BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1871—1875 (1968)

Intramolecular Hydrogen Bonds. XII.[1] The Dipolar-field and the Hydrogen-bonding Effects of the Hydroxyl Group on the Carbonyl Frequencies of Aliphatic Hydroxy-carboxylates

Nobuo MORI, Yuzuru ASANO and Yojiro TSUZUKI
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received September 25, 1967)

The infrared carbonyl-stretching absorption bands of several methoxy- and hydroxy-alkanoates have been measured in dilute carbon tetrachloride solutions, and their frequency shifts from the normal bands of ethyl alkanoates have been explained in terms of the dipolar-field and the hydrogen-bonding effects of the substituents. Further, as regards the direction of hydrogen bonding, the spectral data of the hydroxy-esters lead to essentially the same conclusion as that based on their hydroxyl spectra. However, the magnitudes of the carbonyl-frequency shifts due to hydrogen bonding can not be related to those of the corresponding hydroxyl shifts.

In general, the hydrogen bonding of an alkoxycarbonyl group with a hydroxyl preferably involves the carbonyl group, rather than the alkoxy group, as the proton acceptor; the most striking spectral evidence for this is the lowering in carbonyl frequency which results from the formation of a hydrogen bond,[2,3] this lowering usually being of the order of about 10—20 cm^{-1}. In unusual cases where the alkoxy group participates in the hydrogen bonding, however, the carbonyl frequency rises about 10 cm^{-1} above the usual value.[4] This can be a criterion for deciding which of the two proton-acceptors is involved in the hydrogen bonding.

This spectroscopic method of determination has hitherto been used in elucidating similar problems in several intramolecularly hydrogen-bonded systems, such as alicyclic diol-monoacetates,[5] alicyclic hydroxy-carboxylates,[6] and pyrrole-carboxylates.[7] In their own previous papers[8-10] the present authors reported, on the basis of the hydroxyl spectra exclusively, that the intramolecular hydrogen bonding in aliphatic hydroxy-carboxylates involved predominantly the carbonyl group as the proton acceptor. In the cases of ethyl *d,l*-lactate and *d*-tartrate, the carbonyl frequencies were about 4 cm^{-1} lower in carbon tetrachloride than in ether.[8] However, the extent of frequency-lowering in the former solution did not provide any reliable evidence for the above type of hydrogen bonding. In order to elucidate this problem, the carbonyl spectra in dilute carbon tetrachloride solutions have now been measured, together with those of corresponding methylated-hydroxy compounds selected for purposes of comparison.

Experimental

Samples. All the esters examined were known compounds, some of them were commercial products and others, prepared by known methods. They were purified through several fractional distillations; their physical constants were equal or very close

---

[1] Part XI: N. Mori, Y. Takahashi and Y. Tsuzuki, This Bulletin, **40**, 2720 (1967).

[2] R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2820 (1952).

[3] S. Searles, M. Tamres and G. M. Barrow, *ibid.*, **75**, 71 (1953).

[4] H. B. Henbest and B. J. Lovell, *J. Chem. Soc.*, **1957**, 1965.

[5] H. B. Henbest, G. D. Meakins and T. I. Wrigley, *ibid.*, **1958**, 2633; F. Dalton, J.I. McDougall and G. D. Meakins, *ibid.*, **1963**, 4063; R. West, J. J. Korst and W. S. Johnson, *J. Org. Chem.*, **25**, 1976 (1960); T. C. Bruice and T. H. Fife, *J. Am. Chem. Soc.*, **84**, 1973 (1962).

[6] H. R. Cole and G.T.A. Müller, *J. Chem. Soc.*, **1959**, 1224; J. Castells and J. Palau, *ibid.*, **1964**, 4398.

[7] R. Grigg, *ibid.*, **1965**, 5149.

[8] N. Mori, Y. Tsuzuki and H. Tsubomura, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **77**, 459 (1956).

[9] N. Mori, S. Omura, O. Yamamoto, T. Suzuki and Y. Tsuzuki, This Bulletin, **36**, 1401 (1963).

[10] N. Mori, S. Omura, N. Kobayashi and Y. Tsuzuki, *ibid.*, **38**, 2149 (1965).

to the literature values. The carbon tetrachloride was fractionally distilled over phosphorus pentoxide.

