

ON C-N, C=O AND C=S BONDS IN AMIDES AND THIOAMIDES

K. VENKATA RAMIAH

Department of Physics, Osmania University Post-Graduate Centre, Warangal-1 (A.P.)

AND

V. VENKATA CHALAPATHI

Department of Physics, Sri Venkateswara University Post-Graduate Centre, Ananthapur (A.P.)

IN amide molecules, no single valence bond structure is consistent with all their properties. Two possible structures contribute to the resonance hybrid with the dipolar resonance structure making substantial contribution to the ground state of these molecules giving partial single and double characters to the C=O and the C-N bonds. The bond lengths of the C=O and the C-N bonds of several amides have been determined by X-ray diffraction and microwave spectroscopic methods.¹⁻⁵ Using this bond length data, Morris and Orville-Thomas⁶ have calculated the bond orders of the C=O and the C-N bonds of the amides taking into consideration (i) the presence of delocalised π -bonding, and (ii) the ionic character of the bond. The values of the bond lengths and the bond orders of the C=O and C-N bonds thus obtained are given in Table I.

TABLE I

Amide	Bond length in Å		Bond order	
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \\ \text{N} \end{array}$	$\begin{array}{c} \text{N} \\ \\ \text{C} \\ \diagup \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \\ \text{N} \end{array}$	$\begin{array}{c} \text{N} \\ \\ \text{C} \\ \diagup \\ \text{O} \end{array}$
Formamide (solid)	1.255	1.30	1.61	1.71
Formamide (vapour)	1.193	1.376	1.69	1.63
Oxamide (solid) ..	1.25	1.31	1.63	1.69
Succinamide (solid)	1.243	1.315	1.64	1.68

Suzuki^{7,8} and Venkata Chalapathi and Venkata Ramiah⁹ have carried out the normal co-ordinate treatment of primary, secondary and tertiary amides. The force constants proposed by these workers for the C=O and C-N stretching vibrations are of the order of 8.8 to 9.0 md/Å and 6.15 to 6.8 md/Å respectively. It is thus obvious that the bond lengths, bond order, and the stretching force constants of the C=O and C-N bonds in amides have intermediate values of those of the idealised C=O and C-N bonds.

Venkata Chalapathi and Venkata Ramiah¹⁰ measured the integrated intensities of the carbonyl band in a number of amides and Barrow¹¹ measured the intensities of the same band in

aldehydes, ketones, and esters. These values are given in Table II.

TABLE II

Compound	Carbonyl band	
	Frequency (in cm^{-1})	Intensity ($\text{moles}^{-1} \text{ litre-cm}^{-2} \times 10^4$) in solution of CCl_4
N-methylacetamide ..	1691	3.5
Dimethylacetamide ..	1657	5.2
N-methylpropionamide ..	1688	3.6
Dimethylpropionamide ..	1667	4.4
Propionaldehyde ..	1738	1.55
Benzaldehyde ..	1710	2.10
Acetone ..	1709	1.55
Acetophenone ..	1692	2.1
Methylacetate ..	1751	2.2

The observations in Table II indicate that the integrated intensities of the carbonyl band in amides are much higher than those of the same band in aldehydes, ketones and esters. The intensities of the N-H stretching absorption bands of N-methylamides and N-methylthioamides as measured by Usha Bai and Venkata Ramiah¹² are given in Table III.

TABLE III

Amide	N-H stretching absorption band	
	Frequency (in cm^{-1})	Intensity ($\text{moles}^{-1} \text{ litre-cm}^{-2} \times 10^4$) in solution of CCl_4
N-methylacetamide ..	3470	0.52
N-methylpropionamide ..	3467	0.55
N-methylthioacetamide ..	3408	0.73
N-methylthiopropionamide ..	3407	0.73

The intensities of the N-H stretching absorption bands of the amides given in Table III are much higher than the intensity values of the same bands in amines¹³ which are of the order of 0.20 to 0.28 intensity units.

Apart from the description of the amides as the resonance hybrids between $\text{O}=\text{C}-\text{N}$ and $\text{O}^--\text{C}=\text{N}^+$ groups, Cannon^{14,15} discussed this problem in terms of interaction and mixing of the π -orbitals of the C=O group and 2p orbitals of the nitrogen atom in the SP^2 hybrid

configuration. Cannon explains that this π -P orbital mixing lengthens the bond length of the C=O bond and shortens that of the C-N bond relative to the valence bond structure and is responsible for the high polarity of the C=O group. The above experimental results can thus be accounted for on the basis of the assumption of electron delocalisation in amides. This imparts considerable double bond character to the C-N bond resulting in a restricted internal rotation about the same bond. A consequence of this fact is that the proton resonance signals of the methyl groups of the tertiary amides occur at different fields at room temperature. A vibrational frequency, recorded in the region of 350 cm^{-1} in the Raman spectra of tertiary amides, is in fact assigned to the torsional mode of the C-N bond.⁹

Examples of rotation about partial double bonds are provided by amides and a number of papers describing the application of NMR methods for the measurement of rotational barriers of tertiary amides have appeared in recent years. The experimental activation energy E_a identified with the barrier height restricting internal rotation about the central C-N bond of the amides, is obtained from the measurements of the rate of internal rotation $1/2\tau$ at a series of temperatures and fitting the data to the Arrhenius equation. The barrier heights, obtained by Rogers,¹⁶ Loewenstein *et al.*¹⁷ and Newman *et al.*¹⁸ for a number of dimethylamides and dimethylthioamides are given in Table IV.

