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ON THE RATE OF HYDROLYSIS OF TRIMETHYLPHENOXYSILANE

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Summary

Trimethylphenoxysilane is shown to undergo hydrolysis rapidly in 96% ethanol at ambient temperature; therefore ethanol is unsuitable for taking UV absorption spectra of Me_3SiOPh.

Introduction

Nagy and Hencsei [1] have analysed the structure of methylphenoxysilanes by use of UV spectrophotometry. The UV spectra were recorded as solutions in 96% ethanol, and as such, formed the basis of quantum-chemical investigation of the nature of the bonding between the phenoxy group and silicon. Our experience [2] suggested that in such solutions hydrolysis of the Si—O—Ph bond would occur readily, so that the spectra discussed by them would refer to a mixture of methylphenoxysilanes and phenol:

$$Me_{4-n}Si(OPh)_n + nHOH \rightarrow Me_{4-n}Si(OH)_n + nPhOH$$

In confirmation of our criticism we now describe a study of the rate of hydrolysis of trimethylphenoxysilane in 96% and 99.8% ethanol.

Results and discussion

The identity of our compound was confirmed by comparing the IR spectra with that obtained by Nagy et al. [4].

Figure 1 shows the UV spectrum of a solution of trimethylphenoxysilane in 99.8% ethanol, and Fig. 2 spectra of solutions of phenol and trimethylphenoxysilane in 96% ethanol recorded 10 min after preparation of the solutions. Table 1 lists the absorption maxima in the UV spectra (in nm and wave numbers) and the molar absorptivities, E_{max}, as obtained in this work (1), as reported by Nagy and Hencsei (2) [1], and as reported by Åkerman (3) [5].

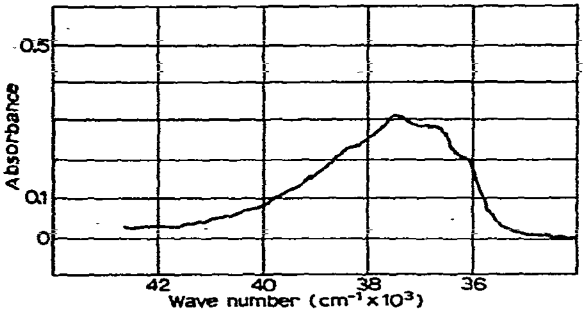

Fig. 1. UV spectrum of trimethylphenoxysilane recorded in 99.8% ethanol.

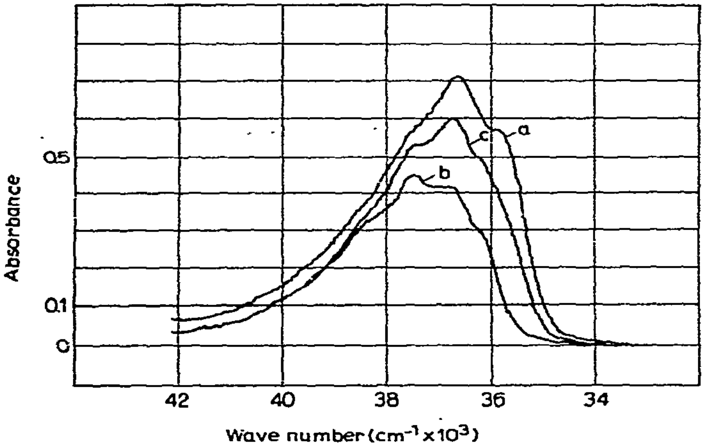

Fig. 2. UV spectra of: (a) phenol in 96% ethanol, (b) trimethylphenoxysilane in 96% ethanol recorded 10 min after preparation of the solution, (c) trimethylphenoxysilane in 96% ethanol recorded 20 h after preparation of the solution.

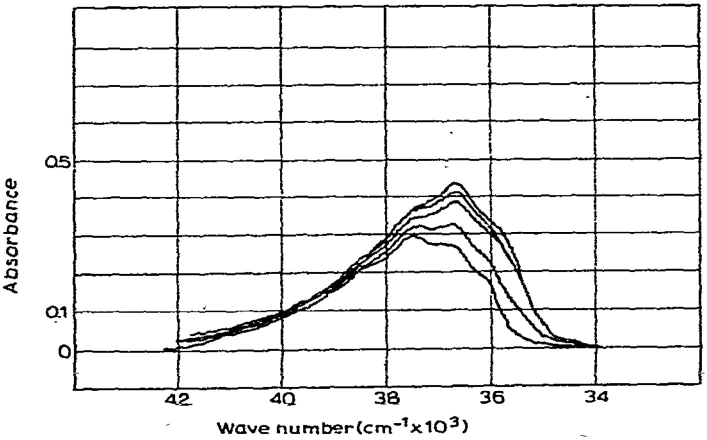

Fig. 3. Changes in the UV spectrum observed during the course of hydrolysis of trimethylphenoxysilane in 96% ethanol.

TABLE 1

UV ABSORPTION MAXIMA OF TRIMETHYLPHENOXYSILANE TAKEN FROM DIFFERENT SOURCES

No.	λ (nm)	ν (cm^{-1})	E_{max}	Ref.
1	266	37600	1177	
2	273	36630	1960	1
3	265[a]	37750[a]	1050[a]	5

[a] Approximate values as taken from the published spectrum.

Typical changes in the UV spectra taking place during hydrolysis of trimethylphenoxysilane in a 96% ethanolic solution are shown in Fig. 3. As the hydrolysis proceeds, the absorption maximum shifts from 266 to 273 nm with an increase in absorption. The hydrolysis shows first-order kinetics with a mean rate constant k of 4×10^{-3} min^{-1}.

This relatively high value of the rate constant, together with the shape and extremal parameters of the spectra (λ_{max}, and E_{max}) indicate that trimethylphenoxysilane is sensitive to the water present in 96% ethanol and hydrolyzes to liberate phenol.

The disagreement between the numerical values of λ_{max} and E_{max} presented in rows 1 and 3 of Table 1 with those of row 2 indicates that substantial hydrolysis of trimethylphenoxysilane had occurred under the conditions used by Nagy and Hencsei [1]. For this reason, their conclusions about the structure of methylphenoxysilanes based on the UV spectra are invalid.

Experimental

Trimethylphenoxysilane was obtained by reaction of equimolar quantities of phenol and trimethylchlorosilane in the presence of pyridine in benzene. The product was isolated from the reaction mixture by fractional distillation, a fraction boiling at 182-183°, n_D^{20} 1.4783, being collected (Lit. data [3]: b.p. 182.5°/736 mm, n_D^{20} 1.4782).

The IR absorption spectra of trimethylphenoxysilane were recorded with a Perkin—Elmer Model 357 spectrophotometer, using a liquid film.

The UV spectra were taken with a Specord UV-VIS (C. Zeiss, Jena) spectrophotometer in a 1-cm cell, using 96% ethanol of spectral purity or AR-grade 99.8% ethanol, both manufactured by POCh, Gliwice, Poland.

The rate of hydrolysis of trimethylphenoxysilane in 96% ethanol was measured spectrophotometrically at 273 nm, at 25 ± 1°. The concentration of solutions ranged from 2.55×10^{-4} to 2.57×10^{-4} mole/dm^3. The first spectrum was recorded 10 min after preparation of the solution. The rate constant was calculated from the following equation:

$$k = \frac{2.303}{t} \log \frac{A_\infty - A_0}{A_\infty - A_t}$$

where t is time, and A_0, A_t, and A_∞ are absorbances at the beginning of the reaction ($t = 0$), after time t and after total hydrolysis of the compound, respectively.

References

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