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The Infra-red Absorption Spectrum and Structure of Urea

by

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In the course of our investigation of infra-red absorption spectra of urea inclusion compounds [1] it was necessary to examine the absorption spectrum of urea itself.

So far a number of authors have examined the infra-red spectrum of urea [2]—[9], but the existing data required revision in the light of our own results [1].

Our experiments have been carried out by means of a Hilger double-beam H-800 spectrometer with sodium chloride optics. Pure urea (m.p. 132.5°) was examined in Nujol mull.

Our results (Fig. 1) are tabulated together with the bands reported by earlier authors (Table I).

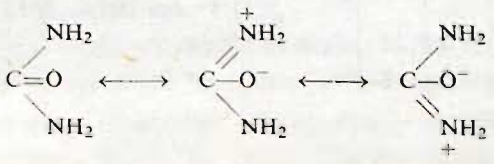
The samples crystallized from methanol were investigated as a film formed on the sodium chloride plate by evaporation of the solution. These samples were kept under various conditions and again investigated, as described below.

It has been noticed in the present work that urea freshly crystallized from water, methanol or ethanol gives a clear shoulder at the frequency of *c.* 1650 cm^{-1} (Fig. 2) which did not disappear when the sample was kept for two days under an atmosphere saturated with the same solvent and protected from light (Fig. 3). It disappeared, however, after a few days (e.g., two days) of keeping the samples under a dry atmosphere and protected from light (Fig. 4).

Discussion and assignements

It is known (on the basis of X-ray analysis by Wyckoff and Corey [10]) that the C=O bond in urea is longer than that usually found in the carbonyl group and the C—N bond is shorter than in amines and amides. This led to accepting the resonance structures (*A*), (*B*) and (*C*):

(I)



A *B* *C*

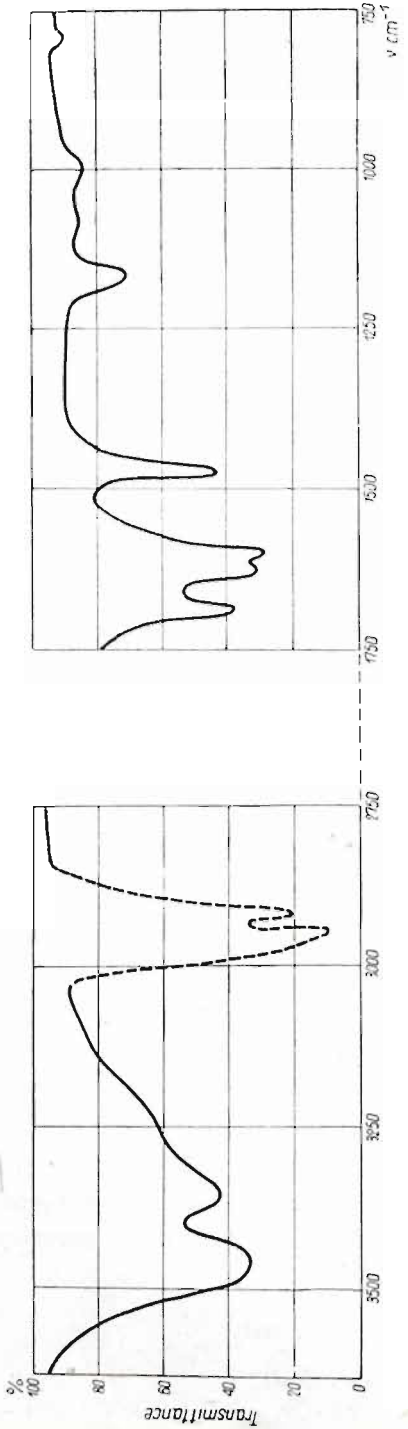


Fig. 1. Spectrum of urea (in Nujol mull)

