Identification of the Enol Content in Some Monoketones by an IR Spectroscopic Method

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The enol contents in methyl-ethyl-ketone and cyclohexanone have been detected and determined from infrared spectra. The determination is based on the absorption peak of the ν_{OH} stretching vibration resulting from the enol content. The temperature dependence of the overall equilibrium constant of tautomerism and association were determined from the enol content and so the overall reaction enthalpy could be calculated.

(Keywords: Keto-enol tautomerism; IR spectroscopy; Association; Equilibrium constant)

Identifizierung des Enolgehaltes in einigen Monoketonen durch eine IR-spektroskopische Methode

Der Enolgehalt in Methyl-ethyl-keton und Cyclohexanon wurde aufgrund der IR-Spektren identifiziert und bestimmt. Grundlage der Bestimmung bildet die IR-Absorption der OH-Valenzschwingung der Enolgruppierung. Aus dem Enolgehalt konnte der Wert der Gleichgewichtskonstante der Gesamtreaktion von Tautomerisation und Assoziation bestimmt werden. Die Temperaturabhängigkeit der Gleichgewichtskonstante ermöglichte die Bestimmung der Reaktionsenthalpie des Gesamtprozesses.

Introduction

The amount of the enol form in monoketones is not more then 1–2%. The percentage of the enol present in several monoketones has been reported and is given in Table 1.

The determination of the enol content has been carried out by the modified *Kurt-Meyer* titration, diluting the pure ketone by a bromine solution. The problem is that the keto-enol equilibrium may be displaced by the dilution.

Table 1. *The percentage of enol present in some monoketones*

Component	Enol content %	Reference
Acetone	$1.5 \cdot 10^{-4}$	[1]
	$2.5 \cdot 10^{-4}$	[2]
Methyl-ethyl-ketone	$1.2 \cdot 10^{-1}$	[1]
Methyl-propyl-ketone	$8.6 \cdot 10^{-3}$	[1]
Methyl-butyl-ketone	$1.1 \cdot 10^{-1}$	[1]
Methyl-isobutyl-ketone	$2.7 \cdot 10^{-1}$	[1]
Methyl-pentyl-ketone	$9.6 \cdot 10^{-2}$	[1]
Cyclopentanone	$8.8 \cdot 10^{-2}$	[1]
	$4.8 \cdot 10^{-3}$	[3]
Cyclohexanone	1.2	[1]
	$2.0 \cdot 10^{-2}$	[3]

In the course of our study an enol content with a maximum of 1–2% was detected by an IR spectroscopic method; quantitative results were also obtained. As in our experiment only pure and not diluted components were used a shift of the equilibrium was avoided.

Theory

The consequence of keto-enol transformation is a decrease in the intensity of the carbonyl stretching band in the IR spectrum. This means that new bands could be observed caracterising the $C = C$ double bond and the OH group.

The stretching vibration of the $C = C$ double bond appears at a wave number of $1\,647\,cm^{-1}$. This band, however, is generally weak (except in case of some β-diketones), and we planned to study ketones containing only 1–2% of enol; so the determination of the enol content based on the absorption of the $C = C$ double bond is not accurate enough. Other possibilities, e.g. the measurement of the bending vibrations, was not suited either, because this region is very rich in absorption peaks and the concentration is usually very low.

In our study the stretching vibration bands of the OH group has been used in order to identify the enol content in the ketones. The wave number region where the v_{OH} absorption occurs is between $3\,600$ and $3\,100\,cm^{-1}$, but this values can be shifted until $3\,760$ and $1\,800\,cm^{-1}$, e.g. because of association. A hydrogen bond of $1\,kJ$ enthalpy can shift the v_{OH} by $8–9\,cm^{-1}$ in the direction of lower wave numbers. As the v_{OH} absorption band are quite intensive the appearance of the enolic v_{OH} band was also expected.

The identification of the enolic OH can be disturbed by the water content of the ketones. The v_{OH} band of the water appears at 3 600–3 100 cm^{-1} and overlaps the other (enolic) v_{OH} bands.

At 3 380–3 400 cm^{-1} a sharp maximum can be found in the IR spectra of monoketones which is due to the overtone of the $C=O$ stretching vibration. In the region of 3 400–3 600 cm^{-1} there is a less intensive band caused by the water content of the ketone, according to *Wiegel* and *Kirchner* [4].

We supposed, however, that this band is due to the water and enol content of the ketone together. In order the prove the validity of our statement the following characteristics of the keto-enol equilibrium were used [5].

By the dilution with simple hydrocarbons the equilibrium is shifted in the direction of enol formation. Consequently, if the intensity of the band is increased after dilution with hydrocarbon, this indicated an enolic OH absorption in this region.

