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Conformations of the Esters. II.[1] The Conformation of Alkyl Acetates

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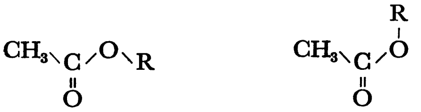
Alkyl acetates which carry secondary and tertiary alkyl groups have been found to have bifurcated bands in the carbonyl region of the infrared spectra. The origin of the bifurcated bands has been studied carefully, and it has been concluded that the Fermi resonance is the most probable origin of the phenomenon.

The conformation of the ester group has long been believed to be *s-trans*. The conformation of acetates is not an exception; it has been reported that alkyl acetates take the *s-trans* conformation, judging from the results of dipole-moment measurements,[2] electron diffraction,[3] and infrared spectroscopy.[4] The only exception is the report by Monaham[5] which postulates that the *s-cis* conformer exists in poly(*t*-butyl acrylate) and *t*-butyl acetate after irradiation by light, as revealed by the temperature dependence of the infrared spectra in the lower-frequency region. In the light of the fact that the *s-cis* conformer can exist together with the *s-trans* in some esters of formic acid which carry a bulky alkyl group,[1] it seems that it would be interesting to reinverstigate the situation of the acetate esters. Since it is believed that the *s-cis* conformation can exist in formates, because hydrogen is the smallest alkyl group in *n*-alkanoic acids and the steric repulsion between the alkyl group of an alcoholic part and hydrogen must be the least, the methyl group in acetates serves as a critical example in diagnosing the conformations of the ester group derived from the higher alkanoic acids: if no *s-cis* conformation exist in acetates, other higher alkanoic acid esters can not possibly show signs of the existence of the stable *s-cis* conformer. Thus, the infrared and nuclear magnetic resonance spectra of acetates have been reexamined. The purpose of this paper is to report the results of this investigation.



s-trans *s-cis*

Fig. 1. Two conformers of acetate.

Experimental

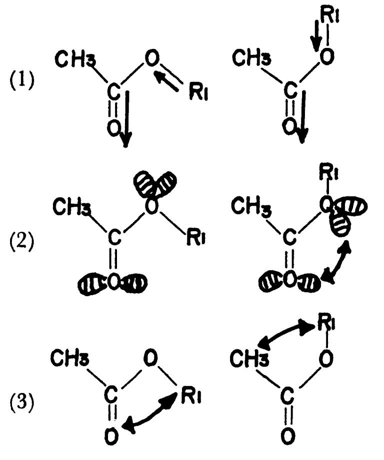
Materials. Various alkyl acetates were prepared according to the standard method. The purity of the samples was checked by means of their physical constants, infrared spectra, nuclear magnetic resonance spectra, and results of gas chromatography. *t*-Butyl acetate-d_3 (CD_3CO_2t-Bu) was prepared from *t*-butyl alcohol and acetyl-d_3 chloride in the presence of pyridine.

Spectra. The infrared spectra were measured by using a Hitachi EPI-G2 grating infrared spectrophotometer (4000——400 cm^{-1}) and a Perkin Elmer 112G single-beam grating spectrophotometer (3600—3300 cm^{-1}, 1800—1700 cm^{-1}). The latter instrument is more precise; the error is estimated to be 0.4 cm^{-1} at 1750 cm^{-1}. The absorption curves due to the carbonyl stretching of alkyl acetates were graphically separated, and it was confirmed that almost all the peaks were in good agreement with the calculated Lorenzian curves. The nuclear magnetic resonance spectra were recorded on a JNM-4H-100 spectrometer.

Results and Discussion

As has previously been described,[1] the chief factors governing the preference of the conformations of the ester group can be considered to include the following three: 1) the dipole-dipole interaction between C=O and O–R bonds, 2) the repulsion between lone-pair electrons of two oxygen atoms, and 3) the steric repulsion between either C=O and R or CH_3 and R (Fig. 2).

