# The Infrared Spectra of Carbonyl Compounds in Alcohols

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The infrared spectra of carbonyl compounds in alcohols have not been studied extensively, but the shift due to the hydrogen bonding is regarded as rather small. Rasmussen et al.[1], for example, report that the carbonyl absorption of diacetone alcohol occurs at 1712 cm$^{-1}$ despite the fact that the hydroxyl frequencies indicate the presence of strong hydrogen bonding. Grove and Willis[2] estimate the influence of hydrogen bonding on some ketones as being not greater than 10 cm$^{-1}$, and Searles et al.[3] have shown that the carbonyl shift in an equimolar mixture of carbon tetrachloride and methanol is about 8 cm$^{-1}$ with esters, and 7 to 15 cm$^{-1}$ with lactones, depending upon the ring size.

Becker[4] determined the infrared spectra of benzophenone in ethanol and in tetrachloroethylene, and in ethanol observed two bands of about equal intensity at 1666 cm$^{-1}$ and

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[1] R. S. Rasmusssen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

[2] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, **1951**, 877.

[3] S. Searles, M. Tamres and G. M. Barrow, *J. Am. Chem. Soc.*, **75**, 71 (1953).

[4] R. S. Becker, *J. Molecular Spectroscopy*, **3**, 1 (1959).

1656 cm$^{-1}$, and, in tetrachloroethylene, a single band at 1668 cm$^{-1}$. It appears that this phenomenon has not been mentioned elsewhere, including the excellent reviews on hydrogen bonding recently published[5,6]. In order to obtain general knowledge about carbonyl absorption in alcohols and, particularly, to clarify the nature of the double peak, this investigation was undertaken.

## Experimental

**Materials.**—Methyl *t*-butylperoxy carbonate was prepared by the drop-by-drop addition of a cooled sodium hydroxide solution to an equimolar mixture of *t*-butyl hydroperoxide and methyl chloroformate at −5°C. All the other chemicals were those of the best grade commercially available in the United States and were used without further purification.

TABLE I. CARBONYL BANDS IN CARBON TETRACHLORIDE AND METHANOL

| | In $CCl_4$ wave number | In $CH_3OH$ wave number | | $\nu_2-\nu_1$ | $\frac{(O.D.)_{\nu_2}}{(O.D.)_{\nu_1}}$ |
|---|---|---|---|---|---|
| | $\nu_0$ | $\nu_1$ | $\nu_2$ | | |
| **Carbonate** | | | | | |
| Di-*t*-butyl carbonate | 1739 | 1739 | 1712 | 27 | 0.53 |
| Di-*m*-cresyl carbonate | 1783 | 1783 | 1761 | 22 | 0.68 |
| Di-*n*-butyl carbonate | 1745 | 1745 | 1727 | 18 | 0.78 |
| Di-*o*-cresyl carbonate | 1779 | 1779 | 1757 | 22 | 0.80 |
| Diethyl carbonate | 1748 | 1748 | 1730 | 18 | 0.81 |
| Ethylene carbonate | 1818 | 1805 | 1779 | 26 | 0.87 |
| Methyl *t*-butylperoxy carbonate[a] | 1795<br>1764 | 1795 | 1776 | 19 | 1.25[a] |
| **Aldehyde** | | | | | |
| Benzaldehyde | 1706 | (1704)[a] | (1695)[b] | 9 | |
| *p*-Anisaldehyde | 1704 | (1692)[b] | (1681)[b] | 11 | |
| **Ketone** | | | | | |
| Acetone | 1718 | | 1709 | 9[c] | |
| 2-Heptanone | 1718 | | 1706 | 12[c] | |
| 4-Heptanone | 1715 | | 1704 | 11[c] | |
| 2, 6-Dimethylheptanone-4 | 1712 | | 1704 | 8[c] | |
| Diacetone alcohol | 1712 | | 1701 | 11[c] | |
| Triacetone alcohol | 1698 | | 1698 | 0 | |
| Benzophenone | 1667 | 1667 | 1656 | 11 | 0.91 |
| Fluorenone | 1724 | | (1712)[b] | 12[c] | |
| **Lactone** | | | | | |
| $\gamma$-Butyrolactone | 1779 | | (1764)[b,d] | 15[c] | |
| $\gamma$-Valerolactone | 1783 | | (1764)[b,d] | 19[c] | |
| **Ester** | | | | | |
| Methyl 3, 5-dinitro benzoate | 1742 | 1739 | (1724)[e] | 15 | (0.27) |
| Methyl benzoate | 1727 | 1727 | 1709 | 18 | 0.75 |
| Phenyl benzoate | 1742 | 1742 | 1727 | 15 | 0.78 |
| Ethyl benzoate | 1724 | 1721 | 1704 | 17 | 0.84 |
| Ethyl butanoate | 1739 | 1736 | 1718 | 18 | 1.02 |
| Methyl acetate | 1745 | 1745 | 1730 | 15 | 1.09 |
| Isopropyl acetate | 1739 | 1736 | 1715 | 21 | 1.14 |
| Ethyl salicylate | 1684 | 1681[d] | | 3[c] | |