The intensity of the band must decrease with increasing temperature as the equilibrium is shifted towards ketone formation.

Experimental

A SPECORD IR 75 type spectrophotometer equipped with KBr optics was used in all measurements. The cell thickness was varied, determined from interference fringes. The temperature of the cell could be regulated. The water content of the examined monoketones was previously reduced with anhydrous $CaSO_4$ heated at 473 K, then by a destillation to a minimum value of less than 0.1 percent. The water content was controlled by gas chromatography.

The hydrocarbons and alcohols used were high purity chemicals, and since good agreement was found between their physical properties and the corresponding data in the literature, no further purification was made.

Results and Discussion

In Figs. 1 and 2 the spectrum of the methyl-ethyl-ketone and the cyclohexanone is shown. Curves 1 are the spectra of the pure ketone, curves 2 are the spectra after diluting by hexane and cyclohexane. The intensity of the OH band is increased by the dilution indicating a likely existence of the enolic OH.

In Figs. 3 and 4 the effect of temperature can be studied on the band intensity. The maximum value of the band is decreasing with increasing temperature which can also mean a presence of enolic OH.

The assumption that the questionable absorption peak is due not only to the OH of water but also to the enolic OH has been verified.
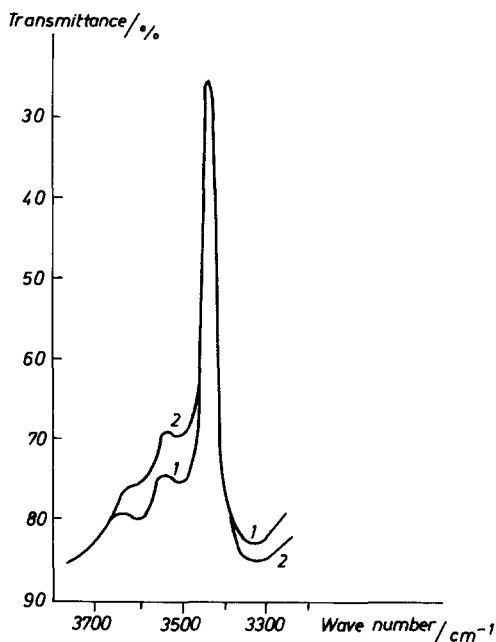
Fig. 1. Absorption spectrum of methyl-ethyl-ketone and methyl-ethyl-ketone + n-hexane mixture

Compound	*1* Methyl-ethyl-ketone	*2* Methyl-ethyl-ketone + + n-hexane
Concentration/ mol per cent	100	50 — 50
Reference material	—	n-hexane
Cell thickness	0.130	0.260
Ref. cell thickness	—	0.130

In order to determine the enol content the molar absorption coefficient of both the enolic and the alcoholic OH were considered to be equal and *Beer*'s law was supposed to be valid.

To the ketone 1 molar per cent alcohol of possibly similar structure and relative molar mass was added. From the increase in the absorption of the above mentioned mixture the enol content could be calculated. The following equation was used

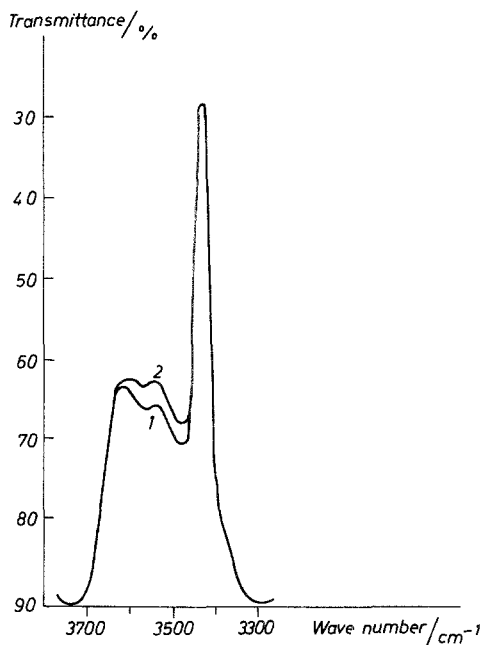$$\frac{x}{0.99\,x + 1} = \frac{\varepsilon_1}{\varepsilon_2} \tag{1}$$

Fig. 2. Absorption spectrum of cyclohexanone and cyclohexanone + cyclohexane
mixture

Compound	*1* Cyclohexanone	*2* Cyclohexanone + + cyclohexane
Concentration/ mol per cent	100	50 − 50
Reference material	—	cyclohexane
Cell thickness	0.130	0.260
Ref. cell thickness	—	0.130

where x is the percentage of enol in the ketone, ε_1 the corresponding absorption, $0.99\,x + 1$ is the OH concentration after adding 1 per cent alcohol, ε_2 the corresponding absorption.