As to the first two factors, the *s-trans* conformer is favored over the *s-cis*. However, the third factor, which makes the existence of the *s-cis* conformer in *t*-butyl formate possible, may also operate in acetates so that the *s-cis* conformer exists. Although, of course, the repulsion between methyl and R groups cannot be overcome by that between R and carbonyl oxygen in a usual sense, there is a possibility that the ester group becomes non-planar because of the severe repulsion in



s-trans *s-cis*

Fig. 2. Factors governing the conformations of acetate.

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[1] M. Ōki and H. Nakanishi, This Bulletin, **43**, 2558 (1970).

[2] a) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1936**, 1383. b) R. J. W. LeFevre and A. Sundaram, *ibid.*, **1962**, 3904.

[3] J. M. O'Gorman, W. Schand, Jr., and V. Schmaker, *J. Amer. Chem. Soc.*, **72**, 4222 (1950).

[4] a) S. Ichikawa and T. Shimanouchi, Tokyo University, private communication. b) J. K. Wilmshurst, *J. Mol. Spectry.*, **1**, 201 (1957).

[5] A. R. Monoham, *J. Polym. Sci. Part A-1*, **5**, 2333 (1967).

[6] The correction for the intensity and for the shapes of the infrared absorption bands of esters, as measured with this spectrometer, has been discussed in detail by Kuratani and Minegishi; see K. Kuratani and A. Minegishi, This Bulletin, **31**, 586 (1958).

Table 1. Absorption maxima due to carbonyl stretching vibration of alkyl acetates and solvent effect

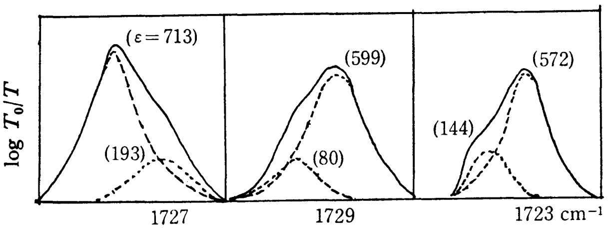
	Compound	Solvent: CCl_4 (2.23)[a) (c=0.0005 mol/l)		Solvent: CH_3CN (37.5)[a) (c=0.05 mol/l)		Solvent: DMSO (48.9)[a) (c=0.05 mol/l)	
I	CH_3CO_2Me	1749.0 cm^{-1} [c)	(824)[b)	1742.2 cm^{-1}	(963)[b)	1738.0 cm^{-1}	(874)[b)
II	CH_3CO_2Et	1741.2[c)	(696)	1736.4	(679)	1732.3	(759)
III	CH_3CO_2*n*-Pr	1742.9	(473)	1734.1[d)	(328)		
IV	CH_3CO_2*n*-Bu	1741.9	(736)	1734.2[d)	(874)		
V	CH_3CO_2*i*-Pr	1728[c) 1737.2	(87) (1000)	1728 1739	(740) (72)	1722 1736	(842) (11)
VI	CH_3CO_2*c*-C_6H_{11}	1728[c) 1735.7	(49) (650)	1717 1729.4	(97) (576)	1719 1728	(264) (844)
VII	$CH_3CO_2CHEt_2$	1729 1736.6	(175) (845)	1727.5[d) 1738	(504) (45)	1725 (broad)	(697)
VIII	CH_3CO_2*t*-Bu	1727 1738.4	(314) (764)	1728.7 1741	(559) (80)	1723.0 1736	(572) (144)
IX	CD_3CO_2*t*-Bu	1728 1735.4	(129) (521)	1720 1733	(364) (297)	1717 1731	(576) (324)
X	CH_3CO_2*t*-Am	1727[c) 1735.6	(142) (701)	1725.4 1737	(685) (124)	1722.0 1733	(646) (162)

a) Numericals shown in parentheses are dielectric constants at 20°C.
b) Numericals shown in parentheses are molar absorption coefficients.
c) c=0.05 mol/l in CS_2.
d) c=0.007 mol/l.

the planar conformation and that, in such a conformation, the *s-cis* becomes relatively favored.

