337. *Infrared Absorption Spectra of Some Urea Complexes.*

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Information about the structure of urea in a urea complex and the endocytic molecules contained therein may be obtained from infrared absorption spectra. Several complexes of aliphatic compounds, including paraffins, bromides, alcohols, acids, and esters, have been examined in this respect.

THE many investigations [1] into the crystalline complexes between urea or thiourea and various organic compounds have been used, in the main, for separation of lower and higher members of homologous series, and of branched from straight-chain compounds. Measurement of the heats of formation [2] of these " adducts " together with *X*-ray diffraction studies [3] showed that no chemical changes had occurred but that the crystal structure of the urea had been altered from a tetragonal to a hexagonal form. Further, the urea molecules were shown to be arranged in a lattice structure such that the holes in the crystals were in the form of spirals. The molecules of the reactant had taken up an endocytic position. This spiral configuration was found to be stable only in the presence of the confined molecule. The molecules inside the spiral were found to be aligned end to end.

Except for a paper by Stuart [4] on the NH stretching frequencies of the urea–cetane complex, no detailed infrared investigation of these complexes has been carried out.* As hydrogen-bond changes which play an integral part in urea-complex formation have been studied extensively by infrared measurements, it was thought that such investigations would provide information on both the changes in structure of the urea and perhaps of the molecules in the complex. So attempts were made to form urea complexes with

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* After this paper had been written, our attention was drawn to work [5] on the NH stretching frequencies of urea complexes containing paraffins, alcohols, mono- and di-carboxylic acids, esters, diamines, and polymethylene halides. The results quoted show that the paraffins, alcohols, and monocarboxylic acids and esters give " normal " complexes with shifts of the asymmetric νNH vibration to longer wavelengths by 43 and 72 cm.$^{-1}$ and the symmetric νNH vibration by 125 cm.$^{-1}$ (urea, 3443 and 3347 cm.$^{-1}$). The complexes of dicarboxylic acids, diamines, and polymethylene halides, however, exhibit different absorptions in the νNH region. Thus these complexes must have a different structure from the " normal " one.

[1] McLaughlin, " The Chemistry of Petroleum Hydrocarbons," Vol. I, Chapter 10, Reinhold Publ. Corp., New York, 1954.

[2] Redlich *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 4153, 4161.

[3] Smith, *Acta Cryst.*, 1952, **5**, 224.

[4] Stuart, *Rec. Trav. chim.*, 1956, **75**, 906.

[5] Illuminati, Grassini, and Scrocco, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1958, **24**, 435.

molecules which had been studied previously by infrared methods. Straight-chain molecules were chosen, as branched-chain and cyclic compounds usually have too large a cross-sectional area to form urea complexes.

Work on similar lines for thiourea complexes will be reported elsewhere.

Experimental.—Spectroscopic measurements were made with a Grubb-Parsons S3 spectrometer (with a sodium chloride prism), with a D.B.1 double-beam radiation unit, and with a Grubb-Parsons G.S.3 grating spectrometer.

The compounds examined were good-quality materials whose physical constants have been reported. The potassium chloride disc technique was used. The potassium chloride was heated for several days in a muffle furnace at 350—400° alternating with grinding to ensure the absence of moisture. The grinding time of the complex and potassium chloride mixture was kept as short as possible as it was thought that long grinding would break up the structure of the complex. Spectra of Nujol mulls of the complexes were essentially similar to those of the discs.

The complexes were prepared by addition of a small amount of the compound to be included to a saturated methanolic solution of urea. The crystalline adduct which formed instantaneously was filtered off under suction and washed rapidly with ether.

Besides the complexes discussed, decane formed a complex, whereas tetramethylene chloride and bromide, pentamethylene and hexamethylene glycol, valeric acid, and disodium adipate did not.