By this method the following enol contents were calculated at 293 K (Figs. 5 und 6).

Methyl-ethyl-ketone	$0.80 \pm 0.2\%$
Cyclohexanone	$1.51 \pm 0.2\%$

These values have the same order of magnitude as those listed in Table 1. We gave $\pm$ 0.2 per cent as the error of the determination. This is due to the small water content and the error of the measurement.
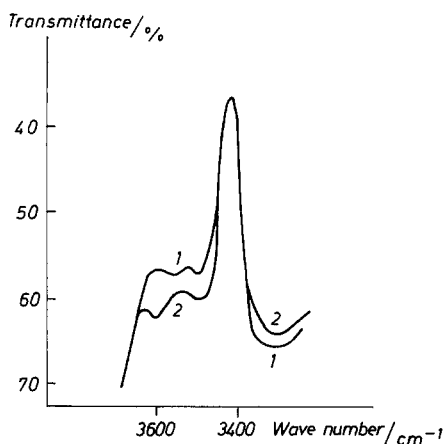
Fig. 3. Absorption spectra of methyl-ethyl-ketone as a function of temperature

Compound	*1* Methyl-ethyl-ketone	*2* Methyl-ethyl-ketone
Reference material	—	—
Cell thickness	0.1	0.1
Temperature/K	298	343
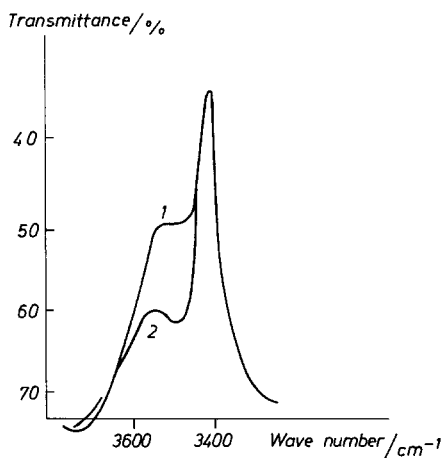
Fig. 4. Absorption spectra of cyclohexanone as a function of temperature

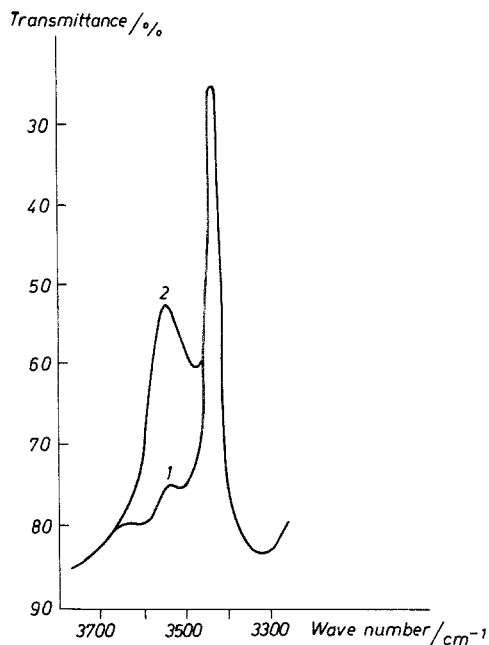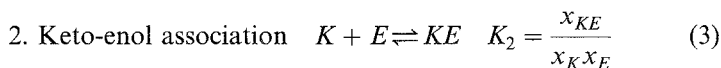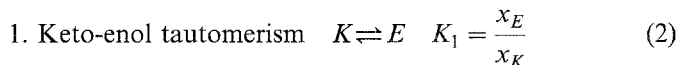| Compound	*1* Cyclohexanone	*2* Cyclohexanone
Reference material	—	—
Cell thickness	0.1	0.1
Temperature/K	298	343

Fig. 5. Absorption spectra for calculation of the enol content in methyl-ethyl-ketone

Compound	*1* Methyl-ethyl-ketone	*2* Methyl-ethyl-ketone + + isobutyl-alcohol
Concentration/ mol per cent	100	99 + 1
Reference material	—	—
Cell thickness	0.150	0.150

By means of the above method, the enol content of methyl-ethyl-ketone and cyclohexanone have been determined as a function of temperature.