Infrared Spectra. From the results obtained with formates[1) it is expected that the *s-cis* and *s-trans* conformations of acetates are reflected in the carbonyl stretching vibration absorptions. Many authors have reported on the infrared C=O stretching spectra of acetates,[7,8) but none has discussed the shapes of the absorptions, most of the attention being devoted to the frequencies and intensities of the bands. The results obtained in this study are shown in Table 1. It can be pointed out immediately that methyl and ethyl acetates give only one absorption (which is sharp and symmetrical) in the solvents studied, whereas isopropyl and *t*-butyl acetates give rise to two absorptions. Clearly those acetates which are derived from primary alcohols give only one absorption, while those derived from secondary and tertiary alcohols give two absorption peaks.

The solvent effect (see Fig. 3) on these absorptions is remarkable. With only one exception (cyclohexyl acetate), the absorption at the higher frequency, which is the stronger one in such nonpolar solvents as carbon tetrachloride and carbon disulfide, becomes the minor absorption in such polar solvents as acetonitrile and dimethyl sulfoxide. In order to make the situation clearer, the solvent effect on the carbonyl-stretching absorption of acetates was studied by changing the mixing ratio of carbon tetrachloride to acetonitrile.



in CCl_4 in CH_3CN in DMSO

Fig. 3. Solvent effect on ν_{CO} of *t*-butyl acetate.

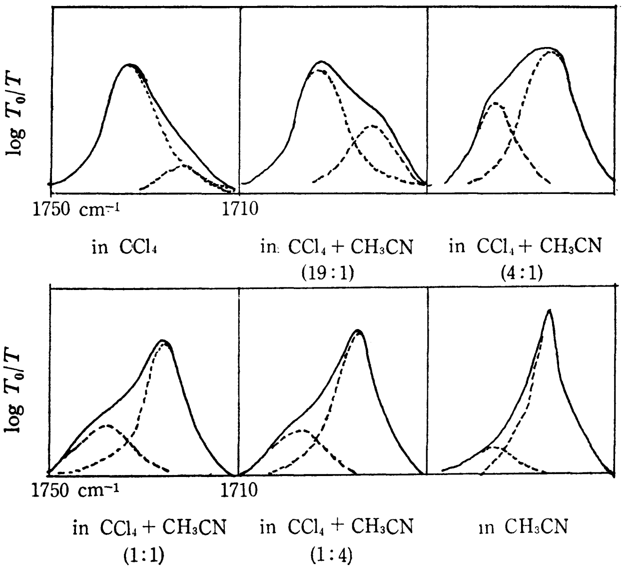


Fig. 4. Effect of solvent on the C=O stretching absorption of *t*-butyl acetate.

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7) a) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, **1945**, 640. b) E. J. Hartwell, R. E. Richards, and H. W. Thompson, *ibid.*, **1948**, 1436. c) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953). d) D. G. I. Felton and S. F. D. Orr, *J. Chem. Soc.*, **1955**, 2170. e) T. L. Brown, *J. Amer. Chem. Soc.*, **80**, 3513 (1958). f) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**,14(1959). g) A. R. Katritzky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, **16**, 964 (1960). h) H. A. Ory, *Anal. Chem.*, **32**, 509 (1960). i) K. Bowden, N. B. Chapman, and J. Shorter, *Can. J. Chem.*, **41**, 2154 (1963). j) N. Mori, Y. Asano, and Y. Tsuzuki, This Bulletin, **41**, 1871 (1968).

8) K. J. Morgan and N. Unwin, *J. Chem. Soc.*, *B*, **1968**, 880.