DISCUSSION.—The spectra of urea and the urea complexes (as potassium chloride discs) are shown in Fig. 1. When compared with that of urea, all show similar changes. The adipic acid complex seems to be peculiar and will be considered below. The absorptions of urea in the free state and in the complexes are added in the Table. The shift of frequencies in the NH stretching region to longer wavelengths in the complexes suggests an increase in hydrogen bonding, this being in accordance with *X*-ray data for N–O distances:[3]

$$\text{Urea}\quad \left.\begin{array}{l} \text{N–H}\cdots\text{O} = 3{\cdot}03\ \text{Å} \\ \text{N–H}\cdots\text{O} = 2{\cdot}99\ \text{Å}\end{array}\right\}\begin{array}{c}\text{Tetragonal}\\ \text{form}\end{array}\qquad \begin{array}{c}\text{Urea–cetane}\\ \text{complex}\end{array}\quad \left.\begin{array}{l} \text{N}^1\text{–H}\cdots\text{O}^3 = 3{\cdot}04\ \text{Å} \\ \text{N}^1\text{–H}\cdots\text{O}^2 = 2{\cdot}93\ \text{Å}\end{array}\right\}\begin{array}{c}\text{Hexagonal}\\ \text{form}\end{array}$$

Aliphatic CH stretching vibrations occur at *ca.* 2920 and 2850 cm.$^{-1}$ and these together with shoulders at *ca.* 1465 cm.$^{-1}$, due presumably to $\delta(CH_2)$ bending vibrations, are the only positive indications that the complexes in Fig. 1 contain endocytic molecules. The changes in the absorptions due to the urea, however, indicate that complexes are formed.

This increase in bond distance in the complex gives rise to different force constants for the C=O groups and also probably different frequencies for the δNH_2 bending vibrations.

The symmetric and the asymmetric νC–N vibrations in urea [6,7] at 1457 and 1000 cm.$^{-1}$ are thought to occur at *ca.* 1485 and *ca.* 1011 cm.$^{-1}$ in the spectra of the complexes. This corresponds to a slight decrease in bond distance which has been measured by *X*-rays (C–N in urea 1·37 Å, in urea–hexadecane 1·33 Å).

The changes in frequency in the 791—717 cm.$^{-1}$ region may well result from the changes in bond angles indicated by *X*-ray evidence,[3] C–N–H$\cdots$O being 116° and 136° in the complex and 99° and 128° in urea.

An alternative explanation, that the frequency changes observed on going from urea to complex may be due to different coupling between molecules in the tetragonal and hexagonal lattices, is thought not to be as good as that put forward here which correlates with *X*-ray measurements of bond distances and angles.

Other bands which occur in the spectra *C*, *D*, and *E* in Fig. 1 are due to the endocytic molecules.

In the spectra of the hexanoic acid–urea complex, the νC=O stretching vibration occurs at the same frequency as in liquid hexanoic acid.[8] Weakish absorptions at 1312, 1292,

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[6] Stewart, *J. Chem. Phys.*, 1957, **26**, 248.

[7] Yamaguchi, Miyazawa, Shimanouchi, and Mizushima, *Spectrochim. Acta*, 1957, **10**, 170.

[8] Corish and Chapman, *J.*, 1957, 1746.

1258, and 1205 (sh) cm.$^{-1}$ show more similarity to the spectrum of crystalline hexanoic acid than to that of the liquid state. These weak bands are intensified on running difference spectra of the complex *versus* urea, both as potassium chloride discs. Similarly for the pelargonic acid–urea complex (*C*), the νC=O stretching vibration corresponds to that in the liquid state[8] whereas weak absorptions at 1450, 1290, 1264, 1230 and ~1195(?) cm.$^{-1}$ correspond more closely to the spectrum of crystalline pelargonic acid. Difference spectra of the complex *versus* urea bring these bands up more strongly. It seems therefore that the $[CH_2]_n$ chains of the monocarboxylic acids are in a *trans*-zig-zag form but that the carboxyl groups are in similar environments to those in the liquid state.