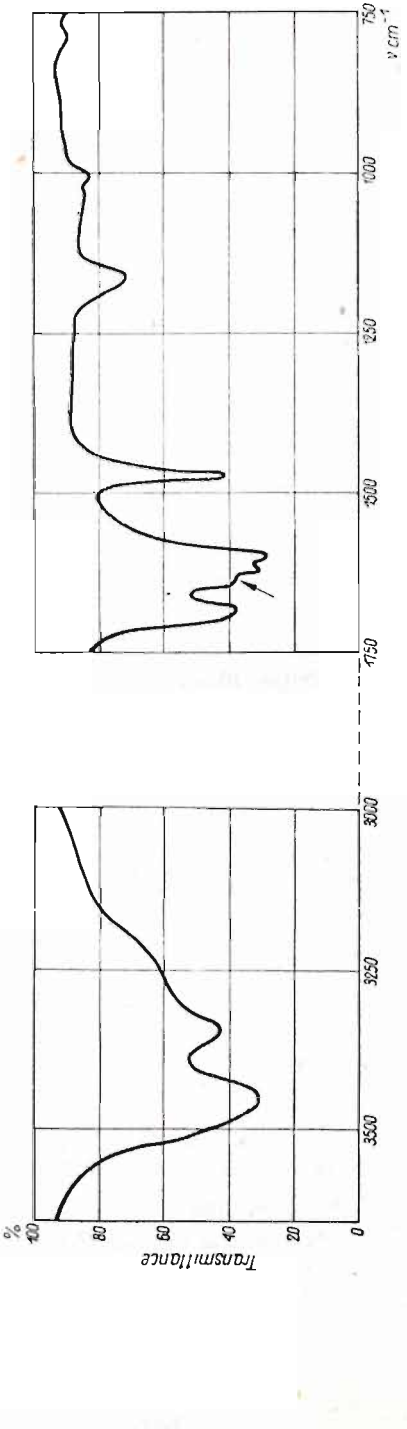
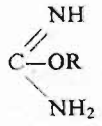


Fig. 2. Urea freshly crystallized from methanol (1650 cm.$^{-1}$ shoulder marked with arrow)

The C—N bond would acquire in *c.* 30 per cent a double bond character and the C—O bond would remain as such in *c.* 40 per cent [11]. Kumler and Fohlen [12] interpreted the dipole moment of urea as indicating a resonance hybrid with 20—30 per cent contribution of highly polar structures. They also pointed out that the structure of urea does not differ essentially from that of simple amides.

N—H stretching modes. According to Stuart [2] the 3420 cm.$^{-1}$ band (in our experiments 3456 cm.$^{-1}$) should be assigned to N—H out-of-phase stretching vibrations. Two other bands: 3360 and 3225 cm.$^{-1}$ (in our experiments 3350 and 3265 cm.$^{-1}$, respectively), are formed by the N—H in-phase stretching vibrations.

1687 cm.$^{-1}$ Mizushima and co-workers [5] assigned this band to both stretching C=O and bending NH_2 motions. On the basis of calculation he found that the contribution of the N bending motion for this band (1686 cm.$^{-1}$ in his paper) is greater than that of the C=O stretching vibration. Other authors, however, [3], [4] assigned this band to C=O stretching vibrations only. According to our earlier experiments [1], this band does not exist in the spectrum of O-alkyl derivatives of iso-urea of type (I) which possess the NH_2 group but do not contain a C=O group. Consequently, it should rather be assigned to C=O stretching modes only, without the share of NH_2.

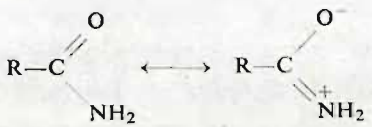


I

It is known that C=O stretching vibrations in saturated aliphatic aldehydes, ketones and acids have frequencies in the range 1740—1700 cm.$^{-1}$. In amides the frequency is lowered to 1690 cm.$^{-1}$ [13]. This lowering cannot be attributed to intermolecular hydrogen bonds as the frequency refers to dilute solutions.

It seems, therefore, probable that the relatively low frequency of C=O in amides is due to the existence of resonance structures (*D*) and (*E*):

(2)



D *E*

In this case the C=O frequency approaches the C—O stretching frequency, which in alcohols is 1410—1260 cm.$^{-1}$ [13].

Also in urea, the C=O frequency should be similar to that in amides and lowering of the frequency could be explained by a shift towards the structures (*B*) and (*C*).

