INFRARED SPECTROSCOPIC STUDIES OF HYDROGEN BONDING IN AMIDE-AMIDE COMPLEXES

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INTRODUCTION

SPECTROSCOPIC studies of hydrogen bonding in terms of frequency changes and variations in the integrated intensity of the absorption bands arising out of stretching and bending modes of vibration give information regarding the nature of the acceptor and donor groups responsible for such bonding. Barrow[1], Tsubomura[2], Huggins and Pimental[3] studied the spectral changes of the O–H stretching absorption band with various donor groups and concluded that these changes are a more reliable indication of the acid-base interactions than can be predicted from the presumed acid strengths. Kartha et al.[4] and Venkata Ramiah et al.[5] studied hydrogen bonds of the type O–H....S, O–H....O=C and S–H....O=C and calculated equilibrium constants. We report in this paper the spectral changes of the free N–H stretching absorption band of N-methylacetamide in the presence of N, N dimethylformamide and N, N dimethylacetamide in order to investigate the strength of the hydrogen bonding in these complexes.

EXPERIMENTAL AND RESULTS

The infrared spectra of the N–H stretching absorption band of N-methylacetamide in solution of carbon tetrachloride and in the presence of dimethylformamide and dimethylacetamide were recorded with Perkin Elmer Model 221 infrared spectrophotometer using NaCl optics and matched quartz cells of 3 cm thickness. The functional groups responsible for hydrogen bonding in N-methylacetamide are the N–H and the C=O linkages. It is well known that N-methylacetamide has a structure with 'O' and 'H' atoms in *trans*-position with respect to the C–N bond[6] with the result that these molecules form an open chain as a result of hydrogen bonding. In solution of CCl_4, these intermolecular associations break down progressively so that in dilute solutions of the order of 0·0008 to 0·0018 molar, only the free N–H stretching band at 3464 cm⁻¹ could be recorded and the bonded N–H stretching band which is in the region of 3340 cm⁻¹ completely disappeared indicating thereby that the intermolecular associations have been eliminated. Thus the effect of dimethylformamide or dimethylacetamide on the

free N–H stretching absorption band has been studied.

The spectra of the N–H stretching band of N-methylacetamide were recorded with various concentrations of the amide in CCl_4 in the sample beam with the CCl_4 in the reference beam. The peak absorbance of the N–H stretching band of N-methylacetamide was plotted against molar concentration of the amide. The analytical curve thus obtained was linear as shown in Fig. 1.
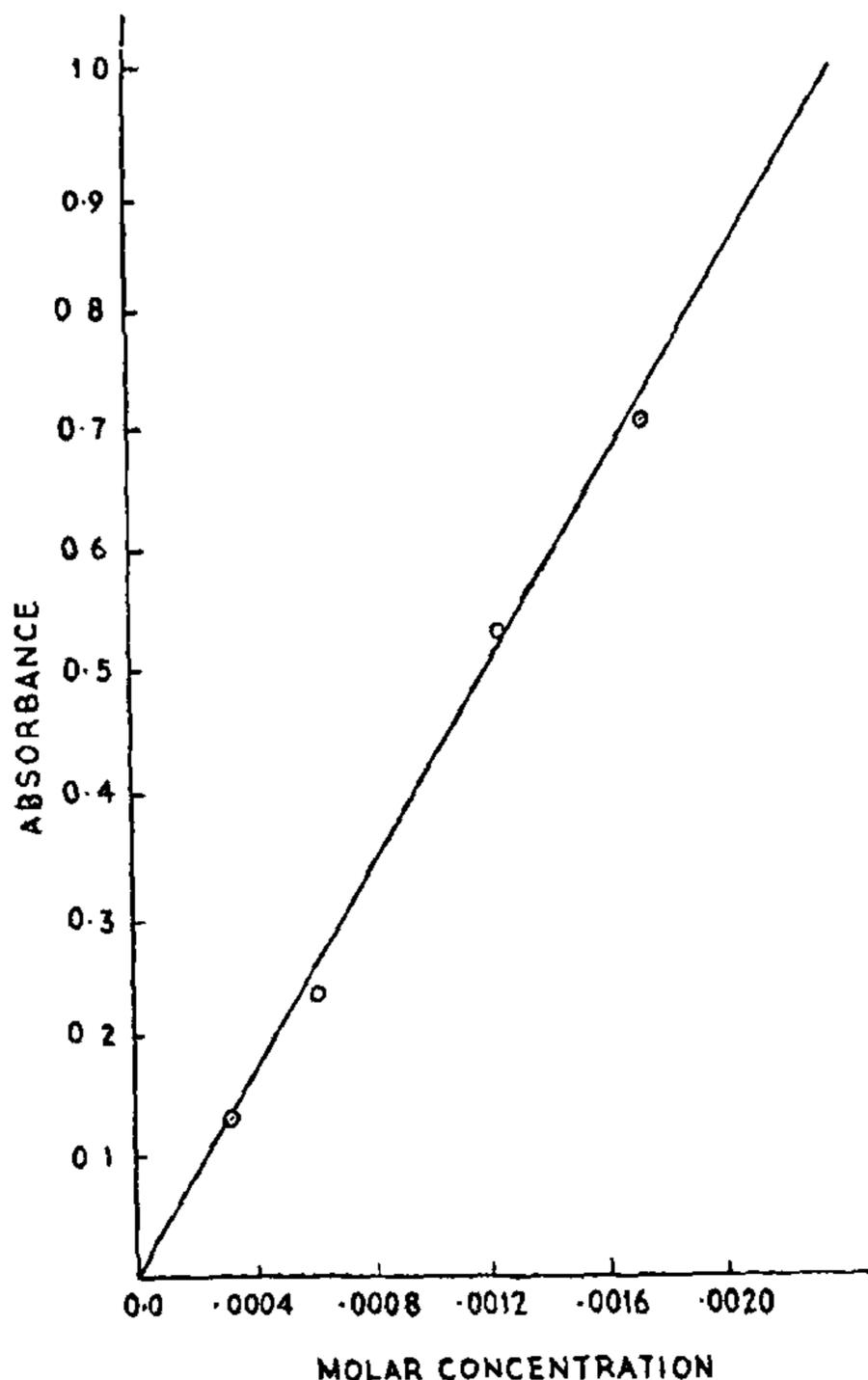

