A Visible and Ultraviolet Spectroscopic Study of the Charge Transfer Complexes Between N-Methyl Lactams and Iodine

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Thermodynamic and spectral data are reported for the addition compounds of iodine with N-methyl lactams, n (ring size) = 5, 6, and 7. The 6-membered ring is the strongest electron donor while the 5- and the 7-membered rings show very similar donor properties. The order of donor-acceptor interaction correlates with the relative magnitude of the blue shift in the visible iodine band and the decrease in the carbonyl stretching frequency on complex formation. A monotonic relationship does not exist between these parameters and the charge transfer energies.

N-Methyl lactams $\overline{(CH_2)_{n-2} - C(O) - N} - CH_3$ are known to form 1 : 1 complexes with phenol[1] and with iodine[2] in which the lone pair electrons on the carbonyl oxygen act as electron donors. The relative basic character toward phenol is 6- > 5- = 7-membered ring based on the equilibrium constants (K_c), while the enthalpies of formation $(-\Delta H°)$ showed a different order 7- > 5- > 6-membered ring.[1] Further information on the ring size effect seemed of interest and a comparison of the three iodine complexes is presented in this paper. The 5- and 6-membered ring lactams had been studied in complex formation with this acceptor,[2] however, the error limits in the $-\Delta H°$ values were rather large. Those results were obtained employing Drago's enthalpy method[3,4] to absorbance values at the blue shifted maximum. In the present work we used the same procedure but the absorbance values were taken at 555 nm which greatly reduced the error limits. The uncertainties in our enthalpy determinations are comparable with those reported by Drago for amide-iodine systems[4] and are estimated as less than ± 0.15 kcal/mol.

EXPERIMENTAL

N-Methyl-γ-butyrolactam and N-methyl-δ-valerolactam both from Aldrich Chemical Co. were dried with silica and purified by repeated vacuum distillations. The constant boiling middle fraction was collected. Refractive indices for these compounds were $n_D{}^{20} = 1.4705$ and 1.4825, respectively. Reported values are $n_D{}^{25} = 1.4666$ and 1.469[1] for the former and $n_D{}^{20} = 1.4818$[5] for the latter compound. N-Methyl-ε-caprolactam was

prepared according to Ruzicka and Hugoson,[6] $n_D^{20} = 1.4835$. Reported values of n_D^{25} were 1.4812 to 1.4833.[1] The lactams were stored in a desiccator over phosphorus pentoxide. Resublimed iodine from Merck was used without purification. Heptane, dichloromethane, and carbon tetrachloride (all Merck *Uvasol* grade) were dried carefully.

Stock solutions of donor and iodine in heptane were made up by weighing into 100 ml volumetric flasks and the mixed solutions were prepared by pipetting aliquot parts into 25 ml flasks. Triiodide ion was apparent in the mixed solutions after 24 h at room temperature. At 40°C the reaction took place more rapidly; however the absorption changes at 555 nm were small.

Instrumental. Absorbance readings employed in the calculation were obtained with a manual Zeiss PMQ II ultraviolet-visible spectrometer equipped with a thermostated cell holder. The cell compartment had been rebuilt for temperature measurements with a thermistor probe.[7] Visible and ultraviolet curves were recorded with a Beckman DK-1 spectrophotometer also equipped with a thermostated cell holder. The ultraviolet spectra of the pure donor molecules were obtained with a Cary model 14 and the infrared spectra with a Perkin-Elmer model 225 recording spectrophotometer.

1 cm matched quartz cells were used for all the measurements in the ultraviolet and visible regions. The infrared cells were of the conventional type with NaCl windows.

