Chemistry

1965

SovietRxiv

structural formulas of the lactam and lactim forms of α-pyridone

Figure 1: structural formulas of the lactam and lactim forms of α-pyridone

Abstract

Full Text

Chemistry

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Investigation of the Tautomerism of Lactams in Vapors by the Method of IR Spectra

(Presented by Academician M. I. Kabachnik, March 2, 1965)

For substances theoretically capable of lactim–lactam tautomerism and possessing dual reactivity, such as α-pyridone,

the tautomeric forms have not been isolated in any case. In condensed phases and in solutions these substances exhibit strong intermolecular hydrogen bonding. On this basis, Hunter (^{1}) advanced the hypothesis of "mesohydrogen" tautomerism, according to which, in the presence of a hydrogen bond $X \cdots H \cdots Y$, the H atom is bonded equally to both heteroatoms X and Y, which was to explain the impossibility of the separate existence of the tautomers. Later it was established (^{2}), using α-pyridone as an example, that the hydrogen bond $N \cdots H \cdots O$ is asymmetric, with N being covalently bonded to H. Subsequently, in a number of works (^{3}-^{5}) it was shown that, by comparing the IR spectra of the unsubstituted compound with the spectra of O- and N-substituted derivatives, the structure of the predominant tautomer can be established. Similar results were obtained by comparison of electronic spectra (^{5}). In the case of substances containing one lactam group, the amide form always predominates (^{6}). Using data from spectral and other methods, attempts were made to establish computationally the presence of tautomeric equilibrium and to calculate its constant (^{7}, ^{8}); however, if the small content of the oxy form is taken into account (fractions of a percent), such calculations are of little evidential value. It therefore seemed of interest to establish the presence of tautomerism and determine the position of equilibrium by observing the IR spectra of free molecules, i.e., in the vapor state, which became the subject of our investigation. A similar attempt had already been made (^{9}), but attention there was directed only to the band of the C=O stretching vibration. This made it possible to detect the presence of the lactam form, but yielded no information on the oxy form. We used the bands of the O–H and N–H stretching vibrations, which made it possible to quantitatively estimate the relative content of both forms. α-Pyridone and δ-valerolactam, including their N-deuterated derivatives, were selected as

Fig. 1. Infrared absorption spectra of α-pyridone in the LiF region: 1 — saturated solution in CCl_4, 2 —vapor $\sim 2 \cdot 10^{-3}$ mol/l at 250°

Figure 2: Fig. 1. Infrared absorption spectra of α-pyridone in the LiF region: 1 —saturated solution in CCl_4, 2 —vapor $\sim 2 \cdot 10^{-3}$ mol/l at 250°

representatives of saturated and unsaturated lactams.

The spectra were recorded on a UR-10 spectrometer in the LiF region. The task was to measure not only the vibration frequency but also the integral intensity of the bands. In these cases the recording was carried out with the following program: slit —4, scanning speed —12, registration time —50, paper scale —50. The spectral slit width was: at $\nu = 3450$ cm^{-1}, 4.37 cm^{-1}; at $\nu = 3620$ cm^{-1}, 5.63 cm^{-1}. Vapors were recorded in a cylindrical quartz-

in a cell 120 mm long with fused-in quartz windows having a low-frequency transmission limit of ~ 2200 cm^{-1}. The cell had a stopcock for evacuation and was heated (including the stopcock and windows) by an electric furnace; the temperature was monitored by a thermocouple with an accuracy of ±5°. After the sample of substance was introduced, the cell was evacuated to a residual pressure of $4 \cdot 10^{-2}$ mm Hg and brought as rapidly as possible to the specified temperature, after which the spectrum was recorded in a narrow region including the frequency of the O—H or N—H vibration; in other cases both bands were recorded rapidly one after the other. The vapor concentration calculated from the weighed sample was $1 \div 2 \cdot 10^{-3}$ mol/l.

