[CONTRIBUTION FROM CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, THE FIRESTONE TIRE AND RUBBER CO.]

Quantum Yields of Decomposition Products from the Copolymer of Vinylidene and Vinyl Chloride

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I. Introduction

A number of investigators have studied the loss of hydrogen chloride from chloride-containing polymers under the influence of heat or light.[1,2,3,4] However, no quantitative relation between amount of hydrogen chloride evolved and light absorbed by solid polymer films has been reported. In view of the commercial importance of the coloration and embrittlement of polymers by ultraviolet light it was decided to make a quantitative study.

Solid films of 90/10 vinylidene chloride–vinyl chloride copolymer have been decomposed in a special thin quartz cell using substantially monochromatic light of 2537 Å. wave length; the quantity of light absorbed and amount of hydrogen chloride evolved have been measured. The production of another condensable gas, probably water, has been observed.

II. Experimental Details

Preparation of Polymer Films.—Saran B115 powder from Dow Chemical Company was extracted with petroleum ether in a Soxhlet extractor for several days to remove plasticizer and stabilizer. The resulting material was a 90/10 copolymer of vinylidene chloride and vinyl chloride, and will be referred to here as "polyvinylidene chloride" for the sake of brevity.

The powder was pressed into films using a small size platen steam press at 180°. All films were carefully checked with a hand micrometer after cutting into shape to fit the reaction cell: Any film not measuring exactly 0.005 in. thick was discarded. After cutting, the slips of film were stored in a desiccator for at least a week to allow any residual water to diffuse out.

Light Source and Intensity Measurement.—A Hanovia SC-2537 tube was used as a light source. This source supplies mostly 2537 and 1849 Å. radiation; the latter was removed by a one centimeter path of 0.167 molar acetic acid.[5] Radiation obtained in this way is about 90% 2537 Å. and 10% visible light. Indirect confirmation of the wave length of the source was obtained by measuring the absorption spectrum of the 5 mil. polyvinylidene chloride film. The optical density was 0.78 at 2537 Å. corresponding to 70% absorption. Average absorption of the films measured with the 2537 Å. source and using the phototube as described below was 66%, indicating satisfactory agreement. The absorption of the film falls off quite rapidly as longer wave lengths are approached.

Quartz lenses and a diaphragm were used to condense the light into a narrow beam passing through the polymer film and focusing on the cathode of the phototube directly behind the reaction vessel. The reaction vessel was constructed of quartz by the Eck and Krebs Company. It consists of a quartz tube of 22 mm. i.d. flattened at one end in such a way as to contain and support the film between two plane quartz faces about 0.007 in. apart. The flattened portion measures about 2 × 2 cm. and is shaped so that the film can be readily slipped in and out from the top. The quartz tube is connected through a graded seal to a pyrex tube which is in turn connected to the vacuum system. At the end of each run the pyrex tube was cut off, the polymer film removed, new film inserted, and the pyrex tube joined again to the vacuum system. The 22 mm. i.d. quartz and pyrex tube allowed plenty of room to manipulate the film in and out of the flattened section of the tube.

Light intensity was measured with an RCA phototube no. 935. This tube exhibits high sensitivity in the ultraviolet and low sensitivity to visible light. A potential of 125 volts d. c. was impressed on the phototube when measuring light intensity, and it was connected through an appropriate Ayrton shunt arrangement to a Leeds and Northrup 2500-f galvanometer. This galvanometer is of the swinging mirror type and the deflection is read by means of a telescope and scale arrangement. The sensitivity of the galvanometer is about 10^{-4} microampere.

Centimeters of galvanometer deflection were calibrated in terms of quanta per second by using the oxalate actinometer. The actinometer solution was 0.001 molar in uranyl oxalate and 0.005 molar in oxalic acid. The calibration procedure consisted in determining the rate of oxalate decomposition corresponding to a given galvanometer deflection. The amount of oxalate decomposed was determined by titration with 0.01 N potassium permanganate solution, and since the quantum yield of oxalate decomposition was known[6] the light intensity in quanta/second could be calculated. The result was corrected for reflection of light from the face of the acti-

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[1] R. F. Boyer, *J. Phys. and Colloid Chem.*, **51**, 80 (1947).

[2] C. S. Marvel, G. D. Jones, T. W. Mastin and G. L. Schertz, THIS JOURNAL, **64**, 2356 (1942).

[3] C. S. Marvel, J. H. Sample and M. F. Roy, *ibid.*, **61**, 3241 (1939).

