CARBONYL STRETCHING VIBRATIONS AND ELECTRONIC TRANSITIONS DUE TO NONBONDING ELECTRONS IN SATURATED RING KETONES

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ABSTRACT

The carbonyl stretching frequency and intensity in saturated ring ketones show marked variations with the ring size. The position of the $n \rightarrow \pi^*$ transition band of the carbonyl group also varies with the ring size. The $n \rightarrow \sigma^*$ bands of the carbonyl group in these compounds have been tentatively assigned.

Considerable interest has been evinced in recent years in correlating the infrared and ultraviolent absorption spectra of related groups of organic molecules with their structure. Recently, Rao and coworkers [1-3] investigated the infrared and the near ultraviolet absorption spectra of aliphatic carbonyl derivatives and explained the data quantitatively in terms of different structural parameters. We have now recorded the absorption spectra of several saturated ring ketones in order to study the effect of ring size on the frequency and intensity of the carbonyl stretching vibration and on the $n \rightarrow \pi^*$ transition[2, 3] of the carbonyl group.

EXPERIMENTAL

All the saturated ring ketones were commercially available and were purified by fractionation before use.

The infrared spectra were recorded in carbon tetrachloride solutions using a Perkin-Elmer, Model 21, spectrometer with NaCl optics. The solutions were about 0.06 molar and the liquid cells were of 0.1 mm. thickness. All the measurements were made under the same experimental conditions in order to get the minimum possible error. The infrared absorption curves were measured over a frequency range of 100 cm^{-1} on either side of the maximum of the carbonyl stretching vibration. A base line was drawn between the ends of the wings and from it a perpendicular to the maximum. The apparent molecular extinction coefficient was calculated by the expression :

$$\epsilon = \frac{1}{Cl} \log_{10} \frac{I_0}{I}$$

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It was realized that the molecular extinction coefficients do not truly measure the intensities of infrared bands. But they have been used for comparing and characterizing relative intensities of bands in related groups of molecules.[4, 5]

The apparent half-intensity band widths, $\Delta\nu^{\frac{1}{2}\epsilon}$, were measured directly at half ϵ values.

The ultraviolet absorption spectra were recorded in *iso*-octane, methanol and water solutions employing a Cary, Model 11, recording spectrophotometer. The positions of the absorption maxima are recorded in $m\mu$ and the intensities in terms of molar extinction coefficients.

RESULTS AND DISCUSSION

Infrared Spectra:—The infrared frequencies and the apparent molecular extinction coefficients of the carbonyl stretching vibrations of the saturated ring ketones are summarized in Table I. The carbonyl stretching frequencies reported in this communication are in good agreement with those reported in the literature.[5] Only one carbonyl band was observed at 1748 cm^{-1} in the case of cyclopentanone. The other band due to intramolecular vibration[6] was not observed under the working conditions (low resolution). The stretching frequency is highest for cyclobutanone and decreases with increase in the ring size. The stretching frequency for cyclohexanone is about the same as that for a simple aliphatic ketone like acetone[1], (1715 cm^{-1}). For ring ketones larger than cyclohexanone, the frequency is slightly lower.

TABLE I

Carbonyl Stretching Vibrations in Saturated Ring Ketones

	Infrared Spectra			Dipole Moment, Debye[7, 8]
	$\nu_{c=0}$, cm^{-1}	ϵ	$\Delta v^{\frac{1}{2}\epsilon}$, cm^{-1}	
Cyclobutanone	1788	490	23	2.76
Cyclopentanone	1748	405	19	2.86
Cyclohexanone	1718	378	23	3.08
Cycloheptanone	1709	345	14	3.04
Cyclooctanone	1708	320	21	2.93
Cyclononanone	1708	275	18	2.82
Cyclodecanone	1708	240	20	2.72

For the most stable configuration of a ketone, the angle between the two bonds attached to the carbonyl group is 120°. In cyclobutanone and cyclopentanone, this angle is much smaller than 120° and the molecules are strained. The strain results in an increased *s*-character of the carbonyl group.

