The Carbonyl Group Frequency. Part IV.[1] Aliphatic Aldehydes

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The carbonyl frequencies for vapours and solutions of a series of simple alkyl aldehydes have been recorded. The variation in frequency with substitution is less regular than with the corresponding ketones and the variation with solvent requires the operation of a specific interaction which is identified with the nucleophilic properties of the solvent. Application of simple vibrational models to the analysis of the change in the carbonyl group frequency between acetone and acetaldehyde indicates that changes in mass and geometry, in the carbonyl force constant, and in the symmetry of the vibration can individually all produce substantial effects; the overall small change in frequency arises from the cancellation of these effects.

FOR solutions of aliphatic aldehydes in carbon tetrachloride the infrared spectra are expected[2] to contain a carbonyl band in the frequency range 1740—1720 cm^{-1}. The group frequency varies within this range with changes in the attached alkyl group but changes in solvent or state may yield a considerably wider range of frequencies. This behaviour appears similar to that of aliphatic ketones[3] and esters[4] but in contrast to these systems few systematic studies[5,6] have been reported of the effects of structure and experimental conditions on the group frequency for aliphatic aldehydes. In an attempt to define the important factors and to facilitate direct comparison with other carbonyl compounds the spectra of a number of simple aldehydes have been measured for vapours and for solutions in a wide range of solvents.

TABLE 1

Carbonyl stretching frequencies (cm^{-1}) of aliphatic aldehydes

	MeCHO	EtCHO	PrCHO	Pr^{i}CHO	Pr^{i}CH$_2$CHO	Bu^{t}CHO	r_1 [a]
Vapour	1746	1749	1746	1752	1744	1740	
Solvent							
Hexane	1734	1739	1734·5	1739	1733	1727	0·964
Cyclohexane	1734	1739	1734	1739	1733	1727·5	0·966
NEt$_3$	1731	1731	1731	1737	1730	1729	0·858
CCl$_4$	1730·5	1736	1730	1736	1729·5	1725·5	0·962
CS$_2$	1728·5	1733·5	1728	1733	1726·5	1724	0·950
1,4-Dioxan	1721	1726	1721	1724	1719	1722·5	0·543
MeCN	1723	1727	1724	1725	1720·5	1719	0·869
Pyridine	1723	1722·5	1718	1719	1716	1719	0·224
MeNO$_2$	1722	1726	1721	1720	1720	1723	−0·042
CH$_2$Cl$_2$	1724	1727	1721·5	1726	1721	1718	0·898
CHCl$_3$	1724·5	1728	1722·5	1726	1722·5	1719	0·867
CHBr$_3$	1721	1725	1720	1722	1718	1718	0·762
Me$_2$SO	1717·5	1721	1716	1714	1715·5	1719	−0·294
r_2 [b]	0·958	0·971	0·971	0·947	0·970	0·960	
m	0·89	0·96	1·02	1·25	1·01	0·74	
d	200·86	89·10	−17·06	−421·98	−5·58	455·99	

[a] Regression coefficient for equation (1). [b] Regression coefficient for modified Bellamy–Hallam–Williams plot [equation (2)].

EXPERIMENTAL

Aldehydes were commercial samples purified by conventional routes; in all cases the purity of the spectroscopic samples was more than 99% as shown by gas chromatography.

Carbonyl frequencies were measured in 0·1 mm cells for *ca.* 0·1M solutions in acetonitrile, dimethyl sulphoxide, dioxan, nitromethane, pyridine, and triethylamine; for other solvents 1·0 mm cells with *ca.* 0·01M solutions were used. Frequencies for hydrogen-bonded systems were measured with 1·0 mm cells for *ca.* 0·05M solutions of phenol or pyrrole in carbon tetrachloride made 0·8 and 0·4M respectively with aldehyde: for all the aldehydes the associated hydrogen stretching frequencies were constant at 3440 ± 2 cm^{-1} (phenol) and 3438 ± 2 cm^{-1} (pyrrole). Vapours were examined in a 10 cm cell at pressure of 5—10 mmHg achieved where necessary by the use of a RIIC CH5 heated cell.

Spectra were recorded on a Perkin-Elmer model 225 spectrometer with dry air flushing. Calibration was by interpolation from external water vapour bands.

Vibrational frequencies were calculated from conventional F and G matrices[7] by use of a computer programme supplied by Professor I. M. Mills with the University of Lancaster I.C.L. 1909 computer.