Supposing that all the enol content forms associated complexes with the ketone, the overall equilibrium constant of the following two reactions could be calculated.
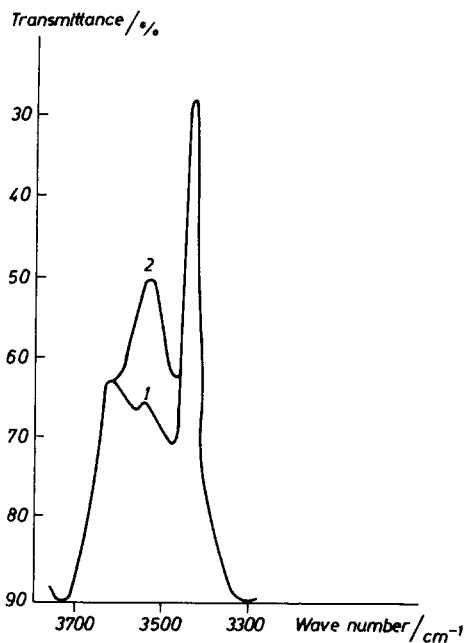
$$1. \text{ Keto-enol tautomerism} \quad K \rightleftharpoons E \quad K_1 = \frac{x_E}{x_K} \qquad (2)$$

$$2. \text{ Keto-enol association} \quad K + E \rightleftharpoons KE \quad K_2 = \frac{x_{KE}}{x_K x_E} \qquad (3)$$

Fig. 6. Absorption spectra for calculation of the enol content in cyclohexanone

Compound	*1* Cyclohexanone	*2* Cyclohexanone + + cyclohexanol
Concentration/ mol per cent	100	99 + 1
Cell thickness	0.150	0.150
Reference material	—	—

The overall reaction

$$2\,K \rightleftharpoons KE \tag{4}$$

the corresponding equilibrium constant

$$K = K_1 \cdot K_2 = \frac{x_{KE}}{x_K^2} \tag{5}$$

Taking the mole number change into account, the overall equilibrium constant can be calculated:

$$K = \frac{x_{KE}}{(1 - x_{KE})^2} \tag{6}$$

where

$$x_{KE} = \frac{E\%}{100 - E\%} \tag{7}$$

From the temperature dependence of the equilibrium constants the reaction enthalpy can be calculated. The measured and calculated data are summarised in Table 2.

By linear regression the data listed in Table 2 gave the following equations:

$$\text{for methyl-ethyl-ketone} \quad \ln K = \frac{546 \cdot 9}{T} - 6.669$$

$$\text{for cyclohexanone} \quad \ln K = \frac{790 \cdot 3}{T} - 6.843$$

From these equations, in comparison with the *vant'Hoff* equation, the brutto reaction of the enol formation followed by association could be calculated:

$$\Delta H_{MEK} = 4\,581 \text{ J/mol}$$

$$\Delta H_{\text{cyclohexanone}} = 6\,573 \text{ J/mol}$$

Table 2. *Measured and calculated data based on the IR spectra of the ketones*

Methyl-ethyl-ketone			
Temperature K	Enol content %	$10^3 \cdot x_{\text{Enol}}$	$10^3 \cdot K$
293	0.797	8.030	8.161
303	0.766	7.716	7.836
313	0.703	7.082	7.183
323	0.676	6.802	6.895
333	0.645	6.487	6.572
Cyclohexanone			
Temperature K	Enol content %	$10^3 \cdot x_{\text{Enol}}$	$10^3 \cdot K$
293	1.515	1.538	1.586
303	1.356	1.394	1.434
313	1.317	1.335	1.345
323	1.182	1.196	1.225
333	1.098	1.111	1.136
343	1.062	1.073	1.097
353	0.908	0.962	0.984

In the literature the following two data were found for the enthalpy of association:

for secondary amines: $\Delta H_{ass} = 8.4 - 9.6\,kJ/mol$ [6]

for primery n-alcohols where one molecule can form two hydrogen bonds:

$$\Delta H_{ass} = 20\text{–}25\,kJ/mol \quad [7]$$

This means that the hydrogen bond between one ketone and one enol is much weaker that at the above mentioned two types of compounds and the ΔH values of the ketones contain in addition the reaction enthalpy of the tautomerism too.

References

[1] *Gero A* (1954) J Org Chem 19: 469, 1960
[2] *Schwarzenbach G, Felder E* (1944) Helv Chim Acta 27: 1044
[3] *Schwarzenbach G, Wittwer C* (1947) Helv Chim Acta 30: 669
[4] *Wiegel E, Kirchner HH* (1961) Z Analyt Chem 178: 421—259
[5] *Ratkovics F, Palágyi B, Wilde Á* (1984) Magyar Kémiai Folyóirat 90: 64—74
[6] *Ratkovics F, Domonkos L* (1976) Acta Chim Hung 39: 325
[7] *Woycicka MK, Recko WM* (1972) Bull Acad Polon Sci Ser Sci Chim 20: 783