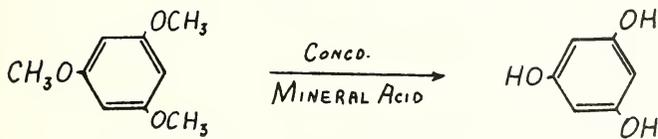
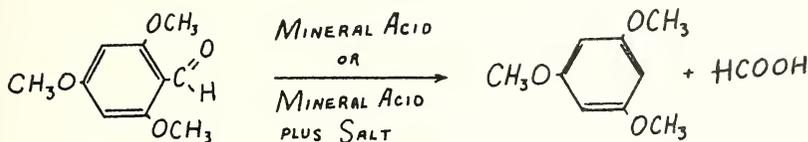


# Acid-Catalyzed Decarbonylation of 2,4,6-Trimethoxybenzaldehyde. An Anomalous Oxidation Reaction.<sup>1</sup>

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## Introduction

Normally when 2,4,6-trimethoxybenzaldehyde at ca.  $10^{-5}$  to  $10^{-4}$  molar concentration is treated with mineral acids and mineral acid salts, the only product obtained is the decarbonylation product, 1,3,5-trimethoxybenzene, or at higher acid concentrations, phloroglucinol by demethylation of the initial product (1).



## Discussion

Using perchloric acid-sodium perchlorate solutions, the sequence of changes of the ultraviolet spectrum were different from those otherwise observed, and the reaction mixture was noticeably yellow. Although decarbonylation proceeded at a comparable rate with or without the added sodium perchlorate (as indicated by following the disappearance of the 315-320  $m\mu$  absorption in the ultraviolet spectrum), the final spectra were dissimilar. The most distinctive feature was the development of a strong absorption band at 288-292  $m\mu$ . (See Fig. 1)

Similar final spectra were obtained when 1,3,5-trimethoxybenzene and phloroglucinol were substituted for 2,4,6-trimethoxybenzaldehyde, although there was a slight shift of the 288-292  $m\mu$  absorption band to a shorter wavelength in the latter case.

In order to investigate the role played by sodium perchlorate, 1,3,5-trimethoxybenzene was treated with solutions of 5.02 molar perchloric acid which were 1.00 molar in sodium chloride, 0.50 molar in magnesium perchlorate, and with a solution which was 6.00 molar in sodium perchlorate. The solution of perchloric acid-magnesium perchlorate gave results identical to those obtained using perchloric acid-sodium perchlorate; the solution of perchloric acid-sodium chloride and the solution of

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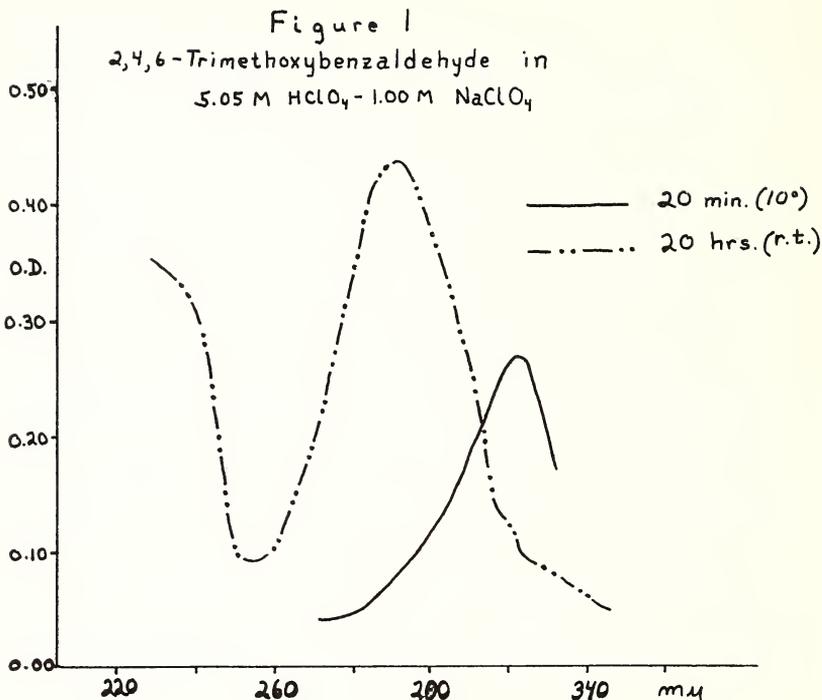


Figure 1

1. The product prepared by the published method (2) was purified by chromatography over alumina using chloroform as the solvent. The melting point of the best sample was 255-256°. The reported melting point is 253-254.5°.