Infrared Measurement. The carbonyl-stretching spectra were measured at *ca.* 25°C, using a Hitachi EPI-2 double-beam spectrophotometer equipped with a sodium chloride prism. The measurement was carried out both in the neat state and in solutions of such low concentrations (of about 1—2 mmol/*l*) that any intermolecular hydrogen bonding, as revealed by the hydroxyl spectra,8—10) was negligible. For the solution measurement, both the reference- and the sample-cell used had a path length of 1.0 cm. The observed frequencies were calibrated against the spectrum of a standard polystyrene film.

Results and Discussion

For purposes of comparison, a series of alkyl alkanoates (1—8) also were examined under the same conditions, since there have been no descriptions of their carbonyl data being measured in concentrations as low as 1 mmol/*l*; the spectra in solutions were almost equal to those in the neat state and they were essentially symmetric with respect to the ordinate at the apparent maximum. The peak frequencies are equal to, or very close to, the

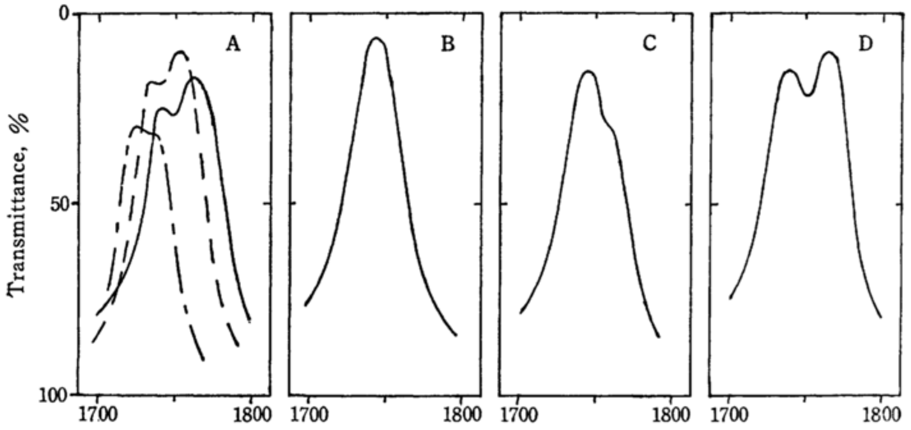


Fig. 1. Carbonyl spectra of methoxy-esters in solutions.

A: ethyl methoxyacetate (9) ——; ethyl α-methoxypropionate (10) — — —; ethyl α-methoxyisobutyrate (11) — — —
B: ethyl β-methoxypropionate (12)
C: dieteyl monomethoxysuccinate (13)
D: diethyl D-α,β-dimethoxysuccinate (14)

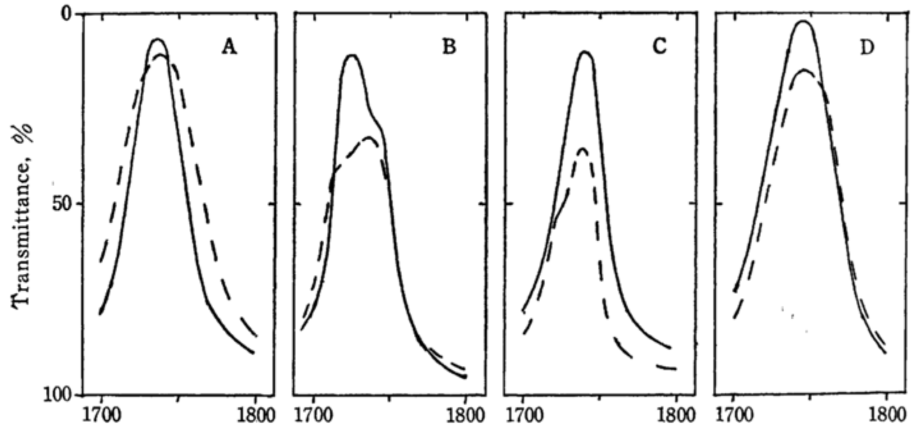


Fig. 2. Carbonyl spectra of hydroxy-esters in solutions —— and in the neat state — — —.

