PHOTOREDUCTION OF GASEOUS IRON(III) CHLORIDE WITH SUNLIGHT AND OTHER LIGHT SOURCES

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Preliminary experiments demonstrate that light in the wavelength range 300-450 nm will photoreduce iron(III) chloride vapor at 160-250°C to iron(II) chloride and chlorine.

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We have observed that gaseous iron(III) chloride can be photoreduced with sunlight, and with light from various tungsten lamps, to a white solid, with concomitant generation of chlorine gas, identified by its absorption spectrum. While the white solid was not subjected to elemental analysis, its appearance, volatility and high temperature vapor absorption spectrum were found to correspond to those of iron(II) chloride.(1,2) Samples were prepared in a Pyrex-quartz high vacuum system with precautions to ensure the absence of water vapor and oxygen. Reduction of iron(III) chloride is an essential step in numerous metallurgical and chemical processes and in certain thermochemical cycles proposed for the production of hydrogen from water.(3,4) It is believed that photoreduction may serve to increase the overall efficiency of such operations markedly. Photoreduction of iron(III) chloride coupled with the back-reaction of iron(II) chloride with chlorine may also have potential as an energy storage system.

Photoreduction of gaseous iron(III) chloride apparently has not been reported previously. Photolysis of iron(III) chloride in various solvents and in various photoinduced chlorination and polymerization processes has been described.(5) However in these systems irreversible changes involving solvated iron(III) complexes and free radicals, which react with the solvent and/or other solute species, are believed to occur.(5,6) In a recent resonance Raman laser activation study of $Fe_2Cl_6(g)$ and $FeCl_3(g)$, the formation of solid iron(II) chloride at the point of entrance of the beam was reported without mention of the possibility of photolytic reduction.(7)

Photolysis was not detected in our earlier spectrophotometric studies of iron(III) chloride (the sample preparation and handling techniques described there were also used in the present work) (8,9) Observations made in the present work indicate that the effect would not have been noticed in experiments above 300°C where the back reaction of chlorine and iron(II) chloride appears sufficiently rapid to maintain virtually normal thermal equilibrium concentrations even under continuous illumination in the spectrophotometer. At lower temperatures, where the back reaction is relatively slow, saturation vapor pressures above FeCl₃(s) were studied; here, photolyzed vapor can be replaced by vaporization of some of the excess solid phase present during the brief periods of illumination. However, photolysis in the spectrophotometer is readily noticeable, causing a decrease in the concentration of Fe₂Cl₆(g) molecules, when a completely vaporized sample at temperatures between 160 and 250°C is illuminated with light in the wavelength interval 300 to 450 nm.

Following are results of preliminary studies. With a Quartzline lamp (General Electric Co.) in the visible source compartment of the Cary 14H Spectrophotometer (light passes through the monochromator after it has passed through the sample) Corning Glass color filters were used to restrict the photolyzing wavelengths. Fig. 1 shows, for one sample, the time dependence of the concentration of $Fe_2Cl_6(g)$, indicated by measuring (with the color filter removed for a few sec-

onds) the absorbance at 360 nm.(9,10) As photolysis progressed corrections to the baseline were necessitated by deposition on the cell windows of white $\operatorname{FeCl}_2(s)$, which reduced the radiant flux entering the cell. The baselines obtained before vaporizing the sample and after quenching it from the final steady state were compared. A fraction (amount of $\operatorname{Fe}_2\operatorname{Cl}_6$ reduced/total reduced at steady state) of the total shift of the baseline was subtracted from each absorbance measured during the approach to the steady state. After a given series of measurements the initial concentration of $\operatorname{Fe}_2\operatorname{Cl}_6$ was quickly restored by increasing the sample temperature above 300°C. The rate of recombination of $\operatorname{FeCl}_2(s)$ and $\operatorname{Cl}_2(g)$ was followed at 185°C by allowing a photolyzed mixture to stand in the "dark", with brief illumination to measure the absorbance only at the indicated times (Fig. 1). The low molar absorptivity of chlorine precluded direct measurement of its concentration in these experiments.



