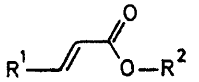
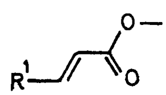
Conformations of Some αβ-Unsaturated Carbonyl Compounds. Part III.[1] Infrared Solution Spectra of Methyl, $[^2H_3]$Methyl, Ethyl, and $[^2H_5]$Ethyl Acrylates and *trans*-Crotonates

By **W. O. George** * and **D. V. Hassid**, School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames, Surrey
W. F. Maddams, Research and Development Department, B.P. Chemicals International Ltd., Epsom, Surrey

Infrared spectra of methyl, $[^2H_3]$methyl, ethyl, and $[^2H_5]$ethyl acrylates and *trans*-crotonates in solution in carbon disulphide are reported. Band intensity measurements at temperatures between −110 and 35 °C together with changes in the appearance of these bands on solidification of the solution are interpreted in terms of conformational equilibria between high- and low-energy forms. The additional enthalpies ($\Delta H°$) of the high-energy forms are remeasured for methyl acrylate as 326 ± 18 cal mol^{-1} and for methyl *trans*-crotonate as 306 ± 30 cal mol^{-1}. The additional entropy ($\Delta S°$) of the high-energy form of methyl *trans*-crotonate is estimated as 1·5 ± 1·0 cal mol^{-1} K^{-1}.

THE i.r. and Raman spectra of methyl and ethyl acrylates and methyl and ethyl *trans*-crotonates have been related[1] to an equilibria between *s-trans* (I) and a form (II) which may be *s-cis* or skew and is hence designated as non-*s-trans*. I.r. spectra measured at temperatures between −110 and 35 °C were used to determine the difference in enthalpy, $\Delta H°$, between these two conformers in solution and vapour states and as an aid to the assignment of the fundamental modes of vibration in each conformer. In the present work i.r. measurements are extended to frozen solution states and more detailed studies of the temperature-dependence of the integrated intensities of selected bands are made. These measurements are used to redetermine values of $\Delta H°$ and also, when feasible, to determine values of the entropy difference, $\Delta S°$, between the two conformers following the procedures outlined by Mizushima, *et al.*[2] and Hartman *et al.*[3] Studies on the temperature-dependence of i.r. bands in the spectra of $[^2H_3]$methyl, ethyl, and $[^2H_5]$ethyl acrylates and *trans*-crotonates have been made to provide further information on the nature of the conformationally sensitive bands in both systems.


(I)


(II)

R^1 = H or Me
R^2 = Me or Et

EXPERIMENTAL

The spectra were obtained on a Perkin-Elmer 457 spectrophotometer having a spectral bandwidth of 2 cm^{-1}. For intensity measurements a scan rate of 50 cm^{-1} min^{-1} was used. The transmission scale was checked by the use of high-speed rotating sectors (20% *T* and 50% *T*). The resolution was checked with ammonia vapour over the region 1250—750 cm^{-1} and the frequency scale was checked (to better than ±2 cm^{-1}) by water vapour and indene.[4]

The Beckman–R.I.I.C. VLT-1 low-temperature unit and TEM-1 temperature controller and observation thermocouples were used in conjunction with 0·5 mm or 0·1 mm cells. With this arrangement temperatures could be held constant to ±1 °C and accurate to ±2 °C. The standards used for the calibration of the potentiometer were acetone–solid carbon dioxide and freezing carbon disulphide. Intermediate temperatures were interpolated with an alcohol thermometer.

Samples were run at concentrations of 1—5% in carbon disulphide. For the frozen solution spectra only the 0·1 mm cell was used because of the level of scattered radiation. In our experience the use of solutions to obtain solid-state spectra has some advantages over the use of the pure liquid because such spectra are more reproducible and appear to have less tendency to form supercooled or metastable forms.