RESULTS

The carbonyl frequencies of the aldehydes as vapours and solutions are in Table 1. The band contours for acetaldehyde, isobutyraldehyde, and pivaldehyde as vapours exhibit rotational fine structure and the quoted frequencies refer

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[1] Part III, A. J. Collings, P. F. Jackson, and K. J. Morgan, *J. Chem. Soc.* (*B*), 1970, 581.

[2] L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1957, ch. 9.

[3] K. J. Morgan and N. Unwin, *J. Chem. Soc.* (*B*), 1967, 1336.

[4] K. J. Morgan and N. Unwin, *J. Chem. Soc.* (*B*), 1968, 880.

[5] E. J. Hartwell, R. E. Richards, and H. W. Thompson, *J. Chem. Soc.*, 1948, 1436.

[6] N. S. Bayliss, A. R. H. Cole, and L. H. Little, *Austral. J. Chem.*, 1955, **8**, 26; J. Depireux, *Bull. Soc. chim. belges*, 1957, **66**, 218; E. Sawicki and T. R. Hauser, *Analyt. Chem.*, 1959, **31**, 523.

[7] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

to the strong central branch. Rotational fine structure is also evident in the symmetrical doublet given by propionaldehyde vapour and here the frequency refers to the band centre. No fine structure is apparent for n-butyraldehyde or isovaleraldehyde. The spectra of the aldehydes in solution are simpler with carbonyl bands showing generally symmetrical contours.

In the spectra of all the aldehydes two bands appear in the region appropriate to the aldehydic C–H stretching frequency (Table 2). For these bands fully satisfactory results were obtained for vapours and for solutions in carbon tetrachloride, tetrachloroethylene, and carbon disulphide. Significant absorption in this region by other solvents gave spectra of poorer quality and those frequencies which for this reason could not be recorded precisely are given in parentheses.

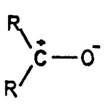
TABLE 2

C–H stretching frequencies (cm^{-1}) of aliphatic aldehydes

	MeCHO		EtCHO		PrCHO		Pr^{i}CHO		Pr^{i}CH$_2$CHO		Bu^{t}CHO	
Vapour	2716	2824	2710	2806	2709	2805	2703	2796	2708	2807	2691	2790
Solution in												
$CHCl_3$	2731	2841·5	2725	2822	2720	2820	2712	2809	2723	2823	2694	(2784)
CH_2Cl_2	2731	2835	2724	2822	2720	2818	2710	2809	2723	2822	2691	(2784)
$CHBr_3$	2728	2828	2721	2819	2720	2817	2711	2807	2719	2819	2695	2795
Pyridine	2726	(2837)	2714		2710	(2810)	2704	(2806)	2710	(2819)	2697	2795
Benzene	2721	2814	2714	2811	2711	(2810)	2701	(2802)	2711	(2812)	2695	2793
CCl_4	2720	2824·5	2713	2813	2711	2810	2703	2802	2709	2811	2684	2785
C_2Cl_4	2719	2819	2712	2811	2708	2807	2700	2800	2708	2810	2692	2794
CS_2	2713	2814	2707	2802	2706	2801	2697	2790	2703	2803	2688	2787

DISCUSSION

Carbonyl Stretching Frequencies.—The chemical properties of the aldehydic carbonyl group are normally described in terms of steric and electronic perturbation of a ketonic carbonyl group. Thus the greater ease of nucleophilic attack on aldehydes is related to the lower steric requirements and greater electronegativity of a hydrogen atom replacing an alkyl group directly attached to the carbonyl centre.[8] It has become conventional to extend this description to the carbonyl group frequencies.[9] In valence-bond terms replacement of alkyl by hydrogen can be expected to destabilise the dipolar canonical structure (1) and so increase the double-bond character (2) of the carbonyl group.[5] The increase of 20 cm^{-1} in the carbonyl group frequency of aldehydes with respect to ketones [2] is then to be attributed to the consequent increase in force constant for the carbonyl bond.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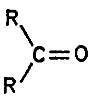
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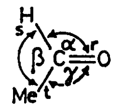

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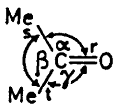

(4)

Although this description provides a useful basis for rationalising the observed frequencies and for empirical assignment of structure it can only be fully valid in so far as the carbonyl group frequency is effectively determined by the stretching constant of the carbonyl bond. Full normal-co-ordinate analyses of acetaldehyde and acetone have been described by Cossee and Schachtschneider.[10] For a variety of models their analyses confirm that the carbonyl group frequency cannot properly be regarded as corresponding to a fully localised vibration: both for acetone and acetaldehyde potential-energy distributions show only *ca.* 70% of the vibrational energy is associated with the C=O bond and that substantial contributions are provided by the deformations of the attached bonds.