a) This peroxycarbonate is exceptional in that it has two carbonyl bands, 1795 and 1764 cm$^{-1}$ (O. D.$_{1764}$/O. D.$_{1795}$=0.32), even in carbon tetrachloride. Recently, Martin reported that di-*t*-butylperoxy carbonate possesses a split carbonyl band, with a high intensity peak at 1825 and a somewhat less intense peak at 1795 cm$^{-1}$ (M. M. Martin, *J. Am. Chem. Soc.*, **83**, 2870 (1961)).

b) The wave numbers in parentheses are inaccurate due to the diffused nature of the bands.

c) These are $\nu_{MeOH}-\nu_{CCl_4}$, not $\nu_2-\nu_1$.

d) The band in methanol is a little broader than that in carbon tetrachloride.

e) These are the shoulders of stronger bands and are not accurate.

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[5] G. C. Pimentel and A. L. McLellan, "The Hydrogen Bond", W. H. Freeman and Co., London (1960).

[6] D. Hadzi (ed.), "Hydrogen Bonding", Pergamon Press, London (1959).

TABLE II. CARBONYL BANDS IN METHANOL AND *t*-AMYL ALCOHOL

| | In methanol wave number $\nu_1$ | In methanol wave number $\nu_2$ | $\frac{(O.D.)_{\nu_2}}{(O.D.)_{\nu_1}}$ | In *t*-amyl alcohol wave number $\nu_1$ | In *t*-amyl alcohol wave number $\nu_2$ | $\frac{(O.D.)_{\nu_2}}{(O.D.)_{\nu_1}}$ |
|---|---|---|---|---|---|---|
| Phenyl benzoate | 1742 | 1727 | 0.78 | 1742 | 1730 | 1.00 |
| Benzophenone[a)] | 1667 | 1656 | 0.91 | 1667 | 1658 | 1.21 |
| Isopropyl acetate | 1736 | 1715 | 1.14 | 1739 | 1721 | 1.74 |

a) In ethanol, $\nu_1=1667\ \mathrm{cm^{-1}}$, $\nu_2=1656\ \mathrm{cm^{-1}}$, $(O.D.)_{\nu_2}/(O.D.)_{\nu_1}=1.0$

TABLE III. CARBONYL BANDS OF ISOPROPYL ACETATE IN MIXTURES OF *t*-AMYL ALCOHOL AND CARBON TETRACHLORIDE

| Vol. % of *t*-AmOH | $\frac{(t\text{-AmOH})}{(i\text{-PrOAc})}$ | Wave number $\nu_1$ | Wave number $\nu_2$ | $\nu_2-\nu_1$ | $\frac{(O.D.)_{\nu_2}}{(O.D.)_{\nu_1}}$ |
|---|---|---|---|---|---|
| 4% | 1.13 | 1739 | | | |
| 8 | 2.25 | 1736 | 1724 | 12 | |
| 20 | 5.6 | 1739 | 1724 | 15 | 0.78 |
| 100 | 28.2 | 1739 | 1721 | 18 | 1.74 |

(The concentration of isopropyl acetate is 0.32 M.)

