450. *Infrared Absorption Spectra of Some Urea Inclusion Compounds.*

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Infrared absorption spectra of urea inclusion compounds with n-paraffins and their 1-bromo- and 1-hydroxy-derivatives are reported. A band 1650 cm.$^{-1}$ is typical for inclusion compounds and corresponds to a C=N bond. An explanation is given on the basis of resonance structures of urea. Owing to hydrogen bonding O–H stretching vibrations of alcohols disappear in the inclusion compounds.

There has been considerable study of the structure of urea inclusion compounds by infrared absorption spectroscopy,[1-4] but some unsolved problems remain. We report here the infrared spectra of inclusion compounds composed of urea with some n-alkanes and their 1-bromo- and 1-hydroxy-derivatives, also a consideration of changes in the structures of urea which occur on formation of complexes, and the effect of the stability of the complexes on the spectra. For comparison, the spectra of a few *O*-alkyl derivatives of isourea have also been examined.

Experimental

Urea, crystallized from methanol, had m. p. 132·5°. The following alcohols were used, having been purified by distillation: octan-1-ol, b. p. 195°, n_D^{20} 1·4331; nonan-1-ol, b. p. 212°, n_D^{20} 1·4332; decan-1-ol, b. p. 230°, n_D^{20} 1·4365; hexadecan-1-ol, b. p. 178—182°/12 mm., m. p. 50°.

Alkyl bromides were prepared from the corresponding alcohols by known methods: 1-bromooctane, b. p. 199—200°, n_D^{20} 1·4526; 1-bromononane, b. p. 220°, n_D^{20} 1·4541; 1-bromodecane, b. p. 148—150°/18 mm., n_D^{20} 1·4551; 1-bromo-hexadecane, b. p. 201—203°/21 mm., m. p. 14°.

The following normal hydrocarbons were prepared from the alkyl bromides by Grignard reactions: octane, b. p. 126°, n_D^{20} 1·3975; nonane, b. p. 150—151°, n_D^{20} 1·4055; decane, b. p. 173°, n_D^{20} 1·4120, hexadecane, b. p. 145°/10 mm., m. p. 20°.

Application of the method of Stieglitz and McKee [5] to cyanamide and the corresponding alcohol gave *O*-methyl-, m. p. 44—45° [hydrochloride (Found: N, 24·55. Calc. for $C_2H_7N_2ClO$: N, 24·8%)], *O*-ethyl-, m. p. 41—42° [hydrochloride (Found: N, 22·8. Calc. for $C_3H_9N_2ClO$: N, 22·65%)], and *O*-propyl-isourea, m. p. 63—64° [hydrochloride (Found: N, 20·2. Calc. for $C_4H_{11}N_2ClO$: N, 20·4%)].

The inclusion compounds of urea and hydrocarbons or alkyl bromides or alcohols were prepared by standard methods,[6] and analyses are reported in Table 1. The complexes were analysed either by evaporating the hydrocarbon (guest) at room temperature or by determining the nitrogen content. The octane and nonane complexes had lost their guests at room temperature only after 3 and 10 days, respectively.

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[1] Stuart, *Rec. Trav. chim.*, 1956, **75**, 906; Lautsch, Bandel, and Broser, *Z. Naturforsch.*, 1956, **11b**, 282; Corish and Chapman, *J.*, 1957, 1746; Corish and Davidson, *J.*, 1958, 927; Caroti and Cassi, *Riv. Combustibili*, 1958, **12**, 451; Illuminati, Grassini, and Serocco, *Atti Accad. Naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1958, **24**, 435; Mecke and Kutzelningg, *Z. analyt. Chem.*, 1959, **170**, 114.

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

[3] Barlow and Corish, *J.*, 1959, 1706.

[4] Fischer and McDowell, *Canad. J. Chem.*, 1969, **2**, 187.

[5] Stieglitz and McKee, *Ber.*, 1900, **33**, 1517.

[6] Schlenk, *Annalen*, 1949, **565**, 204.

TABLE 1.

Inclusion compounds with urea as host.