FIG. 1. Plot of absorbance *versus* molar concentration of the free N–H stretching band of N-methylacetamide in solution of carbon tetrachloride.

The spectra of the free and bonded N–H stretching bands were then recorded with N-methylacetamide

in CCl_4 in the presence of dimethylformamide or dimethylacetamide in the sample beem and a solution of the tertiary amide of the same concentration

The concentrations of NMA, DMF and DMA and the frequencies of free and bonded N–H stretching bands are given in Tables I and II.

TABLE I

The N–H stretching frequencies and equilibrium constants in N-methylacetamide-dimethylformamide complexes

Molar concentration DMF	Molar concentration NMA	Frequency of N–H stretching band		Frequency difference	Absorbance of the free N–H stretching band in the presence of DMF	Equilibrium constant k	Average value of k
		free band in CCl_4	bonded band				
·0125	·001	3,464	3,364	100	0·39	6·9	
.0125	·00150	3,464	3,364	100	0·57	6·9	6·9
0·0250	·001	3,464	3,364	100	0·34	9·9	
0·0250	·00150	3,464	3,364	100	0·49	12·0	11·0

in CCl_4 in the reference beam. Keeping the concentration of DMF or DMA constant, the concentration of NMA was varied and the free and bonded N–H stretching bands were recorded. The same spectra were recorded with different concentration of DMF and DMA. The spectra are given in Fig. 2.
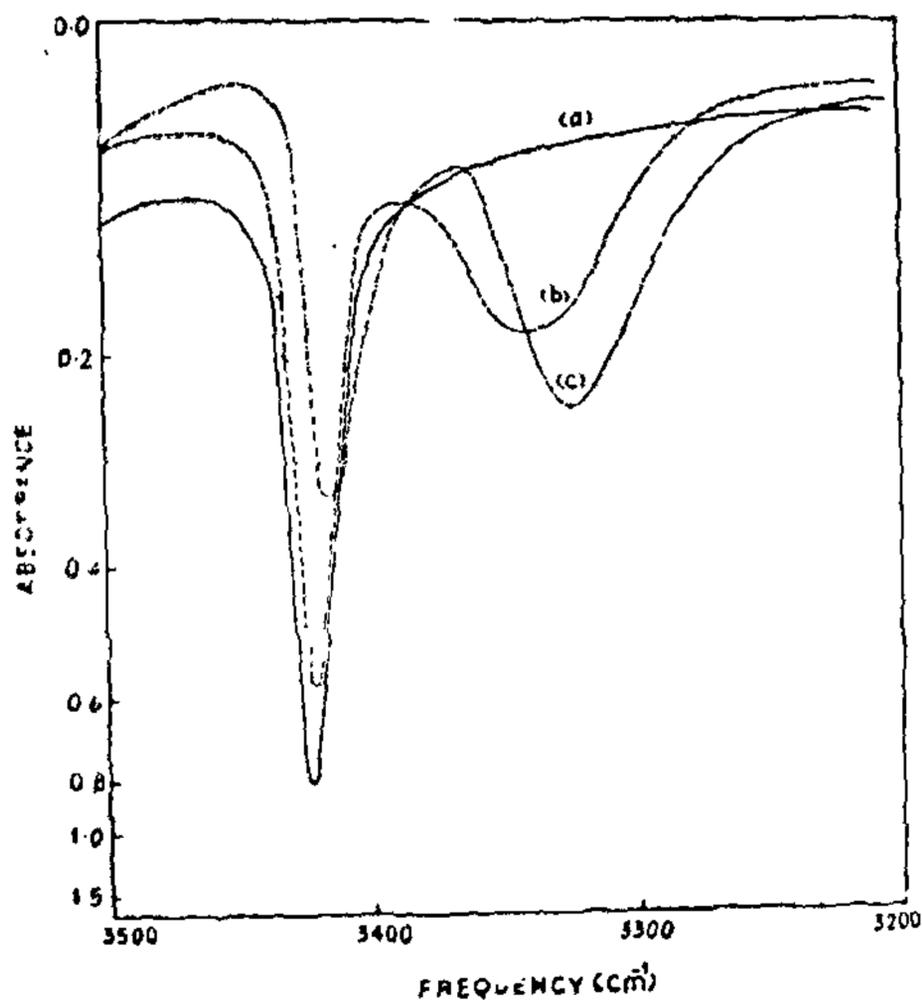

