[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA][1]

The Infrared Absorption Spectra of Diethyl Ketone and its Deuterium Substitution Products

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A comparison of the infrared absorption spectrum of diethyl ketone with the spectra of six deuterium substitution products has permitted the unequivocal identification of the methyl and methylene vibrations in the C–H stretching and C–H bending regions. Bands characteristic of the trideuteromethyl and dideuteromethylene group are also identified between 2300 and 2100 cm.$^{-1}$. A small but significant lowering of the carbonyl stretching frequency occurs on deuteration of the methylene groups.

The use of deuterium substitution to distinguish between methyl and methylene vibrations in the infrared spectra of organic compounds has been described in a preceding publication dealing with steroids.[2] In that article some preliminary observations on the spectra of deuterized diethyl ketones were also included.

The investigation of the spectrum of diethyl ketone (I) has now been extended to include the six deuterized compounds II–VII.

I $CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$
II $CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$
III $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$
IV $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CD_3$
V $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$
VI $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$
VII $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$

It is observed that several of the bands present in the spectrum of normal diethyl ketone disappear on deuteration and the missing bands can be attributed to vibrations localized in the deuterized groups.

Experimental

The deuterium substituted diethyl ketones were synthesized by Dr. L. C. Leitch and Mr. A. T. Morse and the preparative details are reported elsewhere.[3] The deuterium contents, as determined by mass spectrometry, exceeded 96% of the theoretical requirement in all compounds except $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, for which the isotopic purity was 88.4%.

The spectra were measured quantitatively in carbon tetrachloride solution on a Perkin–Elmer Model 12C single beam spectrometer equipped with a calcium fluoride prism, which provided a spectral slit width diminishing from 7 cm.$^{-1}$ at 3000 cm.$^{-1}$ to 3 cm.$^{-1}$ at 1300 cm.$^{-1}$. A control solvent spectrum was recorded on each chart. Duplicate determinations were made for each compound and the curves computed and plotted as apparent molecular extinction coefficients.[4]

Below 1300 cm.$^{-1}$ the spectra were measured in carbon disulfide solution with a sodium chloride prism.

Results and Discussion

C–H Stretching Vibrations (3000–2850 cm.$^{-1}$).—In the spectra of aliphatic hydrocarbons four bands are commonly observed between 3000 and 2850 cm.$^{-1}$. The assignment of two of these to asymmetrical and symmetrical methyl C–H stretching vibrations and the other two to asymmetrical and symmetrical methylene C–H stretching vibrations is well substantiated.[5,6]

In diethyl ketone four bands occur at 2977, 2936, 2902 and 2883 cm.$^{-1}$ (Fig. 1A), and it would seem reasonable *a priori* to assign these two each to the methyl and methylene groups. Francis,[7] in the course of a study of the C–H stretching band intensities observed that the methylene C–H stretching vibrations are quite weak in the –CO–CH$_2$– structure and questioned whether any of these four bands in the diethyl ketone spectrum are associated with methylene vibrations.

That the four bands arise from C–H vibrations of some kind is established by the fact that they are all absent from the spectrum of fully deuterized diethyl ketone (Fig. 1D), but a comparison of Figs. 1B and 1C, for $CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$ and $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$ indicates that the three bands at 2977, 2936 and 2883 cm.$^{-1}$ disappear on deuteration of the methyl group, leaving the 2902 cm.$^{-1}$ band and this alone disappears on deuteration of the methylene groups.

This strongly supports the assignment of the 2977, 2936 and 2883 cm.$^{-1}$ bands to methyl vibrations and the 2902 cm.$^{-1}$ to a methylene vibration. These assignments are further substantiated by the spectra of the unsymmetrically deuterized diethyl ketones shown in Fig. 2. All three of these compounds contain one CH_3 group and show the bands at 2977, 2936 and 2883 cm.$^{-1}$. In $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$, where there is no contribution from CH_2 groups the apparent extinction coefficients of the three bands are 46, 29 and 15, respectively, which approximate reasonably well to half of the values (82, 54 and 29) for $CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$, indicating that each methyl group contributes equally and independently to the total absorption.