Guest	Wt. loss (%)	N (%)	$\frac{\text{Urea}}{\text{Guest}}$ (mol.)	Guest	N (%)	$\frac{\text{Urea}}{\text{Guest}}$ (mol.)	Guest	N (%)	$\frac{\text{Urea}}{\text{Guest}}$ (mol.)
C_8H_{18}	21·0	—	7·2	$C_8H_{17}Br$	32·2	7·2	$C_8H_{17}\cdot OH$	35·4	6·8
C_9H_{20}	22·0	—	7·65	$C_9H_{19}Br$	32·4	7·8	$C_9H_{19}\cdot OH$	35·3	7·45
$C_{10}H_{22}$	—	36·3	8·3	$C_{10}H_{21}Br$	32·9	8·9	$C_{10}H_{21}\cdot OH$	35·2	8·1
$C_{16}H_{34}$	—	35·5	12·1	$C_{16}H_{33}Br$	32·2	12·7	$C_{16}H_{33}\cdot OH$	35·2	12·3

The stability towards organic solvents was examined by passing ether (5 ml.) slowly through a layer of the complex (0·3 g.). The nitrogen contents before and after washing were: hexadecane complex 35·8, 36·8%; 1-bromodecane complex 33·6, 34·95%; hexadecan-1-ol complex, 35·1, 38·7%. However, the compound could gradually be completely washed out; *e.g.*, pure urea resulted from washing of a decan-1-ol complex with ~150 c.c. of ether.

Spectroscopic measurements were made with a Hilger H-800 double-beam spectrophotometer with a 60° sodium chloride prism. Liquids were examined as films between plates of sodium chloride. Solids were mainly used as Nujol mulls. In some instances thin films of inclusion compounds were formed by evaporating a solution of the complexes in ethanol or methanol on sodium chloride plates. Spectra of films of complexes were similar to these of mulls.

The main features of the spectra are given in Tables 2—4.

TABLE 2.

Infrared spectra of alkanes, bromoalkanes, and alkanols (R = C_8H_{17}, C_9H_{19}, $C_{10}H_{21}$, and $C_{16}H_{33}$).

RH	RBr	ROH (in Nujol)	Assignment
		3350—3330	H-bonded O–H stretch
2932—2927s, vs	2932—2020s,	2934—2932s,vs	C–H stretch of CH_3 and CH_2
2668—2850s	2868—2855s	2870—2868s	
1467m	1465—1462m	1467—1465m	CH_2 deformn.
1382w	1380w	1380—1375w	C–CH_3 deformn.
	1255—1250w		C–CH_2Br sheletal
		1120w	OH deformn. C–O stretch
722w	724—722w	725—722w	$[CH_2]_4$ skeletal

TABLE 3.

Infrared spectra of inclusion compounds of urea with the component stated (for assignments see second part of the Table).

(Urea)	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{16}H_{34}$	$C_8H_{17}Br$	$C_9H_{19}Br$	$C_{10}H_{20}Br$	$C_{16}H_{33}Br$
3455s	3450s	3440s	3440s		3429s	3415s	3420s	
3350s	3370s	3365s	3370s	3405s	3372sh	3370s	3380sh	3390s
3265sh	3235s	3220s	3230s	3225s	3224s	3220s	3230m	3225s
1687m	1675s	1680s	1680s	1680s	1678s	1677s	1680m	1677s
	1650sh	1650sh	1650sh	1650vs	1650m	1649s	1651s	1651vs
1627s	1628s	1630s	1630s	1630sh	1630sh	1628w	1631sh	
1600s	1598vs	1600s	1596vs	1595vs	1596s	1595s	1599s	1597vs
1465s	1488m	1488m	1490m	1490s	1495m	1488m	1488m	1490s
1155m	1156m	1156m	1160m	1157m	1155m	1161m	1156m	1160m
1055w	1050m	1050w	1055w	1065m	1060w	1060w	1065w	1052w
1000w	1014w	1014w	1014w	1014w	1014w	1014w	1014w	1014w
790w	792w	792w	792w	792w	792w	792w	792w	792w

$C_8H_{17}\cdot OH$	$C_9H_{19}\cdot OH$	$C_{10}H_{21}\cdot OH$	$C_{16}H_{33}\cdot OH$	
3435s				
3370s	3400s	3380s	3350	N–H stretch
3225s	3225s	3220s	3230s	
1680s	1680s	1680s	1680s	C=O stretch
1655s	1648vs	1650s	1650s	C=N stretch
1630w	1630w			
1600vs	1598vs	1598s	1557vs	C=O stretch & NH deformn.
1486s	1490s	1495s	1493s	C=N stretch
1156m	1161m	1160m	1160m	NH_2 rock
1052w	1055w	1065w	1065w	NH_2 rock or wag
1014w	1014w	1015w	1018w	C–N stretch or CN scissor
792w	792w	795w	795w	C=O and NH wag

Table 4.

Infrared spectra of *N*-methylurea and *O*-alkylisoureas (Me, Et, and Pr^n).