For the present purposes the skeletal vibrations of acetaldehyde [11] and acetone can more conveniently be analysed in terms of simplified tetra-atomic models [1] (3, 4) in which a methyl group is represented as a point mass of 15 a.u. Such models can only yield approximate vibrational analyses but their flexibility allow the effects of structural changes to be indicated. Using a valence force field modified by the inclusion of the appropriate interaction constants and setting the stretching constant for a C–C bond arbitrarily at 4·0 dyn cm^{-1} we obtain satisfactory correlation between the experimental and calculated in-plane vibrational frequencies (Table 3). The force constants and the potential-energy distributions (Table 4) for the carbonyl group vibrations are generally similar to those obtained by Cossee and Schachtschneider.[10] This correspondence demonstrates the utility of the simple model in discussing the carbonyl group frequency.

In view of the potential-energy distributions and the carbonyl group frequencies (1738 and 1745 cm^{-1}) for acetone and acetaldehyde the large difference in the force constants for the C=O bonds (10·42 and 11·95 mdyn Å^{-1}) is particularly striking. A change of this magnitude in the force constant alone would be expected to result in a displacement of the carbonyl frequency of *ca.* 100 cm^{-1}. The vibrational effects of the structural changes when the aldehydic hydrogen atom in acetaldehyde is replaced by a methyl group can be grouped under three headings: (*a*) changes in mass and geometry;

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[8] See, *e.g.*, J. D. Roberts and M. Caserio, 'Organic Chemistry,' Benjamin, New York, 1964, ch. 14; J. Cason, 'Principles of Modern Organic Chemistry,' Prentice-Hall, New Jersey, 1966, ch. 15; K. F. Reid, 'Properties and Reactions of Bonds in Organic Molecules,' Longmans Green, London, 1968, ch. 15.

[9] See, *e.g.*, D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' McGraw-Hill, London, 1966, ch. 3; C. D. Gutsche, 'The Chemistry of Carbonyl Compounds,' Prentice Hall, New Jersey, 1967, ch. 1.

[10] P. Cossee and J. H. Schachtschneider, *J. Chem. Phys.*, 1966, **44**, 97.

[11] J. C. Evans and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 1037.

(*b*) changes in the nature of the carbonyl vibration; and (*c*) changes in the electronic nature of the bonding. Application of the masses and bond lengths necessary to change the acetaldehyde model to acetone produces an increase in the carbonyl group frequency of 41 cm^{-1} (Table 5). A further increase of 45 cm^{-1} follows the modifications to the interaction constants. Only the reduction in the carbonyl force constant, with a consequent decrease of 103 cm^{-1} in the group frequency, acts in the opposite direction for a smaller further positive correction follows from changing the H–C–C bending constant to that for C–C–C. Clearly in terms of the simple models the overall small displacement in carbonyl frequency is consistent with a balance between the essentially mechanical factors associated with the vibrating skeleton and the electronic perturbation of the carbonyl group. In particular it is of interest that the overall change in frequency may not reflect the substantial polar effect of the hydrogen substituent.

TABLE 3

In-plane vibrational frequencies (cm^{-1}) for simplified models * of acetaldehyde and acetone

Vibrational assignment	Acetaldehyde		Acetone	
	Obs.	Calc.	Obs.	Calc.
C–H stretch	2824	2822		
C=O stretch	1746	1746	1738	1738
C–H bend	1409	1402		
Me–C–Me bend			483	482
C–Me stretch	1113	1104	1218(as) 779(s)	1219(as) 781(s)
C=O bend	509	509	528	524

* The following set of force constants and interaction constants was found satisfactory: (i) acetaldehyde: k_{C-H}, 4·3; $k_{C=O}$, 11·95; k_{C-C}, 4·0; h_{CCO}, 0·7; h_{HCC}, 0·3; h_{HCO}, 0·57; $f_{r\alpha}$, 0·3; $f_{t\beta}$, 0·3; $f_{t\alpha}$, −0·3 mdyn Å^{-1}; (ii) acetone: k_{C-C}, 4·0; $k_{C=O}$, 10·42; h_{CCO}, 0·6; h_{CCC}, 0·45; f_{ss}, 0·55 mdyn Å^{-1}. The force constants and interaction constants have not been refined and represent merely possible sets. Variation of k_{C-C} from 4·0 to 5·0 mydn Å^{-1} causes only minor changes in the derived values for $k_{C=O}$, k_{C-H}, and h_{CHO} and in the resultant potential-energy distributions for the carbonyl group vibration. This is not true for the C–C stretching and C–C–O bending vibrations of acetaldehyde or for the corresponding vibrations of acetone; more refined models are needed for a satisfactory description of these vibrational modes.

