[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH AT THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Dehalogenation Reaction. II. Dechlorination of Vinyl Chloride Copolymers[1]

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

A study of the zinc dehalogenation of vinyl chloride/diethyl maleate, vinyl chloride/methyl methacrylate and vinyl chloride/*t*-butylethylene copolymers has been carried out. The results, like those obtained with vinyl chloride/vinyl acetate copolymers, clearly illustrate that the reaction does not consist simply of a random removal of 1,3 halogen with the comonomer acting as an inert spacer. It has been shown that the methyl methacrylate copolymers lose hydrogen chloride in addition to undergoing the normal zinc reaction and this may account for the extremely high extents of dechlorination, fast rates and low induction periods observed with these copolymers. It has been suggested that the only plausible explanation of the high limiting extents of reaction observed with all copolymers is to assume that larger ring formation accompanies 1,3-halogen removal at correspondingly lower rates.

In the first paper of this series,[2] we reported an investigation of the reaction between zinc and vinyl chloride/vinyl acetate copolymers. We found that polyvinyl chloride dehalogenates 86–87% in agreement with the results of Marvel and co-workers[3] and with Flory's[4] calculated value. The limiting extents of reaction observed with the copolymers, however, did not conform to equation (1), developed by Wall[5] and Merz, *et al.*,[6] or agree with the results obtained by Marvel and co-workers.[7]

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

An investigation of several other vinyl chloride copolymer systems has now shown that their reactions with zinc also do not conform to the behavior predicted by equation (1). The systems whose reactions with zinc have been studied and are described here are the vinyl chloride/methyl methacrylate, vinyl chloride/diethyl maleate and vinyl chloride/*t*-butylethylene copolymer systems. The methacrylate copolymers were chosen as a typical vinyl chloride system, the maleates as a system where the comonomer does not add to itself, and the *t*-butylethylene as a comonomer completely devoid of reactive substituents.

Experimental

The vinyl chloride/diethyl maleate and vinyl chloride/*t*-butylethylene copolymers were prepared by a low conversion bulk polymerization at 70°.[8] The vinyl chloride/methyl methacrylate copolymers were prepared in the same manner at 68°.[9] The compositions of the samples selected for study are listed in Table I.

Vinyl chloride is sufficiently more reactive than ethylenic hydrocarbons so that the copolymer having the highest obtainable *t*-butylethylene content still had a mole fraction of 0.83 in vinyl chloride. It was not considered feasible to dehalogenate polymers of lower butylethylene content and attempt to compare the results with the theoretical prediction of equation (1). Pure polyvinyl chloride was dehalogenated alongside the *t*-butylethylene copolymer for comparison purposes.

The dechlorination of these copolymers with zinc has been studied by the same procedure employed previously.[2] Briefly, the reactions were carried out in dilute dioxane solutions at 101 ± 0.5°, the course of the reactions being followed by a Mohr titration of the soluble chloride. All the dehalogenations proceeded smoothly; it was not found necessary to add zinc chloride as was the case with vinyl chloride/vinyl acetate copolymers of low vinyl chloride content. Conversion as a function of time is plotted in Figs. 1–3. Heating dioxane solutions of vinyl chloride/diethyl maleate copolymers and a vinyl chloride/*t*-butylethylene copolymer for long periods of time at 101° in sealed tubes showed that these copolymers were completely stable. The methyl methacrylate/vinyl chloride copolymers however undergo a slow homogeneous loss of hydrogen chloride at 101° as indicated by the presence of titratable chloride, the acidity of the dioxane solutions, and the failure of the Mohr titration except in the presence of an alkaline neutralizing agent.

TABLE I

COMPOSITION OF VINYL CHLORIDE COPOLYMERS

Sample	Mole Fraction of Vinyl Cloride in Copolymer Diethyl maleate	Methyl methacrylate	*t*-Butylethylene
A	0.91	0.70	1.00
B	.82	.61	0.83
C	.75	.34	
D	.63	.16	
E		.06	

Discussion

The conversion curves for the vinyl chloride/diethyl maleate system (Fig. 1) show that the limiting extents of dehalogenation for all copolymers fall between 84 and 87%. The introduction of diethyl maleate into the vinyl chloride chain obviously does not decrease the fraction of chlorine removed by zinc and the behavior does not conform to that predicted by equation (1). Like the vinyl chloride/vinyl acetate copolymers, the induction periods are found to increase with decreasing vinyl chloride content of the copolymer.

