the initial rate by the second order path is 2.4×10^{-4} mole l.$^{-1}$ min.$^{-1}$. When a mole of Ce(IV) is added for each mole of $TSCP^+$ (expt. 7, Table III) the initial rate decreases to 2.5×10^{-5} mole l.$^{-1}$ min.$^{-1}$. It is evident that ceric ion wipes out the second order path completely, substituting for it the first order path, which, at certain concentration levels, is actually slower. A reasonable interpretation for the behavior is that Ce(IV) changes the state of $TSCP^+$ to a type of colloid in which the first order path can operate. This does not necessarily mean that $TSCP^+$ in 68% H_3PO_4 without excess Ce(IV) is homogeneously distributed. It may be present in a colloid structure highly diluted by the solvent, the separation of the molecules of $TSCP^+$ therefore depending on concentration.

The quantitative data discussed in the preceding paragraph show that the solvent exerts an important influence in determining the lifetime of the intermediate by affecting its physical state. The acidity of the medium is another important factor affecting the lifetime. The observations suggest that ring rupture in the phthalocyanine radical is an acid-catalyzed reaction. Another factor in determining lifetime apparently is the activity of water in the reaction medium. This influence is not unexpected since water is a reactant in the net two-electron oxidation. A consideration of these factors makes it seem likely that systems can be formed in which the phthalocyanine radicals have longer life than in those investigated. A promising possibility for further investigation would appear to be systems in which the phthalocyanines are adsorbed on surfaces.

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CHICAGO, ILL. RECEIVED NOVEMBER 8, 1950

[CONTRIBUTION FROM THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN]

The Dehalogenation Reaction. I. Dechlorination of Vinyl Chloride/Vinyl Acetate Copolymers[1]

BY TURNER ALFREY, JR., HOWARD C. HAAS[1] AND CHARLES W. LEWIS

The reaction of polyvinyl chloride and vinyl chloride/vinyl acetate copolymers with zinc, in dioxane, is accelerated by zinc chloride. Polyvinyl chloride dehalogenates to the extent of 86–87% in agreement with Marvel, *et al.*, and Flory. The dechlorination of the copolymers also proceeds to approximately 86%. This indicates that the reaction does not consist simply of the random removal of 1,3 pairs of chlorine atoms to form cyclopropane rings, with vinyl acetate acting as an inert spacer. Simultaneous removal of acetate and chloride, to form zinc chloride–acetate, would account for the high extent of dechlorination in the low-vinyl chloride copolymers; acetate ion is found in the reaction product.

Marvel, Sample and Roy[2] studied the dechlorination of polyvinyl chloride by zinc and observed that 84–86% of the chlorine was removed. The result was in good agreement with the theoretical value of 86.4% predicted by Flory[3] for a head-to-tail polymer and a random removal of pairs of adjacent chlorine atoms. Extension of Flory's theory to the case of vinyl chloride copolymers was made by Wall[4] and Merz, *et al.*[5] These latter treatments assumed that units of the co-monomer (*e.g.*, vinyl acetate) served as inert spacers between sequences of vinyl chloride units, and led to the prediction that the fraction of chlorine removed by zinc should decrease with decreasing mole fraction of vinyl chloride in the copolymer according to the expression

$$f = 1 - e^{-2P_{11}} \qquad (1)$$

(In the special case of vinyl chloride/vinyl acetate copolymers, P_{11} is very nearly equal to the *mole fraction* of vinyl chloride). Marvel and co-workers[6] carried out an experimental study of the dechlorination of vinyl chloride/vinyl acetate copolymers, and observed that the fraction of chlorine removed did decrease with decreasing vinyl chloride content, in approximate agreement with equation (1).

We have now studied this reaction in more detail, and have found that copolymers of different compositions differ in the *rate* of dechlorination, rather than in the final limiting extent of reaction. When sufficient time is allowed, copolymers ranging in composition from 40 to 100 mole per cent. vinyl chloride reach a limiting value for the removal of chlorine of about 87%. Furthermore, the dechlorination reaction has been found to be affected by zinc chloride. Traces of zinc chloride eliminate the induction period otherwise observed and markedly accelerate the dechlorination. By use of zinc chloride, copolymers of low vinyl chloride content, which underwent essentially no reaction with zinc alone within 400 hours, were dechlorinated to approximately the same extent as the other copolymers.