$NH_2\cdot CO\cdot NHMe$	$NH_2\cdot C(OR){:}NH$	Assignment
3435s	3465—3450m	N–H stretch
3330s	3235—3225s	
3220sh	3180—3170s	
1618s	1654—1650s,vs	C=N stretch
	1610—1600m,w	N–H
1578vs		
1420m	1461—1439ms	C–N stretch or C–NH_2 scissor

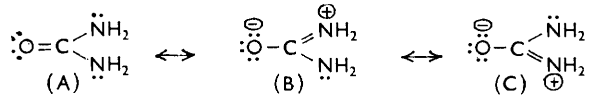
Discussion

Stability of the Inclusion Compounds.—Since urea inclusion compounds with hydrocarbons containing less than 16 carbon atoms are unstable, the compounds studied must be freshly prepared. This applies also to Nujol mulls, since the Nujol may act as solvent. Washing inclusion compounds with ether (to remove an excess of the guest) may extract some of the guest and yield " free " urea. Inclusion compounds of alkyl bromides and alcohols with urea are more stable towards the " ageing " than those of hydrocarbons; however, complexes of alcohols and urea are less stable towards washing with polar solvents. As a result, examination of spectra of less stable inclusion compounds is virtually examination of the superposed spectra of the inclusion compound and " free " urea, this aspect being more pronounced for inclusion compounds which have been treated with solvents. No attention seemed to have been paid so far to these circumstances.

Thus the bands at 3450—3415 cm.$^{-1}$ in our investigations, and similar frequencies found by others,[3,4] should be assigned to NH out-of-phase vibrations of " free " urea, and the bands at 1629—1627 cm.$^{-1}$ to NH_2 bending vibrations of " free " urea,[2,7] contrary to the views of some authors.[3] We believe that " pure " spectra of inclusion compounds have been obtained only for particularly stable inclusion compounds, namely, those of urea with hexadecane, 1-bromohexadecane, nonan-1-ol, decan-1-ol, and hexadecan-1-ol, none of which includes bands at ~3440 and ~1628 cm.$^{-1}$.

Spectra of Urea and its Inclusion Compounds.—The spectra of all the inclusion compounds examined are almost identical and independent of the nature of the guest; this is particularly noticeable for the more stable compounds.

The spectra were similar to that of urea itself, but somewhat shifted, which suggests that the urea is subjected to some modification. It is known [8] that the C–N and C=O bonds of urea are shorter and longer, respectively, than deduced from the conventional formula,



suggesting resonance between structures A, B, and C. Our experiments confirm the resonance; structures B and C are favoured in the inclusion compounds, as appears from the shift of the typical urea bands, *e.g.*, C=O stretching, to lower frequencies.

Band at 1650 *cm.*$^{-1}$. This band is characteristic of a urea inclusion compound. It is very prominent for the stable compounds, with frequencies 1655—1649 cm.$^{-1}$; it appears as a shoulder of the same frequency for the less stable compounds. It is not present in the spectrum of urea but is very strong in spectra of *O*-alkylisoureas at 1654—1651 cm.$^{-1}$. It represents the C=N bond. For the unstable complexes it is superposed on the band 1631—1628 cm.$^{-1}$ due to NH_2 deformation vibrations of " free " urea. Therefore we suggest that the band 1650 cm.$^{-1}$ is the result of the resonance shifting of the molecule of urea in complexes towards the structures B and C.

O–H *Stretching vibrations.* Bands at 3345 cm.$^{-1}$ are present in the spectra of alcohols

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[7] Yamaguchi, Miyazawa, Shimanouchi, and Mizushima, *Spectrochim. Acta*, 1957, **10**, 170.
[8] Wyckhoff and Corey, *Z. Krist.*, 1934, *A*, **89**, 462.

used to form inclusion compounds. They are of medium intensity, broad, and of relatively low frequency, indicating intermolecular hydrogen bonds. The bands completely disappear from the spectra of their inclusion compounds with urea. That this is due to formation of many new strong hydrogen bonds is supported by the fact that hydroxyl bands exist in the spectra of mechanical mixtures of the alcohols and urea.

Influence of Water on the Formation of the Inclusion Compounds.—McAdie and Frost [9] found that in the gaseous state a complex of urea with octane is formed only in the presence of traces of water, methanol, or ethanol vapour. On the other hand it has been suggested [10] that these highly polar solvents stabilize the zwitterion resonance structures. This further supports our view on the presence of the resonance structures B and C in the complexes.

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[9] McAdie and Frost, *Canad. J. Chem.*, 1955, **33**, 1275.

[10] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955.