Band-area measurements were obtained by converting recorded transmission values into digital form on punch-tape; a computer programme was then used to determine the band-area measurements (integrated band intensities) by use of Simpson's rule and to replot the absorbance values of the bands at intervals of one wavenumber. The measurement of the intensities of overlapping bands has been the subject of detailed analysis[3,5-7] involving the simulation of i.r. bands. We used three methods to obtain areas of pairs of overlapping peaks. (*a*) The midpoint between the bands was found from the peak maxima from which a vertical line was dropped. (*b*) The minimum point between the peaks was found from which a vertical line was dropped. (*c*) The areas of the outer halves of the peaks were found and the values doubled.

The more systematic results were obtained from (*a*) and (*b*) and the less systematic results from (*c*); Baker and Yeaman[5] considered (*b*) to be the most reliable method. Only the results of method (*a*) are reported and these are expected to be precise to ±4%.

Commercial methyl and ethyl acrylates and *trans*-crotonates were distilled through a fractionating column and then purified chromatographically with a Wilkins Autoprep 705 instrument equipped with a 4 m Carbowax 20M column at 100—120 °C.

$[^2H_3]$Methyl acrylate was prepared by the dropwise addition of $[^2H_4]$methanol (3 ml) to freshly distilled acryl-

---

[1] Part II, A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc.* (*B*), 1970, 1070.

[2] S. Mizushima, T. Shimanouchi, K. Kuratani, and T. Miyazawa, *J. Amer. Chem. Soc.*, 1952, **74**, 1378.

[3] K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, 1968, **24**, *A*, 157.

[4] I.U.P.A.C. 'Tables of Wavenumber for the Calibration of Infra-Red Spectrometers,' Butterworths, London, 1961.

[5] A. W. Baker and M. D. Yeaman, *Spectrochim. Acta*, 1966, **22**, 1773.

[6] J. Pitha and R. N. Jones, *Canad. J. Chem.*, 1966, **44**, 3031.

[7] J. Pitha and R. N. Jones, *Canad. J. Chem.*, 1967, **45**, 2347.

oyl chloride (12 ml) at 0 °C. The reaction mixture was held at 0 °C for 30 min and then refluxed for 2 h. Octan-1-ol (10 ml) was added, the mixture refluxed for 2 h, and finally fractionally distilled, the fraction of b.p. 70—82 °C being collected. [$^2H_3$]Methyl *trans*-crotonate and [$^2H_5$]-ethyl acrylate and *trans*-crotonate were prepared in a similar manner. In all cases samples were purified by preparative g.l.c.

The purity of all samples was checked on a 2 m 5% P.E.G.A. column and a 1·5 m 10% Apiezon column at 60 °C in a Perkin-Elmer F11 chromatograph.

The ^1H n.m.r. spectra and the mass spectra of the deuteriated esters were consistent with the structures assigned to these compounds.

RESULTS AND DISCUSSION

Acrylates.—We reported [1] that cooling a solution of methyl acrylate in carbon disulphide led to an increase in the relative intensities of the higher-frequency components of two pairs of bands at 1290 and 1273 cm^{-1} and 1203 and 1181 cm^{-1}. We now report the frozen solution-state spectrum of methyl acrylate (Table 1) from which the lower-frequency components have disappeared. This observation adds further support to the existence of a conformation equilibrium as suggested previously. Additional features of the spectrum of methyl acrylate in a frozen solution state are summarised in Table 1. Bands at 1069 and 964 cm^{-1} also tend to disappear in the solid state but do not show the clear-cut systematic variation with temperature leading to a ready correlation with conformational equilibria. Certain splittings do appear; notably the band at 1203 cm^{-1} in the liquid to bands at 1196 and 1220 cm^{-1}. (We consider this more likely than an alternative possibility, that the pair at 1181 and 1203 cm^{-1} in the liquid state shift to 1196 and 1220 cm^{-1} in the solid state.)

