Short communications

STUDIES ON THE STRUCTURE OF THE UREA-ORTHOBORIC ACID COMPLEX

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Thermal and infrared spectral studies of the urea-orthoboric acid complex are reported. The complex is formed through the elimination of 0.5 H_2O molecule. Infrared spectral data show the presence of hydrogen-bonding and the force constant calculated for the N . . . HO bond is found to be $4-5 \times 10^{-5}$ dyne cm^{-1}, which is for the order of a single bond and indicates strong hydrogen-bonding in the complex. A tentative structure for the complex is proposed.

Studies of the solid-state interaction between urea and orthoboric acid have already been reported [1, 2]. Differential scanning calorimetric (DSC) and gas evolution analysis (EGA) studies showed that a definite compound is formed between urea and orthoboric acid in 2 : 1 molar proportion, through the elimination of water at 70°, the heat of reaction being $-$ 221.85 joule g^{-1}. However, no quantitative estimation has yet been carried out to account for the amount of water loss and to study the structure of the complex so formed.

In the present communication an attempt has therefore, been made to elucidate the structure and the nature of the bonding in the solid complex, using TG, DTG and infrared spectral studies.

Experimental

The TG and DTG of the samples were carried out in a manually-operated thermobalance fabricated in this laboratory. About 0.5 g of sample (2 : 1 molar mixture of urea: orthoboric acid) was placed in the platinum container of the balance and heated at a rate of 10°/min from 25 to 100°. The DTG curve was plotted by measuring the weight loss between two successive temperatures against temperature, i.e. dw/dt against t. The infrared spectrum of the complex was recorded on a Beckman IR instrument in the range 600 – 4000 cm^{-1}. The i.r. spectral data on orthoboric acid were taken from standard data [3].

Results and discussion

TG curves of pure urea and pure orthoboric acid (Fig. 1) were featureless in the experimental temperature range, whereas the DTG and TG curves of their 2 : 1 molar mixture showed a sharp change at 70°, which was also observed in the DSC and evolved gas analysis studies [1, 2]. It was noticed there that some reaction oc-

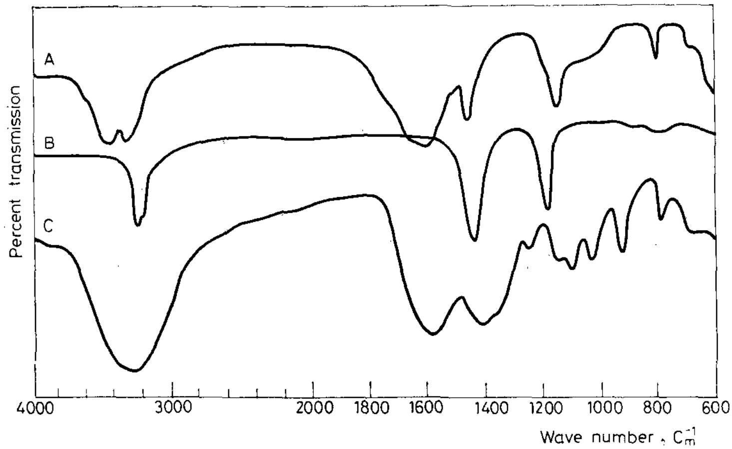


Fig. 1. TG curves of (A) orthoboric acid, (B) urea and (C) complex and DTG of (c) complex

Table 1

Energy data for urea-orthoboric acid complex

Sample designation	Conversion, %	Observed* energy, joule/g	Calculated energy, joule/g
C	16.9	− 37.67	− 33.28
D	29.2	− 64.88	− 66.55
E	58.6	−130.18	−133.12
F	72.4	−160.74	−164.93
G	100.0	−221.85	−221.85
H	74.7	−165.76	−166.60
I	28.6	− 63.62	− 66.56
J	15.7	− 32.87	− 33.27
K	6.6	− 14.65	− 16.66

% conversion, observed and calculated energy data are taken from earlier work [1].
* Calculation work performed by using the equation:

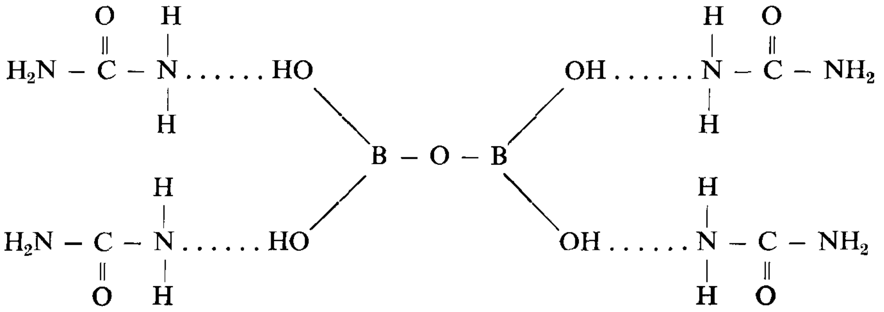
$$H_m \equiv \frac{H_{(T)} X S_{(m)} X W_{(T)}}{S_{(T)} X W_{(m)}}, \text{ employed}$$

for DSC techniques, where $H_{(T)}$ = heat of fusion of tin, $S_{(m)}$ = area of the transition peak of the mixture, $S_{(t)}$ = area of transition peak of tin, $W_{(T)}$ ≡ weight of tin, and $W_{(m)}$ = weight of the mixture.

curred at 70° with evolution of water, and the energy of formation of the complex was -221.85 joule g^{-1} where 100% conversion took place.

In the present investigation the TG curve of the complex shows a weight loss of 4.93%. This corresponds to a loss of 1/2 molecule of water during complexation. Evidently, the "complex molecular unit" so formed is the reaction product of 4 molecules of urea with 2 molecules of orthoboric acid with elimination of 1 molecule of water.

Keeping in view the earlier calorimetric studies and combining these with the present results of TG and DTG, the structure of the compound may tentatively be proposed as follows:



The above structure of the complex was supported by infrared spectral studies.

The i.r. spectra of urea, orthoboric acid and the complex are shown in Fig. 2 and the tentative assignments of the relevant peaks are given in Table 2. The i.r. spectrum of the solid complex is totally different from those of the individual re-

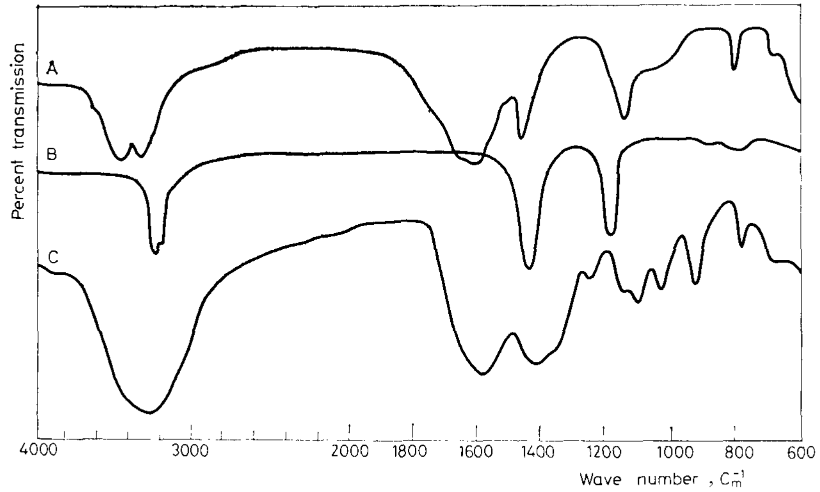


Fig. 2. Infrared spectra of (A) urea, (B) orthoboric acid and (C) 2 : 1 urea : orthoboric acid complex

