CCH_3 as. bend, a' OCH_3 as. bend, a''
1436s			1438m, sh			OCH_3 s. bend, a' CCH_3 as. bend, a''
1375w	1373m	sp	1375w	1376m	sp	CCH_3 s. bend, a'
1335w, sh						
1315vs↑	1317vw, sh	?	1321vs↑	1317vw, sh		CH=CH as. bend, a'(I)
1293s, sh↑	1292m	sp	1296s↓	1290m		CH=CH s. bend, a'(I), CH_3O rock, a'(I)
1276vs↓	1273w, sh	sp				CH=CH as. bend, a'(II)
1267s, sh↓			1272w↓	1273w, sh	sp	CH=CH s. bend, a'(II), CH_3O rock, a'(II)
1195vs↑	1196vw	sp	1198vs	1198m	sp	C–O str., a'(I), CH_3O rock, a''(I)
1178vs↓	1178vw, sh	?				C–O str., a'(II), CH_3O rock, a''(II)
1104s	1104vw	dp	1105w	1101vw	dp	CH_3C rock, a'
			1092s	1088vw, sh	dp	$C(^2H)_3O$ as. bend, a', rock a''
1043m↓	1044w	dp		1050vw, sh	dp	CH_3C rock, a''(II), $C(^2H)_3O$ s. bend, a'
1028m↑	1026w, sh	dp	1040m	1036w	dp	CH_3C rock, a''(I)
968s	989vw	sp	968s	972m	sp	CH=CH as. def., a''
934w	935w	sp	920w	916vw	dp	C–C str. a' $C(^2H)_3O$ s. bend a'
904w	906w	sp	903vw, sh	899vw, sh	?	$C(^2H)_3O$ rock, a', CH_3–O str., a'
				858w, sh	sp	
842m	846m	sp	837w	835w	dp	CH=CH as. def., a''
			786w	784w	sp	$C(^2H)_3$–O str., a'
724w	723m	sp				O–C=O bend, a'
689m	688vw	dp		682m	dp	C=O def., a''
	640vw	?		636vw	?	CH_3–C bend, a'
495w↓	496w↓	sp	490w↓	488w↓ !	sp	C–C–O bend, a'(II)
453m↑	452w↑	sp	440w↑	437vw↑	sp	C–C–O bend, a'(I)
385vw	386s	sp	382vw	378s	sp	C–C bend, a'
				369m, sh	sp	$C(^2H)_3$–O bend, a'
				345vw, sh	sp	
	323vw	sp		305w	sp	C–O–C bend, a'
	240vw, sh	?		220vw, sh	?	CH_3–C def. a'', CH_3–C torsion, a''
	197vw, sh	?		190vw, sh	?	O–CH_3, C–CH_3, and –OCH_3 torsion, a''
	160w	?		155w	?	C–C torsion, a''

† Polarizations: sp = strongly polarized; mp = moderately polarized; dp = depolarized.

2000—1500 cm^{-1}.—In the i.r. spectra of methyl and [$^2H_3$]methyl acrylate a doublet occurs in the C⁚C stretching region (1633 and 1620 cm^{-1}). On cooling both liquid and carbon disulphide solution samples there is no change in relative intensities until the solid state is attained and the samples are repeatedly annealed; the lower wavenumber component then disappears. It is possible that the component at 1620 cm^{-1} is due either to the fundamental of a high energy conformer,[5] or, more probably, to combinations of conformer bands at lower wavenumber in Fermi resonance with the C:C stretching mode.

The i.r. spectra of the *trans*-crotonates contain both high and low wavenumber components to the band near 1660 cm^{-1} (assigned to the C:C stretching mode) which are also present in the solid state spectrum. The band near 1680 cm^{-1} may be due to an overtone of the a' mode at 840 cm^{-1}.

1500—1000 cm^{-1}.—The assignments of the OMe bending modes are based on our studies of various deuteriated acetates [7] and on previous studies of methyl acetate [8] and methyl formate.[8,9] The MeC and MeO rocking modes and the C–O stretching modes are also assigned from these comparisons. The olefinic CH bending modes may be compared with those in acrylonitrile and crotononitrile.[10]

Within this spectral region a number of pairs of conformer bands are detectable in either or both the i.r. and Raman spectra. Bands arising from high energy conformers (↓) become relatively weaker at lower temperatures and are absent in the spectra of the solid. The corresponding band from the low energy conformer (↑) becomes relatively stronger at lower temperatures. Although the conformational splitting is due to differences in the mode of vibration, both components of pairs of conformer bands are given the same description.