The doublet at 1633 and 1620 cm^{-1} is of some interest because of the possible assignment to C=C stretching vibrations of two conformers. This explanation appears to receive support when methyl acrylate is studied as a liquid because on cooling to the solid state the lower-wavenumber component disappears. However in solution in carbon disulphide, carbon tetrachloride, or cyclohexane the two bands are well resolved and their relative intensities do not alter when the liquids are cooled to a solid from which the bands at 1273, 1181, 1069, and 964 cm^{-1} have all disappeared. This further supports the assignment of this pair to a C=C stretching vibration in Fermi resonance with overtones or combinations of low-frequency modes.[1] The disappearance of the 1620 cm^{-1} band from the liquid (as distinct from solution spectra) cannot be explained; it is presumably associated with the more complex selection rules prevailing in the solid state and serves as a warning against drawing conclusions from solid-state spectra in isolation. Spectra of frozen solutions may be expected to give more conformationally meaningful solute spectra when present under dilute conditions in inert solvents. The disappearance of the band at 964 cm^{-1} is also inexplicable. There is little doubt that this band is due to the methylene out-of-plane

TABLE 1

The i.r. wavenumber values (1750—600 cm^{-1}) of methyl, [$^2H_3$]methyl, ethyl, and [$^2H_5$]ethyl acrylates and *trans*-crotonates as solutions in carbon disulphide at different temperatures (25 to −150 °C)

Methyl acrylate: 1728vs—1721vs, 1633w—1635w, 1620w—1620w(i), 1401m—1412w, 1305w,sh—1307w, 1290m,sh—1297m(1), 1273s—absent(1), 1203vs—1220vs,b(2)(ii), absent—1196s, 1181s—(iii)(2), 1069s—absent, 1003m,sh—997s, 984s—990s, absent—982w,sh, 964s—absent, 853m—864m, 811s—813s, 664m—664m.

[$^2H_3$]Methyl acrylate: 1728vs—1721vs, 1634m—1635m, 1620w—1620w, 1401m—1412w, absent—1325w,sh, 1302vs,sh—1305s(1), 1290vs—absent(1), 1212vs—1230vs, 1091vs—1091vs, 1069w—absent(v), 1053w,sh—1053w,(v), 983s—993vs, absent—990s,sh, absent—980m,sh, 964s—963w,(vi), 902w—906w, 809s—810vs, 647w—645m.

Ethyl acrylate: 1724vs—1715vs, 1636w—1638m, 1620w—1620m(i), 1405m—1417m, 1387m—1387m, 1365w—1363vw, 1306w,sh—1308w,sh, 1295s—1302vs,sh(1), absent—1292vs,(1), 1270vs—absent, 1192vs—1208vs,b, 1172w,sh—(iv). 1113vw,sh—1122m(v), 1096w—absent(v), 1063s—1068vw(2), absent—1062vw, 1030m—1028vs(2), 985s—999s, absent—985s, 965m—absent, 915vw,sh—920m(v), 900vw,sh—absent(v), 859w—866s, 809w—826vs, absent—812vs, 660w—674s.

[$^2H_5$]Ethyl acrylate: 1724vs—1715vs, 1637w—1639m, 1618w—1618w, 1402s—1412w, 1300vs,sh—1305m(1), 1291vs—absent(1), 1220m—1232vs, 1211vs—1222s,sh, 1187vs—1190vs, 1177m,sh—1180m,sh, 1097s—1100s, 1086m—1090w,sh, 1059s—1060s, 1046s—1050m,sh, 1009vw—1000m,sh, 984s—980vs,b, 966s—absent, 953vw,sh—950vw, 909vw—932w, absent—913w, 870vw—870w, 810s—812vs, absent—738w, 679vw—673s, 657vw—660m,sh.

Methyl *trans*-crotonate: 1727vs—1710vs, 1680vw—1684vw, 1663m—1661s, 1655w,sh—1652w,sh, 1378w—1383w, 1335w,sh—1335w,sh, 1315vs—1325vs(1), 1296s—1295m(2), 1276m,sh—absent(1), 1267s—absent(2), 1196vs—1203vs(3), absent—1190vs, 1179vs—(iii)(3), 1104m—1108m, 1043m—absent(4), 1028m—1023m(4), 1010w,sh—1010vw,sh, 968s—970s, 939m—927vw, 908w—908vw, 842m—839s, 730w—730w, 692m—700m.