Extents of dechlorination *vs.* time for the reactions between vinyl chloride/methyl methacrylate copolymers and zinc are plotted in Fig. 2. Here again, the behavior does not follow equation (1). The abnormally high limiting extents of reaction which fall between 92 and 100% are believed to result from a homogeneous loss of hydrogen chloride which accompanies the normal zinc reaction with these copolymers. The instability of the vinyl chloride/methyl methacrylate copolymers at 101° resulting in loss of hydrogen chloride and zinc chloride formation probably accounts for the relatively fast rates and short induction periods for copolymers of all mole fractions. The anomalous effect of a decrease in the soluble chloride observed with vinyl chloride/vinyl acetate copolymers of low vinyl chloride content has also been

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

[2] T. Alfrey, Jr., H. C. Haas and C. W. Lewis, THIS JOURNAL, **73**, 2851 (1951).

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

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

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

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

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

[8] T. Alfrey, Jr., J. Bohrer, H. C. Haas and C. W. Lewis, *J. Polymer Sci.*, **5**, 719 (1950).

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

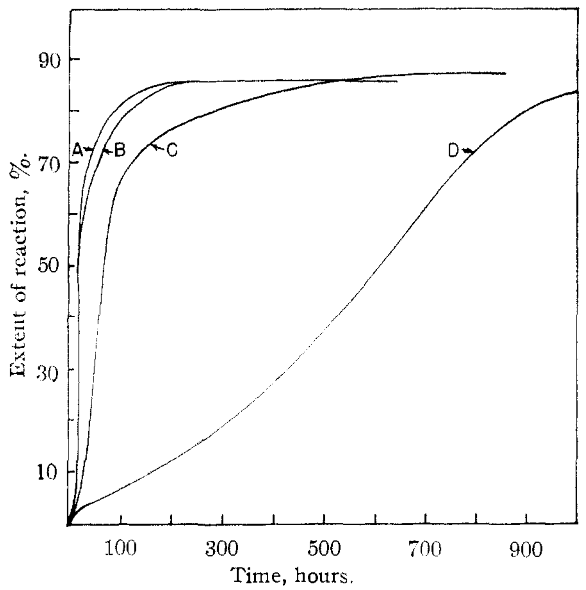

Fig. 1.—Dechlorination of vinyl chloride/diethyl maleate copolymers.

observed with methyl methacrylate copolymers of low vinyl chloride content (Fig. 2, samples D and E). This decrease in soluble chloride is always associated with complete agglomeration of the zinc.

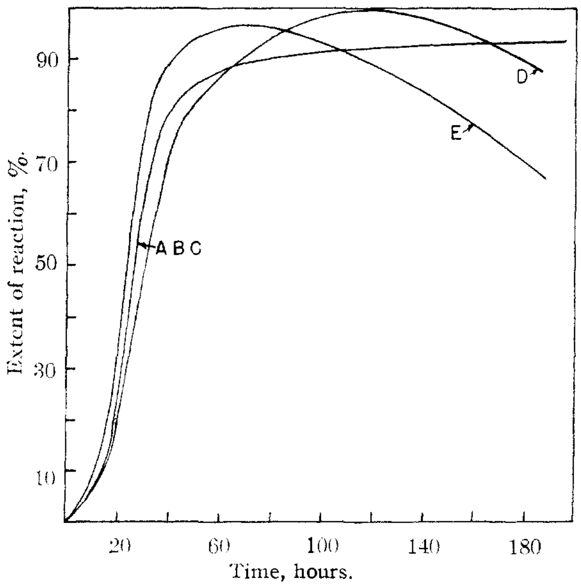

Fig. 2.—Dechlorination of vinyl chloride/methyl methacrylate copolymers.

