
NOTES

The Catalyst in the Gattermann Reaction

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The modification of Gattermann's synthesis for aromatic aldehydes has greatly increased the popularity of this reaction as a synthetic method.¹ It is noteworthy, however, that the zinc cyanide usually prepared in the laboratory is not pure, but it is stated that the material "contains no impurity that interferes with the Gattermann synthesis." We have reason to believe that these impurities are essential to the successful use of this method. An attempt to use pure zinc cyanide (prepared by Eimer and Amend, New York) for the preparation of 4-hydroxy- α -naphthaldehyde resulted in complete failure and after five hours the only product which we could isolate was the starting substance α -naphthol. We have shown repeatedly, however, that the addition of potassium chloride (0.33 mole) to this zinc cyanide will cause the reaction to take place as described when the zinc cyanide was prepared just before using. If the potassium chloride is added at the beginning of the reaction, the mixture may be decomposed after seventy minutes to give the reported yield. It also has been shown that the zinc cyanide usually employed for this reaction will not function if it is thoroughly washed with water before being dried. We have found one sample of commercial zinc cyanide (Eimer and Amend) which did not require an additional salt and gave good yields in seventy minutes. This material was partially leached with water and filtered. The filtrate gave a strong test for chloride ion. The residue after drying underwent the Gattermann reaction in one hundred minutes. The addition of sodium chloride cut this reaction time to seventy minutes.

(1) Adams and Levine, *THIS JOURNAL*, **45**, 2373 (1923).

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The Stability of Chlorine-Water Vapor Mixtures in Light

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The photochemical reaction involving chlorine and liquid water has been the subject of many

papers since its discovery by Berthollet in 1785. The most definite results are those of Allmand, Cunliffe and Madison.^{1,2} They found that solutions of hypochlorous acid as well as those of chlorine yield hydrochloric acid, oxygen and chloric acid in the same relative amounts. For each quantum absorbed, two molecules of chlorine or of hypochlorous acid are decomposed.

A search of the literature failed to disclose any investigation of the photochemical behavior of mixtures of chlorine and water vapor. Allmand, Cunliffe and Madison¹ concluded merely that the reaction, if any, in 3 cc. of vapor phase was negligible in comparison with that in 220 cc. of liquid phase.

The apparatus and method used by us to detect and measure a minimal amount of oxygen photochemically evolved from mixtures of chlorine and water vapor was a modification of that previously used for investigation of the photolysis of hydrogen sulfide.³ Purified chlorine and water were distilled separately into the quartz reaction cell. The pressure of water vapor was read on a mercury manometer and the pressure of chlorine estimated from its volume as a liquid in a calibrated tube. Capillary seals which could be broken by magnetic hammers were used consistently instead of stop-cocks. Several distillations under high vacuum served effectively to remove gases not condensable at liquid air temperature. After long exposure of the cell to radiation the extremely small amount of non-condensable gases was determined by use of a McLeod gage as previously described.³

Each value of ϕ in the last column was calculated upon the assumption that the radiation considered was the sole effective one. The small amounts of non-condensable gases found might have escaped from the walls of the cell, so that the values of ϕ may be considered as upper limits.

Schwab⁴ found that oxygen does not react perceptibly with chlorine atoms, so that oxygen once formed in our reaction mixture could scarcely have been eliminated. The experiments described above therefore indicate the absence of any photo-

(1) Allmand, Cunliffe and Madison, *J. Chem. Soc.*, **127**, 822 (1925).

(2) Allmand, Cunliffe and Madison, *ibid.*, **131**, 655 (1927).

(3) Forbes, Cline and Bradshaw, *THIS JOURNAL*, **60**, 1431 (1938).

(4) Schwab, *Z. physik. Chem.*, **178A**, 123 (1937).