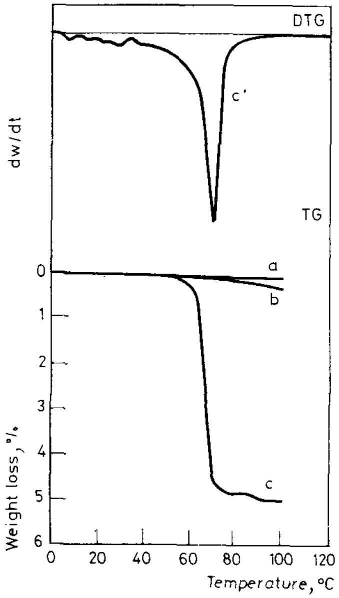


Fig. 3

Table 2

Infrared absorption bands of urea, orthoboric acid complex and their tentative assignments (cm^{-1})

Urea	Assignements	Orthoboric acid	Assignments	2 : 1 Complex	Assignments
3435 bs	νNH				
3340 bs	νNH	3270 bs	νOH	3280 bs	Hydrogen bond (N–H–O)
1670 ms	νC=O and NH$_2$ bending			1600 bs	νC=O and NH$_2$ bending
1620 bs	NH$_2$ bending + νC=O				
1465 s	νC–N	1450 bs 1195 s	νB–O δOH	1395 bs 1250 w 1150 vw	νC–N + νB–O
1150 s	NH$_2$ rocking			1100 m	δ(OH) + NH$_2$ rocking
		885 w	νB–O	1025 m	
				920 ms	
		824 bs	γB–O	785 s	
790 s		648 bs	γOH	690 m	

s = strong, bs = broad strong, m = medium, ms-medium strong, w = weak, vw = very weak.

actants. Such behaviour indicates some interaction between urea and orthoboric acid. The absorption bands observed in urea and orthoboric acid were found to be shifted towards lower wavenumbers in the complex. The i.r. spectrum of the complex has been analyzed in the following manner.

(i) The νOH band of orthoboric acid at 3270 cm^{-7} [3] and the νNH bands of urea at 3435 and 3340 cm^{-1} were combined to give rise to a broad absorption band at 3280 cm^{-1} in the complex. The broad nature of the band in the complex indicates the presence of hydrogen-bonding [4] between an NH_2 group of the urea and an OH group of the orthoboric acid.

(ii) Urea showed two intense absorption bands due to $\nu C{=}O$ and NH_2 bending vibrations, at 1670 cm^{-1} and 1620 cm^{-1}; after formation of the complex with orthoboric acid, these shifted towards lower wavenumber, at 1600 cm^{-1}. It was difficult to analyse the C=O and NH_2 bands, as these were broad.

(iii) The $\nu C-N$ stretching frequency at 1465 cm^{-1} in urea and $\nu B-O$ at 1450 cm^{-1} in orthoboric acid were also affected in the complex spectrum. Two bands of a split nature were found for the complex, in the region 1360–1425 cm^{-1}, due to the $\nu C-N$ and $\nu B-O$ stretching vibrations.

(iv) The νOH and νOH bands of orthoboric acid at 3270 cm^{-1} and 1195 cm^{-1} were found not to be present in the spectrum of the complex. Some additional bands were found at 1100 cm^{-1}, 1025 cm^{-1} and 920 cm^{-1} in the spectrum of the complex, which were probably bands due to urea and orthoboric acid interaction.

(v) The $\nu B-O$ and $\nu B-O$ at 885 cm^{-1} and 824 cm^{-1} in orthoboric acid were found to be shifted after reaction with urea. The complex spectrum showed a band at 785 cm^{-1}, which was most likely shifted $\nu B-O$ of orthoboric acid [5].

The sharp nature of the bands in the spectra of urea and orthoboric acid were found to disappear, to shift from their original positions or to merge to give rise to broad intense bands of a composite nature, which indicated intramolecular hydrogen-bonding in the complex. The value of the force constant (K) calculated [6] for the N . . . HO bond was found to be $4\text{-}5 \times 10^{-5}$ dyne cm^{-1}, which was of the order of a single bond. It is reported [7] that such OH . . . N bonds are stronger than OH . . . O bonds, and thus strong hydrogen-bonding is expected in the complex. This is in good agreement with the formation energy of the complex, 221.85 joule g^{-1}.

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