[$^2H_3$]Methyl *trans*-crotonate: 1725vs—1706vs, 1661m—1660m, 1657w,sh—1658m,sh, 1649vw,sh—1650w,sh, 1375w—1383vw, 1321vs—1337vs(1), 1298s—1303vw,sh(1), absent—1295w, 1272w—absent, 1198vs—1212vs, 1105w—1113w. 1092s—1093vs, 1040m—1038m, 968s—967s, 920w—912m(v), 903vw,sh—absent(v), 837w—837m, 687w—700w, absent—693w, 656w—absent.

Ethyl *trans*-crotonate: 1723vs—1714vs, 1681vw—1685w, 1663s—1660vs, 1655w,sh—1651m,sh, 1391w—1392vw,sh, 1378m—1383w, 1367m—1365m, 1330vw,sh—1330vw,sh, absent—1319s,sh, 1307vs—1312s(1), 1294s—1294m(2), 1273s—absent(1), 1263vs—absent(2), 1183vs—1194vs, 1169m,sh—1172w,sh(iii), 1103s—1121m, absent—1109s, absent—1096w,sh, 1044s—1043s, 969s—991m, absent—973s, 918w—917w, 841m—844m, 815vw—811w(v), 790vw—absent(v), 745vw—745m, 718vw—absent(v), 690m—696s(v).

[$^2H_5$]Ethyl *trans*-crotonate: 1723vs—1713vs, 1663m—1661m, 1656w,sh—1658m,sh, 1650w,sh—1652w,sh, 1375w—1377w,sh, 1323vs—1330s(1), 1295vs—1300vw,sh(1), 1273vw,sh—absent, 1194s,sh—1210m,sh, absent—1190vs, 1182vs—1180m,sh, 1101m—1110m,sh, absent—1103s, 1063m—1065s, 1052w,sh—1055m,sh, 1035vw—1040vw,sh, 1012vw—1009w, 986vw—985s, 970m—980s,sh, 928vw—929vw, 913vw—913w, 838w—843m, 687w—692m.

sh = Shoulder; s = strong; m = medium; b = broad; w = weak; v = very. (n) Systematic change of relative intensity with band of same number. (i) Absent from solid state spectrum of pure compound. (ii) Complex with components at 1235 (sh), 1222 and 1213 cm^{-1}. (iii) See text. (iv) Broad band at 1208 cm^{-1} obscures this band in the solid state spectrum. (v) Too weak and ill-defined for variable temperature study. (vi) Weakens further after annealing.

wagging mode in both conformers. The band at 1069 cm^{-1} may be the high-energy component of a pair for which the low-energy component could be at 1003 cm^{-1}; the intensity-dependence with temperature is somewhat less clear-cut in this case.

Further information on conformational assignments comes from examination of the spectra of [$^2H_3$]methyl acrylate, ethyl acrylate, and [$^2H_5$]ethyl acrylate. All three compounds show similar patterns of behaviour with temperature change. These are summarised in Table 1. One significant feature is the disappearance of bands in the range 1260—1290 cm^{-1} and the intensification of one or more bands in the range 1290—1320 cm^{-1} on cooling from liquid to solid state. This reveals a conformationally sensitive mode associated with the $CH_2\dot{:}CHCO_2$ group, and is in accord with an assignment [1] to a C–H deformation or rocking mode. Single bands are observed at 1212 and 1192 cm^{-1} in [$^2H_3$]methyl acrylate and ethyl acrylate respectively (a shoulder on the side of the band in the latter compound at 1174 cm^{-1} could conceivably arise from conformational doubling). In [$^2H_5$]ethyl acrylate an apparent doublet is observed at 1187 and 1214 cm^{-1}. However there is no relative intensity change with temperature nor does either band disappear on solidification although splittings of each band occur. We therefore conclude that the additional band is associated with a C–^{2}H deformation mode.