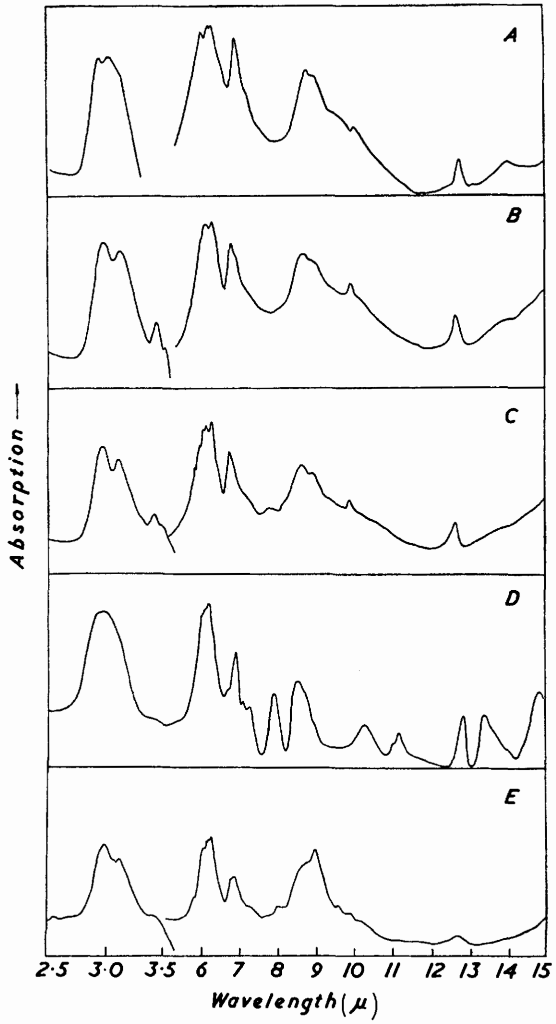

FIG. 1. *Infrared spectra of* (*A*) *urea and urea complexes with* (*B*) *cetane,* (*C*) *pelargonic acid,* (*D*) *adipic acid, and* (*E*) *diethyl adipate* (*all in* KCl *discs*).

The diethyl adipate complex (*E*) has a carbonyl absorption at a frequency corresponding to that of liquid diethyl adipate.[9] An absorption due to a $\delta(CH_3)_s$ vibration at 1382 cm.$^{-1}$ also corresponds more closely to that in liquid diethyl adipate. Weakish, but sharp, absorptions at 1266, 1053, 1018(?), and 866 cm.$^{-1}$ correspond to those in crystalline diethyl adipate. A difference spectrum of a diethyl adipate–urea complex *versus* urea (both as

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[9] Corish and Davison, *J.*, 1958, 927.

Infrared frequencies (*cm.*$^{-1}$).

Urea	Urea in complexes *		Lit.†	Assignments
3404	3350	3400	(3420)[4]	νNH out of phase [4]
		3350	(3360)[4]	
3317	3200		(3225)[4]	νNH in phase [4]
3209(sh)			(3190)[4]	
1668			1686[7]	Combination of CO stretch and NH_2 bend[7]; ν(CO)[6]
1620			1629[7]	NH_2 bending,[7] δNH deformation[6]
1603			1600[7]	Combination of CO stretch and NH_2 bend[7]; δNH deformation[6]
	4 bands 1675–1590			Probably due to different combination of CO stretch and NH bend taken in pairs
1457	1485		1464[7]	ν(C–N)[6, 7]
1150	1160		1150[7]	A_1NH_2 rocking,[6] A_1 and B_2NH_2 rocking[7]
(1120)				
1058	1058(w)		1050[7]	B_2NH_2 rocking,[6] B_1NH_2 wagging[7]
1000	1011		1000[7]	ν(C–N)[6, 7]
786	791		786[7]	Out of plane skeletal[6] mode; NH_2 wagging + CO out of plane
717			717[7]	B_1NH_2 wagging;[6] NH_2 wagging + CO out of plane