Fig. 1. Infrared absorption spectra of α-pyridone in the LiF region: **1** — saturated solution in CCl_4, **2** —vapor $\sim 2 \cdot 10^{-3}$ mol/l at 250°

In the determination of the integral intensity

$$A = I/C$$

there enters, in addition to the quantity I, calculated from the spectrogram, also the concentration (C). The value A cannot be determined from an experiment on an isolated tautomer, and only the ratio could be used to estimate the displacement of the equilibrium:

$$C_{\mathrm{OH}}/C_{\mathrm{NH}} = I_{\mathrm{OH}}/I_{\mathrm{NH}} \cdot A_{\mathrm{NH}}/A_{\mathrm{OH}},$$

where $A_{\mathrm{NH}}/A_{\mathrm{OH}}$ is a certain unknown constant. I was calculated by the Bourgin method (^{10}), the areas being measured with a planimeter. In parallel, spectra of the selected objects were recorded in dilute solutions and in the crystalline state (in KBr pellets and in Vaseline oil).

Of the three fairly intense bands in the vapor spectrum of α-pyridone (see Fig. 1 and Table 1), the bands ~ 3600 and ~ 3445 cm^{-1} undoubtedly belong to

Fig. 2. Infrared spectra of α-pyridone vapors at 300°, recorded: 1—after 60 min, 2—after 140 min, 3—after 180 min from the start of heating of the cell

Figure 3: Fig. 2. Infrared spectra of α-pyridone vapors at 300°, recorded: 1—after 60 min, 2—after 140 min, 3—after 180 min from the start of heating of the cell

free vibrations of the O—H and N—H bonds. This is also confirmed by comparison of the corresponding frequencies in the spectra of H- and D-compounds: $\nu_{\mathrm{NH}}/\nu_{\mathrm{ND}} = 1.350$, $\nu_{\mathrm{OH}}/\nu_{\mathrm{OD}} = 1.355$, whereas by approximate calculation it should be 1.37 and 1.38, respectively. In assigning the third intense band

Infrared absorption spectra of lactam vapors

Table 1

α-Pyridone	α-Pyridone	α-Pyridone	α-Pyridone	α-Pyridone —N—D	α-Pyridone —N—D	α-Pyridone —N—D	α-Pyridone —N—D
T, °C	ν_{CH}, cm^{-1}	$\nu_{\mathrm{N-H}}$, cm^{-1}	$\nu_{\mathrm{O-H}}$, cm^{-1}	T, °C	$\nu_{\mathrm{C-H}}$, cm^{-1}	$\nu_{\mathrm{N-D}}$, cm^{-1}	$\nu_{\mathrm{O-D}}$, cm^{-1}
160	3080	3450	3620	160	30503080	2550	2655
200	3080	34383450	35903610	200	30503080	2550	2655
250	3080	34383453	35933612	220	30503080	2550	2655
300	3080	34383450	35903610	300	30503080	2550	26502665

δ-Valerolactam	δ-Valerolactam	δ-Valerolactam	δ-Valerolactam	δ-Valerolactam —N—D	δ-Valerolactam —N—D	δ-Valerolactam —N—D	δ-Valerolactam —N—D
160	28702955	3445	—				
200	28702950	34303445	—	200	28802955	2555	—
250	28702950	34353445	—	250	28802950	2550	—

($\sim$ 3080 cm^{-1}) and of the weaker broad band at $\sim$ 2900 cm^{-1} must be taken into account by considering the change in their intensity in successive recordings of spectra at constant temperature. Fig. 2 shows successively recorded spectra obtained with an increased sample charge; in this case the vapor concentration apparently increases with the duration of heating. Since the 3080 cm^{-1} band remains unchanged in the spectrum of the D derivative and is absent in δ-valerolactam, and moreover its intensity changes with time in concert with the intensities of the bands at $\sim$ 3445 and $\sim$ 3600 cm^{-1}, this band probably belongs to stretching vibrations of

Fig. 2. Infrared spectra of α-pyridone vapors at 300°, recorded: **1**—after 60 min, **2**—after 140 min, **3**—after 180 min from the start of heating of the cell

the C—H ring. The band at ~ 2900 cm^{-1}, which corresponds to the short-wave part of the broad band observed in solution (see Fig. 1) and increases in intensity with increasing vapor pressure, may be assigned to associated vibrations of the O—H and N—H groups. The latter two assignments are not indisputable. Additional evidence for the presence of the lactam form in the vapors is the presence of an intense band at 1716 cm^{-1} of the free stretching vibration of the C=O group (see also (9)).