Crotonates.—We reported [1] that on cooling a solution of methyl *trans*-crotonate in carbon disulphide bands at 1315 and 1196 cm^{-1} intensified compared with bands at 1294 and 1178 cm^{-1}. We now report the spectrum of a solidified solution (Table 1). It is apparent that bands at 1276, 1267, 1179, and 1043 cm^{-1} disappear from the spectrum on freezing the solution. These are assigned to a high-energy conformer and are probably associated with bands at 1315, 1296, 1196, and 1028 cm^{-1} respectively, arising from corresponding modes in the low-energy conformer.

The pair of bands near 1200 cm^{-1} in methyl *trans*-crotonate resemble the similar pair in methyl acrylate in relation to temperature effects and splittings in the solid state.

The spectra of [$^2H_3$]methyl, ethyl, and [$^2H_5$]ethyl *trans*-crotonates as liquids and as frozen solutions are given in Table 1. These spectra parallel the spectra of the corresponding acrylates in that the only region in which evidence for conformational doubling occurs in all compounds is 1260—1290 cm^{-1} (high-energy form) and 1290—1350 cm^{-1} (low-energy form). The other conformationally sensitive pairs of bands in methyl *trans*-crotonate at 1196, 1179 cm^{-1} and at 1043, 1028 cm^{-1} appear to coalesce into single bands in the [$^2H_3$]-methyl, ethyl, and [$^2H_5$]ethyl forms.

These results for both acrylates and *trans*-crotonates suggest that there are two sets of conformationally sensitive modes; first those in methyl, [$^2H_3$]methyl, ethyl, and [$^2H_5$]ethyl compounds, and secondly those in methyl compounds only. The latter type presumably involve skeletal modes coupled to CH_3 deformation modes in a manner which is conformationally sensitive, a change of conformation bringing a change of coupling and hence frequency. Substitution of methyl by [$^2H_3$]methyl, ethyl, or [$^2H_5$]ethyl presumably removes this conformationally sensitive coupling.

Thermodynamic Parameters.—The standard enthalpy (ΔH°) and entropy (ΔS°) changes for the equilibrium *s-trans* $\rightleftharpoons$ non-*s-trans* forms can be related to the intensity, A, and absorption coefficient, ε, of bands assigned to *s-trans* and non-*s-trans* conformers (designated by subscripts t and n respectively) and measured at different temperatures T. The equilibrium constant, K, for the reaction can be expressed (1) in terms of the Beer–Lambert law, where C is the concentration.

$$K = \frac{C_n}{C_t} = \frac{\varepsilon_t A_n}{\varepsilon_n A_t} \qquad (1)$$

K can be substituted in the van't Hoff equation (2) to give (3). The calculation of ΔH° graphically from (3)

$$RT \ln K = -\Delta H^\circ + T\Delta S^\circ \qquad (2)$$

$$\ln\left(\frac{A_n}{A_t}\right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln\left(\frac{\varepsilon_n}{\varepsilon_t}\right) \qquad (3)$$

on the assumption that $\varepsilon_n/\varepsilon_t$ remains constant with temperature is well established but the calculation of ΔS° from (3) has only been attempted in a limited manner. Mizushima *et al.*[2] in studies on ethylene chlorohydrin measured the intensity A_c of a band common to both conformers and for which it was assumed that the absorption coefficient ε_c changed in the same way with temperature as ε_n and ε_t. From (1) and (2) equations (4) and (5) follow. Since the intensity of the common band, A_c, can be related to the total concentration of the two conformers, $C_n + C_t$, equation (6) follows.

$$\frac{C_n}{C_t} = \exp\left(\frac{-\Delta H^\circ}{RT}\right) \times \exp\left(\frac{\Delta S^\circ}{R}\right) \qquad (4)$$

$$\frac{C_t + C_n}{C_t} = 1 + \exp\left(\frac{-\Delta H^\circ}{RT}\right) \times \exp\left(\frac{\Delta S^\circ}{R}\right) \qquad (5)$$

$$\frac{A_c}{A_t} = \frac{\varepsilon_c}{\varepsilon_t}\left[1 + \exp\left(\frac{-\Delta H^\circ}{RT}\right) \times \exp\left(\frac{\Delta S^\circ}{R}\right)\right] \qquad (6)$$

ΔS° can be calculated from the slope and intercept of a graph of A_c/A_t against $\exp(-\Delta H^\circ/RT)$.

