

The Ultraviolet Spectra of Phloroglucinol and Its Ethers

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The spectrum of phloroglucinol and that of its ether, 1,3,5-trimethoxybenzene, are reported to be identical in neutral (1,2,3), in weak acid (1,3) and in concentrated sulfuric acid (2) solutions. In connection with a study of the mechanism of the acid-catalyzed decarbonylation of 2,4,6-trimethoxybenzaldehyde it became necessary to learn whether or not 1,3,5-trimethoxybenzene was the only initial product of the reaction. The 1,3,5-trimethoxybenzene had been identified by isolation but the yield was not quantitative. A spectrographic method which could be applied directly to the reaction mixture seemed to be the most promising method to give a definitive answer. Hence, in spite of negative reports in the literature, an investigation was undertaken to discover acid conditions in which the spectrum of 1,3,5-trimethoxybenzene would serve to distinguish it from other likely products.

Initially, only phloroglucinol and 1,3,5-trimethoxybenzene were used. In 0-42% perchloric acid the spectra of the two compounds are the same. The only absorption maximum is a very weak one at *ca.* 265m μ . for each. This is consistent with the previous reports for the spectra in neutral and weak acid solutions. In 48.8%, 53.8% and 55.0% perchloric acid the spectra are different (Fig. 1). In 55.0% perchloric acid 1,3,5-trimethoxybenzene has absorption maxima at 252m μ . ($\epsilon = 24 \times 10^3$) and at 346 m μ . ($\epsilon = 14 \times 10^3$). Phloroglucinol in the same acid has maxima at 242 m μ . ($\epsilon = 13 \times 10^3$) and at 342 m μ . ($\epsilon = 9 \times 10^3$). The positions of the maximum absorption are the same in the lower concentrations of acid but the absorption is less intense. The absorption bands at the higher wavelengths are very broad and the maxima are only slightly different; hence, they are not useful for identification. The absorption bands at the lower wavelengths are quite sharp and sufficiently separated to be distinctive.

Since the monomethyl ether and dimethyl ether of phloroglucinol are also plausible products of the decarbonylation reaction, it was necessary to study their spectra. In 55.0% perchloric acid the results in the 340-350 m μ . range were intermediate between those for phloroglucinol and 1,3,5-trimethoxybenzene and were useless for identification. At the lower wavelengths the maxima were at 245 m μ ($\epsilon = 17 \times 10^3$) for the dimethyl ether and at 244 m μ . ($\epsilon = 15 \times 10^3$) for the monoethyl ether. In 48-55% perchloric acid 1,3,5-trimethoxybenzene can easily be distinguished from phloroglucinol and its monomethyl and dimethyl ethers.

In perchloric acid significantly above 55% concentration the spectra of phloroglucinol and 1,3,5-trimethoxybenzene were identical. In 70% perchloric acid, even working rapidly at *ca.* 9° C., the spectra of the two compounds were the same ($\lambda_{\text{max.}} = 242 \text{ m}\mu$.; $\epsilon = 15 \times 10^3$). For 1,3,5-trimethoxybenzene in 60% perchloric acid under the same conditions the absorption maximum was first seen at 245-248 m μ . and rapidly changed to 242m μ . The position of the maximum is that expected for phloroglucinol. That it is actually due to phloroglucinol is indicated by the following. Heating 1,3,5-trimethoxybenzene in 55% perchloric acid at 70° for

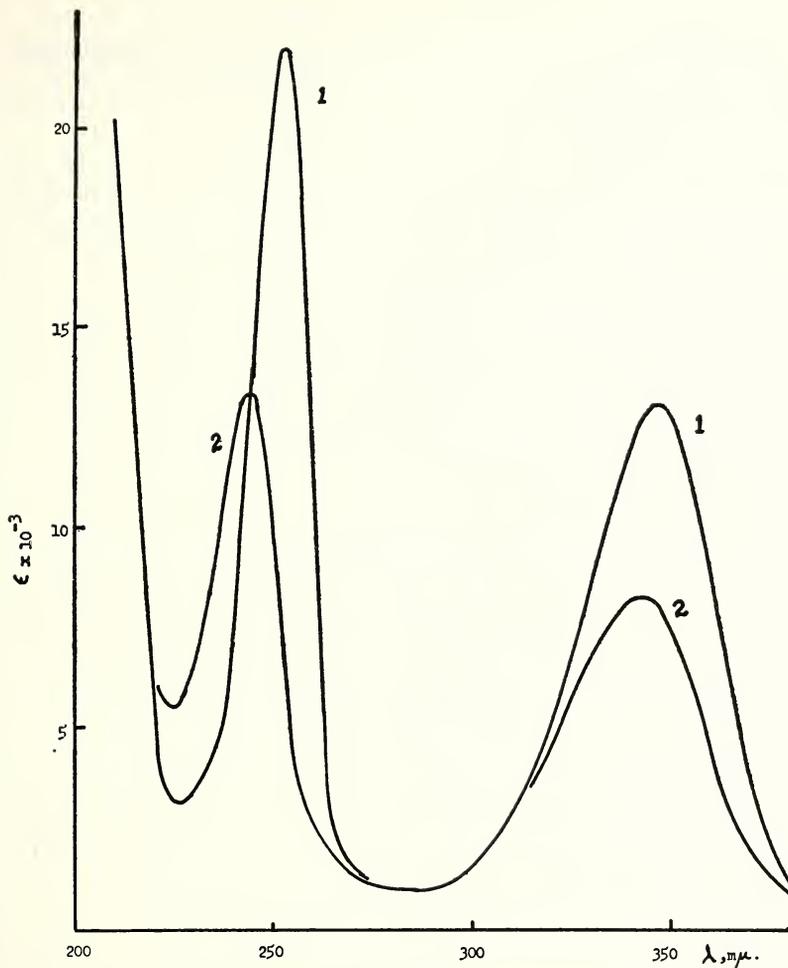


Fig. 1. Ultraviolet Spectra of (1) 1,3,5-Trimethoxybenzene and
(2) Phloroglucinol in 53.8% Perchloric Acid.

twenty minutes or allowing it to stand for over twelve hours at room temperature caused the original spectrum to change to one identical with that of phloroglucinol in the same medium. The same change occurred, but more slowly, in acids of lower concentration. Hence, 1,3,5-trimethoxybenzene cannot be identified in perchloric acid solutions significantly above 55% because hydrolysis to phloroglucinol occurs too rapidly.

The nature and identity of the spectra ($\lambda_{\max.} = 240$; $\epsilon = 10 \times 10^3$) for phloroglucinol and its trimethyl ether in 98% sulfuric acid reported by Valyasko and Voroshin (2) indicate that their results were also due to rapid hydrolysis of the ether to the unsubstituted parent compound.

Methods and Equipment

The phloroglucinol was a carefully purified and dried commercial material. The ethers were prepared by published methods (5).

The ultraviolet spectra were obtained with a Beckmann DU instrument.

The concentrations of the acid solutions were determined by titrating weighed samples with standard alkali. The solutions of the compounds were made in 25 ml. volumetric flasks using fractional milligram samples.

Literature Cited

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