for her assistance in the experimental work, and to Miss Barbara A. McNeice and Mr. William A. Steuer for the analyses reported in this paper.

PITTSFIELD, MASS.

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

The Dehalogenation Reaction. IV. Dechlorination of the Copolymers Vinyl Acetate/*trans*-Dichloroethylene and Vinyl Acetate/Trichloroethylene[1]

BY TURNER ALFREY, JR.,[2] HOWARD C. HAAS AND CHARLES W. LEWIS

RECEIVED MAY 1, 1952

The dechlorination of the copolymers vinyl acetate/*trans*-dichloroethylene and vinyl acetate/trichloroethylene has been investigated. The reaction of the latter is complete after six to ten hours; the former is much slower, and is not complete after three weeks.

The dechlorination of polyvinyl chloride has been shown to go to a limiting conversion of 84–86%.[3] This result is in good agreement with the theoretical value, 86.47%, derived from a statistical treatment based on a head-to-tail structure.[4] It has been assumed that a head-to-head, tail-to-tail structure would give up 100% of its chlorine by way of the sterically favored 1,2-dechlorination. The work described here was undertaken in order to evaluate the correctness of this assumption. The *vic*-dichloro structure that would exist in a head-to-head, tail-to-tail polymer was simulated by using a copolymer of vinyl acetate and *trans*-dichloroethylene. The copolymer of vinyl acetate and trichloroethylene was also studied. These copolymers were dechlorinated in dioxane at 101.5° with zinc dust by the method described in an earlier paper of this series.[5]

Experimental

Vinyl acetate/*trans*-dichloroethylene (16.2% Cl) and vinyl acetate/trichloroethylene (27.1% Cl) were prepared according to the method of Alfrey and Greenberg.[6] In each case, the monomer composition was chosen which would give "azeotropic" copolymerization.[7]

TABLE I

DECHLORINATION OF DICHLOROETHYLENE COPOLYMER

Expt. No.	Copolymer concentration, g./l.	Zinc dust, g./25 ml.	$\frac{-\log(1-x)\times 10^3}{t}$
I-A	24.478	1.000	2.2 ± 0.2
I-B	14.914	1.000	2.1 ± .1
I-C	14.914	2.000	4.1 ± .3
I-D	4.001	1.000	2.2 ± .4

TABLE II

DECHLORINATION OF TRICHLOROETHYLENE COPOLYMER

Expt. No.	Copolymer concentration, g./l.	Zinc dust, g./25 ml.	$x^{1/2}/t$
II-A	11.776	1.000	0.16 ± 0.01
II-B	13.537	1.000	.17 ± .01
II-C	13.537	2.000	.15 ± .01
II-D	6.761	0.500	.11 ± .01
II-E	6.761	1.000	.13 ± .01

The method used in following the rate of dechlorination has already been described.[5] The systems studied are outlined in Tables I and II, and the conversion data for each system are plotted in Figs. 1 and 2.

Discussion

In order to interpret the results, it will be assumed that the mechanism of the reaction is the same in both cases, and that the differences in the conversion curves arise from differences in the constants governing the rate-determining step. It is reasonable to expect that the equilibrium reactions,

$$2\mathrm{ZnCl_2} \rightleftarrows \mathrm{ZnCl^+} + \mathrm{ZnCl_3}$$

and

$$\mathrm{ZnCl_2} + \mathrm{RCl_2} \rightleftarrows \mathrm{RCl^+} + \mathrm{ZnCl}$$

take place to a small extent, and are governed by the equations

$$[\mathrm{ZnCl^+}][\mathrm{ZnCl^3}\ ]/[\mathrm{ZnCl_2}]^2 = K_1 \qquad (1)$$

$$[\mathrm{RCl^+}][\mathrm{ZnCl^3}\ ]/[\mathrm{RCl_2}][\mathrm{ZnCl_2}] = K_2 \qquad (2)$$

Finally it is postulated that the rate-determining reaction is

$$\mathrm{RCl^+} + \mathrm{Zn} \longrightarrow \mathrm{R} + \mathrm{ZnCl^+}$$

and therefore

$$\mathrm{d[R]}/\mathrm{d}t = k[\mathrm{RCl^+}] \qquad (3)$$

Here $\mathrm{RCl_2}$ represents a polymerized di- or trichloroethylene molecule, $\mathrm{RCl^+}$ the carbonium ion produced from it by removal of a chloride ion, and R, the dechlorinated molecule. The rate constant, k, is a function of the amount and physical condition of the zinc used. Equations (1), (2) and (3) may be solved simultaneously to give

$$\mathrm{d}x/\mathrm{d}t = kK_2(1-x)\left[\frac{x}{(K_1-K_2)x+K_2}\right]^{1/2} \qquad (4)$$

where x is the extent of reaction.