Hartman *et al.*[3] in studies on halogenated butadienes considered a further assumption that ε_t and ε_n are independent of temperature. If this assumption is valid A_t should be a linear function of A_n according to equation (7) where l is the cell path length. The assumption can be tested by plotting A_t against A_n, and if linear, the slope of the graph ($-\varepsilon_t/\varepsilon_n$) can be calculated, and substitution of $\varepsilon_t/\varepsilon_n$ in (3) enables ΔS° to be estimated.

$$A_t = -\frac{\varepsilon_t}{\varepsilon_n} A_n + \varepsilon_t l(C_t + C_n) \qquad (7)$$

The central considerations in using integrated intensity measurements to determine entropy changes is whether the absorption coefficients of pairs of bands associated with pairs of conformers and that of one or more common bands all vary with temperature in the same way (the assumption of Mizushima *et al.*[2]) or whether the absorption coefficients of pairs of bands remain constant (the assumption of Hartman *et al.*[3]). If either assumption is valid ΔS° can in principle be determined and it necessarily follows that the ratio of the absorption coefficients of the pair of bands is constant with temperature change so that ΔH° can be calculated.

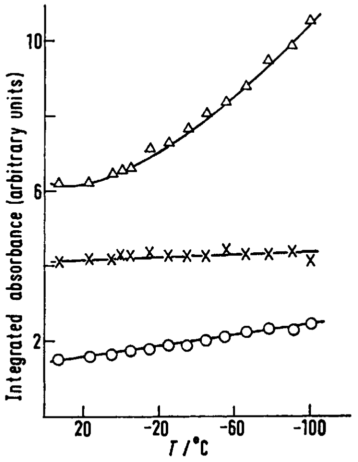


FIGURE 1 Integrated absorbances of bands in methyl acrylate at 1·7% (v/v) in CS$_2$ and 0·1 mm path-length at different temperatures: △, 1203 cm^{-1}; ×, 1181 cm^{-1}; ○, 808 cm^{-1}

In order to obtain more background to these questions the integrated intensities were measured on some model compounds. It has been found[8] that for a band at 1087 cm^{-1} in acetone the absorption coefficient increases linearly with decreasing temperature, whilst for a band at 1213 cm^{-1} in chloroform the absorption coefficient is constant with temperature change. It therefore follows that specific bands may or may not fulfil the various assumptions about temperature-dependence and this problem is being further investigated. A possible source of instrumental interference arises in these measurements because the sample and detector are at different temperatures possibly leading to net transfer of energy from detector to sample. In order to investigate this possibility, measurements were repeated on an instrument (Perkin-Elmer 180 spectrometer) where the radiation from the source was chopped before and after passing through the sample. The results were essentially identical which indicated that the effects were not attributable to instrumental effects but were molecular in origin.

The integrated intensity values of the pair ot bands at 1181 and 1203 cm^{-1} in methyl acrylate and that of a band at 808 cm^{-1} at various temperatures are shown in Figure 1. The value of ΔH° determined from equation (3) was 326 ± 18 cal mol^{-1} (Table 2) in good agreement with the previously determined value of 315 ± 42 cal mol^{-1}. Attempts to determine ΔS° were unsuccessful by use of either equation (6) (the method of Mizushima *et al.*[2]) or equation (7) (the method of Hartman *et al.*[3]). It was concluded that the absorption coefficients of the bands studied did not change with temperature in accordance with either set of assumptions. Figure 1 shows that the 1181 cm^{-1} band is considerably weaker than that at 1203 cm^{-1}. The effect of overlap may be more difficult to assess in this case than where the bands are of approximately equal intensity.