TABLE IV

Amide	Solvent	Activation energy E_a in Kcal/mole
NNDMF	.. Pure	18.3 ± 0.7
NNDMTF	.. "	27.9 ± 1.1
NNDMF	.. Formamide	26.3 ± 2.6
NNDMA	.. "	24.7 ± 0.8
NNDMTA	.. "	43.7 ± 5.6

The internal rotation of NNDMF has been reinvestigated by the NMR total line shape (TLS) treatment in recent years¹⁹ taking into account both the variance of non-exchanging N-methyl doublet chemical shift and the coupling between the formyl and N-methyl protons. The activation energy E_a obtained in these studies in 20.5 ± 0.2 Kcal/mole which is in broad agreement with that obtained by Rogers.

Loewenstein *et al.*¹⁶ obtained the activation energy in case of dimethylthioformamide by measuring the intensity ratio of the peaks since

the coalescence temperature in case of this amide is very high. In case of dimethylacetamide and dimethylthioacetamide, Newman *et al.* used formamide as a solvent because of its non-interfering protons and the fact that it would dissolve the thioamides easily. From the observations in Table IV, it is obvious that the height of the barrier in thioamides is much higher than that in the case of the corresponding amides. The higher values for the rotational barriers of the tertiary amides with formamide as a solvent are due to the solvent interaction which is the hydrogen-bonding of the type C=O...H-N or C=S...H-N.

An almost similar result is obtained from the studies of infrared spectra of the amides in pure and vapour states. In vapour state, the intermolecular associations in primary and secondary amides break down with the result that the double bond character of the C-N bond diminishes. Experimental evidence to this effect comes from the reduction in the value of C-N stretching frequency in vapour state^{20,21} as shown in Table V.

TABLE V

Amide	C-N stretching frequency of	
	Pure amide	Amide in vapour state
Formamide	.. 1309	1253
N-methylformamide	.. 1248	1201
N-methylacetamide	.. 1300	1257

This result is further substantiated by the fact that the bond length of the C-N bond increases and the bond order of the same bond diminishes from pure amide to vapour state as indicated by values in Table I.

The vibrational frequencies assigned by various workers to the C-N stretching vibration in primary, secondary and tertiary amides and thioamides^{7-9,22-24} on the basis of the normal co-ordinate analysis are given in Table VI.

TABLE VI

Amide	Mode	Frequency (in cm^{-1})
Formamide	.. ν (C-N)	1309
Thioformamide	.. ν (C-N)	1325 and 1443
N-methylformamide	.. Amide III	1248
N-methylthioformamide	.. Amide III	1297
Dimethylformamide	.. ν (C-N)	1502
Dimethylthioformamide	.. ν (C-N)	1540

On the basis of computations of potential energy distribution of each normal mode among various symmetry co-ordinates, the bands at 1443 cm^{-1} and 1325 cm^{-1} in thioformamide are

considered as due to the combined contribution of $\nu(\text{C-N})$ and $\delta(\text{C-H})$ vibrations. It is seen from Table VI that the C-N stretching frequencies in thioamides are higher than of those in the corresponding amides. In addition, the observations in Table III indicate that the intensities of the N-H stretching absorption bands of N-methylthioamides are much higher than those of the corresponding N-methylamides.

The experimental results of higher C-N stretching frequencies, higher values of the intensities of N-H stretching absorption bands and greater values for the rotational barriers in thioamides than in the corresponding amides thus lead to a basic and important conclusion that the double bond character of the C-N bond in thioamides is greater than that in the corresponding amides.

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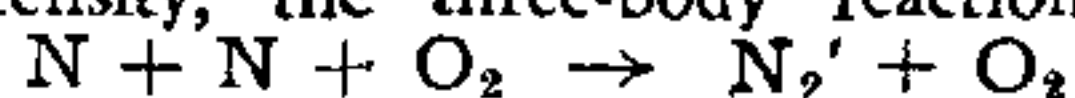
EFFECT OF O₂ ON N₂ AFTERGLOW

A. N. SRIVASTAVA, R. V. SHUKLA AND S. K. GUPTA

J.K. Institute of Applied Physics and Technology, University of Allahabad, Allahabad, India

ABSTRACT

Effect of molecular oxygen on the afterglow of nitrogen has been studied photometrically in a dynamical flow system at room temperature. Using large O₂ concentrations, it has been found that intensity of the afterglow decreases linearly with partial pressure of O₂. To account for the decrease in intensity, the three-body reaction



is proposed and its rate coefficient is estimated to be $3.22 \times 10^{-34} \text{ cm}^6 \text{ sec}^{-1}$.

1. INTRODUCTION

N₂ first positive bands were first detected in the afterglow of nitrogen by Fowler and Strutt.¹ Detailed studies of these bands, their excitation mechanism and the effect of various physical factors were carried out later on.²⁻⁵ Kistiakowsky and Volpi⁶ and Mavroyannis and Winckler⁷ observed that O₂ has practically no effect on N₂ first positive system at room temperature. At higher temperatures, O₂ molecules react with N atoms and consequently the intensity of these bands decreases with O₂ concentration. In these experiments, the concentration of O₂ molecules used was small. In order to find out whether molecular oxygen has at all any effect on N₂ first positive bands, large amount of O₂ gas was used in the present investigation.

2. PROCEDURE AND OBSERVATIONS

The experimental arrangement used was the same as in the earlier work.⁸ For the production of N₂ afterglow, N atoms were produced by dissociating molecular tank nitrogen by a Raytheon microtherm. Flow of O₂ and N₂ gases were varied by Hoke Needle valves. Pressure inside the reaction chamber was measured by a NRC thermocouple gauge. The experiment was performed at room temperature.

To obtain an intense afterglow, tank N₂ was introduced into the evacuated system through a needle valve. Before entering the reaction chamber, it was partly dissociated by the microtherm discharge. As the pressure of N₂ was gradually increased, the reaction chamber began to fill up with straw-yellow afterglow. At 0.315 torr, a workable intensity of the