The solution of (4) is quite unwieldy, and requires the simultaneous manipulation of three constants in order to fit it to the data. For the present purpose it will be more instructive to examine three special cases

A. $K_1 >> K_2$.—In this case eq. (4) reduces to

$$\mathrm{d}x/\mathrm{d}t = kK_2K_1^{-1/2}(1-x)$$

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(1) Taken in part from the Ph.D. thesis submitted by Charles W. Lewis, Polytechnic Institute of Brooklyn, May, 1950.

(2) Dow Chemical Co., Midland, Michigan

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

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

(5) T. Alfrey, H. C. Haas and C. W. Lewis, *ibid.*, **73**, 2851 (1951).

(6) T. Alfrey and S. Greenberg, *J. Polymer Sci.*, **3**, 297 (1948).

(7) Azeotropic copolymerization occurs when the polymer formed has the same composition as the monomer mixture. Copolymers formed in this way have the greatest degree of homogeneity, particularly at higher degrees of conversion. *Cf.* R. Simha and L. A. Wall, *J. Research Natl. Bur. Standards* **41**, 521 (1948).

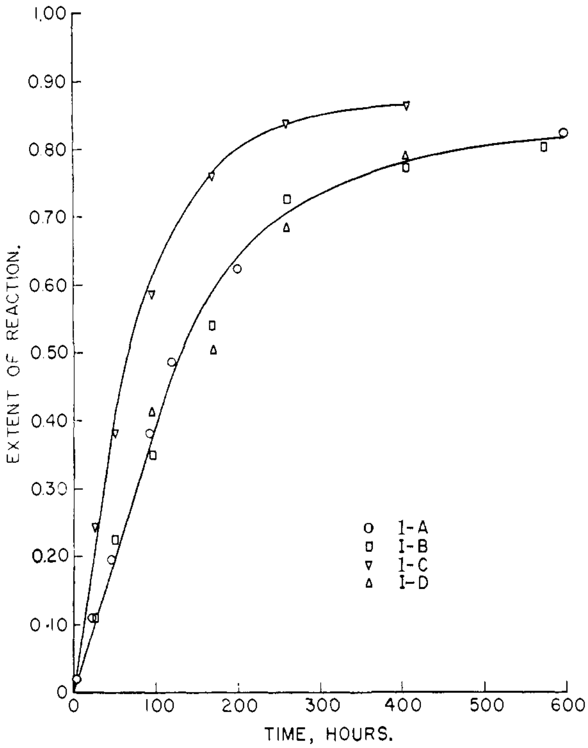

Fig. 1.—Dechlorination of vinyl acetate/*trans*-dichloroethylene copolymer.

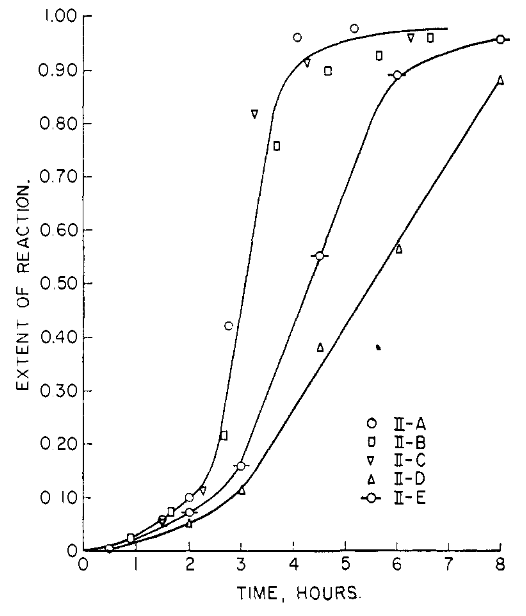

Fig. 2.—Dechlorination of vinyl acetate/trichloroethylene copolymer.

which yields upon integration

$$-\ln(1 - x) = kK_2K_1^{-1/2}t \qquad (5)$$

B. $K_1 = K_2$

$$dx/dt = kK_2^{1/2}(1 - x)x^{1/2}$$

$$\tanh^{-1}x^{1/2} = {}^1/_2kK_2^{1/2}t \qquad (6)$$

C. $K_1 << K_2$

$$dx/dt = kK_2^{1/2}(1 - x)^{1/2}x^{1/2}$$

$$\sin^{-1}x^{1/2} = {}^1/_2kK_2^{1/2}t \qquad (7)$$

For values of x not larger than 0.2, the functions $\tanh^{-1}x^{1/2}$ and $\sin^{-1}x^{1/2}$ do not differ appreciably from $x^{1/2}$. Under these conditions (6) and (7) reduce to

$$x^{1/2} = {}^1/_2kK_2^{1/2}t \qquad (8)$$

Since it is not likely that the value of K_1 is influenced by the particular system undergoing dechlorination, the treatment above leads to the conclusion that the over-all kinetic behavior is dominated by K_2, with larger values leading to faster reactions.