TABLE 2

Calculated thermodynamic parameters on methyl acrylate and methyl *trans*-crotonate

(*a*) ΔH° values

$CH_2{:}CHCO_2Me$ (cm^{-1})	ΔH°/ cal mol^{-1}	$CH_3CH{:}CHCO_2Me$ (cm^{-1})	ΔH°/ cal mol^{-1}
1288 1273	X	1315 1276	X
1203 1181	326 ± 18	1296 1267	X
1069 1003	X	1196 1179	300 ± 30
		1043 1028	313 ± 30

(*b*) ΔS° values for methyl *trans*-crotonate

Bands (cm^{-1})	Procedure	ΔS°/cal mol^{-1}K^{-1}
1028 1043	Hartman *et al.*[3]	2·0 ± 1·0
1196 1179 +968	Mizushima *et al.*[2]	1·1 ± 1·0

The ΔH° and ΔS° values ± standard deviations are determined from least-squares values of linear graphs. X: measurements precluded by band overlap.

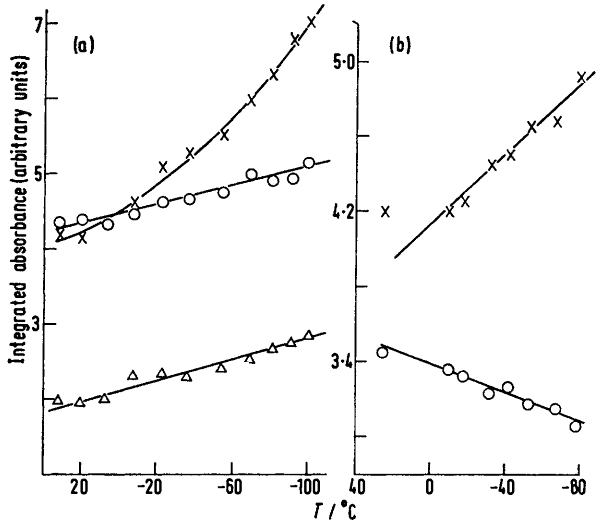


FIGURE 2 Integrated absorbances of bands in methyl *trans*-crotonates at 2% (v/v) in CS$_2$: (a) ×, 1196 cm^{-1}; ○, 1179 cm^{-1}; △, 968 cm^{-1}; (b) ×, 1028 cm^{-1}; ○, 1043 cm^{-1}

The integrated intensity values of pairs of bands at 1196 and 1179 cm^{-1} and at 1043 and 1028 cm^{-1} and a band at 968 cm^{-1} in methyl *trans*-crotonate at various

---

[8] W. O. George, D. V. Hassid, and W. F. Maddams, to be published.

temperatures are shown in Figure 2. The two values of ΔH° in Table 2 for the two pairs of bands assigned to pairs of conformers are in good agreement with each other (300 ± 30 and 313 ± 30 cal mol^{-1} respectively). The ΔH° values for methyl *trans*-crotonate are significantly lower than previous values.[1] The values of ΔH° reported here and previously were measured on different instruments. In order to resolve any instrumental uncertainties the measurements were repeated on a Perkin-Elmer 180 instrument for which the photometric accuracy was carefully checked. The value of ΔH° derived from the pair of bands at 1196 and 1179 cm^{-1} was determined as 304 ± 21 cal mol^{-1} from which we conclude that the previous value of ΔH° for methyl *trans*-crotonate was in error.