TABLE 2. EFFECT OF SOLVENT ON ν_{co} OF *t*-BUTYL ACETATE (c=0.05 mol/l)

Solvent		Band A	Band B	A/B
CCl_4 %	CH_3CN %	cm^{-1} (ε)	cm^{-1} (ε)	
100	0	1738.4 (764)	1727 (314)	2.43
95	5	1736.4 (639)	1725 (340)	1.88
75	25	1739 (301)	1727 (620)	0.49
50	50	1737 (266)	1725.5 (698)	0.38
25	75	1735 (213)	1726 (678)	0.31
0	100	1738 (80)	1725.5 (599)	0.13

The results obtained with *t*-butyl acetate are shown in Fig. 4 and Table 2. Apparently, as the polarity of the mixed solvent increases, the absorption at higher wave number diminishes, whereas the absorption at lower wave number increases, in intensity.

The bifurcation of the carbonyl bands of the acetates which carry secondary or tertiary alkyl groups could be explained as resulting from any one of the following causes: 1) solute-solvent interaction, 2) solute-solute interaction, 3) equilibrium between *s-cis* and *s-trans* conformational isomers, and 4) Fermi resonance (including a fairly strong overtone or combination tone).

The first two possibilities may be ruled out for the following reasons: 1) The bifurcation of the carbonyl band in nonpolar solvents because, in these solvents, solute-solvent interactions are negligibly samll. 2) It is very difficult to explain, from the intermolecular interaction, why methyl and ethyl acetates show only one band, whereas secondary and tertiary alkyl acetates show two bands. 3) The concentration of the solution is so low that the intermolecular solute-solute interaction is hardly possible. 4) *t*-Butyl acetate gives essentially the same absorption curves at 0.5, 5, and 50 mmol/l concentration.

If the populations of the rotational isomers change according to the polarity of the solvents, this change must be reflected in the skeletal vibrations. Thus, the infrared spectra of *t*-butyl acetate at lower frequencies (1100—400 cm^{-1}) were recorded in the range of 23°C and —150°C, the three phases being covered by this technique. The results are shown in Figs. 5 and 6. No clear change in the absorptions could be found.

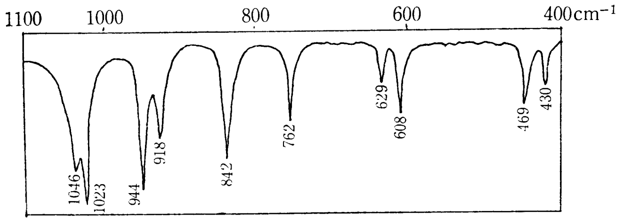


Fig. 5. Infrared spectra of *t*-butyl acetate in the range of 1100—400 cm^{-1} in liquid state.

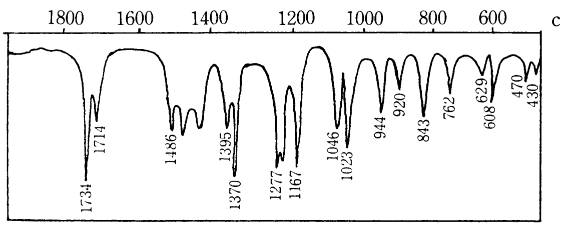


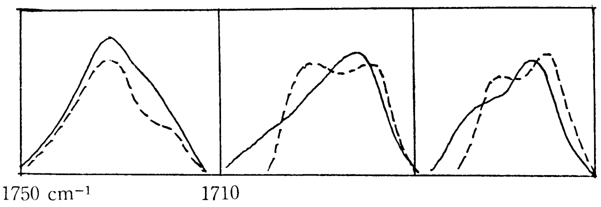
Fig. 6. Infrared spectra of solid state *t*-butyl acetate at lower temperature.

The *s-cis* conformer of the ester is considered to be more polar than the *s-trans*, because the arrangement of bond dipoles implies the more polar nature and because the calculated dipole moments, calculated using the usual C–O and C=O bond dipoles, are 3.40 and 1.53D for the *s-cis* and *s-trans* conformers respectively. These considerations necessarily mean that the population of the *s-cis* conformer will become denser in a polar solvent relative to a non-polar solvent. Thus, the infrared spectra in 1100—400 cm^{-1} region were again scanned with solutions made by dissolving *t*-butyl acetate in solvents of various polarities (CS_2, $CHCl_3$, CH_3CN, DMSO, and $HCONMe_2$). The results showed essentially no change in the spectra, the one exception being a band at 918 cm^{-1} which became stronger in polar solvents.