TREATMENT OF DATA

The K_c value at 25°C and the absorption coefficient $\varepsilon_c - \varepsilon_I$ (ε_c and ε_I are the molar absorptivities for the complex and free iodine, respectively) were calculated from the general Lang equation.[8] The procedure had been programmed for the CD-3300 computer.[9] Nine to twelve solutions were employed in these calculations and the results showed good agreement with those obtained by the graphical method.[10] The concentration ranges of the lactams and iodine were, respectively, (M) $(0.9-9.5) \times 10^{-2}$ and $(0.9-1.9) \times 10^{-3}$ for the $n=5$, $(1.0-5.3) \times 10^{-2}$ and $(0.8-2.0) \times 10^{-3}$ for the $n=6$, and $(1.1-6.9) \times 10^{-2}$ and $(1.1-1.5) \times 10^{-3}$ for the $n=7$ lactam. The calculated value for $\varepsilon_c - \varepsilon_I$ at 25°C was employed to determine K_c by means of the equation:[3]

$$K_c^{-1} = \frac{A - A_0}{\varepsilon_c - \varepsilon_I} - (C_I + C_D) + \frac{C_I C_D (\varepsilon_c - \varepsilon_I)}{A - A_0}$$

where $(A - A_0)$ is the measured absorbance, and C_I and C_D represent initial concentrations of iodine and lactam. $(A - A_0)$ was measured directly by placing a solution of iodine and lactam in the sample cell and a solution of iodine of the same initial concentration in the reference cell. K_c values were calculated at eight temperatures in the range $9-38$°C for each of the twelve solutions assuming temperature invariance in $(\varepsilon_c - \varepsilon_I)$. A least squares treatment of the temperature variation in K_c gave the corresponding $-\Delta H°$ value for each solution. The average of these values are listed in Table 1 with error limits calculated for 95 % confidence level.

The blue shifted iodine band. An isosbestic point near 490 nm appeared in each of the two lactam-iodine systems in the previous study.[2] We also observed an isosbestic point for the $n=7$ lactam, indicating the presence of only one complex, probably of 1 : 1 stoichiometry. In order to compare the interaction in the three lactams we also re-examined the blue shifted iodine band in the two former complexes. The data are listed in Table 2.

The charge transfer (CT) band. Overlap with the strong lactam absorption obscured the low wavelength side of the CT band in heptane. A somewhat

better separation of the two bands occurred in dichloromethane due to the red shift of the CT band in this solvent. However, the formation of triiodide ion prevented the observations in the case of the $n = 6$ lactam. The empirical relationship suggested by Briegleb [11] was employed in the determination of the half intensity width. The data are listed in Table 3.

RESULTS AND DISCUSSION

The higher precision in our measurements as compared to the reported data seems to arise from our choice of wavelength. A prerequisite for this method is the temperature invariance of $\varepsilon_c - \varepsilon_I$ which would hardly be fulfilled at the blue shifted maximum. An examination of a heptane solution of iodine alone showed a negligible temperature variation in ε_I at 555 nm and the resolution of the complex curve revealed a low ε_c value at this wavelength, indicating a small change in $\varepsilon_c - \varepsilon_I$ with temperature.

It appears from the data in Table 1 that the larger interaction takes place between iodine and the 6-membered ring, while the two other lactams show

Table 1. Thermodynamic parameters of *N*-methyl lactam-iodine complexes in heptane.

Lactam	K_c^{25} (M^{-1})	$-\Delta G^\circ_{25}$ (kcal/mol)	$-\Delta H^\circ$ (kcal/mol)	$-\Delta S^\circ$ (e.u.)
$n = 5$	21.1 ± 0.3^a $(18.7 \pm 0.4)^c$	1.80 ± 0.01^b $(1.74 \pm 0.04)^c$	5.52 ± 0.10^b $(5.6 \pm 0.3)^c$	12.5 ± 0.3^b
$n = 6$	29.7 ± 0.4^a $(31.1 \pm 1.2)^c$	2.01 ± 0.01^b $(2.01 \pm 0.04)^c$	5.75 ± 0.05^b $(6.0 \pm 0.3)^c$	12.5 ± 0.2^b
$n = 7$	22.4 ± 0.3^a	1.83 ± 0.01^b	5.52 ± 0.07^b	12.4 ± 0.2^b

[a] Present work, uncertainties as standard deviations. [b] Present work, uncertainties as error limits at 95 % confidence level. [c] Reported data, 90 % confidence level.

Table 2. Spectral characteristics for the BS band of *N*-methyl lactam-iodine complexes in heptane.