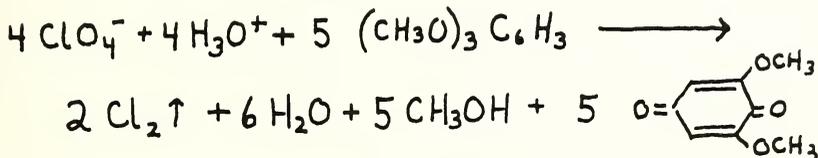
sodium perchlorate gave no absorption band in the 288-292  $m\mu$  region of the ultraviolet spectrum.

Among the possible compounds which might be producing the 288-292  $m\mu$  absorption band, an oxidation product was considered, the most probable being 2,6-dimethoxybenzoquinone-1,4. An authentic sample of this compound was prepared by a published method (2). The ultraviolet spectrum of this yellow compound in various perchloric acid-perchlorate salt and perchloric acid solutions was identical to the final spectrum observed when 1,3,5-trimethoxybenzene or 2,4,6-trimethoxybenzaldehyde were treated with perchloric acid-perchlorate salt solutions. In addition to this spectral evidence, the oxidation product from the perchloric acid-sodium perchlorate treatment was identified by isolation.

Since it seemed possible that a contaminant in the sodium perchlorate was responsible for the oxidation, several commercial samples of sodium perchlorate were tried. All gave oxidation of 1,3,5-trimethoxybenzene to the quinone. In addition, a perchloric acid-sodium perchlorate solution was prepared from concentrated stock solutions of perchloric acid and sodium hydroxide. The final solution was 3.50 molar in perchloric acid

and 4.36 molar in sodium perchlorate. When a sample of 1,3,5-trimethoxybenzene was treated with this solution, no reaction took place even after three days at room temperature or after four hours at 90°. Addition of a small amount of potassium chlorate caused the oxidation to proceed at a comparable rate to those observed in previous experiments. In 8.00 molar perchloric acid which was  $2 \times 10^{-4}$  molar in potassium chlorate, the oxidation proceeded at a rate too fast to be measured at 30°.

In order to determine the stoichiometry of the reaction, weighed amounts of 1,3,5-trimethoxybenzene were added to a solution of 8.00 molar perchloric acid which was  $2.9 \times 10^{-3}$  molar in potassium chlorate and the optical density at 290  $m\mu$  was determined after each addition. The reaction stopped corresponding to a 5:4 molar ratio of the trimethoxybenzene to potassium chlorate. A balanced equation corresponding to this ratio is shown below. The odor of chlorine was noted in those reactions producing oxidation.



### Experimental

#### Materials

The 2,4,6-trimethoxybenzaldehyde, prepared by a known method and recrystallized several times from ethanol or water, melted at 117.5-118° (3).

Perchloric acid solutions were made by appropriate dilution of analytical reagent grade concentrated acid. Acid concentration was determined by titration with sodium hydroxide. Reagent grade salts were used and their concentrations were determined by calculation.

#### Spectra

The ultraviolet absorption spectra were obtained on a Beckmann Model DU quartz spectrophotometer. The temperature was regulated to  $30.00^\circ \pm 0.03^\circ$ .

#### Isolation of 2,6-Dimethoxybenzoquinone-1,4

To 20 mg. of 2,4,6-trimethoxybenzaldehyde was added 40 ml of a solution which was 5.05 molar in perchloric acid and 2.00 molar in sodium perchlorate (analytical reagent grade, anhydrous). The mixture was warmed to 40° with shaking until the aldehyde was all dissolved and was maintained at this temperature for one hour. After dilution with 80 ml of water and cooling, the resulting yellow solution was extracted with chloroform in several portions. The yellow chloroform solution was dried over magnesium sulfate and evaporated to dryness. The yellow solid was washed three times with boiling ethanol. The insoluble residue, yellow needles, melted at 253-254°. A mixed melting point with authentic 2,6-dimethoxybenzoquinone-1,4 gave a melting point of 254-255°. The infrared spectra of the two materials were identical.

### Stoichiometry

To 25.00 ml of an 8.00 molar solution of perchloric acid was added 0.908 mg. of potassium chlorate and 0.369 mg. of 1,3,5-trimethoxybenzene. The optical density was measured at  $290\text{ m}\mu$  and was found to be 0.559. Similarly 0.710 and 1.045 mg. samples of 1,3,5-trimethoxybenzene were added giving optical densities of 0.673 and 0.671 respectively.

From this data the molar ratio of 1,3,5-trimethoxybenzene to potassium chlorate was calculated to be 5.00:4.09.

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