Since the *s-cis* conformer of the formates is known to give an absorption at a higher frequency than the *s-trans* in the carbonyl-stretching absorption region, and since this arrangement agrees with the consideration of intramolecular dipolar interactions, it is natural to assume that it is the *s-cis* conformer of the acetate which gives rise to an absorption at a higher frequency. However, this consideration leads to a conclusion which is the reverse of actuality: namely, the absorption band which is enhanced in polar solvents is the one located at the lower frequency (see Fig. 4).

All these discussions favor the absence of the *s-cis* conformer of the acetates.[9] Thus, the third possibility may be disregarded also.

Further support for ruling out the possibility of conformational heterogeneity as being the reason for the bifurcation of the carbonyl band could be obtained by studying the overtone region of the carbonyl stretching. Thus, the infrared spectrum of *t*-butyl acetate in the region of 3600—3400 cm^{-1} was carefully recorded. It was made clear that *t*-butyl acetate has only one symmetrical sbsorption, at 3447.6 cm^{-1} (ε=4.00), in carbon tetrachloride at the low concentration of 0.01 mol/l. This result suggests that the most probable cause of the



in CCl_4 (c=0.0005 mol/l) in CH_3CN (c=0.05 mol/l) in DMSO (c=0.05 mol/l)

Fig. 7. Infrared spectra of ν_{CO} of *t*-butyl acetate and *t*-butyl acetate-d_3.
—— line: CH_3CO_2t-Bu
---- line: CD_3CO_2t-Bu

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[9] Morgan and Unwin[8] recently suggested that the *s-cis* conformer might be present in isopropyl and *t*-butyl acatetes, judging from the abnormal solvent effect on the carbonyl-stretching vibration in the infrared spectra. However, since their discussion assumed that these compounds show only one carbonyl absorption, their results must be reinvestigated in the light of the fact reported above.

Table 3. Infrared spectra absorptions of lower region of alkyl acetates (in CS_2)

I CH_3CO_2Me	II CH_3CO_2Et	V CH_3CO_2*i*-Pr	VIII CH_3CO_2*t*-Bu	IX CD_3CO_2*t*-Bu	X CH_3CO_2*t*-Am
1247 (s)		1240 (s)	1277 (s)	1274 (s)	1253 (s)
1180 (w)		1066 (s)	1255 (s)	1260 (s)	1204 (m)
1156 (w)		1049 (s)	1174 (s)	1165 (s)	1158 (s)
1049 (s)	1097 (s)	1026 (s)	1046 (m)	1108 (m)	1140 (s)
981 (m)	1040 (s)	970 (m)	1023 (s)	1079 (m)	1066 (m)
846 (m)	1003 (m)	909 (m)	944 (m)	1035 (m)	1051 (s)
639 (m)	938 (m)	897 (m)	918 (m)	901 (m)	1018 (m)
604 (m)	914 (m)	856 (m)	842 (s)	875 (m)	950 (m)
431 (m)	846 (m)	777 (m)	762 (m)	825 (s)	940 (s)
	787 (m)	651 (s)	629 (s)	757 (m)	926 (s)
	635 (m)	625 (s)	608 (m)	728 (m)	830 (m)
	609 (m)	503 (s)	467 (m)	666 (s)	784 (s)
	463 (m)		430 (s)	614 (s)	750 (s)
	440 (m)			564 (s)	747 (s)
				536 (s)	625 (s)
				442 (s)	609 (s)
					505 (s)
					460 (s)

s=strong, m=medium, w=weak

bifurcation of the carbonyl band is not the confromational heterogeneity, but the overtone or combination tone, which is enhanced by Fermi resonance.

