

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Rigid Purification of Chlorine

BY PAUL M. FYE AND J. J. BEAVER¹

One of the most essential and yet most difficult experimental phases of gas kinetic studies involving chain reactions is the purification of the reactant gases to the extent required for consistent and reproducible work. Various anomalies of the reaction rates in photochemical studies involving chlorine have been attributed to impurities in this gas.²

Manninen³ has shown that the photochemical formation of phosgene from carbon monoxide and chlorine is either retarded or is caused to exhibit an induction period by minute amounts of impurities. These findings we have now confirmed by numerous measurements of the velocity of phosgene formation using chlorine which has been rigorously purified by a process of sublimation-crystallization at very low temperatures and pressures. Such retardation or induction period provides a means of detection of small traces of impurities present in the chlorine.

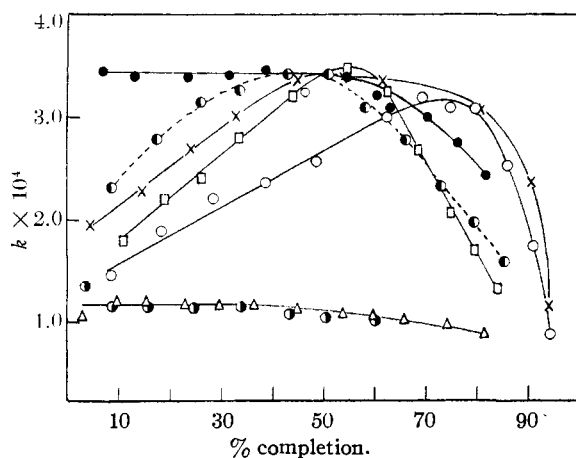


Fig. 1.—O, No. 86; Δ , 87; \square , 88; \times , 89; \bullet , 90; \bullet , 92; \bullet , 106.

The velocity measurements were carried out as follows. The cylindrical Pyrex glass reaction cell had a volume of 72.5 ml. The rate of reaction was followed at all times by the pressure decrease in the reaction cell as indicated by a quartz spiral manometer which was used as a null point instrument in conjunction with a carefully constructed

mercury manometer. All pressure measurements were made in the dark to eliminate the Draper effect. All stray light was excluded from the cell, which was contained in a thermostat regulated at $25.00 \pm 0.02^\circ$.

The illuminating system consisted of two 100-watt projection bulbs placed 32 cm. from each face of the cell. The light beam was rendered roughly parallel by two condensing lenses and filtered by glass filters (BG12 and GG3, Schott). The voltage of the lamps was regulated to 100 ± 0.10 volts by the method of Hughes and Hurka⁴ and the intensity checked by a calibrated Moll thermopile.

The entire apparatus with the exception of two quartz cells for the storage of the purified chlorine was made of Pyrex glass. All stopcocks were of a standard high-vacuum type having mercury seals and were lubricated with a phosphoric acid lubricant.⁵

The sublimation-crystallization process as finally developed consisted in passing commercial chlorine⁶ through a 70-cm. gas-washing tower filled with Pyrex glass chips containing concentrated sulfuric acid, a 6-cm. coil of 6 turns of 8-mm. Pyrex tubing immersed in a dry ice-acetone-bath (-80°), a tube maintained electrically at 350° and, finally, through a stopcock lubricated with phosphoric acid into a manifold with two successive traps maintained in boiling nitrogen (-196°). The entire train was evacuated continuously with a mercury diffusion pump backed by a Hyvac oil pump. This permitted the continuous removal of gases not condensable at -196° . The collection of the chlorine was very slow, 20 cc. of liquid chlorine collecting in seventy hours. The chlorine was then distilled between the two quartz side arms of the manifold; the temperature of the distilling chlorine was maintained at -80° and that of the condensing chlorine at -196° . The first and last fractions were discarded, each fraction being about one-tenth the total volume. After this distillation the chlorine was frozen (-196°) and pumped (10^{-5} mm. pressure) for an hour. At this point a check run still showed an induction period in the rate, indicating the presence of traces of impurities. The chlorine was then distilled from one of the quartz storage cells (-80°) to a second trap immersed in a liquid-solid mixture of ethyl bromide (-119°) with continuous pumping. The pressure maintained in the manifold was below 1 mm. of mercury and the rate of evaporation was sufficient to keep the chlorine in the first trap a solid (-101.6°). It is believed that the 17° temperature gradient within a few degrees of the melting point of chlorine which resulted in a very slow sublimation-crystallization process (15 g. in twenty-four hours) is the means of removal of the final traces of impurities. Definite crystals of chlorine two to three mm. in size were formed during the crystallization. There was no measurable change in this chlorine when stored in quartz cells at -80° over a period of several weeks.

(1) Excerpt from the thesis submitted by P. M. Fye to the Faculty of Pure Science, Columbia University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1939.