A copolymer of vinyl chloride and *t*-butylethylene having a mole fraction of 0.83 in vinyl chloride also dehalogenates 86–87%. A zinc dehalogenation of pure polyvinyl chloride carried out simultaneously with the butylethylene copolymer and under identical conditions dehalogenates to the same extent (Fig. 3). Equation (1), based on a random removal of 1,3-halogen from a polymer in which vinyl chloride sequences have a head-to-tail structure and in which the comonomer acts as an inert spacer, predicts a 79% removal of chloride from this copolymer. Once more equation (1) is not obeyed.

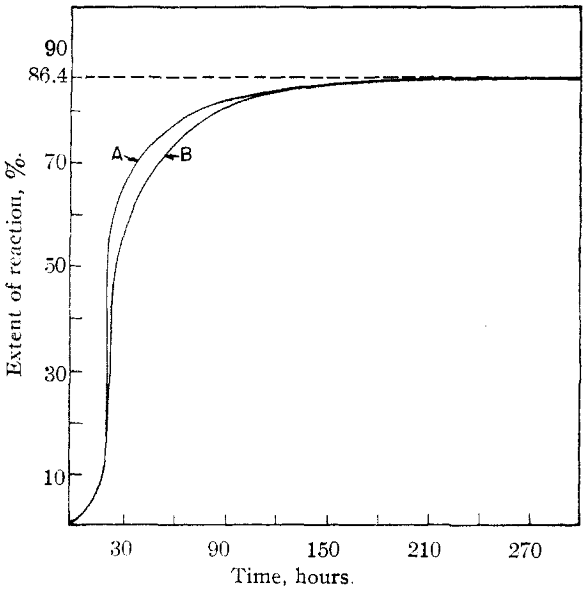

Fig. 3.—Dechlorination of vinyl chloride/*t*-butylethylene copolymers.

All vinyl chloride copolymer systems which have been studied show a high, more or less constant removal of halogen which appears completely independent of copolymer composition. The reactions obviously do not consist of a random removal of 1,3-chlorine with the comonomer serving as an inert spacer and increasing the expectancy of isolated halogen. The question arises as to what mechanism can account for this behavior. Except for the methyl methacrylate copolymers which dechlorinate more than the 86–87% usually observed, the copolymers are stable to loss of hydrogen chloride. Intermolecular loss of halogen is highly improbable because of the dilute solutions involved and the failure to ever observe crosslinked insoluble polymer formation in any of these reactions. It has been shown that the vinyl acetate copolymers lose acetate during zinc dehalogenation and this may be associated with the high removal of halogen for these copolymers. Formation of RZnCl followed by a Reformatsky type condensation is a possibility which may be present in those copolymers containing ester groups. The vinyl chloride/*t*-butylethylene copolymer however completely devoid of all reactive groups except halogen, still undergoes the normally observed 86–87% reaction. The only readily understandable means by which this behavior might be explained is to assume that in addition to 1,3-halogen removal, rings larger than three-membered rings are being formed. This of course would allow chlorine atoms, isolated as regards a 1,3-reaction, to take part in larger ring formation and could account for the observed 86–87% removal independent of copolymer composition. This assumption is not without some experimental substantiation. If during a zinc dehalogenation of pure polyvinyl chloride, reaction is allowed to continue for a considerably longer time than that required to reach

86–87% dechlorination, points are obtained which are higher than expected for an extrapolation of the smooth rate curve. This additional halogen removal may be resulting from the utilization of isolated chlorine atoms for the formation of larger rings. Because of entropy effects, one would expect the rate of ring formation to decrease with increasing ring size. Experimentally one finds that as the vinyl chloride content of a copolymer decreases, thereby requiring a greater degree of larger ring formation to reach 87% dehalogenation, the rates of dehalogenation fall rapidly to a point where, for very low vinyl chloride contents, no reaction is observed within 400 hours. Thus we feel that the normal zinc dehalogenation reaction consists of rapid random removal of 1,3-chlorines and this is followed by the 1,5, etc. reactions at correspondingly lower rates. Superimposed on the normal zinc reaction are complicating factors such as the removal of acetate in the case of the vinyl chloride/vinyl acetate copolymers and loss of hydrogen chloride by vinyl chloride/methyl methacrylate copolymers.