Since the *s*-character increases the stretching frequency, cyclobutanone and cyclopentanone exhibit higher carbonyl stretching frequencies than cyclohexanone.

The apparent molecular extinction coefficient of the carbonyl stretching band is also found to be maximum in the case of cyclobutanone and decreases with the increase in ring size. A similar trend (from cyclopentanone on) in the integrated absorption intensities of the carbonyl stretching band has been found by Bürer and Günthard.[7] But they have not measured the carbonyl absorption intensity in cyclobutanone. It is not easy to explain the variation of band intensity with ring size. Band intensities are related to electrical properties of bonds such as dipole moments, polarizabilities, etc. From the data in Table I it may be seen that there is a simple relation between the molecular extinction coefficients and the dipole moments[7, 8] only for the larger ring ketones. The half-intensity band widths, $\Delta\nu^{\frac{1}{2}\epsilon}$, do not show any regular trend with the ring size.

Near ultraviolet absorption spectra:—The long-wavelength low-intensity absorption between 260 and 300 $m\mu$ in carbonyl compounds has been shown[9, 10]

TABLE II

Carbonyl Group Electronic Transitions Due to Nonbonding Electrons in Saturated Ring Ketones

	$n\rightarrow\pi^*$ Transitions				Tentative assignments of $n\rightarrow\sigma^*$ Tratsitions	
Compound	In *iso*-octane [a]		Methanol[c]	Water[c]	In *iso*-octane	Methanol
	L	ϵ_{max}	L	L	L	L
Cyclobutanone	281	19.2	278	273	210 [b]	215
Cyclopentanone	300	19.1	287.5	282	211 [b]	217.5
Cyclohexanone	290	15.8	282.5	277	211 [b]	215 [b]
Cycloheptanone	292	18.6	283	277.5	215 [b]	215 [b]
Cyclooctanone	290	16.8	283	277	......	......
Cyclononanone	288	16.2	281.5	276	......	......
Cyclodecanone	289	15.4	283	277	......	......
2, 2-Dimethlcyclopentanone	298	......	292.5	......	215	215
3-*t*-Butylcyclopentanone	300	......	287	282	215	218
2-Methylcyclohexanone	289	......	283	278	215 [b]	215
3-Methylcyclohexanone	289	......	282.5	277.5	222	231
4-Methylcyclohexanone	291	......	282.5	277.5	217	223

a. Center of the band.

b. Appears as a shoulder or as part of a band extending to the vacuum ultraviolet region.

c. ϵ_{max} valuos are similar in magnitude to those in *iso*-octane solution.

$L = \lambda_{max}, m\mu$

to be due to a singlet-singlet symmetry forbidden transition ($1_U - 1_G$) arising from the excitation of an electron from a non-bonding atomic orbital (*n* orbital) to an antibonding molecular orbital (π^* orbital). Empirical criteria which permit distinctions between pure π-electron transitions and $n \rightarrow \pi^*$ transitions have been formulated[11-13]. The solvent effects on $n \rightarrow \pi^*$ transitions have been characterised[12] and in general, the transition energies are found to increase with the increase in the polarity of the solvent. The $n \rightarrow \pi^*$ transition wavelengths and intensities of the saturated ring ketones are given in Table II. The data