The determination of ΔS° for methyl *trans*-crotonate was attempted by both methods described. It was found that the pair of bands at 1196, 1179 cm^{-1} together with one at 968 cm^{-1} appeared to show a temperature-dependence in accord with the assumption of Mizushima *et al.*[2] The 968 cm^{-1} band is the olefinic out-of-plane deformation of the *trans*-C–H groups and is unresolved into components due to the two conformers. The intensity of the 968 cm^{-1} band [Figure 2(a)] increases in an approximately linear manner with decreasing temperature. The rate of increase is higher than that of the band at 1179 cm^{-1} assigned to the high-energy conformer but lower than that of the band at 1196 cm^{-1} assigned to the low-energy conformer. The plot of the ratio of the absorbances of the bands at 968 and 1196 cm^{-1} against the exponential temperature factor (Figure 3) is reasonably linear in accord with equation (6) which suggests that the underlying assumptions of Mizushima *et al.*[2] for these bands are valid. From the slope and the intercept of this graph the value of ΔS° was determined as $1{\cdot}1 \pm 1{\cdot}0$ cal mol^{-1} K^{-1} (Table 2). The large value of the uncertainty arises because in equation (6) it is clear that relatively small errors in the integrated absorbance values cause large errors in the intercept and slope and hence to a large error in ΔS°, Figure 2(a) shows that the assumptions underlying the method of Hartman *et al*[3] for ΔS° are not valid for the pair of bands at 1196, 1179 cm^{-1} since the absorption coefficients are not constant for these bands but clearly increase with decreasing temperature. However the temperature-dependence of the pair of bands at 1028 and 1043 cm^{-1} [Figure 2(b)] reveals that the intensity of the 1043 cm^{-1} band (high-energy conformer) decreases as the intensity of the 1028 cm^{-1} (low-energy conformer) band increases. The plot of the integrated intensity of the 1028 cm^{-1} band against that of the 1043 cm^{-1} band (Figure 4) is reasonably linear in accordance with equation (7) which implies that the underlying assumptions of Hartman *et al*[3] are valid in the case of these bands. From the slope, ΔS° is calculated to be $2{\cdot}0 \pm 1{\cdot}0$ cal mol^{-1} K^{-1} (Table 2).

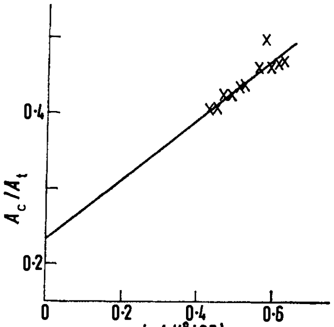


FIGURE 3 Determination of ΔS° in methyl *trans*-crotonate by the method of Mizushima *et al.*[2]

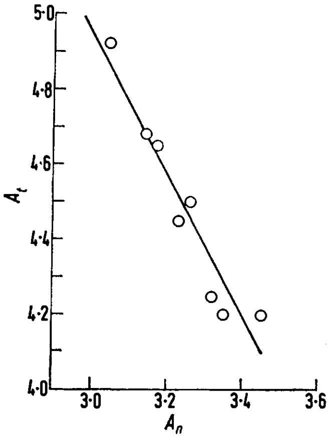


FIGURE 4 Determination of ΔS° in methyl *trans*-crotonate by the method of Hartman *et al.*[3]

The measurements made in the present work therefore suggest that the non-*s*-*trans*-conformers of methyl acrylate and *trans*-crotonate have an additional enthalpy (ΔH°) of 326 ± 18 cal mol^{-1} and 306 ± 30 cal mol^{-1} respectively and an additional entropy of $1{\cdot}5 \pm 1{\cdot}0$ cal mol^{-1} K^{-1} (measurable for methyl *trans*-crotonate only) above that of the *s*-*trans*-conformer. The standard deviations indicate that the precision is remarkably good on ΔH° values but poor on ΔS° values. The accuracy of these values may be affected by systematic errors. It would be desirable to measure these parameters by alternative methods to investigate this problem. These parameters measure the tendency of the *s*-*trans* form to change to the non-*s*-*trans* form in terms of the formation of a structure with greater strain energy but with a more disordered structure [equation (2)]. The ΔH° values are probably a measure of the greater strain energy in terms of non-bonded interactions of the non-*s*-*trans* form; the ΔS° values are a measure of greater disorder probably arising from alternative non-*trans* structures or from lower torsional frequencies in the non-*s*-*trans* form.

We thank the Royal Borough of Kingston upon Thames for a Research Assistantship to one of us (D. V. H.) and Dr. F. E. Dunstan and Perkin-Elmer Ltd., for the use of a Perkin-Elmer 180 instrument.

[1/1591 *Received*, 1*st September*, 1971]