Experimental

Vinyl chloride (Monsanto) was purified as described previously.[7] Polyvinyl chloride was prepared by solution polymerization at 67° of the following mixture: C.P. methanol, 40 ml.; vinyl chloride, 15 g.; benzoyl peroxide, 50 mg. The polymer was purified by precipitation in hexane from a dioxane–methylethyl ketone mixture, filtered and dried in vacuum. *Anal.* Calcd. Cl, 56.7. Found: Cl, 56.6.

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[1] Taken in part from the Ph.D. thesis submitted by Howard C. Haas, Polytechnic Institute of Brooklyn, November, 1948.

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

[3] P. J. Flory, *ibid.*, **61**, 1518 (1939).

[4] F. T. Wall, *ibid.*, **62**, 803 (1940).

[5] E. Merz, T. Alfrey and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

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

[7] P. Agron, T. Alfrey, Jr., J. Bohrer, H. C. Haas and H. Wechsler, *J. Polymer Sci.*, **3**, 156 (1948).

Vinyl chloride/vinyl acetate copolymers were prepared by low conversion bulk polymerization at 68°.[7] Table I lists the composition of the samples selected for study.

TABLE I

Sample	Mole fraction of vinyl chloride in copolymer	Sample	Mole fraction of vinyl chloride in copolymer
A	1.00	G	0.45
B	0.93	H	.25
C	.85	I	.17
D	.70	J	.30
E	.58	K	.21
F	.53	L	.14

C.P. zinc dust was purified as described by Marvel.[2] Dioxane (Will Corporation, Technical) was purified by refluxing with hydrochloric acid and then with sodium as described by Fieser.[8] This purification was found to be absolutely necessary; freshly distilled C.P. dioxane contains sufficient impurities to lead to erratic results.

The dechlorination was carried out in the following manner: Sample A (0.9006 g.) was dissolved in dioxane and diluted to 250 ml. Twenty-five ml. aliquots were pipetted into each of eight 25 × 20 mm. Pyrex test-tubes, each containing 1.000 g. of purified zinc. The tubes, which had been previously constricted about one inch from the top, were sealed off and tumbled in an oil-bath held at 101.5 ± 0.5°. Tubes were removed after various time intervals, cooled to room temperature and allowed to stand until the zinc had settled. The tubes were then opened and duplicate 10-ml. aliquots of the supernatant liquid were analyzed for chloride by the method of Mohr.[9] Thirty ml. of distilled water, ten drops of 5% sodium chromate and a small amount of calcium carbonate were added to each aliquot. The solution was then titrated using 0.1011 *N* silver nitrate solution. Extent of dechlorination *vs.* time is shown in Fig. 1. The limiting value of 86.4% removal (dotted line) was obtained by an extrapolation to infinite time on a $1/t$ plot. Two repeat experiments were performed, both giving a value of 86.6% final dechlorination and exhibiting a similar induction period. These results are in complete agreement with those of Marvel.

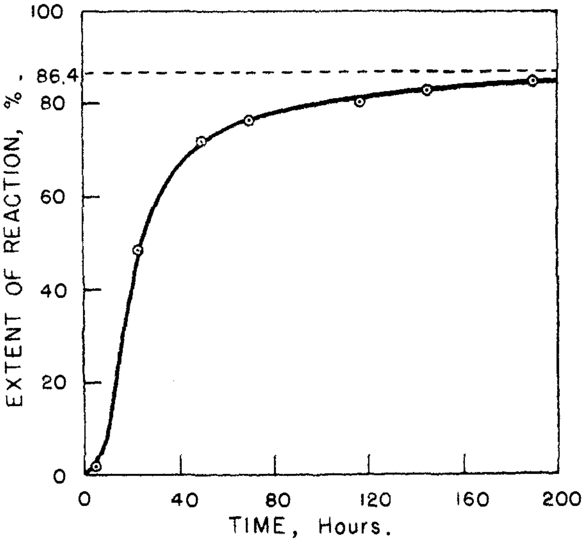

Fig. 1.—Dechlorination of polyvinyl chloride as a function of time (first 200 hr.).

Several auxiliary experiments were also carried out to confirm the applicability of the method used. Solutions of polyvinyl chloride in dioxane were heated for long periods of time at 101.5°, and found to be completely stable in the absence of zinc. Solutions of zinc chloride in dioxane, after several hundred hours of heating in sealed tubes at 101.5°, showed no apparent change and titration showed a constant chloride content. Moreover, tubes containing 25-ml. portions of a dioxane solution of zinc chloride in contact with 1 g. of zinc, also underwent no change in appearance or chloride content. If several per cent. of water were added to the tubes containing zinc chloride solution and zinc, and the tubes were heated to 101.5°, a white coating appeared on the inside of the tubes. In addition, the zinc assumed a black appearance, considerable pressure was built up inside the tubes by the generation of hydrogen, and titration showed a decrease in soluble chloride. When only small traces of water were present, no decrease in chloride was observed after heating at 101.5°. Therefore, no special precaution was taken throughout this work to seal the tubes under completely anhydrous conditions.