C–D Stretching Vibrations (2250–2050 cm.$^{-1}$).—Diethyl ketone does not absorb significantly in this region (Fig. 1A) but the fully deuterized compound (Fig. 1D) shows four bands. In $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$ (Fig. 1C) there are three bands, at 2233, 2129 and 2078 cm.$^{-1}$, which must be correlated with the trideuteromethyl groups. The 2173 cm.$^{-1}$ band must be inference by a dideuteromethylene band.

These assignments are substantiated by the spectra of the unsymmetrically deuterized compounds. Thus $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ (Fig. 2A) shows the 2233, 2129 and 2078 cm.$^{-1}$ bands with apparent absorption coefficients of 24, 10 and 11, respectively. The introduction of the second CD_3 group (Fig. 1B) approximately doubles these to 51, 21 and 17.

The absorption of the CD_3 and CD_2 groups are

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(2) R. N. Jones, A. R. H. Cole and B. Nolin, THIS JOURNAL, **74**, 5662 (1952).

(3) L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **31**, 785 (1953).

(4) R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, THIS JOURNAL, **74**, 80 (1952).

(5) J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A167**, 257 (1938); **A175**, 208 (1940).

(6) N. Sheppard and D. M. Simpson, *Quarterly Rev. Chem. Soc.*, **7**, 19 (1953).

(7) S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

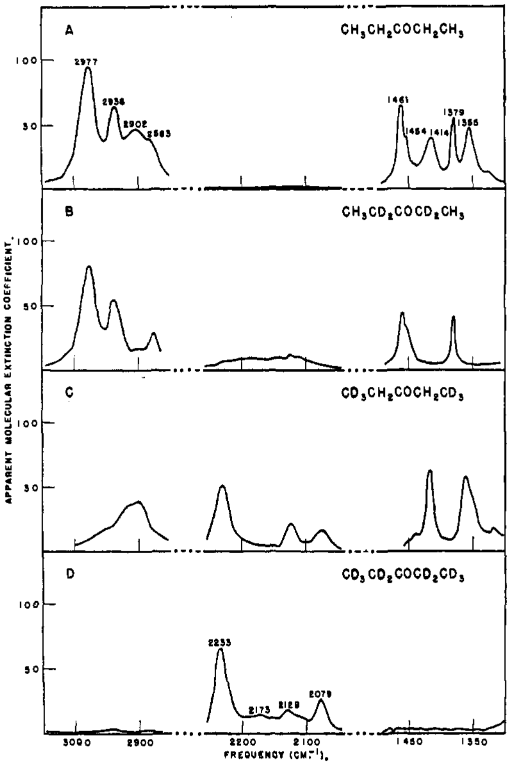

Fig. 1.

appreciably weaker than the corresponding CH_3 and CH_2 groups. Indeed, the CD_2 absorption is so weak that the band might well be overlooked or confused with weak overtone bands if its presence in the compound was not anticipated.

C–H Bending Vibrations (1470–1320 cm.$^{-1}$).—Five prominent bands are shown by diethyl ketone in this region (Fig. 1A) at 1461, 1454, 1414, 1379 and 1355 cm.$^{-1}$. From normal coördinate vibration analyses of aliphatic hydrocarbons,[6] these can most probably be associated with C–H bending vibrations. This is confirmed by the fact that fully deuterized diethyl ketone does not absorb in this region (Fig. 1D). The 1414 and 1355 cm.$^{-1}$ bands of diethyl ketone are missing from the spectrum of $CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$ (Fig. 1B) and are therefore to be assigned to the methylene groups. In accord with this it is observed that in $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$ the two bands at 1414, 1355 cm.$^{-1}$ are present and the other three absent.