The dechlorination of the dichloroethylene copolymer is reasonably well described by (5) for conversions up to 75% (see Fig. 3). The last column of Table I shows the best-fitting values of $-t^{-1}\log(1 - x)$. This constant was approximately doubled when the amount of zinc was doubled.

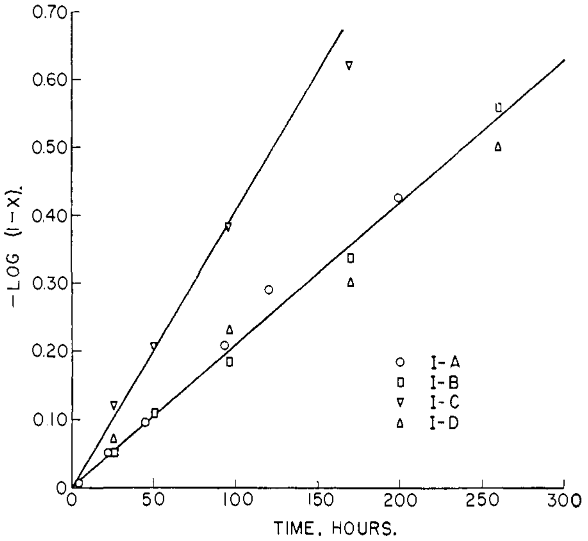

Fig. 3.—Dichloroethylene copolymer data fitted to Eq. 5.

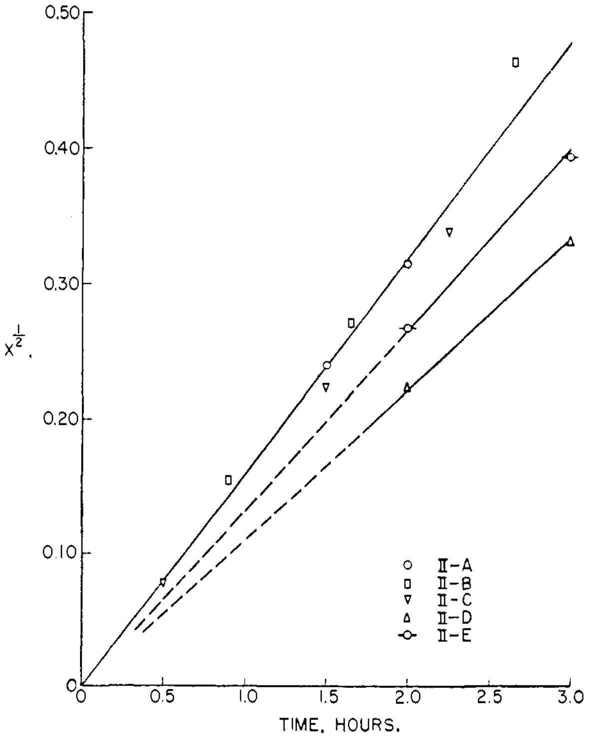

Fig. 4.—Trichloroethylene copolymer data fitted to Eq. 8.

The dechlorination of the trichloroethylene copolymer shows fair agreement with (8) in the range from 0 to 20% conversion (see Fig. 4). In every case, however, the reaction seemed to go faster in the conversion range beyond 20% than would be expected from (6) or (7). Furthermore, the anticipated dependence on the amount of zinc was not realized, as may be seen from the last column of Table II. It is obvious that the proposed mechanism is not entirely adequate.

The failure to achieve 100% dechlorination in the case of the dichloroethylene copolymer requires some comment. It was found that when either copolymer was heated in solution in the absence of zinc, HCl was formed. This reaction was too slow to compete with the dechlorination by zinc of the trichloroethylene copolymer, but may very well take place to a measurable extent during the dechlorination of the dichloroethylene copolymer. The removal of one molecule of HCl between two adjacent chlorinated carbon atoms will cause the remaining chlorine atom to be inert. Hence the dechlorination will not go to completion.

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BROOKLYN, N. Y.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Racemization of *d*(+)-3-Methylhexane[1]

BY HOWARD E. HELLER[2,3]

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The racemization and isomerization of *d*(+)-3-methylhexane in the presence of aluminum bromide and various promoters at 23–24° have been studied. Racemization proceeds more rapidly than isomerization, and the ratio of the two rates is not constant. The implications of these data are discussed in terms of the carbonium ion theory.