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Kinetics of the Polymerization of Methyl Methacrylate with Aliphatic Azobisnitriles as Initiators[1]

BY L. M. ARNETT

Methyl methacrylate has been polymerized in bulk and in benzene solution with each of three aliphatic azobisnitriles which have decomposition rates in a range whose extremes differ by a factor of 100. The initial rate of polymerization is found to be proportional to the square root of the initiator concentration, to the square root of the specific rate constant for initiator decomposition, and to the first power of the monomer concentration. The relationship between the number average molecular weight and the initiator concentration indicates that approximately one-half of the radicals generated by decomposition of the initiator start polymer chains. It is also indicated that the termination reaction is combination of two growing chains.

In studies of the mechanism of vinyl polymerization, several investigators have related the rate of initiation of growing polymer chains to the rate of decomposition of benzoyl peroxide used as initiator.[2–4] Their results show that, although the decomposition of this peroxide appears to be a first order reaction under a given set of conditions, the rate constant calculated for a first order reaction varies widely with changes in reaction medium and peroxide concentration.[2–5] This deviation from a true first order reaction is generally attributed to free radical attack on undecomposed peroxide to produce induced decomposition which makes no contribution to the sum total of initiating radicals.[4] As a result, the rate of generation of free radicals from decomposing peroxide is always less by an uncertain amount than the rate of decomposition of the peroxide.

The discovery that certain aliphatic azobisnitriles are excellent initiators of vinyl polymerization[6] prompted an investigation of the decomposition of typical azobisnitriles. This work indicated that the aliphatic azobisnitriles decompose thermally in solution by a true first order reaction not influenced by solvent or concentration. This conclusion is in agreement with that of other workers as reported recently in the literature.[7–9] It is therefore to be expected that when azobisnitriles are used as vinyl polymerization initiators, the rate of generation of free radicals may be set equal to the rate of decomposition of the initiator. This ideal behavior of the azobisnitrile initiators has been used in this investigation to obtain evidence concerning the mechanism of the polymerization of methyl methacrylate.

Experimental Methods

Decomposition of Azobisnitriles.—The azobisnitriles used in this study were prepared by the method of Thiele and Heuser.[10] The decomposition of the azobisnitrile was carried out in solution in a glass vessel immersed in a vapor-bath or water thermostat. The reaction medium was brought to the temperature of the bath, and the gas space swept out with purified nitrogen (less than 20 p.p.m. O_2). A known weight of azobisnitrile was added to the liquid, and the vessel was closed and agitated to bring about solution. The evolved nitrogen was collected in a gas buret, and the volume noted as a function of time.

Monomer Purification.—Methyl methacrylate monomer containing phenols as polymerization inhibitors was washed with 5% sodium hydroxide solution and then with distilled water. The monomer was dried with Drierite and then fractionated in a stream of purified nitrogen at 100 mm. in a 12-inch column packed with Fenske rings. The middle fraction boiling at 46° was stored under purified nitrogen in a glass bottle at 0–5°. This monomer polymerized at 70° with benzoyl peroxide at a rate in good agreement with that

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(1) Presented orally at the Division of High Polymer Chemistry, American Chemical Society, Cleveland, Ohio, April 9, 1951.

(2) S. G. Cohen, THIS JOURNAL, **67**, 17 (1945).

(3) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

(4) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946); *ibid.*, **68**, 1686 (1946).

(5) D. P. Brown, *ibid.*, **62**, 2657 (1940).

(6) Madison Hunt (to du Pont) U. S. Patent 2,471,959 (5/31/49).

(7) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(8) C. Walling, *ibid.*, **71**, 1930 (1949).

(9) C. G. Overberger, M. T. O'Shaughnessy and Harold Shalit, *ibid.*, **71**, 2661 (1949).

(10) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).