The assignments of the 1461, 1454 and 1379 cm.$^{-1}$ bands to methyl groups and the 1414 and 1355 cm.$^{-1}$ bands to methylene groups are substantiated by the spectra of the unsymmetrically deuterized ketones in Fig. 2. $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ (Fig. 2A) and $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ (Fig. 2B) possess the same bands as normal diethyl ketone, except for a diminution in intensity. In the former, where there are one methyl group and two methylene groups, the intensity of the methyl bands is approximately halved and the intensity of the methylene not greatly affected. In the latter, where one methyl and one methylene only are present, all five bands are approximately halved in intensity.

A methylene bending band at 1430–1410 cm.$^{-1}$ is commonly observed where the methylene group is adjacent to a carbonyl group,[2,7,8] being displaced down from 1465 cm.$^{-1}$ where it occurs in saturated hydrocarbons. Francis has concluded from intensity measurements[7] that the methylene group in the $-CH_2-CO-$ structure also absorbs between 1355 and 1370 cm.$^{-1}$ and the identification of the 1355 cm.$^{-1}$ with the methylene group confirms this.

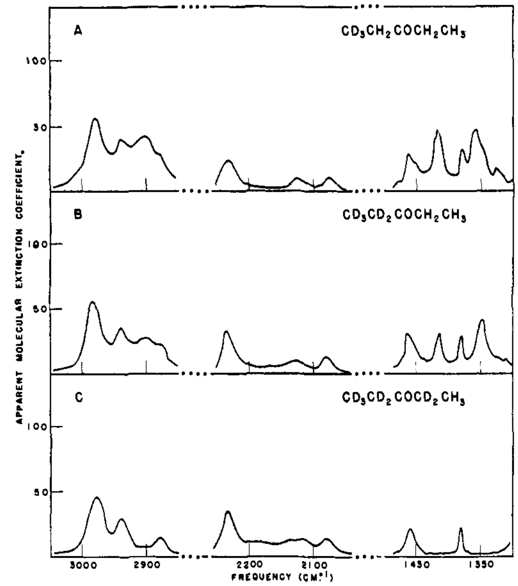

Fig. 2.

The 1379 cm.$^{-1}$ band arises from the symmetrical bending vibration of the methyl group, and the 1461 cm.$^{-1}$ band and its 1454 cm.$^{-1}$ satellite are probably associated with the non-symmetrical methyl bending vibration, although the presence of two peaks in this region is at present unexplained.

Carbonyl Stretching Vibrations (1720–1714 cm.$^{-1}$).—Diethyl ketone gives a moderately intense band at 1720 cm.$^{-1}$ in carbon tetrachloride solution which is the well recognized C=O stretching vibration. The position of this band in the various deuterized derivatives is listed in Table I. In the fully deuterized compound the band maximum is displaced down to 1714 cm.$^{-1}$ The deuterium atoms in the methylene group are mainly responsible for this displacement since $CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$ also absorbs at 1714 cm.$^{-1}$ and $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$ at 1720 cm.$^{-1}$. In the unsymmetrically deuterized ketones the deuteromethyl

TABLE I

CARBONYL STRETCHING BANDS IN DIETHYL KETONES

Ketone	Frequency, cm.$^{-1}$	True mol. extinction coefficient,[a] mole/l. cm.	True integrated intensity,[a] $\times 10^4$ l./mole cm.^{2}
$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	1720	355	1.78
$CH_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$	1714	360	1.84
$CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$	1720	290	1.92
$CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CD_3$	1714	295	1.88
$CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	1718	290	1.94
$CD_3{\cdot}CD_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	1716	325	1.83
$CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$	1716	335	2.02

[a] See reference 4 of text.

