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The Addition Reaction of Phosphorus Trifluoride with Chlorine

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The addition of phosphorus trifluoride vapor to chlorine vapor is complete at room temperature within 1% or less. The reaction is photosensitive and is catalyzed by glass surfaces; the homogeneous dark reaction, if it occurs at all, is much slower than the heterogeneous reaction; the latter has a negative temperature coefficient. The liquefied product of the reaction rapidly attacks glass at room temperature.

Some years ago a preliminary study of the kinetics of the above reaction was made using all glass reaction vessels.[2] The work was discontinued because the reaction was found to be heterogeneous with rates difficult to reproduce. The findings are summarized here for the benefit of others who may be interested in this reaction.

(1) At 0° in lightly baked out Pyrex glass vessels (150°, 10^{-5} mm.) the vapor-phase addition reaction goes to completion within experimental error as judged from pressure measurements (final pressure of product PF_3Cl_2, 12–20 cm.; final pressure of the reactant in excess, 0.6 to 4.0 cm.; reaction complete within 1% or better).

(2) Under these conditions the reaction is heterogeneous; the rate follows the equation

$$\frac{d}{dt}(PF_3Cl_2) = k\frac{S}{V}\frac{(PF_3)(Cl_2)}{1 - ap}$$

where p is the total pressure and S/V is the ratio of surface to volume of the reaction vessel. The values of k and of a usually remained sensibly constant during a reaction but varied from experiment to experiment. The value of a usually fell in the range 0.010 to 0.013 (cm.)$^{-1}$, though in one case it fell to 0.00; it showed no obvious correlation with the magnitude of the specific surface, which varied over the range 0.90 to 5.75 cm.$^{-1}$. The value of k varied with the treatment of the glass surface; with glass that had been exposed to a previous reaction, rinsed with distilled water and baked out, it covered the range 8.0 to 11.5 cm.^{4} mole^{-1} sec.$^{-1}$ in four experiments. With new glass k was about 6. Coating the glass with potassium chloride had little effect on the rate; in a vessel coated with silver chloride the rate was approximately doubled and the kinetics were erratic.

(3) The rate of the reaction was approximately halved by raising the temperature from 0 to 25°.

(4) At 25° the rate in a paraffin-coated glass vessel was less than one-tenth as great as in a similar uncoated glass vessel; whether the reaction is still heterogeneous under these conditions was not established. The reaction is photosensitive in glass, being accelerated approximately 2.5-fold by exposure to a 100-watt incandescent lamp and reflector placed beside a 300-ml. Pyrex reaction vessel (in all other experiments the reaction vessel was protected from light).

(5) The reaction in the liquid phase at temperatures below the boiling point of the mixture at a few cm. pressure is many-fold more rapid than it is in the gas phase at 0°. Whether this liquid-phase reaction is heterogeneous was not established.

(6) The liquefied product of the reaction (frozen out together with excess reactant, sealed in a glass tube and warmed) rapidly attacks glass at room temperature. Small flocks of fluffy white material appear in the liquid and increase in amount; in a few hours the initially clear liquid is replaced by a gelatinous mass which is white or yellow depending on whether phosphorous trifluoride or chlorine is present in excess. The nature of this reaction was not investigated; it may have been catalyzed by traces of water sorbed on the walls of the reaction vessel.

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[1] Shell Development Company, Emeryville, California.

[2] J. N. Wilson, disssertation, California Institute of Technology, 1939.