**Infrared Spectra.**—The infrared spectra of carbonyl compounds were determined in carbon tetrachloride, methanol or *t*-amyl alcohol by using calcium fluoride cells 0.2 mm. in thickness with a Perkin-Elmer Model 21 infrared spectrophotometer. The concentrations of the carbonyl compounds ranged from ca. 0.1 to 0.3 M, and were chosen so as to show the double peak clearly in alcohols.

## Results

The infrared spectra of various carbonates, aldehydes, ketones, lactones and esters were determined in carbon tetrachloride and alcohols. The wave numbers of carbonyl bands in carbon tetrachloride ($\nu_0$) and in alcohols ($\nu_1$ and $\nu_2$), together with the ratios of the optical density of the two bands in alcohols, are shown in Tables I, II, III and IV. The spectrum of the carbonyl absorption of isopropyl acetate in methanol is shown in Fig. 1; this will serve as an example of the doublet bands and also shows the independence of the relative band intensities of the concentration.

The results shown in Tables I—IV may be summarized as follows.

TABLE IV. CARBONYL BAND OF ISOPROPYL ACETATE OF THE VARIOUS CONCENTRATIONS IN METHANOL

| Isopropyl acetate mol./l. | $\frac{(O.D.)_{\nu_2}}{(O.D.)_{\nu_1}}$ |
|---|---|
| 0.404 | 1.12 |
| 0.305 | 1.13 |
| 0.152 | 1.21 |
| 0.122 | 1.09 |
| 0.061 | 1.25 |

($\nu_2=1715$, $\nu_1=1736\ \mathrm{cm^{-1}}$)

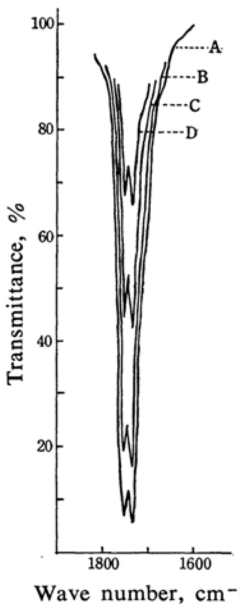

Fig. 1. Carbonyl band of isopropyl acetate in methanol.
Concentration of *i*-PrOAc; A, 0.404; B, 0.305; C, 0.122; D, 0.061 M. Spectral slit-width, 2 cm⁻¹.

1) Except for ethyl salicylate and methyl 3, 5-dinitrobenzoate, all the esters and carbonates appear to give two carbonyl bands in methanol, one at a wave number almost identical with the one in carbon tetrachloride, and the other lower by 15～27 cm⁻¹.

2) Carbonyl bands of aliphatic ketones shift by 9～15 cm⁻¹ but do not give two bands in methanol. Benzophenone gives two bands, 11 cm⁻¹ apart, while fluorenone seems

to give one broad band which may well in fact consist of two bands.

3) Diacetone alcohol, the carbonyl group of which is already hydrogen-bonded, suffers a further shift as much as 11 cm$^{-1}$ in methanol, whereas the carbonyl absorption of triacetone alcohol is not affected by the change of solvents.

4) Aldehydes seem to give one broad band which may well in fact consist of two bands. The shift of the center of the band is 6∼18 cm$^{-1}$.

5) Lactones gives one broad band in methanol, shifted by 15∼19 cm$^{-1}$.

6) The (Optical density of $\nu_2$)/(Optical density of $\nu_1$) ratio increases as the alcohol is changed from methanol to *t*-amyl alcohol.

7) No significant change in the ratio of the band intensities was observed for various concentrations of isopropyl acetate in methanol.