The dechlorination of vinyl chloride/vinyl acetate copolymers was studied by the same procedure. Figure 2 shows the conversion *vs.* time for samples B through I. It may be noted that samples of low vinyl chloride content react more slowly and exhibit longer "induction periods."

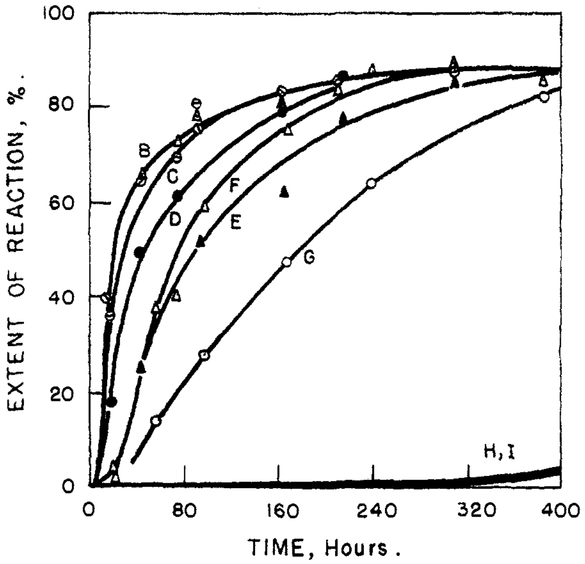

Fig. 2.—Dechlorination of vinyl chloride/vinyl acetate copolymers as a function of time.

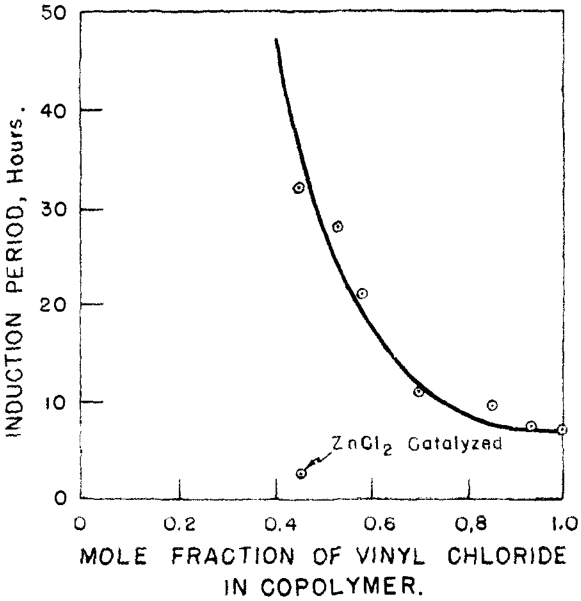

Fig. 3.—Induction period for dechlorination as a function of copolymer composition.

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(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., p. 368.

(9) A. J. Berry and J. E. Driver, *Analyst*, **67**, 730 (1939).

The induction periods (obtained by extrapolation of the linear portion of the curves to zero conversion) *vs.* mole fraction of vinyl chloride in the copolymer are given in Fig. 3.

The upward curvative observed in the early stages of the conversion curves suggested autocatalysis. The effect of added zinc chloride on the dechlorination of polyvinyl chloride and the copolymers was therefore investigated. It was found that small initial amounts of zinc chloride markedly reduced the time necessary for the reaction. The magnitude of this effect can be seen in Fig. 3 by comparing the induction periods of the catalyzed *vs.* the uncatalyzed reactions for Sample G. The dechlorination of Samples J, K, and L was, therefore, studied in the presence of added zinc chloride. The results are shown in Fig. 4. Dechlorination proceeded rapidly. The amount of soluble chloride found did not, however, approach a limiting maximum in the case of these samples but rose to a maximum of about 82–84% and then decreased with time. This anomaly will be discussed in detail in a later paper. The only conclusion we wish to draw here is the observation that this effect makes it impossible to fix with certainty the limiting value of the dechlorination from these experiments. All that can be said with any confidence is that dechlorination proceeds at least to the values indicated.