A: ethyl lactate (17); B: ethyl β-hydroxypropionate (20);
C: ethyl ε-hydroxycaproate (22); D: diethyl D-tartrate (26)

TABLE 1. CARBONYL FREQUENCIES OF ALKANOATES*

No.	Compound	$\nu_{C=O}$ cm^{-1} CCl$_4$ soln.	$\nu_{C=O}$ cm^{-1} Neat
1	CH_3COOCH_3	1751	1748
2	$CH_3COOC_2H_5$	1745	1744
3	$CH_3COO\textit{i}\text{-}C_3H_7$	1740	1741
4	$CH_3COO\textit{t}\text{-}C_4H_9$	1740	1740
5	$C_2H_5COOC_2H_5$	1741	1739
6	$(CH_3)_2CHCOOC_2H_5$	1737	1736
7	$(CH_3)_3CCOOC_2H_5$	1731	1728
8	$(CH_2COOC_2H_5)_2$	1741	1736
9	$CH_2(OCH_3)COOC_2H_5$	1741, 1761	1736, 1754
10	$CH_3CH(OCH_3)COOC_2H_5$	1737, 1752	1739, 1751
11	$(CH_3)_2C(OCH_3)COOC_2H_5$	1733, 1742 sh	1736
12	$CH_2(OCH_3)CH_2COOC_2H_5$	1743	1741
13	$CH_3OCHCOOC_2H_5$ $CH_2COOC_2H_5$	1744, 1759 sh	1736, 1751 sh
14	$CH_3OCHCOOC_2H_5$ $CH_3OCHCOOC_2H_5$ (D-form)	1739, 1765	1736, 1756

* Unless otherwise noted, the esters are of the racemic form.
sh = shoulder.

TABLE 2. CARBONYL AND HYDROXYL FREQUENCIES OF HYDROXY-ALKANOATES*1

No.	Compound	CCl$_4$ soln. $\nu_{C=O}$*3 I	$\nu_{C=O}$*3 III	ν_{O-H}[9,10]*2,*3 I	ν_{O-H} II	ν_{O-H} III	Neat $\nu_{C=O}$	Neat ν_{O-H}[9]
15	$CH_2(OH)COOC_2H_5$	1743		3550	3618 w		1745	3427
16	$CH_3CH(OH)COOCH_3$	1741		3549	3616 w		1740	
17	$CH_3CH(OH)COOC_2H_5$	1736		3543	3613 w		1738	3436
18	$CH_3CH(OH)COO\textit{i}\text{-}C_3H_7$	1738		3544	3614 w		1735	
19	$(CH_3)_2C(OH)COOC_2H_5$	1732		3544	3606 w		1733, 1744 sh	3478
20	$CH_2(OH)CH_2COOC_2H_5$	1725	1744 sh	3584		3640 w	1723 sh, 1734	3426
21	$CH_3CH(OH)CH_2COOC_2H_5$	1725	1743 sh	3560		3626 w	1723 sh, 1738	3430
22	$HO(CH_2)_5COOC_2H_5$		1741	3542 w		3640	1738, 1718 sh	
23	$HO(CH_2)_6COOC_2H_5$		1738			3638	1738, 1720 sh	
24	$HO(CH_2)_8COOC_2H_5$		1738			3638	1739, 1721 sh	
25	$HOCHCOOC_2H_5$ $CH_2COOC_2H_5$	1743		3535	3590 sh		1742	3441
26	$HOCHCOOC_2H_5$ (D-form)	1746		3532	3588 w		1745	3454
27	$HOCHCOOC_2H_5$ (meso-form)	1745		3534	3584 sh			
28	$CH_3CH(OH)CH(OH)COOC_2H_5$ (Threo)	1738		3522	3585*4		1740	
29	$CH_3CH(OH)CH(OH)COOC_2H_5$ (Erythro)	1736		3533	3588*4		1738	

*1 Unless otherwise noted, the esters are of the racemic form.

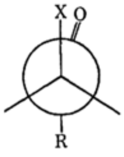
*2 The frequencies are those of the apparent band-peaks described in the literature.

*3 I, II and III denote the types of hydrogen bonding : I = $C=O\cdots HO$; II = $\rangle O\cdots HO$; III = Unbonded. w = weak; sh = shoulder.

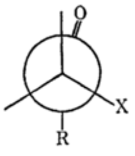
*4 This is the bonded β-OH frequency to be associated with the OH(β)-to-OH(α) bonding.[11]

reported values, and they depend on both the type of the alcohol part and the type of the acid part, as is shown in Table 1. According to the generally-accepted explanation, this dependence can be attributed predominantly to the electronic effects, operating along the bonds, of both parts on the double-bond character of the carbonyl group. Therefore, the ethyl esters of methoxy- and hydroxy-alkanoic acids, which are the most popular, have been examined in the present study. Some typical spectra are shown in Figs. 1 and 2, while the carbonyl data are summarized, together with the hydroxyl data, in Tables 1 and 2.