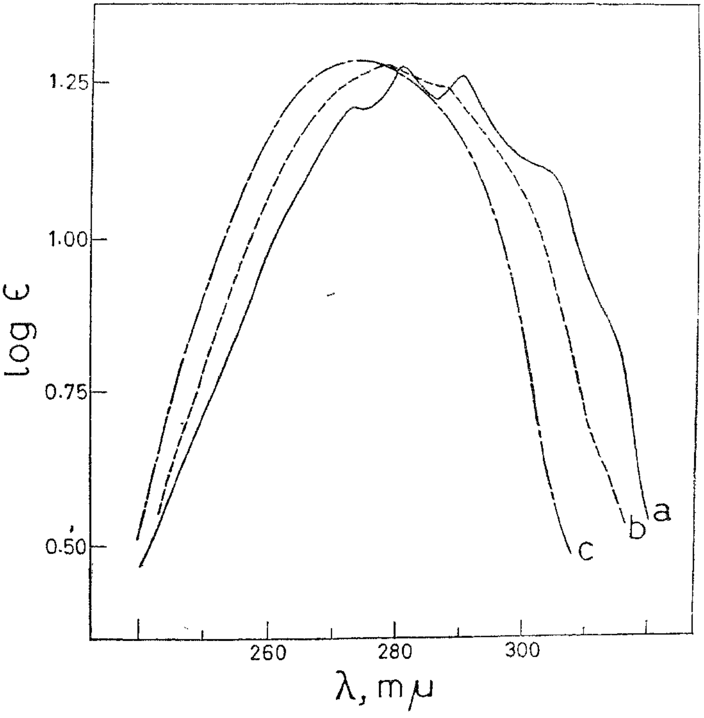

FIG. I
Carbonyl $n \rightarrow \pi^*$ Transition Band of Cyclobutanone
a. in *iso*-octane, *b*. in methanol and *c*. in water

satisfy all the necessary criteria[11-13] proposed for $n \rightarrow \pi^*$ transitions. The intensities of the bands are weak in all the ring ketones studied. All of them show vibrational fine structure in *iso*-octane. The fine structure is more pronounced in the case of cyclobutanone and cyclopentanone. The fine structure diminishes in methanol and nearly vanishes in water. The $n \rightarrow \pi^*$ bands of cyclobutanone in *iso*-octane, methanol and water solutions are shown in Figure I. All the ring ketones show increasing $n \rightarrow \pi^*$ transition energies (decreasing wavelengths) with increasing polarity or hydrogen-bonding ability of the solvents.

Of all the ring ketones, the wavelength corresponding to the $n \rightarrow \pi^*$ absorption maximum is lowest in the case of cyclobutanone and largest in the case of cyclopentanone. In ring ketones larger than cyclohexanone, the wavelength remains nearly constant. The explanation for the observed trend in the $n \rightarrow \pi^*$ band positions in these ring ketones is not clear at present. The positions of the $n \rightarrow \pi^*$ bands of cyclopentanone and cyclohexanone do not seem to be affected by alkyl substitution.

In addition to the $n \rightarrow \pi^*$ transitions, carbonyl groups also exhibit the $n \rightarrow \sigma^*$ transitions ($1_W - 1_G$) at lower wavelengths.[10, 13] In the case of the $n \rightarrow \sigma^*$ transitions, the transition density at the oxygen atom contains a one center ($2s$, $2p$) term which transforms like a local electric dipole, *i.e.*, the σ^* orbital has some $2s$ character at the oxygen atom. The assignment of $n \rightarrow \sigma^*$ transition bands has not been straight-forward since they occur in the vacuum ultraviolet region in most carbonyl compounds.

Many of the ring ketones investigated exhibit shoulders or absorption maxima towards the edge ($\sim 220\, m\mu$) of the near ultraviolet region. Some of them show vibrational fine structure. These shoulders or maxima are tentatively assigned to the $n \rightarrow \sigma^*$ transitions (Table II). The absorption intensities of these bands have not been reported because the observed bands appear to extend further to the vacuum ultraviolet region. Alkyl substitution in 3- or 4-position seems to shift the $n \rightarrow \sigma^*$ bands of cyclopentanone and cyclohexanone to longer wavelengths. Some of the $n \rightarrow \sigma^*$ bands undergo marked solvent red-shifts (increase in wavelength with increase in polarity of the solvent).

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