After establishing the origin of the bifurcation of the carbonyl band of some acetates, it seemed that it would be interesting to know what kind of vibration is responsible for the Fermi resonance. Thus, the deuteration of the acetyl methyl of *t*-butyl acetate was carried out and the infrared spectra were measured. The reason for this deuteration was the fact that there are numerous examples of carbonyl compounds which show Fermi resonance in the carbonyl region attributed to the resonance between the carbonyl fundamental and the overtone of the α C–H deformations.[10–14] The results with *t*-butyl acetate-d_3 are shown in Fig. 7, together with the curves of undeuterated samples for the sake of comparison. As may be seen in Fig. 7 and also in Table 1, *t*-butyl acetate-d_3 also has two absorptions in the carbonyl region in both polar and nonpolar solvents, this behavior being similar to that of the nondeuterated specimen; the only difference between the deuterated and nondeuterated compounds is the fact that the former always give a somewhat stronger band on the higher-frequency side. Thus, it is unlikely that any of the vibrational modes involving hydrogen is responsible for the Fermi resonance.

The infrared spectra of some acetates in carbon disulfide at the lower frequencies are given in Table 3. The skeletal vibrations are expected to be sensitive to the mass of R in CH_3CO_2R; the results shown in Table 3 conform with this expectation. Nevertheless, all the secondary and tertiary alkyl acetates studied so far give rise to a bifurcated band. Thus, we prefer that a common band at 1280—1240 cm^{-1}, which may be assigned to the antisymmetric stretching mode of the C–O–C of the esters, be chosen as one of the origins for the bifurcation in the carbonyl region. Then another band which is responsible for this phenomenon should be found at *ca.* 460 cm^{-1}. Indeed, we can see that those substances which give two bands in the carbonyl region have a fairly strong absorption at 505—430 cm^{-1}, although the assignment of these bands is still obscure. Thus, it can tentatively be concluded that the bifurcation of the carbonyl bands of some acetates can be attributed to the Fermi resonance between the carbonyl fundamental and a combination tone arising from the antisymmetric C–O–C stretching mode and an unknown mode of vibration which gives absorption at 505—430 cm^{-1}.

Nuclear Magnetic Resonance Spectra. The proton magnetic resonance spectra of *t*-butyl acetate in a mixed solvent of carbon disulfide and dichloromethane were measured at various temperatures. The *t*-butyl and acetyl methyl signals appear at 1.40 and 3.07 ppm downward from TMS at room temperature. The chemical shifts are almost the same at −50, −70, and −95°C. No sign of a decrease in the peak heights of these peaks is found as the temperature is lowered.[15] Thus, the results conform with those obtained by the infrared spectral study in that the conformational heterogeneity is not observed with *t*-butyl acetate.

The authors wish to express their hearty thanks to Professor T. Shimanouchi and S. Ichikawa for their helpful discussions.

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[10] a) R. N. Jones, C. L. Angell, T. Ito, and R. J. D.Smith, *Can. J. Chem.*, **37**, 2007 (1959). b) R. N. Jones and B. S. Gallagher, *J. Amer. Chem. Soc.*, **81**, 5242 (1959).

[11] C. L. Angell, P. J. Krueger, R. Lauzon, L. C. Leitch, K. Koack, R. J. D. Smith, and R. N. Jones, *Spectrochim. Acta*, **1959**, 926.

[12] R. P. M. Bond, T. Cairns, J. D. Connolly, G. Eglinton, and K. H. Overton, *J. Chem. Soc.*, **1965**, 3958.

[13] P. Yates and L. L. Williams, *J. Amer. Chem. Soc.*, **80**, 5896 (1958).

[14] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, (1959).

[15] Lojo *et al.* measured the NMR spectra of methyl acetate in the range of 120°—−40°C and found no outstanding change. O. R. Lojo, C. K. Hancock, and A. Danti, *J. Org. Chem.*, **31**, 1899 (1966).