Ethyl Methoxy-alkanoates. In solutions, each of the α-methoxy-esters (9—11) shows two bands; one of them appears at the normal frequency characteristic of the corresponding ester with a methyl group instead of a methoxy group, and the other, at a higher (by *ca.* 10—20 cm^{-1}) frequency. The appearance of such a boublet band has hitherto been observed in many α-halo-carbonyl compounds,[12-14] such as some α-halogenated ketones, alkanoates, aldehyds, acid halides, and amides, and, further, in several α-alkoxy-ketones[15] and in some phenoxy- and ethoxy-acetates.[13,16] The doublet has been attributed to the existence of rotational isomers showing two carbonyl frequencies, such as the forms I and II, which can be represented by Newman's projection along the C_1–C_2 bond :



cis Form (I)



gauche Form (II)

where X is a highly polar group or atom. The nature of the effects causing the frequency shift has been discussed by Bellamy and Williams,[14] who attributed it primarily to the dipolar field effect operating across the space. When the negatively-charged atom or group X is close in space to the readily polarisable, negatively-charged oxygen atom of the carbonyl group, as in the form I, such a geometry results in a mutual induction of opposite charges; consequently, the carbonyl group becomes less polar, and its vibrational frequency rises above the frequency of the carbonyl group, which is twisted away from X, as in the form II. This mechanism can conveniently explain the present case ; the higher frequency band can be associated with the cis form, and the lower frequency band, with the gauche form. Further, the α-methoxy group in the gauche form does not lead to any appreciable carbonyl-frequency shift (*i. e.*, the lower frequency is almost equal to the normal carbonyl frequency of the corresponding ester with a methyl group instead of a methoxy group). This does not necessarily suggest, however, that all inductive effects are absent; rather, it could be due to the cancellation of the inductive effects by small residual field effects, which in that form would be expected to operate in the opposite direction. Such a cancellation has been suggested in accounting for a similar behavior of α-halogens observed in several carbonyl compounds.[14]

Ethyl β-methoxypropionate (12) shows a single band that is identical in both shape and frequency with that of ethyl propionate (5). This indicates that the methoxy group in the β-position, and probably also in a more separated position, has no influence on the carbonyl double-bond character.

Diethyl mono- and di-methoxysuccinate (13 and 14) each shows a doublet band the peak-frequency and relative intensity of which agree with that would be expected from their structures; the monomethoxy-ester shows the overlapped spectra of ethyl α- and β-methoxypropionates (10 and 12), while the dimethoxy-ester shows nearly the same spectrum as that of ethyl α-methoxypropionate.

Ethyl Hydroxy-alkanoates. The α-hydroxy-esters (15—19) show, in solutions, a single, almost symmetric band at nearly the same frequency as the lower-frequency band of the corresponding α-methoxy-esters. This suggests that the hydroxy-esters exist predominantly in an internally-bonded cis-geometry. If the carbonyl and the hydroxyl group (X) are in the cis-relationship, as in the form I,

---

11) N. Mori, S. Omura and Y. Tsuzuki, *ibid.*, **38**, 2199 (1965).

12) S. Mizushima, T. Shimanouchi, T. Miyasawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953); L. W. Daasch and R. E. Kagarise, *J. Am. Chem. Soc.*, **77**, 6156 (1955); L. J. Bellamy, L. C. Thomas and R. L. Williams, *J. Chem. Soc.*, **1956**, 3704; R. N. Jones and E. Spinner, *Can. J. Chem.*, **36**, 1020 (1958).

13) M. L. Josien and R. Calas, *Compt. rend.*, **240**, 1641 (1955).

14) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, **1957**, 4294.

15) N. H. Cromwell, R. E. Bambury and J. L. Adelfang, *J. Am. Chem. Soc.*, **82**, 4241 (1960); N. H. Cromwell, F. H. Schumacher and J. L. Adelfang, *ibid.*, **83**, 974 (1961); J. L. Adelfand, P. H. Hess and N. H. Cromwell, *J. Org. Chem.*, **26**, 1402 (1961).

