

IR VARIABLE TEMPERATURE SPECTROSCOPY (I). HYDROGEN BONDING IN 1,2,3,4-TETRAHYDRONAPHTALIL HYDROPEROXIDE

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The aim of this work was to study the effect of controlled heating on the 1,2,3,4-tetrahydronaphthalil hydroperoxide in tetraline solutions. Using two solvents, CCl_4 and tetraline, it was systematically observed the change of IR spectra, carried out at different temperatures. It was determined the activation energy, E_a , of the hydrogen bonding for hydroperoxide of tetraline (HPT).

Introduction

Hydroperoxydes are, in general, used as initiators in process of polymerisation because of their high reactivity [1]. The type of their decomposition is a very interesting characteristic.

Thus, kinetics of the decomposition for hydroperoxide of 1,2,3,4 tetrahydronaphtalene (HPT) was studied in different conditions: in presence of polyoxyethylene complexes with CoCl_2 , of Co (II) and Cu (II) salts, or some acids [2-4].

In relation with this we are interested in the spectral and theoretical studies of hydrogen bonding of different compound in various matrices [5,6]. The breaking of these bonds in process of heating is a preliminary physical stage to that of decomposition.

We use in this study the IR variable temperature spectroscopy as differentiating technique. As is known, the existence of hydrogen bonding affects all the modes of vibrations related with the polar groups X-H.[7] But the effect of temperature on IR spectra of HPT solutions must be the most spectacular.

Experimental

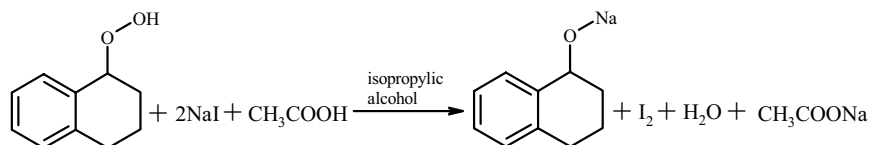
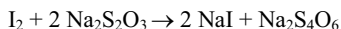
The IR spectra were obtained using SPECORD IR-71 Carl Zeiss Jena spectrophotometer within the range $4600\text{-}650\text{ cm}^{-1}$. For this study we used a variable temperature IR-cell and an electrical heating system, made by the same firm, which was calibrated by us to assure a suitable temperature control (to 1°C) in the range of temperature -180 to $+250^\circ\text{C}$ /6/. The time necessary to attend the thermal equilibrium was 15-30 minutes to temperature below 70°C and approximately one hour for highest temperatures. IR spectra of HPT solutions were carried out only after stabilization of thermal equilibrium. For one solution on the same spectrogram were registered distinctly the spectra at 3-4 temperatures at two rates of

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scanning (4.4 minutes and 8.8 minutes for whole spectrum). The reference beam was attenuated by Hartmann device.

The solutions of HPT in Cl_4C were prepared using pure crystalline solute with molecular weight $M=164$ and m.p. 49.5°C . The concentrations were in interval 1-2% (suitable for spectroscopic observations with minimal errors). Additional density determinations were made for postcalcul of molar concentrations of these solutions.

The solutions of HPT in tetraline were prepared starting from samples, extracted from oxidation process of tetraline with known content of HPT (8.87%), determined by iodometric method in accord with the reactions:



Again the starting samples were diluted to the concentrations suitable for spectrophotometric determinations. The obtained solutions were introduced in the variable temperature IR cell by injection. We have been used Cl_4C fresh distilled to wash the IR cells. At the end of every experiment a flow of inert gas was circulated through cell.

Results and Discussions

As precedence of this work IR spectrum of pure crystalline HPT was registered by KBr pellets technique and was interpreted after literature data and with the help of EXP-AIR program [5,6].

The IR spectra of the solution containing 1.5% HPT in CCl_4 were carried out at four different temperatures between 18.5 - 66.99°C . They are done in Fig. 1 in region of OH stretching vibrations. This shows the decrease of intensity of the OH stretching band corresponding to associated by hydrogen bonding HPT molecules and the relative increase in intensity of the bands assigned to them unassociated (this is a physical process of destruction of hydrogen bonding).

Fig. 2a shows the same type of changes observed in the IR spectra of solution containing 1.66% HPT in tetraline, solvent which permit the extension of observed temperature range. Fig. 2b shows the spectral changes observed nearly 1700 cm^{-1} region (characteristic to carbonyl groups) [5]. It is obvious a spectacular intensity increase of the carbonyl stretching band, which demonstrate the progressive decomposition of HPT with tetralone formation at highest temperature regime (a chemical process), which will be separately considered in the future paper.