Lactam	λ_{max}^a (nm)	$\Delta\lambda_{max}^b$ (nm)	λ_{IBP}^c (nm)	ε_{max} (M^{-1}cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	f (M^{-1}cm^{-2})	D (debye)
$n = 5$	450	71	490.5	1190	3800	0.020	1.37
$n = 6$	443	78	490	1310	4240	0.024	1.50
$n = 7$	451	70	491.5	1200	3790	0.020	1.38

[a] Obtained after resolution of the complex curve. The concentration of uncomplexed iodine was calculated from K_c^{20}. [b] Blue shift. [c] Isosbestic point.

Table 3. Spectral characteristics of the CT band of N-methyl lactam-iodine complexes in heptane.

Lactam	λ_{max} (nm)	ε_{max} (M^{-1}cm^{-1})	$\Delta\nu_{\frac{1}{2}}$ (cm^{-1})	f (M^{-1}cm^{-2})	D (debye)
$n = 5$	247(253)[a]	16100	7100	0.50	5.10
$n = 6$	250 —	14500	7500	0.47	5.00
$n = 7$	253.5(261)[a]	13000	9000	0.50	5.21

[a] Dichloromethane.

Table 4. The ultraviolet absorption and the carbonyl stretching frequency of the N-methyl lactams.

Lactam	$\lambda_{max}{}^{a}$ (nm)	$\nu_{C=O}{}^{b}$ (cm^{-1})	$\Delta\nu_{C=O}{}^{b,d}$ (cm^{-1})
$n = 5$	< 195	1699	41
$n = 6$	198	1652[c]	44
$n = 7$	199	1653	40

[a] $\pi \rightarrow \pi^*$ in hexane. [b] Carbon tetrachloride. [c] 1667 cm^{-1}, reported in Ref. 2. [d] Frequency decrease on complex formation with iodine.

Table 5. Thermodynamic data for 1 : 1 adduct formation between phenol and N-methyl lactams in carbon tetrachloride.[a] Errors given in standard deviations.

Lactam	$K_c{}^{25}$ (M^{-1})	$-\Delta G_{25}{}^{\circ}$ (kcal/mol)	$-\Delta H^{\circ}$ (kcal/mol)	$-\Delta S^{\circ}$ (e.u.)
$n = 5$	150 ± 3	2.95 ± 0.15	5.95 ± 0.15	10.04 ± 0.49
$n = 6$	186 ± 3	3.11 ± 0.12	5.62 ± 0.12	8.42 ± 0.40
$n = 7$	149 ± 3	2.98 ± 0.11	6.41 ± 0.11	11.52 ± 0.38

[a] Ref. 1.

nearly similar electron donor properties. The order of electron donor ability is not consistent with the variation in the CT maxima listed in Table 3, however, the relative magnitude of the shifts in the visible iodine maximum and in the carbonyl stretching frequency (Tables 2 and 4) conform with the thermodynamic data. Also the K_c values for the complexes with phenol showed the same order, but this acceptor seemed to form the strongest bond with the

7-membered ring (Table 5). The higher flexibility and greater capacity for adjustment to the steric and spacial restrictions in the complex have been proposed as an explanation.[1] With iodine as acceptor the flexibility of the ring seems less important. This effect would be more pronounced for the larger acceptor molecule.

A correlation between the carbonyl stretching frequency and the hydrogen bonding ability was found for the cyclic ($n = 4$ to 7) ketones [12] and the ($n = 4$ to 6) lactones,[13] which also co-ordinate *via* the carbonyl oxygen. The observed lowering in the carbonyl frequency with increasing ring size was accompanied by an increase in the enthalpy for the hydrogen bond formation, presumably due to loosening of the carbonyl bond. This effect seems parallelled in the 5- and 6-membered ring lactams when comparing the donor properties toward iodine. Ring strain tends to reduce amide resonance [14,15] and shorten the carbonyl bond, which may explain the lower donor ability of the 5-membered ring. A strainless conformation in which the amide group shows some departure from coplanarity has been found for ($n = 6$)α-chloro-δ-valero-lactam from X-ray diffraction studies,[16] while weak strain and strong electron delocalisation was assumed for ($n = 7$)ε-caprolactam from infrared investigations.[17] A comparison of the carbonyl frequencies and the ultraviolet absorptions of the *N*-methyl lactams (Table 4) indicate strong electron delocalisation in the 7-membered ring. Thus factors other than amide resonance seem to determine the relative stability of the iodine complexes formed by the two larger rings.

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