16) M. Ōki and M. Hirota, This Bulletin, **34**, 374 (1961); T. L. Brown, *J. Am. Chem. Soc.*, **80**, 3513 (1958).

the dipolar electrical forces operating across the space between the groups would raise the carbonyl frequency, much as in the case of the α-methoxy-esters, while the possible hydrogen bonding between them should have the effect of decreasing the carbonyl frequency. On the other hand, if the groups are situated as in the form II, the carbonyl frequency may be expected to be nearly equal to the lower frequency of the corresponding α-methoxy-esters, while the possible hydrogen bonding between the hydroxyl and the ethoxy group (R) should raise the carbonyl frequency. The observed frequencies indicate the preferential existence of the internally-bonded cis-form or the internally-unbonded gauche-form. In reality, however, the latter can not be considered. Nevertheless, this does not obviate the existence of the internally-bonded gauche-form, *i. e.*, another type of hydrogen bonding which involves the ethoxy group as a proton acceptor, because the resolution power of the instrument used is not strong enough to detect a weaker band which may appear at a slightly separated position. The above indication is in good agreement with the conclusion, previously reported on the basis of the hydroxyl spectra,[8-10] that the hydrogen bond is predominantly formed on to the carbonyl group, the ethoxy group being involved to only a minor extent.

In solutions, the β-hydroxy-esters (20 and 21) show, apart from the normal-frequency band appearing as a shoulder, a stronger band at a lower (by *ca.* 20 cm^{-1}) frequency. Since the β-hydroxyl group is expected to have no field and electronic effects, like the β-methoxy group, the strong band can reasonably be assigned to the bonded carbonyl group,[*1] and the shoulder, to the free carbonyl group. This provides other striking evidence for the conclusion, previously deduced from their hydroxyl spectra,[10] that the hydrogen bonding in these esters involves the carbonyl group predominantly, while their unbonded molecules are much lower in proportion.

The other higher ω-hydroxy-esters (22—24) show no bonded-carbonyl band, although their hydroxyl spectra indicated that only one of them, ethyl ε-hydroxycaproate (22), was internally bonded to a very small extent.[10] Accordingly, a very weak band due to the bonded carbonyl group in the ester (22) probably overlaps the observed free-carbonyl band.

Diethyl malate (25) and tartrates (26 and 27) show a single band, whose frequency is close to the lower frequency of the corresponding mono- or di-methoxysuccinate (13 or 14). Therefore, the type of hydrogen bonding in these esters is essentially the same as in the α-hydroxy-esters, as was previously concluded on the basis of their hydroxyl spectra.[8,9] Similarly, ethyl α,β-dihydroxybutyrates (28 and 29) form a hydrogen bond between the α-hydroxyl and the carbonyl group, as is indicated by their having the same carbonyl data as the α-hydroxy-esters and as was previously conjectured on the basis of their hydroxyl spectra.[11]

In the neat state, the spectra of all the mono- and di-hydroxy-esters are interesting in comparison with their spectra in solutions. Although the hydroxyl bands in the neat state are very broad and shift greatly towards the lower-frequency side as compared with the spectral bands in solutions, the carbonyl bands, except for those of the β- and the higher ω-hydroxy-esters, remain nearly unchanged in both frequency and band shape. In the β-hydroxy-esters (20 and 21), the relative intensities of the higher-frequency bands to the lower ones are reversed, while in the higher ω-hydroxy-esters (22—24) a new band appears as a shoulder on the lower-frequency side. The authors can not give any decisive explanation for this observation, because more complex, unknown intermolecular interactions are probably involved in the liquid state.

The authors wish to thank Mr. Yutaka Kikuchi of this University for his infrared measurements. Their thanks are also due to the Ministry of Education for its grant-in-aid for Fundamental Scientific Research.

[*1] Note Added in Proof : We have recently been informed by Professor P. von R. Schleyer of Princeton University of his study of intramolecular hydrogen bonding between the π-electrons on a carbonyl oxygen atom and a hydroxyl group in hydroxy-carbonyl compounds. He regards, exclusively on the basis of a comparison of $\Delta\nu_{\mathrm{OH}}$'s and possible conformations, that the hydrogen bonding in β-hydroxy-ketones involves the π-electrons as the predominant proton acceptor, while in α-hydroxy-ketones the n-electrons on the oxygen atom is the proton acceptor. The same may be suggested in the cases of the α- and β-hydroxy-esters examined, since they have essentially the same $\Delta\nu_{\mathrm{OH}}$ values and possible conformations as have the corresponding hydroxy-ketones.