In the vapor spectrum of δ-valerolactam, a band of N—H vibrations is observed (see Table 1), and again the ratio $\nu_{\mathrm{NH}}/\nu_{\mathrm{ND}} = 1.350$ is close to the theoretical value. The bands at ~ 2880 and ~ 2960 cm^{-1}, equally present in the H and D derivatives, undoubtedly correspond to the symmetric and antisymmetric vibrations of the CH_2 group. The band of free O—H vibrations is completely absent.

Special experiments were carried out in which the vapor spectrum was recorded at a constant temperature at certain time intervals, and then I_{OH} and I_{NH} were measured. As Table 2 shows, the ratio $I_{\mathrm{OH}}/I_{\mathrm{NH}}$, and consequently also $C_{\mathrm{OH}}/C_{\mathrm{NH}}$, practically does not change with time, which suggests the rapid establishment of an equilibrium state. Experiments carried out at different temperatures (Table 2) show that $I_{\mathrm{OH}}/I_{\mathrm{NH}}$, even if it depends on temperature (a decrease at 300°), does so only very slightly. In view of the insufficient accuracy of these measurements, associated with the difficulty of maintaining constant temperature and vapor concentration throughout the entire volume of the cell, it is not possible to calculate from the data obtained the heat of the tautomeric transformation.

Of the results obtained, the most interesting appears to be the fundamental difference between α-pyridone and δ-valerolactam in the ratio

tautomeric forms. This can be explained on the basis of the difference in the conjugation energies of the two molecules. Calculation of bond energies from Pauling' s data gives, for the lactam form, a value greater by 10 kcal. In agreement with this, the unconjugated molecule of δ-valerolactam is in the lactam form in all states. In the case of α-pyridone, the conjugation energy is, for the lactim form, ~43 kcal (ring) + 7 kcal (conjugation with the OH group); for the lactam form, ~21 kcal (acid amide) + 3.5 kcal (diene). Taking both components of the energy into account, this gives a gain in favor of the lactim of ~15.5 kcal. These calculations are of a purely approximate character and, moreover, the values found characterize differences in heat contents (H), which, as is known, do not unambiguously determine the position of equilibrium. Nevertheless, the calculation, if not quantitatively, then at least qualitatively confirms the assumption that the difference in the behavior of the two substances is determined by the effect of conjugation.

Table 2

Change in $I_{\mathrm{OH}}/I_{\mathrm{NH}}$ for α-pyridone vapors with temperature (A) and with time at a constant temperature of 300° (B)

A	A	B	B
Temp., °C	I_{OH}/I_{NH}	Spectrum Nos.**	I_{OH}/I_{NH}
140 ($n = 2$)*	2.50	1	1.89
200 ($n = 8$)	2.47	2	1.89
250 ($n = 18$)	2.64	3	1.84
300 ($n = 10$)	2.01	4	1.84
		5	1.84

* n is the number of measurements.
** Numbers of consecutively recorded spectra; no intervals were made between them. The recording time of the registered region was 35 min.

Received
2 III 1965

CITED LITERATURE

1. L. Hunter, J. Chem. Soc., 1945, 806; J. Chem. Soc., 1950, 2857.
2. B. R. Penfold, Acta Crystallogr., 6, 591 (1953).
3. Yu. N. Sheinker, V. M. Reznikov, DAN, 102, 109 (1955).
4. Yu. N. Sheinker, Yu. N. Pomerantsev, ZhFKh, 1, 79 (1956).
5. A. R. Katritzky, Advances in Heterocyclic Chemistry, 1, London, 1963, p. 347.
6. M. I. Kabachnik, Zhurn. Vsesoyuzn. khim. obshch. im. D. I. Mendeleeva, 7, 263 (1962).
7. A. Albert, J. N. Phillips, J. Chem. Soc., 1956, 1294.
8. S. F. Mason, J. Chem. Soc., 1958, 676.
9. K. Nakamura, J. Chem. Soc. Japan (pure chem. sect.), 80, 231 (1959).
10. D. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).

Note: Figure translations are in progress. See original paper for figures.