A study of the reactions of paraffins begun several years ago has been interrupted before completion. However, because of the close relationship between the results obtained by this author and the recent findings of other workers, it seems desirable to note some of the results at this time. Some of the findings of a study of the racemization and isomerization of optically active 3-methylhexane in the presence of promoted aluminum bromide are summarized here.

Experimental

Reagents.—Fractional distillation of U. S. I. "Refined Amyl Alcohol" through Podbielniak Heligrid columns yielded *d*(−)-2-methyl-1-butanol of the following characteristics after three passes: $n^{20}\text{D}$ 1.4102, d^{23}_4 0.814, $\alpha^{23}\text{D}$ −4.62°, $[\alpha]^{23}\text{D}$ −5.68°.

Saturation of the alcohol under reflux with anhydrous hydrogen bromide at 100° and atmospheric pressure for 24 hours yielded *d*(+)-2-methyl-1-bromobutane. The product, washed twice with water, dried over potassium carbonate, and passed twice through towers of silica-gel, had the properties: $n^{20}\text{D}$ 1.4450, d^{23}_4 1.220, $\alpha^{23}\text{D}$ +3.70°, $[\alpha]^{23}\text{D}$ +3.03°. Fractional distillation was attempted and abandoned, because even at reduced pressure (48 mm.) isomerization to the tertiary halide occurred.

Synthesis of *d*(+)-3-methylhexane was accomplished by two different methods:

(a).—By action of the Grignard reagent on diethyl sulfate: Diethyl sulfate (1.0 mole) diluted with about an equal volume of ether was added rapidly to an ether solution of the Grignard reagent prepared from 0.44 mole of active amyl bromide in 5.6 times its volume of ether. Careful drying of all reagents and apparatus, and an atmosphere of pure nitrogen were employed. After refluxing overnight with vigorous stirring, the reaction mixture was decomposed with dilute hydrochloric acid. The ether layer was dried with potassium carbonate and distilled. Yields were 55–60% of crude 3-methylhexane and 5–10% of optically active diamyl. Difficulties in stirring reduced yields in larger scale runs.

(b).—Through the malonic ester synthesis: Active amyl malonic ester was prepared according to the procedure of Adams and Kamm[4] for *n*-butylmalonic ester. The product, stripped of low boiling impurities by vacuum distillation, was treated by the method of Vliet, Marvel and Hsueh[5] to give γ-methylcaproic acid.

Lithium aluminum hydride reduction of the crude acid gave a poor yield of 4-methyl-1-hexanol. The recovered acid was converted to its ethyl ester by saturating a thirty-one volume per cent. solution of the acid in absolute ethanol with anhydrous hydrogen chloride and warming to 80° for eight hours. The mixture poured onto ice, washed with water, and dried with calcium chloride, yielded the ester. Reduction of the ester followed standard methods.[6]

Crude 4-methyl-1-hexanol heated with seven times its volume of concentrated hydriodic acid for eight hours with stirring at 90° yielded the corresponding iodide. This was separated, washed with water, dried with potassium carbonate, and used without further purification.

The iodide in twice its volume of ether was reduced to 3-methylhexane by addition to a fourfold excess of lithium aluminum hydride solution containing 1.79 moles of hydride per liter.[7,8]

Early purification work on the hydrocarbon, keeping separate the material prepared by the two paths, indicated the presence of a common impurity not removable by any of the ordinary hydrocarbon purification methods.[9] On exhaustive application of those methods, the ultraviolet absorption of both samples approached the same limiting "tail" below 2500 Å., and the optical rotation approached the same limiting value, +5.51°. The combined samples were hydrogenated over one-twentieth their total weight of platinum oxide at 45 pounds pressure and room temperature for 24 hours. The ultraviolet transparency increased over the former limit, but repeating the procedure gave no further improvement. No racemization appeared to occur during this process.

The hydrocarbon, sealed with one-seventh its weight of

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[1] The material presented herein is abstracted from the Ph.D. thesis of Howard E. Heller, the University of Chicago, 1949.

[2] Naval Research Laboratory Fellow, 1945–1947.

[3] Photo Products Department, E. I. du Pont de Nemours and Company, Parlin, New Jersey.

[4] R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.

[5] E. B. Vliet, C. S. Marvel and C. M. Hsueh, *ibid.*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 416.

[6] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

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[9] W. G. Brown and M. H. Reagan, *ibid.*, **69**, 1032 (1947).