Fig. 1

Time dependence of $Fe_2Cl_6(g)$ concentration. Quartz cell, 10 cm path length, 19 mm i.d., volume 29 cm³. Light source: Quartzline lamp with color filters (beam cross section 0.95 cm²); wavelength range (nm) and initial radiant flux (milliwatt) for the various series of measurements were: (a) unfiltered; 6.5 (b) $\lambda > 300$, 6.1 (c) $\lambda > 350$, 5.7 (d) $\lambda > 410$, 5.1 (e) $\lambda > 480$, 5.3 (f) $\lambda > 520$, 5.4. The time scale for the recombination rate curve ----- must be multiplied by ten.

The same sample was also heated to <u>ca</u>. 200°C in a cylindrical furnace (one closed end) and exposed to sunlight for 15 minutes. Subsequent measurement of the vapor absorbance (at 185° C) showed that 70% of the Fe₂Cl₆(g) had been photolyzed. When sunlight was focused (with a simple 4 inch magnifying reading lens) on another sample of solid FeCl₃ in an evacuated Pyrex container, a white deposit, presumably FeCl₂, appeared immediately at the point of entrance of the beam.

In another series of experiments <u>ca</u>.10 mg of FeCl₃ (giving an excess of solid) in a 1 cm quartz cell (volume 4 cm³) was photolyzed in the Cary 14H at 200°C with unfiltered light until sufficient chlorine was generated to determine, with reasonable accuracy, its concentration $(4 \times 10^{-4} \text{ M})$ from its absorbance at room temperature.(11) The fine white crystals of FeCl₂ which deposited on the walls of the cell during this exposure increasingly limited the entry of light until photolysis was virtually stopped. After the FeCl₂ was sublimed off the windows (with a flame and with chlorine condensed in a side arm cooled with liquid nitrogen), photolytic reduction of the remaining FeCl₃ could be continued. It was found that two 500 watt Radiant spotlight bulbs (mounted in parabolic caluminum reflectors placed on opposite sides of the sample) simultaneously illuminated and heated the cell to <u>ca</u>. 200°C and gave a more intense light source which

greatly increased the rate of formation of chlorine. Deposition of FeCl_2 was still a problem, however. After clearing the windows several times, a pressure as high as 60 torr of Cl_2 (as indicated by its absorbance) was developed in the cell. Illumination of the sample while the side arm was immersed in liquid nitrogen led to sublimation of FeCl₃ without appreciable reduction. Apparently, under these conditions, the vapor concentration of Fe₂Cl₆ was not high enough in the evacuated cell for photolysis to occur at an appreciable rate.

The approach to a steady state seen in Fig. 1 appears to represent a balance between the rate of photolysis and the back-reaction of chlorine and FeCl_2 . We see no definite evidence in these preliminary experiments that the chlorine concentration affects the actual rate of photolysis; the rate appears to depend mainly on the Fe_2Cl_6 vapor concentration and the radiant energy wavelength and density.

Photolysis of a third sample (<u>ca</u>. 10 mg FeCl₃, 10 cm quartz cell, volume 30 cm³, 19 mm i.d.) to which a pressure of 376 torr of N_2 (at 25°C) was also added, led to formation of larger crystals of FeCl₂. These seemed to interfere less with the transmission of light and gave significantly improved rates of reduction, both in the Cary 14H and with spotlight illumination.

It is suggested that solar energy (perhaps supplemented by other suitable low level heat sources) might be used to heat iron(III) chloride to temperatures of 160 to 200° C, sufficient to permit vapor phase photolysis by the sunlight. While the reaction $\text{Fe}_2\text{Cl}_6(g) = 2 \text{ FeCl}_2(s) + \text{Cl}_2(g)$ is slightly exothermic, in the vicinity of 500 K AG^o = - 6200 + 16.6 T,(1) the unfavorable entropy change leads to a very small equilibrium pressure of chlorine at these temperatures. However, photolysis drives the reaction to the right. In the presence of an excess of solid iron(III) chloride, vapor removed by photolysis would be replaced by the endothermic vaporization of the solid, for which $\Delta G^o = 32700 - 56.0 \text{ T cal.}(1)$ giving a net capture (from the heat source) of 26.5 kcal mole⁻¹ of chlorine. By trapping or cooling the products, the release of this energy by the reverse reaction 2 FeCl₂(s) + Cl₂(g) = 2 FeCl₃(s) could be delayed, giving the possibility of a cyclic energy capture system. A somewhat similar cycle based on the photolysis of aqueous iron(III) bromide has also been suggested.(12)

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