FIG. 2. (a) Free N–H stretching band of NMA in CCl_4 (0·00175 molar); (b) Free and bonded N–H stretching bands of NMA in solution of CCl_4 in the presence of dimethylformamide. (0·025 molar) and (c) Free and bonded N–H stretching bands of NMA in solution of CCl_4 in the presence of dimethylacetamide (0·025 molar).

In case of these amide-amide complexes, the hydrogen bonding was assumed on the basis of 1 : 1 complex and the equilibrium constants were calculated using the expression[5]

$$K_t = \frac{\left[M_N - \dfrac{a-c}{m}\right]}{\left[M_D - M_N + \dfrac{a-c}{m}\right]\dfrac{a-c}{m}} \qquad (1)$$

where M_N and M_D are the molar concentrations of N-methylacetamide and dimethylformamide or dimethylacetamide respectively and 'a' is the absorbance of the free N–H stretching band in the presence of dimethylformamide or dimethylacetamide. 'm' and 'c' which are the slope and intercept of the analytical curve are determined and used for computing the equilibrium constants. In this case, the value of the intercept is zero. These values are also given in Tables I and II. The frequency differences of free and bonded N–H stretching absorption bands in N-methylacetamide-dimethylformamide and N-methylacetamide-dimethylacetamide complexes are 100 cm^{-1} and 124 cm^{-1} respectively indicating the manifestation of strong hydrogen bonding.

DISCUSSION

In amides, two possible resonance structures contribute to the resonance hybrid and the contribution of the dipolar resonance structure makes substantial contribution to the ground state of the molecule enhancing the polarity of the $C=O$ group. The interaction of the π-orbitals of the $C=O$ group and the $2p_\pi$ orbitals of the N-atom in the $O=C–N$ group of the amide has been discussed by Cannon[7,8]

TABLE II

The N–H stretching frequencies and equilibrium constants in N-methylacetamide-dimethylacetamide complexes

Molar concentration DMA	Molar concentration NMA	Frequency of N–H stretching band		Frequency difference	Absorbance of the free N–H stretching band in the presence of DMA	Equilibrium constant k	Average value of k
		free band in CCl$_4$	bonded band				
0·0127	·0008	3,464	3,340	124	0·250	32	
0·0127	·00125	3,464	3,340	124	0 39	30	32·3
0 0127	·001845	3,464	3,340	124	0·546	35	
0·02539	·0008	3,364	3,340	124	0·127	66	
0·02539	·00125	3,464	3,340	124	0·208	64	66
0·02539	·001845	3,464	3,340	124	0·276	68	

and the high polarity of the C=O group has been attributed to the π-p orbital mixing. This explains[1] the formation of strong hydrogen bonding with the C=O group of dimethylformamide and dimethylacetamide. The hydrogen bond is stronger in case of dimethylacetamide due to hyperconjugation as a result of the contribution of the structure

$$H^{+}H_3C=\overset{\overset{\displaystyle O^{-}}{\displaystyle /}}{C}-NR_2.$$ The infrared spectrum of N-methylacetamide in solution of CCl$_4$ of moderate concentration has two absorption bands at 3330 cm^{-1} and 3470 cm^{-1} and these are assigned to the bonded and free N–H stretching absorptions. It is significant to note that this frequency difference is nearly the same as that of the bands arising out of the same modes in N-methylacetamide-dimethylacetamide complex.

The equilibrium constants calculated for various concentrations of N-methylacetamide with the same concentration of dimethylformamide or dimethylacetamide are found to be constant, but when the concentration of dimethylformamide or dimethylacetamide was varied, the values of the equilibrium constants also change. For the same concentration

of dimethylformamide or dimethylacetamide, the value of the equilibrium constant in N-methylacetamide-dimethylacetamide complex is much higher than that in N-methylacetamide-dimethylformamide complex.

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