It is possible to affirm that in the domain of low temperatures the needed time to attend the thermal equilibrium is little enough in comparison with the time of reaction (the time to maintain the installation, attached to IR spectrometer at one value of temperature). Thus, in

working temperature range (291,65÷340,15 K) the logarithm of rapport of intensity^a of the band corresponding to ν_{OH} associated and intensity of the band corresponding to ν_{OH} unassociated may be assimilate with $\log K$ (equilibrium constant for breaking of hydrogen bonds) Table 1.

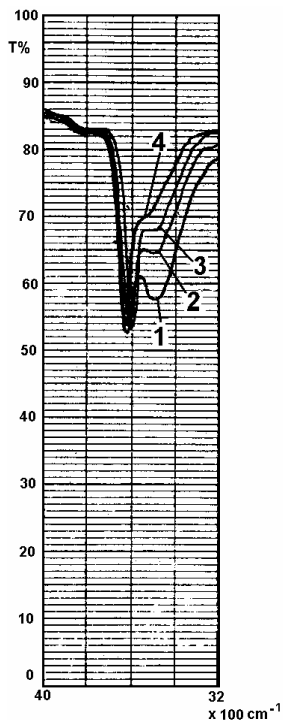


Fig. 1: IR spectra of HPT in CCl_4 at four temperatures: 1) 18.5 °C; 2) 36.86 °C; 3) 50.68 °C; 4) 66.99 °C

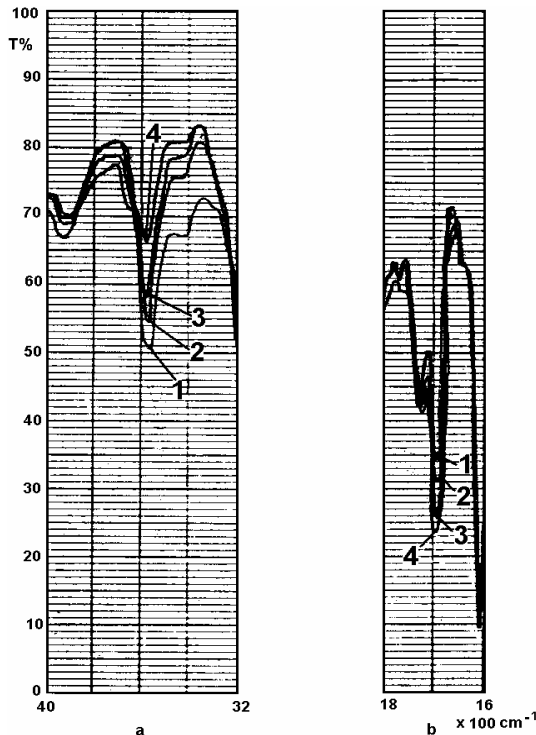


Fig. 2: IR spectra of tetraline at four temperatures: 1) 19 °C; 2) 65.06 °C; 3) 115.38 °C; 4) 161.95 °C; a) 4000÷3200 cm^{-1} b) 1800÷1600 cm^{-1}

Table 1. IR spectral data for HPT in Cl_4C solution at different temperatures

No	T (K)	$1/T$ (K^{-1})	$h_{band\ assoc}$ (mm)	$h_{band\ unassoc}$ (mm)	$K = \frac{h_{b-assoc.}}{h_{b-unassoc.}}$	$\lg K$
1	291.65	$3.4 \cdot 10^{-3}$	42	36	1.166	0.0667
2	310.00	$3.22 \cdot 10^{-3}$	43	26	1.65	0.217
3	323.83	$3.09 \cdot 10^{-3}$	44	22	2	0.309
4	340.15	$2.94 \cdot 10^{-3}$	44	18	2.44	0.387

^a Intensity is approximate as the height of the bands, determined by baseline method.

The obtained Arrhenius equation:

$$\lg K = 1.025 - 666.667 \frac{1}{T}$$

corresponds to a value for $E_a = 3.051 \pm 0.013$ (kcal/mol).

The obtained E_a values for the process of hydrogen bonding destruction of HPT in Cl_4C solutions is in accord with them reported in literature for the association by hydrogen bonding of methanol, t-butylic alcohol and benzylic alcohol (s. table 2) in the same solvent, CCl_4 . [8]

Table 2. Literature data concerning E_a

No	Alcohol	$E_{\text{assoc}} \pm S_E$ (kcal/mol)
1	Methanol	4.72 ± 0.09
2	t-Butylic	5.30 ± 0.5
3	Benzylic	4.60 ± 0.2

Conclusions

By IR variable temperature spectroscopy we determined in the case of HPT solutions in Cl_4C , as solvent, the energy E_a corresponding to destruction of hydrogen bonding. The obtained value is in concordance with other literature data for the same solvent.

Acknowledgement

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