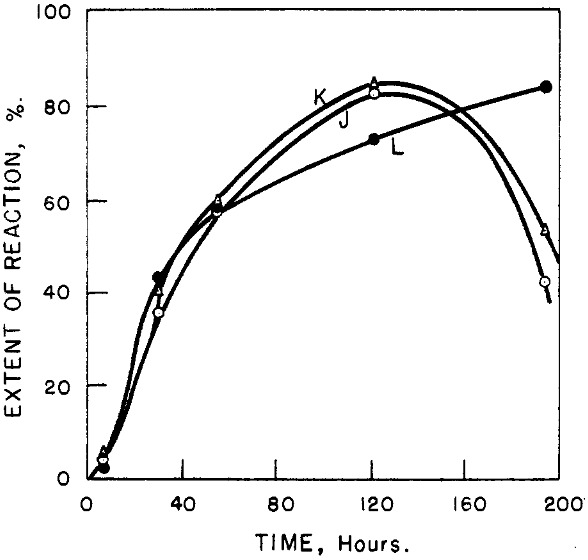

Fig. 4.—Catalyzed dechlorination of low vinyl chloride copolymers.

The limiting fractional extents of dechlorination, as a function of copolymer composition, are plotted in Fig. 5. Over most of the composition range, the limiting dechlorination is scattered around the value of 86.4%, observed for polyvinyl chloride. The maximum observed dechlorination for the low vinyl chloride copolymers also falls in this range. (However, because of the anomaly observed at long reaction times, these observed values must be taken as possible lower limits to the actual values. This uncertainty is indicated in Fig. 5.)

In an attempt to explain the observed high chlorine removal for these copolymers, several additional experiments have been performed. It has been found that the copolymers, like polyvinyl chloride, are completely stable in dioxane at 101.5°. The exchange of acetate and chloride groups between the copolymer and zinc chloride in solution was considered as a definite possibility. This would allow the removal of chlorine atoms normally considered to be isolated. To test this possibility, solutions of polyvinyl acetate in dioxane containing zinc chloride were heated at 101.5°, both with and without zinc. No decrease in the chloride concentrations of these solutions was observed. A similar experiment carried out between polyvinyl chloride and zinc acetate also gave no evidence for exchange. Furthermore, heating vinyl chloride/vinyl acetate copolymers in a dioxane solution containing zinc chloride yielded highly colored solutions but gave no test for acetate ion. However, if the normal zinc dehalogenation of one of these copolymers is performed, we have been able to show that the solution contains acetate ion. This was done by adding distilled water to the reaction mixture, dialyzing through a regenerated cellulose membrane against distilled water, followed by distillation and identification of acetic acid in the distillate by the lanthanum nitrate test.[10] A complete series of blanks have been carried through to verify that the presence of acetate does not arise from the thermal decomposition of the polymer at 101.5° or the hydrolysis of acetate groups during dialysis. Thus it seems that the removal of acetate is closely allied with the mechanism of the zinc reaction itself and may in part explain the high removal of chlorine. This follows if it is assumed that zinc can remove an acetate group and a chloride as well as two chlorides. Another possibility is that rings larger than cyclopropane can be closed, although at lower rates. A definitive resolution of this mechanism, however, would seem to require the investigation of the dechlorination of low molecular weight analogs—*e.g.*, 4-chloro-2-pentyl acetate.

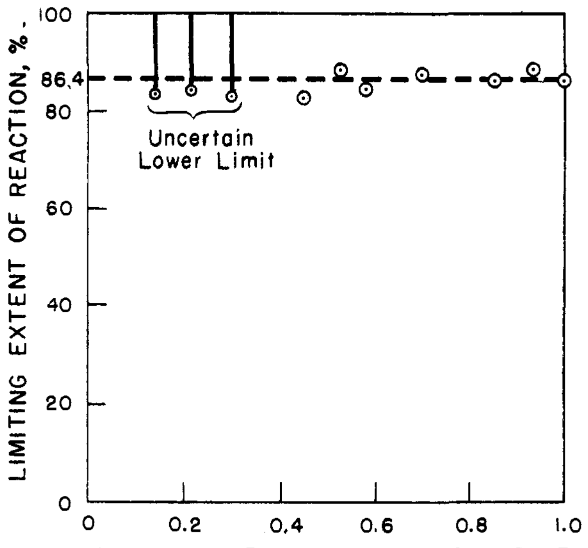

Fig. 5.—Limiting extent of dechlorination as a function of copolymer composition.

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RECEIVED DECEMBER 15, 1950

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[10] F. Feigl, "Spot Tests," Elsevier Pub. Co., New York, N. Y., p. 397.