## Discussion

The infrared literature contains numerous examples of monocarbonyl compounds that exhibit two or more prominent bands between 1900 and 1650 cm$^{-1}$. In the absence of other acceptable explanations, both bands are usually assigned to vibrations involving the carbonyl groups. These doublet carbonyl peaks have been attributed to equilibria between conformational isomers, to Fermi resonance, or to some form of interaction between carbonyl compounds and solvents.

It is not possible to write pairs of stable, conformationally isomeric structures for the carbonyl compounds considered here. In order for the equilibria between conformational isomers to be the cause of the doublet carbonyl bands, it is necessary for the energy difference between two forms to be small enough to allow a significant concentration of the less stable form to exist in equilibrium at room temperature, and the inductive, mesomeric and field effects on the carbonyl group must differ sufficiently in the two forms to induce a significant displacement of the two carbonyl frequencies.

Next, the possibility of attributing these doublet carbonyl bands to Fermi resonance should be examined. Yates and his collaborators[7,8] found that some cyclopent-2-enones exhibited doublet carbonyl bands, the relative intensities of which were dependent on solvents. By a careful examination of the infrared spectra of 5, 5-dimethylcyclopent-2-enone, deuterated cyclopent-2-enone and other substituted cyclopent-2-enones, they showed unambiguously that these doublet carbonyl bands arose from Fermi resonance between the carbonyl vibration and the out-of-plane bending vibration of the single ethylenic C–H bond. Angell et al.[9] attributed the double bands of cyclopentanone to the Fermi resonance.

However, the Fermi resonance does not seem to be an acceptable explanation for the doublet carbonyl bands of esters and carbonates in alcohols for the following reason. It is highly unlikely that an accidental degeneracy between the carbonyl stretching mode and an overtone or combination bands would occur through such a wide range of different types of structure. Although Jones et al.[10,11] reluctantly and tentatively attributed the doublet carbonyl bands of unsaturated lactones to Fermi resonance, they were not satisfied with their choice of explanation for the same reason. Yates and Williams[8] found that while 3, 4-diphenylcyclopent-2-enone showed a doublet carbonyl absorption at 1718 and 1695 cm$^{-1}$ due to the Fermi resonance with an overtone of the out-of-plane bending vibration of the single ethylenic carbon-hydrogen bond at 860 cm$^{-1}$, 3, 4-diphenyl-5, 5-dimethylcyclopent-2-enone showed a singlet carbonyl band since its ethylenic carbon-hydrogen absorption was at 873 cm$^{-1}$. It is utterly unlikely that the doublet carbonyl bands of all the compounds in Table I arose from an accidental degeneracy between the carbonyl stretching mode and an overtone or combination band, from, i. e., a Fermi resonance.

If these doublet carbonyl bands observed in alcohols cannot be attributed either to equilibria between conformational isomers or to a Fermi resonance, one is forced to believe that these doublet bands are due to some form of interaction between carbonyl compounds and solvents.

If these doublet carbonyl bands in alcohols are due to the hydrogen bonding between the carbonyl oxygen and solvent alcohols, the following three sets of species are conceivably responsible for the doublet bands: 1) non-hydrogen-bonded carbonyl and hydrogen-bonded carbonyl, 2) hydrogen-bonded carbonyl with monomeric alcohol and with polymeric alcohol, and 3) mono-hydrogen-bonded carbonyl and di-hydrogen-bonded carbonyl.

The first set of species does not seem acceptable because of the following two reasons.

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[7] P. Yates, N. Yoda, W. Brown and B. Mann, *J. Am. Chem. Soc.*, **80**, 202 (1958).

[8] P. Yates and L. L. Williams, ibid., **80**, 5896 (1958).

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

[10] R. N. Jones, C. L. Angell, T. Ito and R. J. D. Smith, *Can. J. Chem.*, **37**, 2007 (1959).

[11] R. N. Jones and B. S. Gallagher, *J. Am. Chem. Soc.*, **81**, 5242 (1959).