[4] R. M. Fuoss, *Trans. Electrochem. Soc.*, **74**, 110 (1938).

[5] J. E. Cline and G. S. Forbes, THIS JOURNAL, **61**, 717 (1939).

[6] G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

nometer cell.[7] The absorption of the 2537 Å. light increased from about 66% at the start of the run to as much as 85% at the end, depending upon the duration of the run and the intensity employed. The constancy of the light source was quite good; intensity rarely changed more than 1 or 2% during the run.

Quartz Fiber Gage.—In the early experiments on the irradiation of polyvinylidene chloride film it was found that two distinct product gases were being produced, one condensable by cooling with Dry Ice and acetone and the other only condensable by liquid nitrogen. The one not condensable by Dry Ice was identified as hydrogen chloride on the grounds of its high vapor pressure at low temperature, the fact that it was completely absorbed by dry sodium hydroxide, and the fact that hydrogen chloride had been identified as a product by other workers. The other product, showing less than one micron of pressure at dry ice temperature, was tentatively assumed to be water because it was also completely absorbed by dry sodium hydroxide, and because of its vapor pressure behavior as described below.

It was therefore necessary to measure the pressure of two gases as a function of time during the irradiation of the film. It was found possible to do this by using the quartz fiber gage. The bifilar type of gage suggested by Coolidge[8] was used in which a small glass pointer suspended from two thin quartz filaments swings back and forth before a scale. The time for the amplitude of the swing to decrease by half can be measured with a stop watch and related to the gas pressure by the following equation[9]

$$P = \frac{B}{\sqrt{M}}\left(\frac{1}{t_{1/2}}\right) - \frac{C}{\sqrt{M}} \qquad (1)$$

where P is the pressure of the gas, M is the molecular weight of the gas, $t_{1/2}$ is the half damping time of the swing, and B and C are constants characteristic of the gage. A plot of P *versus* the reciprocal of the half damping time gives a straight line. Such a plot was made using pure, dry oxygen and B was calculated to be 6.68 from the slope of the line. The data are shown in Table I. From the reciprocal of the half damping time in a vacuum, C was found to be 0.0003. Knowing the gage constants, B and C, and the molecular weights of water and hydrogen chloride, calibration curves of each of these gases relating pressure to gage damping time were drawn.

Oxygen pressures were measured with a McLeod gage. Pumping out was always accomplished using a mercury diffusion pump backed by a Cenco Hyvac pump; mercury diffusion into the quartz fiber gage was prevented by a Dry Ice trap.

TABLE I

CALIBRATION OF QUARTZ FIBER GAGE WITH OXYGEN

P, mm.	$t_{1/2}$, sec.	B
0.0295	41	6.86
.0210	56	6.70
.0165	72	6.76
.0129	92	6.77
.0096	115	6.26
.0076	155	6.73
.0032	312	5.75
.0012	1,020	7.21
~ .00001	22,300	..

To measure water vapor pressure in a mixture of water vapor and hydrogen chloride, the water was first frozen out in a Dry Ice trap and the pressure of hydrogen chloride alone measured. Then equation (2) was utilized[9]

$$P_1\sqrt{M_1} + P_2\sqrt{M_2} = B\left(\frac{1}{t_{1/2}}\right) - C \qquad (2)$$

where P_1 and P_2 are the pressures of the two gases, M_1 and M_2 are the corresponding molecular weights, and the other symbols are as defined above. It was shown that water vapor pressure in a mixture of water vapor and hydrogen chloride vapor could be calculated with good accuracy by reading the total pressure on the water calibration curve and subtracting 1.42 times the known hydrogen chloride pressure. The calibration curve for oxygen departs from linearity above about 0.030 mm., but water and hydrogen chloride pressures above this value can be approximated by applying an empirical correction.

It can be seen that equation (1) provides an approximate method for the determination of the molecular weight of a gas by measuring the damping time at several known pressures. This method was applied in the case of the HCl product, using a McLeod gage to measure pressures. A value of about 36 was found for the molecular weight (actual 36.45), supplying further confirmation of the identity of the hydrogen chloride.

The quartz fiber gage was used to measure the vapor pressure of the product mixture as a function of temperature. Plotting vapor pressure *versus* temperature was suggested by Sebastian and Howard[10] as a means of analysis for small quantities of gases. When a mixture of gases is slowly warmed from a sub-zero temperature each gas begins to vaporize at a temperature quite characteristic of the gas.