N—H deformation (bending) vibrations. We recorded the bands 1627 and 1600 cm.$^{-1}$. Both should be assigned to N—H deformation vibrations in agreement with Becher [3] and Stewart [4]. Mizushima [5] suggested that the

TABLE I

Infra-red absorption bands of urea (ν cm^{-1})

Our experimental data	Literature data					Assignement
3456	3420 [2]	3404 [6]	3440 [7]			NH out-of-phase [2]
3350	3360	3317	3320			NH in-phase [2]
3265	3225, 3190	3209	3250			
1687		1668	1685	1686 [4]	1680 [3]	ν (O + NH) [5]; ν CO [3]; ν CO [4]
1627		1620	1620	1629	1625	δ NH [5]; δ_s NH [4]; δ_s NH_2 [2]
1600		1603	1608	1603	1600	(CO and δ NH_2) [5]; δ NH_2 [4]; δ_s NH_2 [3]
1465		1457	1470	1464	1468	ν (C—N) [5], [4]; ν_{as} CN_2 [3];
1155		1150	1155	1150	1160	ϱ NH_2 [4]; ϱ NH_2 [5]; ϱ NH_2 [3]
1055		1055	1058	1050	1060	ϱ NH_2 [4]; γ NH_2 [5]; γ NH_2 or ϱ NH_2 [3]
1000		1000	1000	1000	1010	ν (C—N) [4], [5]; ν_s CN_2 [3]
790		786	790	786	788	γ CO [3]; γ NH_2 + CO out-of-phase [6]

ν_s — symmetric stretching, ν_{as} — asymmetric stretching, δ — bending, δ_s — symmetric bending, γ — wagging, ϱ — rocking.

former (1629 cm.$^{-1}$ in his experiments) corresponds to almost pure NH_2 bending vibration, and the latter (1603 cm.$^{-1}$ in his experiments) is due both to C=O stretching and NH_2 deformation.

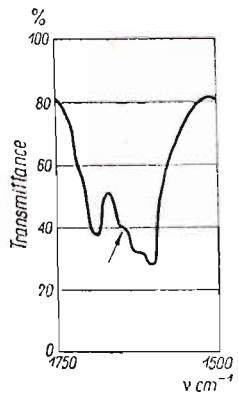


Fig. 3. 1700—1500 cm.$^{-1}$ region. Urea crystallized from methanol kept two days under atmosphere saturated with methanol (1650 cm.$^{-1}$ shoulder marked with arrow)

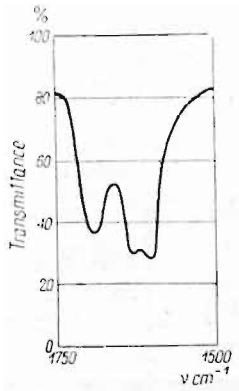


Fig. 4. 1700 cm.$^{-1}$ region. Urea crystallized kept two days under dry atmosphere

We found a frequency of 1610—1600 cm.$^{-1}$ in the spectra of O-alkyl derivatives of iso-urea [1], although they do not contain the carbonyl group. This would support the view that the band 1600 cm.$^{-1}$ corresponds to pure NH_2 bending vibrations.

C—N stretching vibrations. The frequency 1465 cm.$^{-1}$ should be assigned to C—N stretching vibrations in agreement with results of former investigators [4]—[6]. Becher [3] assigned it (1468 cm.$^{-1}$) to $C\begin{smallmatrix}N\\N\end{smallmatrix}$ asymmetric (scissoring) vibrations.

It should be pointed out that the usual frequency of C—N stretching vibrations in aliphatic amines is 1220—1020 cm.$^{-1}$ [11].

The band is evidently shifted towards higher frequency which approaches C=N (1690—1640 cm.$^{-1}$ [11]) in accordance with the structures (*B*) and (*C*).

Another band which should be assigned to C—N stretching vibration is that of frequency 1000 cm.$^{-1}$ [4]—[6]. Becher assigned it (1010 cm.$^{-1}$) to $C\begin{smallmatrix}N\\N\end{smallmatrix}$ symmetric modes.

Band or shoulder 1650 cm.$^{-1}$. As previously pointed out [1], this band is very typical for urea inclusion compounds. The more stable the inclusion compound, the more prominent this band. We assigned it to the C=N bond in the resonance structures of urea (*B*) and (*C*) and suggested that urea in the inclusion compounds has the resonance structure shifted towards the zwitterionic structures (*B*) and (*C*). Indeed, according to Wheland [14], the zwitterionic resonance structure is stabilized by polar solvents. This would suggest that the crystallization of urea

from a polar solvent would promote this shifting. Subsequently, the shoulder 1650 cm.$^{-1}$ should appear in the spectrum.