(2) Bodenstein, Lehner and Wagner, *Z. physik. Chem.*, **53**, 459 (1929); Schumaker, *ibid.*, **130**, 422 (1927); Bodenstein and Unger, *ibid.*, **511**, 256 (1931).

(3) Manninen, Columbia Dissertation, 1938.

(4) Hughes and Hurka, *Rev. Sci. Instruments*, **6**, No. 9, 289 (1935).

(5) Stevens, *THIS JOURNAL*, **52**, 635 (1930).

(6) Penfield and Cushing, *Ind. Eng. Chem.*, **31**, 377 (1939), report commercial chlorine may be secured with impurities as low as 0.2%.

Commercial chlorine was also purified by extensive distillation in a multiple-plate still designed by Crist and Brown.⁷ The highest values of the velocity constants obtained in 24 experiments using this chlorine are shown by curves nos. 87 and 90 in the accompanying figure.⁸ The corresponding constants obtained with the final crystalline product of the sublimation-crystallization process are typified by the curve no. 106. It is evident from the increased velocity of Expt. 106 that the latter chlorine is purer than that obtained by distillation.

As a further check on our results, measurements of velocity constants were made using the chlorine purified by distillation in the 240 cm. column still to which amounts of air corresponding to pressures of 1.3, 1.1, 0.6, and 0.1 mm. were added. The results thus obtained are shown in curves 86, 88, 89, and 92, respectively. These curves

(7) The design of the still together with a detailed method of operation will be published by Crist and Brown. It consisted essentially of a two-liter boiler and a 240 cm. packed column.

(8) Weber (Columbia Dissertation, 1933) found that commercial chlorine purified merely by passage in succession through a water scrubber, sulfuric acid and a heater maintained at 350°, often gave a product exhibiting the rate of phosgene formation normal for the very purest chlorine. In other cases he found that several distillations were necessary and sufficient to produce the same results. We attempted to use this method for the purification of chlorine from seven tanks but in no case did the resulting chlorine give the high velocity constants characteristic of the purest chlorine.

show an increased velocity over nos. 87 and 90 as well as the typical oxygen induction period due to the added air. Since it is difficult to account for the increase in reaction rate upon the addition of an impurity (air) and since addition of air to reaction mixtures containing the purest chlorine always resulted in a lowered rate,⁹ this is further evidence that an impurity still exists in the chlorine prepared by distillation.

The successful purification of chlorine by the sublimation-crystallization process was accomplished using chlorine from several sources. It is believed that this method can be applied wherever small amounts of extremely pure chlorine are needed.

Summary

A low-pressure sublimation-crystallization process for the rigorous purification of chlorine depending upon a 17° gradient close to the melting point of chlorine is described.

A method for the detection of traces of impurities in the chlorine utilizing the photochemical formation of phosgene is reported.

NEW YORK, N. Y.

RECEIVED SEPTEMBER 18, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Attempted Exchange of Radiophosphorus between Ortho-, Pyro- and Metaphosphoric Acids

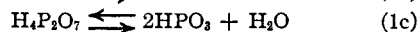
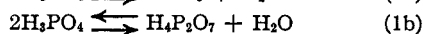
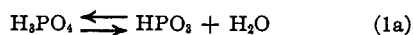
BY D. E. HULL

Several attempts have been made to discover an exchange of radioactive phosphorus between acids of phosphorus in different oxidation states, but so far no case has been found in which such exchange occurs.^{1,2} Phosphorus in the +5 oxidation state forms several acids differing in the degree of hydration, the most important of which are orthophosphoric acid, pyrophosphoric acid, and metaphosphoric acid. It would be of interest to know whether any exchange of phosphorus takes place between these acids in aqueous solution under various conditions of concentration, acidity, and temperature. This paper is to report a few exploratory experiments carried out in dilute solutions.

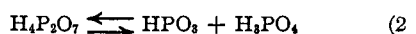
In aqueous solution the ortho acid is the stable form; both the meta and the pyro acids change to the ortho. The change is fairly slow at room temperature, requiring something less than one day for half conversion of the meta acid, and about

four days for the pyro.³ The rate is accelerated by an increase in concentration, acidity, or temperature. The pyro acid is ordinarily an intermediate in the conversion of the meta acid to ortho. In order that these reactions might not obscure the results of an attempted exchange, the more hydrated acid was the one marked with the radioactive indicator in each case, and the less hydrated acid was used in the inactive form.

We may postulate two mechanisms by which an exchange could be effected between the acids of +5 phosphorus. First, reactions in which water is reversibly split off and taken up, thus



Secondly, a reaction whereby pyrophosphoric acid dissociates reversibly into the ortho and meta acids



(1) Perrier and Segre, *Ricerca sci.*, **9**, 638 (1938).

(2) Wilson, *This Journal*, **60**, 2697 (1938).

(3) Durgin, Lum and Malowan, *Trans. Am. Inst. Chem. Engs.*, **33**, 643 (1937).