NOTES

The Catalyst in the Gattermann Reaction

By Richard T. Arnold and Joseph Sprung

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).

Department of Chemistry
University of Minnesota
Minneapolis, Minnesota

Received May 16, 1938

The Stability of Chlorine–Water Vapor Mixtures in Light

By James E. Cline and George S. Forbes

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 Madison[1] 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 stopcocks. 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.

Schwab[4] 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).

DATA

Source	λ considered	P_{Cl_2} mm.	P_{H_2O} mm.	Estimated quanta absorbed	P_{O_2} mm.	Molecules O_2	$\phi \frac{O_2}{\text{quanta}}$
Mazda	Visible	2000	7.2		$<7 \times 10^{-4}$		
Hg arc	365 mμ	77	13	$>0.8 \times 10^{20}$	$<3 \times 10^{-4}$	$<8 \times 10^{15}$	$<1 \times 10^{-4}$
	313 mμ			$>1 \times 10^{20}$			$<0.8 \times 10^{-4}$
"Fluorolight"	254 mμ	2000	7.2	$>1 \times 10^{20}$	$<5 \times 10^{-4}$	$<1.3 \times 10^{15}$	$<1.3 \times 10^{-4}$

chemical reaction between chlorine and water vapor, unless the improbable hypothesis is made that all products are completely condensable at liquid air temperature.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED MAY 13, 1938

COMMUNICATIONS TO THE EDITOR

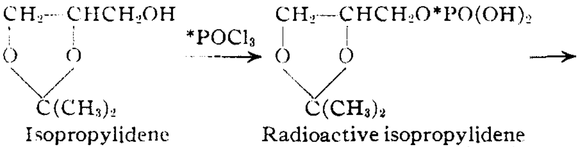
SYNTHESIS OF A RADIOACTIVE ORGANIC COMPOUND: α-GLYCEROPHOSPHORIC ACID

Sir:

The use of radioactive elements as labels in the study of metabolic processes, as initiated by G. Hevesy, already has given highly significant results in a number of cases. Most of the biochemical work accomplished so far has made use of the unstable phosphorus isotope $^{32}_{15}P$. The usual experimental procedure involves the administration to animals of a sodium phosphate solution containing a minute amount of radioactive sodium phosphate and the study of the distribution of the radioactive phosphorus in various organs or chemical fractions isolated from them. While valuable results may be obtained in this manner, it is obvious that the application of organic derivatives of radioactive phosphorus offers even greater possibilities. The development of methods for the synthesis *in vitro* of such compounds is therefore of interest. Biochemical synthesis, while theoretically possible, would be expected to yield products of lower activity and less definitely controllable composition.

For these reasons the synthesis of radioactive phosphorus oxychloride, $^*POCl_3$,[1] was carried out, which, as is well known, is an excellent reagent for the introduction of phosphoric acid into organic compounds. The radioactive phosphorus was obtained by the action of fast neutrons liberated by a radon-beryllium source on carbon disulfide. For this material we are indebted to Dr. J. R. Dunning of the Department of Physics of Columbia University. To the reddish residue remaining after the evaporation of the carbon disulfide [*cf.* O. Chievitz and G. Hevesy, *Kgl. Danske Videnskab. Selskab., Biol. Medd.*, **13**, 9 (1937)] a small amount of dry red phosphorus was added and the mixture converted into the chlorides which were sublimed at a pressure of 10^{-5} mm. The sublimate was converted into $^*PCl_3$, diluted with ordinary PCl_3 and rectified by distillation. The radioactive PCl_3 obtained was oxidized to $^*POCl_3$ by means of potassium chlorate [F. Ullmann and A. Fornaro, *Ber.*, **34**, 2172 (1901)], and the *radioactive phosphorus oxychloride* was purified by fractionation.

With this material the synthesis of *radioactive α-glycerophosphoric acid* was carried out according to E. Fischer and E. Pfähler [*Ber.*, **53**, 1606 (1920)]. The synthesis involved the following steps:



Isopropylidene glycerol

Radioactive isopropylidene α-glycerophosphoric acid

$CH_2(OH)CH(OH)CH_2O^*PO(OH)_2$

Radioactive α-glycerophosphoric acid

The barium salts of the radioactive α-glycerophosphoric acid and of its acetone derivative were both obtained in crystalline form, the former

---

[1] In writing formulas, analytical figures, etc., for compounds containing an unstable isotope it is proposed to express this fact by using an asterisk before the letter symbol for the particular element, e. g., *P, *S