First, diacetone alcohol, the carbonyl group of which is already hydrogen-bonded, absorbs at 1712 $\text{cm}^{-1}$ in carbon tetrachloride, while 2, 6-dimethylheptanone-4 absorbs at 1712 $\text{cm}^{-1}$ and heptanone-4 absorbs at 1715 $\text{cm}^{-1}$ in the same solvent, the latter two not being hydrogen-bonded. Second, the carbonyl absorption of diacetone alcohol, which is already hydrogen-bonded, is shifted as much as 11 $\text{cm}^{-1}$ when its spectrum is taken in methanol.

The second set was chosen by Becker[4] as responsible for the doublet bands of benzophenone in ethanol. He attributed the absorption at 1666 $\text{cm}^{-1}$ to the carbonyl group hydrogen-bonded to the monomeric alcohol and the absorption at 1656 $\text{cm}^{-1}$ to the carbonyl group hydrogen-bonded to the polymeric alcohol. However, it seems highly unlikely that the ethanol monomer can exist in pure ethanol. The oxygen of the ethanol molecule hydrogen-bonded to a carbonyl group is more basic and should be hydrogen-bonded to other molecules of ethanol.

Therefore, in the absence of other acceptable explanations, the most reasonable explanation for the double bands seems to be that carbonyl compounds in alcohols may exist as both a mono-hydrogen-bonded form and a di-hydrogen-bonded form[12,13]. In Tables I, II and III, $\nu_1$ is attributed to the mono-hydrogen-bonded carbonyl and $\nu_2$ is attributed to the di-hydrogen-bonded carbonyl. These assignments are made on the basis of the following observations: (a) The carbonyl absorption of diacetone alcohol occurs at 1712 $\text{cm}^{-1}$ in carbon tetrachloride despite the fact that the hydroxyl frequencies indicate strong hydrogen-bonding (3484$\text{cm}^{-1}$), while 2, 6-dimethylheptanone-4 and heptanone-4 absorb in the same solvent at 1712 and 1715 $\text{cm}^{-1}$ respectively, these latter two not being hydrogen-bonded. This fact indicates that the carbonyl absorption of a mono-hydrogen-bonded carbonyl compound occurs at nearly the same wave-number as that of a non-hydrogen-bonded carbonyl compound. (b) Triacetone alcohol, in which two intramolecular hydrogen bondings are possible, absorbs in carbon tetrachloride at 1698 $\text{cm}^{-1}$ (compare this value with 1712 $\text{cm}^{-1}$ of diacetone alcohol). The carbonyl absorption of triacetone alcohol does not suffer any shift at all when the solvent is changed from carbon tetrachloride to methanol. These facts indicate that a carbonyl absorption is shifted a great deal when the compound is subjected to a condition where di-hydrogen-bonding may take place, and that the carbonyl absorption of a di-hydrogen-bonded carbonyl compound is not affected at all by changing the solvent from carbon tetrachloride to methanol, while that of a mono-hydrogen-bonded carbonyl compound is shifted almost as much as that of a non-hydrogen-bonded carbonyl compound by changing the solvent from carbon tetrachloride to methanol.

It is an interesting question why mono-hydrogen-bonding gives only a small shift while di-hydrogen-bonding gives a rather large shift. A plausible explanation is that, since a carbonyl oxygen probably uses one of its p-orbitals in forming the $\sigma$-bond with carbon and another p-orbital in forming the $\pi$-bond, two unshared electron pairs are in the 2s and 2p orbitals. Therefore, the first hydrogen-bonding probably takes place by making use of the rich electron density of the unshared p-orbital. This hydrogen bonding probably will not affect the stretching frequency of a carbonyl bond very much. The second hydrogen bonding, however, may strongly affect the stretching frequency of the carbonyl bond, if use must be made of the electrons closer to the carbon-oxygen bond. In other words, extensive hybridization of oxygen orbitals would be required for the formation of two hydrogen bonds, whereas little hybridization would be required to form a single hydrogen bond.