TABLE 4

Approximate potential-energy distribution for carbonyl group vibration in simplified models of acetone and acetaldehyde

	C=O Stretch	C–H Stretch	C–C Stretch	C–H Bend	CCC Bend	CCO Bend
Acetone	82·9		10·3		6·8	
Acetaldehyde	82·6	0·7	4·8	11·2		0·6

TABLE 5

Effects of structural perturbation on in-plane vibrational frequencies of MeCHO

	Vibrational frequencies (cm^{-1})					$\Delta\nu_{CO}$
Acetaldehyde (calc.)	2822	1746	1402	1103	508	
Bond lengths and atomic masses put to values for acetone	1787	1366	739	517	434	+41
Interaction constants changed to value for acetone	1832	1248	795	539	435	+45
$k_{C=O}$ Put to value for acetone	1729	1248	788	539	434	−103
Other stretching and bending constants put to values for acetone	1738	1219	781	524	482	+9

Although the carbonyl vibrations in aldehydes and ketones differ, some similarity might be expected within each series for the effects of substituents on the carbonyl frequency. It is unlikely that steric factors are important for aldehydes but the normal polar effects might be expected to operate and to lead to frequencies in the order Me > Et > Pr^i > Bu^t. The observed sequence, *viz.*, Pr^i > Et > Me > Bu^t, must then arise by the superposition of other perturbations. The change in effective mass of the substituent can be shown to have a negligible effect. There remain only small changes in the force constants of the bonds to the adjacent atoms and in the nature of the carbonyl vibration as sources of perturbation. It is probable that increased branching in the alkyl group will lead to some variation [12] in the C–H bending constant but the effects of this on the carbonyl frequency should be small; concurrently branching will remove the CH_3 out-of-plane rocking vibration which Cossee and Schachtschneider [10] show contributes *ca.* 3% of the energy of the carbonyl vibration of acetaldehyde. The cumulative effect of these perturbations is probably small but it may well be of the same magnitude as the apparently small effects of substituent polarity in aldehydes. Further clarification of this requires results from a wider range of substituents than those of simple aliphatic aldehydes.

In solution the carbonyl group frequency falls to lower values. With non-polar solvents the frequencies for aliphatic aldehydes correspond to satisfactory straight lines of the form [3] (1). This relationship, indicating

$$\nu_{soln} = n\nu_{vap} + c \qquad (1)$$

that the effects of intermolecular forces on the carbonyl frequencies are proportional to the effects of intramolecular forces, permits the use of these solution frequencies in discussion of intramolecular effects. However even for hexane, cyclohexane, and carbon tetrachloride solutions the linear correlation (Table 1) is less precise than for solutions of aliphatic ketones and esters.[3,4] For more polar solvents the value of the gradient, *n*, decreases and of the intercept, *c*, increases: these changes are accompanied by a marked decrease in linearity. This anomalous behaviour is alternatively shown in modified Bellamy–Hallam–Williams plots [13] by use of pentan-3-one as the reference compound according

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[12] *Cf.* E. F. Worden, *Spectrochim. Acta*, 1962, **18**, 1121; U.S. Atomic Energy Commission, UCRL-8508.

[13] L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

to the expression (2). Again the regression coefficients (Table 1) are significantly less than those normally

$$\nu = m\nu_{\text{ref}} + d \qquad (2)$$

shown in related correlations but they are improved by the ommision of the four basic solvents (dioxan, Me_2SO, $MeNO_2$, pyridine) or by using acetaldehyde as the reference compound. The departures from linearity of these plots imply intervention of solvent–solute interactions specific to aldehydic carbonyl compounds.

Special solvent–solute interactions have been detected for carboxylic acids[14] and for acetylenic ketones[15] operating by virtue of hydrogen bonding of the acidic hydrogen atom to the solvent. For aldehydes an alternative interaction lies in the nucleophilic properties of the solvent becoming effective in specific interactions at the carbonyl carbon atom. The solvents showing irregularities are those expected to have nucleophilic properties and it is particularly significant that triethylamine which behaves as a strongly basic but weakly nucleophilic solvent has comparatively little special effect on the carbonyl frequencies. Such interaction is in accord with the better fit and lower solvent-sensitivity of the carbonyl frequency of the sterically hindered pivaldehyde and with results for substituted benzaldehydes and pyrrole aldehydes which, being less susceptible to nucleophilic attack, give good Bellamy–Hallam–Williams plots.[16] Conversely, such plots for chloral, where nucleophilic interaction is expected to be important, show poor correlation (regression coefficient with reference to pentan-3-one, 0·85).