In the present case the product gases were condensed in a trap immersed in ethyl alcohol enclosed by a liquid nitrogen bath. After evaporation of the liquid nitrogen the temperature of the alcohol rose slowly, about 1° every five minutes. Pressures were read on the fiber gage and temperature measured with a pentane thermometer; the data are plotted in Fig. 1. Below −80° only the vapor pressure of the hydrogen chloride

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(7) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 84.

(8) A. S. Coolidge, THIS JOURNAL, **45**, 1637 (1923).

(9) S. Dushman, "Scientific Foundations of High Vacuum Technique," John Wiley and Sons, New York, N. Y., 1949, p. 284.

(10) Sebastian and Howard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 172 (1934).

is measured. The second gas to come off shows a vapor pressure of about one micron at −72°; the known vapor pressure of water is one micron at −75°. This agreement may be taken as tentative identification of the second gas as water vapor.

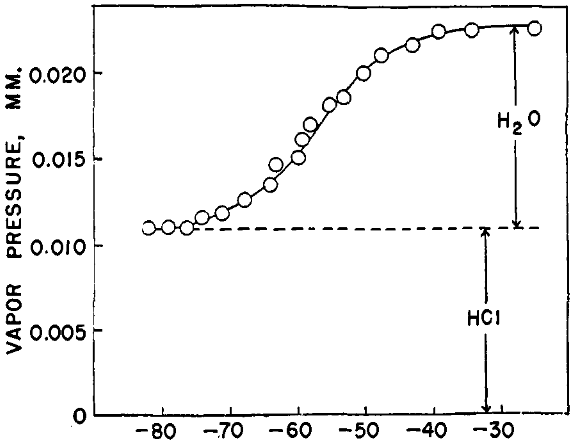

Fig. 1.—Vapor pressure of typical product mixture *versus* temperature; 90/10 copolymer of vinylidene chloride–vinyl chloride, 2537Å.

Experimental Procedure.—In making a run, a slip of polymer film was placed in the reaction cell and its light absorption measured; the proper correction was applied for absorption and reflection of light by the quartz surfaces of the cell. The apparatus was then pumped out overnight before starting the run. Pumping out was always done through a long spiral trap immersed in liquid nitrogen to prevent the slightest diffusion of mercury into the reaction cell or the quartz fiber gage. After the pumping out treatment the diffusion of dissolved gases from the film in the dark amounted to considerably less than 0.001 mm. per day, as repeatedly checked.

In calculating quantum yields, the total quanta absorbed by the film were calculated by multiplying quanta absorbed per second by duration of the run in seconds. The light absorption used was always taken as the value measured at the start of the run; as the run progressed the light absorption of the film increased because brown colored substances were formed in addition to the clear polymeric material. No correction was made for reflection from the face of the polymer film since insufficient data were available on the magnitude of this reflection. The molecules of water or hydrogen chloride produced in a run were calculated from the measured pressure and known volume of the reaction system, 513 cc., and quantum yields are equal to the total number of molecules produced divided by the total number of quanta absorbed. In making a run, the reaction system was sealed off from the McLeod gage and pumps so that the product gases came in contact with clean pyrex and quartz walls only.

III. Results and Discussion

Figure 2 shows the typical results obtained when a film of polyvinylidene chloride is irradiated with 2537 Å. light. There was always an induction period of one to five hours before the hydrogen chloride began to come off; the lower the intensity the longer the induction period. Some question arose as to whether the induction period was caused by a small amount of remaining stabilizer which had not been extracted. To check this point, runs were made on films of Saran B118-3234, a polymer of the same composition but prepared without stabilizer and made available through the courtesy of the Dow Chemical Company; the induction period remained as before. In calculating quantum yields the steady, linear rate of hydrogen chloride evolution after the induction period was always used.

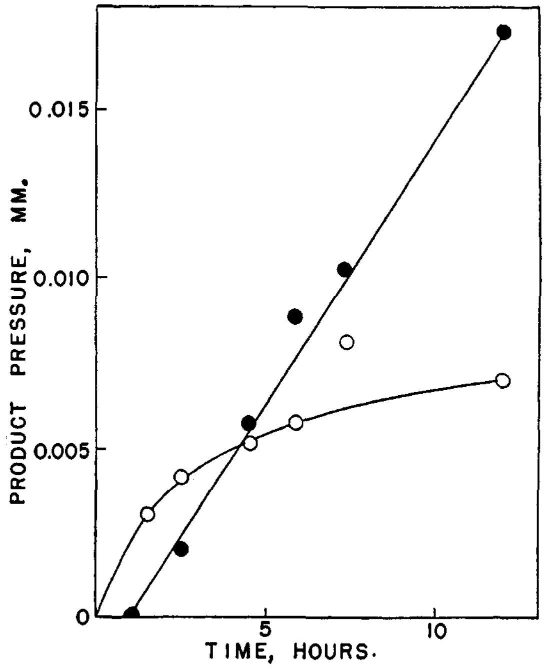

Fig. 2.—●, HCl; O, H_2O; typical high intensity run; 12.3×10^{14} quanta/second; 2537Å.; 90/10 copolymer of vinylidene–vinyl chloride.