Alkyl ketones are exceptional in that they show only one carbonyl band in methanol, one shifted by 8∼12 $\text{cm}^{-1}$. They lack the conjugated $\pi$-system which is present in esters, carbonates and aryl ketones. The lack of conjugation and the presence of electron-releasing alkyl groups make alkyl ketones form di-hydrogen-bonds more easily than esters, carbonates or aryl ketones, in which the $\pi$-electrons of the carbonyl bond are somewhat spread to the conjugated $\pi$-system. In methyl 3, 5-dinitrobenzoate, the $\pi$-electrons of the carbonyl bond are strongly pulled to the benzene ring and di-hydrogen-bonded forms are present in a very small quantity, if at all. Methyl trichloroacetate and methyl trifluoroacetate, both of which are esters of strong acids, show only one band in methanol[14], presumably

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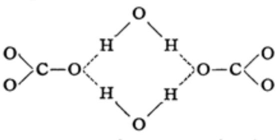
[12] The positions of two molecules of water in the crystalline structure of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ are as follows (Ref. 5, p. 264):



[13] The oxygen atoms of water molecules are pictured as hydrogen-bonded to two hydrogens of other water molecules. See, for example, E. S. Gould, "Inorganic Reactions and Structure", Henry Holt and Co., New York (1955), p. 32.

[14] T. G. Traylor, private communication.

due to the absence of the di-hydrogen-bonded carbonyl.

In the case of ethyl salicylate, the carbonyl $\pi$-electrons are completely spread to the quasi-six membered ring and are not available to form an additional hydrogen-bond. As may be seen in Table I, the carbonyl band of ethyl salicylate is not affected by changing the solvent from carbon tetrachloride to methanol. Its carbonyl band in carbon tetrachloride is at 1684 cm$^{-1}$, which is 40 cm$^{-1}$ lower than that of ethyl benzoate in carbon tetrachloride and 20 cm$^{-1}$ lower than that of ethyl benzoate in methanol.

Searles et al.3) found that the shift of the carbonyl band by changing the solvent from carbon tetrachloride to an equimolar mixture of carbon tetrachloride and methanol is 7 cm$^{-1}$ for $\beta$-propiolactone, 12cm$^{-1}$ for $\gamma$-butyrolactone, and 15 cm$^{-1}$ for $\delta$-valerolactone. These are shifts of the centers of the broad band, and so the bigger shifts may mean a more di-hydrogen-bonded form. The carbonyl band of $\gamma$-butyrolactone is further shifted when its infrared spectrum is determined in pure methanol (15 cm$^{-1}$; see Table I).

The higher (Optical Density of $\nu_2$)/(Optical Density of $\nu_1$) ratio with *t*-amyl alcohol than with methanol may be explained by the fact that self-hydrogen-bonding is much weaker in *t*-amyl alcohol than in methanol15). Therefore, the equilibrium, self-bonded alcohol $\rightleftharpoons$ carbonyl-bonded alcohol, is shifted more to the right in the case of *t*-amyl alcohol, even though methanol is a stronger acid. It is presumably only as a hydrogen acceptor that *t*-amyl alcohol is ineffective; accordingly, we have a carbonyl compound able to compete with the oxygen of *t*-amyl alcohol in the hydrogen acceptor role, whereas the carbonyl oxygen cannot compete so well with the oxygen of methyl alcohol.

## Summary

The infrared spectra of some esters, lactones, carbonates, ketones and aldehydes in methanol and *t*-amyl alcohol have been determined. With few exceptions, they showed either two carbonyl peaks separated by 15~27 cm$^{-1}$ or a broad carbonyl peak shifted by 9~19 cm$^{-1}$ from the wave number as determined in carbon tetrachloride. The relative intensities of the two bands are independent of the concentration. Some possible explanations for this phenomenon have been discussed, and as a result these doublet carbonyl bands have been attributed to the mono-hydrogen-bonded carbonyl and the di-hydrogen-bonded carbonyl.

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15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley, New York (1959), p. 101.