In both *trans*-crotonate spectra a conformer pair is observed near 1315 and 1276 cm^{-1}; these are assigned to the a' antisymmetric CH bend because of the large i.r. intensity. A second pair of conformer bands near 1293 and 1267 cm^{-1} is present in the *trans*-crotonate and acrylate spectra; these are prominent in the Raman (polarized) and also in the i.r. This pair is assigned to an overlapping a' symmetric CH bend and an a' MeO rocking mode. A third pair of conformer bands near 1200 and 1180 cm^{-1} for all four species is prominent in the i.r. but weak in the Raman and is assigned to an overlapping a' C–O stretch and an a'' OMe rocking mode.

The fourth and lowest pair in this region occurs near 1070 and 1000 cm^{-1} in the acrylates (assigned to the a' CH_2 rocking mode) and near 1048 and 1028 cm^{-1} in the *trans*-crotonates (assigned to the a'' CH_3C rocking mode).

1000—500 cm^{-1}.—The two high frequency o.p. CH deformation modes of the vinyl group have been well characterized [11] and are considered in a more general study.[12] The third CH_2:CH o.p. mode at lowest wavenumber was assigned, on the basis of resolved fine structure, at 593 cm^{-1} in acraldehyde.[13] In methyl acrylate this has been assigned at 811 cm^{-1} on the basis of comparison with vinyl acetate,[5] and at 664 cm^{-1} on the basis of comparison with ethyl acrylate.[14] The present comparisons with [$^2H_3$]methyl acrylate support the latter assignment since in both species bands occur near 650 cm^{-1} which are Raman depolarized. These bands are intensified at lower temperature in the i.r. and Raman, and bands at 30—40 cm^{-1} to lower values become correspondingly weaker, suggesting conformational splitting for this mode. This splitting is readily explicable in terms of geometrical models which show considerable differences in the environment of the o.p. vinyl mode for the two conformers.

The o.p. CH:CH antisymmetric deformation in methyl and [$^2H_3$]methyl *trans*-crotonate spectra occurs near 968 cm^{-1}. The corresponding o.p. CH:CH symmetric deformation is less well characterized but has been assigned [10] to 768 cm^{-1} in *trans*-crotonitrile, 845 cm^{-1} in fumaronitrile, and 746 cm^{-1} in *trans*-but-2-ene. In the present work i.r. and Raman bands near 840 cm^{-1} are assigned to this mode.

The assignment of most of these o.p. CH modes is well established on the basis of i.r. intensities and vapour contours; it is therefore surprising that for certain of these modes the corresponding Raman bands are partly polarized. In a planar molecule o.p. vibrations should be completely depolarized in the Raman. These results may mean that these acrylates and *trans*-crotonates are not completely planar. Careful polarization measurements of these modes in a selected series of compounds would provide information on this matter.

In the 800—950 cm^{-1} region strong i.r. and Raman bands are observed. One very strong polarized Raman band at 856 cm^{-1} is observed in methyl acrylate and appears to shift to 781 cm^{-1} in the Raman spectrum of [$^2H_3$]methyl acrylate. This is therefore assigned to an Me–O stretching mode since this can have mass dependence. Prominent bands near 810 cm^{-1} in i.r. and Raman of both acrylates are likewise assigned to a C–C stretching mode on account of the absence of mass dependence. It is likely that the true modes involve a contribution from C–C and C–O bands in each case, and the intensities are likely to be high in the Raman if the C–C contribution is significant, and high in the i.r. if the C–O contribution is significant. The corresponding bands in the *trans*-crotonates are less intense, suggesting a smaller degree of localizations of the modes in comparison with acrylates.

Other modes which may be expected in this region

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[7] W. O. George, T. E. Houston, and W. C. Harris, *Spectrochim. Acta*, 1974, **30A**, 1035.

[8] J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1957, **1**, 201.

[9] H. Suzi and T. Zell, *Spectrochim. Acta*, 1963, **19**, 1933.

[10] J. R. Durig, C. K. Tong, C. W. Hawley, and T. Bragin, *J. Phys. Chem.*, 1971, **75**, 44.