At the absorbed intensity of the run shown in Fig. 2, 12×10^{14} quanta per second, water always evolved rapidly at first and then slowed down after a few hours. At intensities of the order of 1×10^{14} quanta per second the evolution of water was generally linear with time from the start of the irradiation. In the case of both water and hydrogen chloride the rates fell off markedly after about 20 microns had been evolved. In calculating quantum yields for water the linear evolution following the rapid initial burst was used. Quantum yield results for water were very erratic and hard to reproduce; this would be expected since the water must be produced from small, variable quantities of oxygen-containing impurities present in the film. These oxygen-containing impurities may be peroxidic in nature; vinylidene chloride is known to form peroxides with ease, even at Dry Ice temperature,[11] so that some peroxides might have formed during the original polymerization.

There seemed to be a trend toward higher quantum yields of water at lower values of absorbed intensity; thus at 0.93×10^{14} quanta/sec. the quantum yield was 1.60×10^{-2}, compared with 0.13×10^{-2} at 12.3×10^{14} quanta/sec. However, yields of water were very erratic, and it was produced from impurities; hence this relation is of doubtful significance.

Quantum yields of hydrogen chloride at various intensities are presented in Fig. 3. The yield appears to be independent of intensity in this range, at least within experimental error. It can be seen from the graph that the average deviation from the mean is about ±10%.

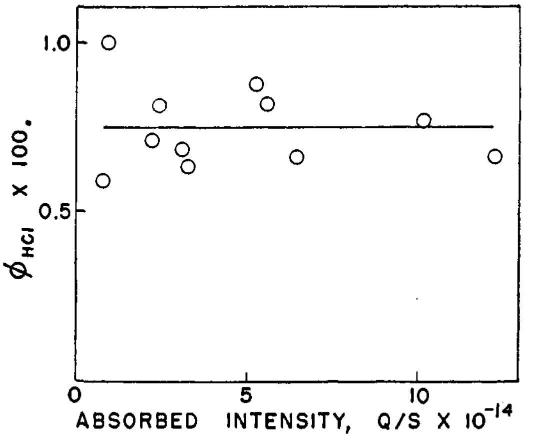

Fig. 3.—Quantum yield of hydrogen chloride *versus* absorbed intensity; 2537Å.; 90/10 copolymer of vinylidene chloride–vinyl chloride.

The small size of the quantum yield of hydrogen chloride is noteworthy. In a typical run the light passed through a volume of film weighing about 0.01 g., and 0.020 mm. of hydrogen chloride was liberated in a volume of 513 cc. Assuming a polymer molecular weight of 20,000 it can be seen that about one molecule of hydrogen chloride was lost per molecule of polymer. The average molecule contains about 200 monomer units, so that one out of every 200 monomer units lost hydrogen chloride.

The film always developed a deep yellow-brown color in the area irradiated. It has been shown by G. N. Lewis[12] that in order to observe color in a system of carbon–carbon double bonds about four or five double bonds must occur in conjugation. In the present experiments the four or five molecules of hydrogen chloride would be lost from the same polymer molecule in only a small fraction of the cases. It was also observed that visible color appeared in the polymer film near the start of the run when only 10% or less of the total hydrogen chloride loss had occurred.

From these observations it appears unlikely that the characteristic yellow-brown color of irradiated polyvinylidene chloride results from conjugation produced by hydrogen chloride loss alone. It would seem more reasonable that part of the color results from the action of light on the oxygen-containing impurities known to be present.

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Summary

1. Quantum yield of HCl evolution from the solid copolymer of vinylidene and vinyl chloride is essentially constant at 0.7×10^{-2} over a tenfold range of intensity using 2537 Å. light.

2. Yield of hydrogen chloride is so small that production of colored systems of conjugated double bonds by hydrogen chloride loss alone is questionable.

3. Evolution of another product gas, probably water, was observed.

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[11] Pamphlet, "Handling Precautions for Vinylidene Chloride," Dow Chemical Company.

[12] G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).