* These frequencies relate to complexes of urea with cetane, cetyl bromide, lauryl alcohol (which give essentially similar spectra), and to urea complexes of hexanoic acid, pelargonic acid, and diethyl adipate, but not to that of adipic acid. † Values quoted are for urea only.

potassium chloride discs) brings out these similarities more clearly. Fig. 2 shows the difference spectrum and also spectra of liquid and crystalline diethyl adipate run at the same time over the same chart. It may be deduced that the $[CH_2]_4$ part of diethyl adipate is in the *trans*-zig-zag form, but the CO_2Et part is in a similar environment to that in the liquid state.

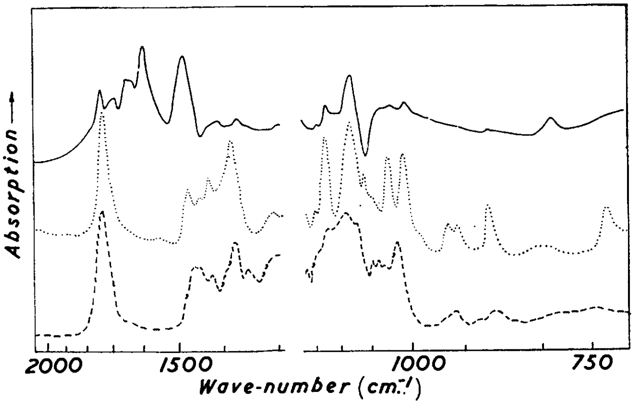

FIG. 2. *Difference spectrum of a diethyl adipate–urea complex.*

—— *Difference spectrum of complex versus urea* (both as KCl discs).
. . . . *Diethyl adipate* (*crystalline*).
– – – – *Diethyl adipate* (*liquid*).

The adipic acid–urea complex (*D*) is of different structure. The complex appears to have been formed, as the bands due to the urea, *i.e.*, at 1656, 1618, 1451, and 780 cm.$^{-1}$, differ from those in urea but they also differ from those in the other complexes. In particular, the 786 cm.$^{-1}$ band due to a skeletal mode in urea has apparently moved to a longer wavelength (780 cm.$^{-1}$) and not to a shorter wavelength (791 cm.$^{-1}$) as in the urea–paraffin complexes. The absorptions due to the adipic acid, however, are somewhat different from those in the crystalline state.[10] There is a rather broad band at 747 cm.$^{-1}$, the δ(OH) out-of-plane deformation vibration at 921 cm.$^{-1}$ has moved to 975 cm.$^{-1}$ and weakened, and several additional absorptions (compared with the spectrum of crystalline adipic acid) are present. It is thought that some of the adipic acid molecules are constrained into a non-*trans*-configuration, perhaps *ttg*, where *t* = *trans*, *g* = *gauche* (cf. dimethyl and diethyl pimelate[10]). This would account for the shorter-wavelength band (747 cm.$^{-1}$) and for the

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[10] Corish and Davison, *J.*, 1955, 2431.

additional absorptions at 892 and 907 cm.$^{-1}$. A shoulder at 1685 cm.$^{-1}$, however, is the same as in crystalline adipic acid, so that the C=O group is still similarly hydrogen-bonded The 3 μ region reveals little detail, a broad OH band being centred about 3290 cm.$^{-1}$. The possibility that a reaction between urea and adipic acid causes some of these peculiarities in spectrum was eliminated, since washing with water gave a residue of pure adipic acid. The complex therefore seems to have been formed.

From the foregoing it is seen that use of the potassium chloride disc technique reveals whether a urea complex has been formed, what changes have occurred in the urea structure, and also sometimes information about the structure of the endocytic molecules. The use of differential or difference spectroscopy is valuable for this work.

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