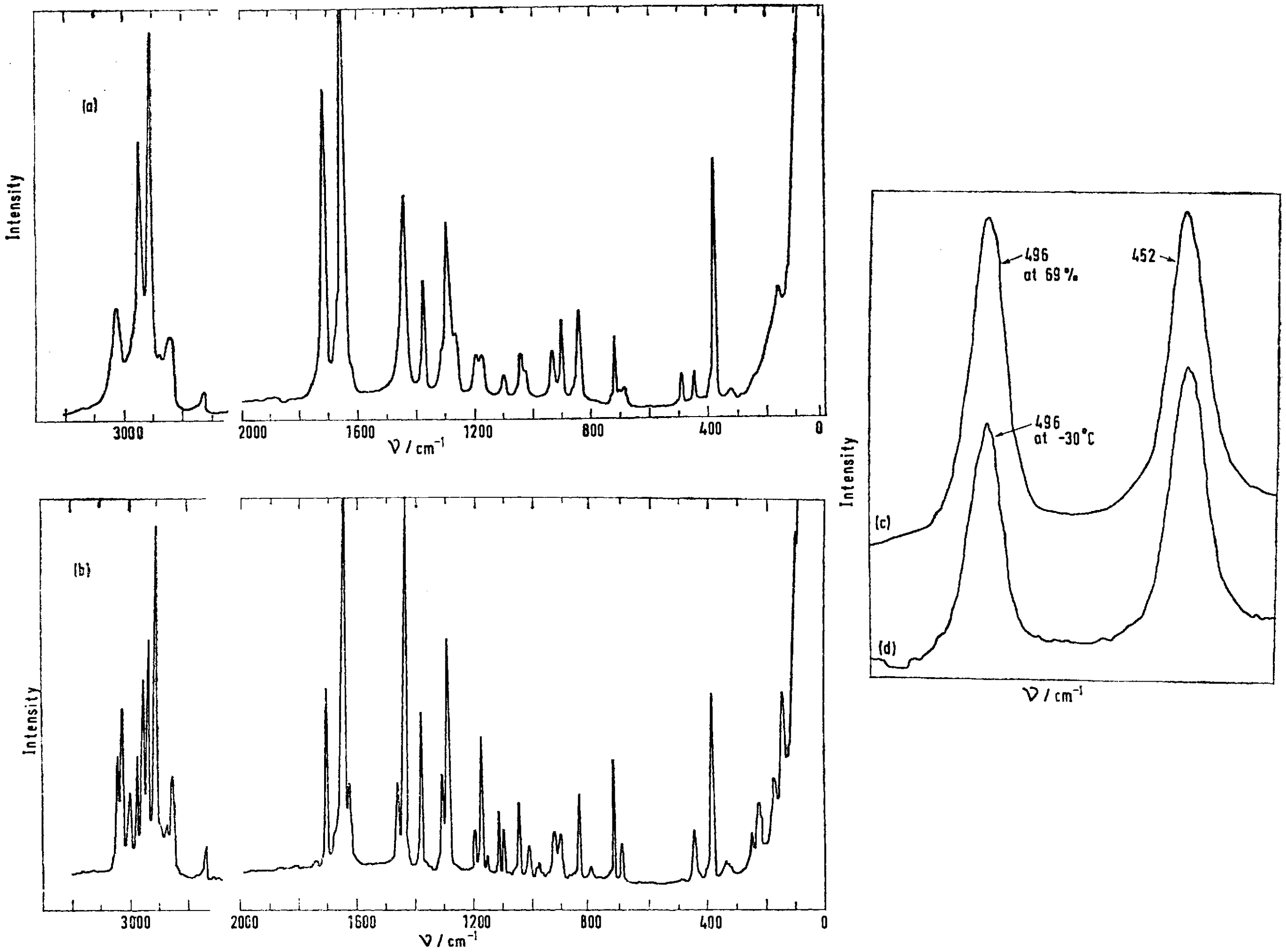
[11] W. E. Potts and R. A. Nyquist, *Spectrochim. Acta*, 1959, **15**, 679.

[12] J. R. Cowles, W. G. Fateley, and W. O. George, following paper.

[13] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc.* (*B*), 1969, 810.

[14] A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc.* (*B*), 1970, 1010.

are the *a*′ and *a*″ O–C=O bends, which are assigned near 700 cm^{-1} as coincident bands in the acrylates but as resolved bands in the *trans*-crotonates.