Attempts to study the effects of solvents on skeletal vibrations other than those evident in the C–H and C=O bands are made difficult by the strong absorbtion of many solvents. Of the usual solvents only with carbon tetrachloride, chloroform, carbon disulphide, and pyridine could complete sets of in-plane vibrational frequencies be recorded (Table 6). Application of the tetra-atomic model to these solution frequencies shows that for satisfactory fit changes may be required in the three stretching constants (C–H, C=O, C–C) and the HCO bending constant (Table 6). Apart from the expected correlation between the stretching constants and frequencies for the C–H and C=O vibrations the small changes appear to correspond to a complex interaction with the solvent species. In particular the changes in C–H stretching and bending constants are not those expected for a dominant hydrogen-bonding interaction but together with the changes in C=O stretching constant imply a change in the apparent electronegativity at the central carbon atom.

C–H *Stretching Frequency*.—The C–H stretching frequency of the aldehyde group occurs in the region 2850—2700 cm^{-1}, a frequency lower than that of other C_{sp^3}–H bonds. Previous studies of aldehydes have shown the occurrence of two bands in this range and the proper assignment of these bands has been the subject of several studies. Pozefsky and Coggeshall[17] suggested the possibility that the two bands could arise by Fermi resonance between the C–H stretching mode and an overtone of a skeletal vibration. Pinchas[18] assigned the lower frequency band to the aldehydic C–H stretching vibration and the higher-frequency band to the first overtone of the aldehydic in-plane C–H bending vibration; Eggers and Lingren[19] indicated the possibility of Fermi resonance between these two transitions and this was confirmed by Sauer, *et al.*[20] although Pinchas[21] subsequently modified his assignment.

The observed frequencies (Table 2) show reasonably similar solvent-dependence. Were one of the observed bands to arise from an uncoupled C–H stretching frequency and the other from the overtone of the C–H bending frequency or from a combination band then the two frequencies would be expected to show different solvent-dependence. In contrast if weak Fermi resonance were involved it would be expected that the vibrational coupling would be destroyed by a solvent-

TABLE 6

Frequencies (cm^{-1}) and force constants *(mdyn Å^{-1}) for in plane vibrations of acetaldehyde in solution

	Vapour		Solvent							
			CCl_4		CS_2		$CHCl_3$		Pyridine	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
	2824	2822	2824	2822	2814	2814	2841·5	2841·5	2837	2838
	1746·5	1746	1730	1731	1729	1728	1724·5	1724·5	1723·5	1724
	1409	1402	1423	1422	1471	1416	1399	1397	1421·5	1421
	1112·5	1104	1107	1104	1106·5	1104	1111·5	1104	1111	1111
	509	509	511	509	510	509	513	508		511
k_{CO}		11·95		11·68		11·65		11·63		11·55
k_{CO}		4·0		4·0		4·0		4·0		4·1
k_{CH}		4·3		4·3		4·28		4·36		4·35
h_{CHO}		0·57		0·6		0·59		0·56		0·6

* Force constants other than those listed and interaction constants retained values given in Table 3.

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[14] A. J. Collings and K. J. Morgan, *J. Chem. Soc.*, 1963, 3437.

[15] J. S. Byrne, unpublished results.

[16] M. K. A. Khan and K. J. Morgan, *J. Chem. Soc.*, 1964, 2579.

[17] A. Pozefsky and N. D. Coggeshall, *Analyt. Chem.*, 1951, **23**, 1611.

[18] S. Pinchas, *Analyt. Chem.*, 1955, **27**, 2.

[19] D. F. Eggers and W. E. Lingren, *Analyt. Chem.*, 1956, **28**, 1328.

[20] E. L. Saier, L. R. Cousins, and M. R. Basila, *J. Phys. Chem.*, 1962, **66**, 232.

[21] S. Pinchas, *Analyt. Chem.*, 1957, **29**, 334.

induced decrease in the C–H stretching and increase in the C–H bending frequencies. Neither of these situations is revealed. The observed behaviour is in good accord with the assignment to strong Fermi resonance interaction in which neither band can usefully be assigned solely to a C–H stretching frequency.

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