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(8) R. N. Jones and A. R. H. Cole, THIS JOURNAL, **74**, 5648 (1952).

groups do appear to exercise some effect on the carbonyl frequency. In $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ the frequency is lowered by 2 cm.$^{-1}$ to 1718 cm.$^{-1}$; although small this is considered a significant shift and is substantiated by the fact that in $CD_3{\cdot}CD_2{\cdot}CO{\cdot}CD_2{\cdot}CH_3$ the carbonyl frequency is raised by 2 cm.$^{-1}$ in comparison with the fully deuterized compound.

The true integrated absorption intensities and the true maximal molecular extinction coefficients are also given. These were determined by methods described previously.[4] The intensity is about the same as that of carbonyl stretching bands in steroids[4] and deuteration has no significant effect upon it.

Absorption below 1300 cm.$^{-1}$.—The absorption below 1300 cm.$^{-1}$ is complex, and the spectra are changed very considerably by the introduction of deuterium. This region requires more extensive study and will not be dealt with here.

Concluding Remarks

The characteristic frequencies established in this investigation are summarized in Table II. They indicate that the methyl and methylene groups in diethyl ketone undergo stretching and bending vibrations which are localized and show little evidence of interaction; no cross effects between the alkyl groups on opposite sides of the carbonyl group are detected.

Table II

Summary of Characteristic Vibration Frequencies between 3000 and 1300 Cm.$^{-1}$ in Diethyl Ketones

Band frequency, cm.$^{-1}$	Related group	Nature of the band
2977	CH_3	Attributed tentatively to a pure asymmetrical stretching vibration
2936, 2883	CH_3	Could arise from coupling between the symmetrical stretching vibration and a harmonic of the 1461 cm.$^{-1}$ band
2902	CH_2	Symmetrical stretching motion
2233	CD_3	Similar to the 2977 cm.$^{-1}$ band
2173	CD_2	Stretching vibration
2129, 2078	CD_3	Could arise from coupling between the symmetrical stretching vibration and an overtone of the CD_2 bending vibration near 1050 cm.$^{-1}$
1720	CO	Carbonyl stretching vibration
1461, 1454	CH_3	Probably associated with the non-symmetrical bending vibration
1414	CH_2	Bending vibration
1379	CH_3	Symmetrical bending motion
1355	CH_2	Identified with the methylene group in $-CH_2-CO-$

In most respects these conclusions substantiate the interpretation of the diethyl ketone spectrum based on the intensity studies of Francis[7] and the more generalized considerations of specific group frequencies established for organic compounds of all types. The only feature calling for special comment is the association of three bands in the 3000–2850 cm.$^{-1}$ with the methyl groups.

In terms of vibration theory only two of these could be simple stretching vibrations and it must be inferred that the third band arises from resonance coupling with an overtone of a lower frequency vibration. Tentatively it is suggested that the most intense of the bands, at 2977 cm.$^{-1}$ is a pure asymmetrical methyl stretching vibration, the analog of the 2962 cm.$^{-1}$ band of aliphatic hydrocarbons. The weaker bands at 2936 and 2883 cm.$^{-1}$ could arise from coupling between the symmetrical methyl stretching vibration and the first harmonic of the methyl bending band at 1461 cm.$^{-1}$. Since the trideuteromethyl group also gives three bands in the C–D stretching region, a similar explanation might apply with the 2233 cm.$^{-1}$ arising from a pure CD_3 asymmetrical stretching vibration and the 2129 and 2078 cm.$^{-1}$ from coupling of the symmetrical CD_3 stretching band and a harmonic of a CD_2 bending vibration near 1050 cm.$^{-1}$.

The presence of only one methylene stretching band in the spectrum is also unanticipated but the unsymmetrical contour of the residual CH_2 band in $CD_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CD_3$ suggests the presence of a second weak component near 2955 cm.$^{-1}$ which is totally submerged when methyl groups are also present.

These results illustrate the value of the deuterium substitution technique in interpreting the infrared spectra of complex molecules, and other organic compounds are at present being studied in a similar manner.

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