This expectation is in agreement with our experiments. The shoulder appeared in urea freshly crystallized from methanol (Fig. 2). It disappeared when keeping the crystallized urea sample under a solvent free-atmosphere (Fig. 3), but it did not disappear when crystallized urea was kept under an atmosphere saturated with the same solvent (Fig. 4).

TABLE II

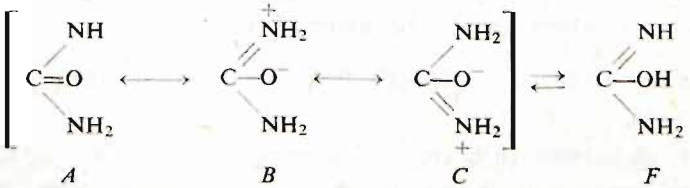
Infra-red absorption bands of urea (ν cm.$^{-1}$)

Urea in Nujol mull	Urea freshly crystallized from methanol; film	Urea crystallized from methanol kept two days under an atmosphere saturated with methanol vapours; film	Urea crystallized from methanol kept two days under dry atmosphere; film
3456	3454	3450	3454
3350	3352	3348	3350
3265	3267	3270	3266
1687	1690	1688	1689
	1651 sh	1650 sh	
1627	1625	1628	1628
1600	1603	1600	1603
1465	1465	1468	1467
1155	1155	1156	1155
1055	1050	1050	1058
790	792	791	792
Fig. 1	Fig. 2	Fig. 3	Fig. 4

The definite presence of the band 1650 cm.$^{-1}$ in Figs. 2 and 4 and the frequency close to that of compounds with the C=N bond, undistorted by resonance structures, such as Schiff's bases, seems to suggest that the shifting to the resonance structures might go so far as to reach the imidolic form (*F*).

This might be expressed diagrammatically:

(3)



The presence of the form (*F*) would account both for intensity and frequency of the 1650 cm.$^{-1}$ band.

This would be, at the same time, a novel kind of tautomery which could be thus presented in general terms

(4) $$[X \leftrightarrow Y] \rightleftarrows Z .$$

Here, X and Y are mesomeric structures of a compound which under certain circumstances (such as, e.g., action of a solvent) can furnish a tautomeric form Z.

It is also possible to extend the diagram of resonance combined with tautomery, by accepting resonance structures of both tautomeric forms, e.g.:

(5) $$[X—Y] \rightleftarrows [Z \leftrightarrow V] .$$

With regard to our studied case, there is no evidence that any resonance structures should be assigned to iso-urea (F), and, therefore, Eq. (5) does not seem to be applicable.

The form (F) in freshly crystallized urea should involve the presence of an OH band in the spectrum. However, taking into consideration that urea was examined in the solid state, strong hydrogen bonds may shift the frequency of the OH band and reduce its intensity. The concentration of the tautomeric form (F) is probably low. Therefore, both hydrogen bonds and low concentration may lead to undetectability of the OH band. It may, besides, be obscured by the presence of NH stretching modes in the 3500—3200 cm.$^{-1}$ region.

The same was recently pointed out by Kutzelnigg and Mecke [9].

NH_2 rocking vibrations. According to all earlier authors, the NH_2 rocking vibrations are seen in the region 1160—1150 cm.$^{-1}$. In our experiments they have the frequency 1155 cm.$^{-1}$.

NH_2 wagging (or rocking) vibrations. Earlier authors assigned the band 1060—1050 cm.$^{-1}$ to the NH_2 wagging vibrations [3], [5], although some of them [4] suggested that it is produced by NH_2 rocking vibrations. In our spectra it has the frequency 1055 cm.$^{-1}$.

Frequency 790 cm.$^{-1}$. This frequency was assigned by Becher [3] to C=O wagging vibrations. Barlow and Corish [6] assigned it to mutual NH_2 and CO out-of-plane wagging vibrations. We found [1] the same frequency in the spectra of O-alkyl derivatives of iso-urea which do not contain the C=O group. It is more likely that the frequency is due to NH_2 wagging or rocking vibrations only.

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