Raman spectra of methyl *trans*-crotonate: (a) 0—4000 cm^{-1} (room temperature); (b) 0—4000 cm^{-1} (annealed at −50 °C); (c) 425—525 cm^{-1} (at 69 °C); (d) 425—525 cm^{-1} (at −30 °C)

500—100 cm^{-1}.—Since bands in this region have not been well characterized, the assignments to skeletal deformations are only tentative. Conformer pairs of bands were observed in the spectra of the *trans*-crotonates near 490 and 445 cm^{-1}; the higher wavenumber band is absent from i.r. and Raman spectra measured for the solid state. These bands are assigned to the C–C–O bending vibration, which is likely to be susceptible to the conformational equilibrium (I) $\rightleftharpoons$ (II). I.r. bands (with Raman counterparts) at 476 and 456 cm^{-1} in the acrylates are similarly assigned to the C–C–O bending mode; a band near 520 cm^{-1} may be the corresponding mode in the high energy conformer since it is weakened considerably in the i.r. spectrum on cooling. However, there is no marked weakening for this band in the Raman so the assignment is doubtful. A prominent polarized Raman band near 380 cm^{-1} in the *trans*-crotonates with i.r. counterparts can be assigned to a C–C bend in the $CH_3{\cdot}CH{:}CH$ group on the basis of the absence of a band in the corresponding $CH_2{:}CH$ compounds. Bands at lower wavenumbers are observed in the Raman spectra with intensification from samples of frozen solids. It was not possible to assign the torsional modes in the spectra of methyl acetate and the various [$^2H_3$] forms. The corresponding –OMe and O–Me torsions with respect to two- and three-fold barriers in the present compounds are also likely to be very weak. Depolarized Raman bands near 190 cm^{-1} are tentatively assigned to both these modes. The torsion of the C–C bond forming a two-fold barrier between the two unsaturated groups is expected in the 100—165 cm^{-1} region,[15] and may be tentatively assigned near 160 cm^{-1} in the *trans*-crotonates. These interesting torsional assignments merit a detailed far-i.r. study involving vapour as well as liquid and solid phases in order to measure the barrier heights associated with the various conformers described.

Conformational Equilibria.—Measurements [2] of intensities of i.r. bands for selected conformer pairs in acrylates

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[15] R. K. Harris and R. E. Witkowski, *Spectrochim. Acta*, 1964, **20**, 1651.

and *trans*-crotonates have been made between −100 and 35 °C. It is assumed that the high energy band (↓) is associated with (II) and the low energy band (↑) with (I). Vibrational spectroscopy does not provide definitive evidence on these conformational assignments for molecules of this complexity. These assignments are based on comparison with simpler molecules[13] in which rotational fine structure or band contours may be related to molecular conformations.

In the present work, variable temperature Raman studies were made to provide independent information on the equilibrium (I) $\rightleftharpoons$ (II). Tables 1 and 2 reveal a number of pairs of Raman bands corresponding to i.r. conformer bands. This is confirmation of an equilibrium. In the current studies the Raman conformer bands are less amenable to quantitative measurements of intensity variation with temperature than the i.r. bands. No quantitative measurements were feasible on methyl acrylate because the relevant bands were weak or overlapped. For methyl *trans*-crotonate [Figure (a) and (b)] the Raman spectra of liquid and frozen solid are compared. A weak pair of conformer bands is observed at 496 and 452 cm^{-1}; these are sufficiently well separated for measurements of intensity variation with temperature. Eleven spectra were recorded at temperatures between −30 and 69 °C and the two extreme spectra are shown in the Figure [(d) and (c)]. Plots of log (I_{496}/I_{452}) against $1/T$ were made by using both peak height measurements and integrated peak area measurements. These yielded values of ΔH^0 for (I) $\rightleftharpoons$ (II) of 384 ± 41 (on the basis of peak heights) and 371 ± 68 cal mol^{-1} (on the basis of peak areas).

As in the previous i.r. study, a value is quoted with its standard deviation as an indication of precision. Since the standard deviation is determined from the statistics of the scatter of the points about the slope derived from the least squares plot, this is insensitive to the many systematic errors inherent in the method, which may lead to a result having good precision but poor accuracy. However, comparison of the mean value of ΔH^0 (377 ± 56 cal mol^{-1}) derived from the present Raman study with a mean value of 306 ± 30 cal mol^{-1} derived from the previous i.r. study shows very good agreement. Vibrational spectroscopy can only provide indirect information on the structure of the conformers participating on the equilibrium for these types of compound. Studies of saturated esters[7] have indicated that the ester group normally is stabilized in the form in which the $-CO_2R$ group is in the planar *cis* form shown in (I) and (II), and comparisons with other αβ-unsaturated carbonyl compounds[13] suggest that these are the low and high energy forms, respectively.

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