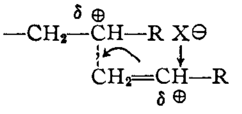
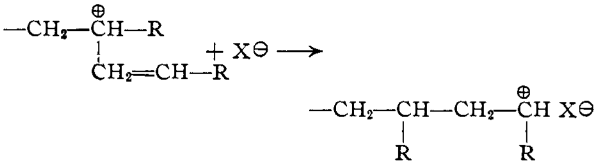
curve. It is of interest to note that Fig. 6 could likewise be drawn as a curve and if σ values for the *p*-methoxy and *p*-dimethylamino group were included in Fig. 2, a similar curve to that obtained by Swain would be obtained. One might interpret these results to indicate that the addition of R^+X^- to an olefin is also termolecular with a transition state somewhat similar to that proposed for concerted displacement reactions as indicated. With substituent groups in our system, bond breaking (polarization of double bonds by positive portion of ion pair) is largely taking place as indicated by the negative ρ's.



$$\begin{array}{l} -CH_2-\overset{\delta\oplus}{C}H-R\ X^{\ominus} \\ CH_2{=}\underset{\delta\oplus}{C}H-R \end{array}$$

Groups such as *p*-methoxy and *p*-dimethylamino which will stabilize the partial positive charge on carbon in the transition state would change the ρ to even a larger negative value. This evidence points to an ion pair in the propagation step in which the anionic fragment is utilized in the bond polarization. A π-complex scheme may also be applicable. The σ-plots seem applicable in this case as carbon X in the transition state would bear a partial positive charge.



$$\begin{array}{l} -CH_2-\overset{\oplus}{C}H-R \\ \quad | \qquad\qquad + X^{\ominus} \longrightarrow \\ CH_2{=}CH-R \end{array}$$

$$-CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{\oplus}{C}H}\ X^{\ominus}$$

Since α-methylstyrene is more reactive with *p*-chlorostyrene than is *p*-methylstyrene, it appears that the methyl group in the α-position has a greater activating effect than has the *p*-methyl group.

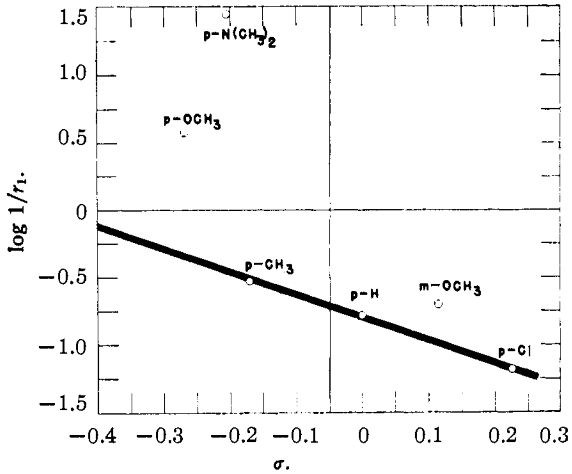


Fig. 6.—Plot of log relative reactivity towards an α-methylstyrene carbonium ion *vs.* Hammett σ-value for various substituted styrenes.

In contrast with radical copolymerizations no alternation tendency has been found for systems subject to acid catalysis. Due to the low activation energy of reactive monomers in acid-catalyzed systems, disubstituted monomers having electron rich double bonds can compete favorably with monosubstituted monomers for growing carbonium ions. Disubstitution does appear to reduce the reactivity. Thus, *p*-methoxystyrene is more reactive with styrene than is anethole with *o*-chlorostyrene.[24]

[24] T. Alfrey, Jr., L. Arond and C. G. Overberger, *J. Polymer Sci.*, **4**, 539 (1949).

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE NEW PRODUCTS DEVELOPMENT LABORATORY, GENERAL ELECTRIC COMPANY, CHEMICAL DIVISION]

Acetylenic Silicon Derivatives*

BY KURT C. FRISCH AND ROBERT B. YOUNG

RECEIVED MARCH 27, 1952

Acetylenic silicohydrocarbons and chlorosilanes were prepared by treating acetylenic Grignard compounds with chlorosilanes in the presence of cuprous chloride as a catalyst. The acetylenic chlorosilanes were converted first to the acetoxysilanes or were directly hydrolyzed to the corresponding silanols or siloxanediols without rupture of the $\equiv C-Si$ bond. Some addition products of the acetylenic derivatives were prepared.

Very little is known concerning the chemistry of acetylenic silicon derivatives. Volnov and Reutt[1] prepared (phenylethynyl)-triethoxysilane and bis-(phenylethynyl)-diethoxysilane by the reaction of phenylethynylmagnesium bromide with ethyl orthosilicate

$$C_6H_5C{\equiv}CMgBr + Si(OC_2H_5)_4 \longrightarrow C_6H_5C{\equiv}C-Si(OC_2H_5)_3 + (C_6H_5C{\equiv}C)_2Si(OC_2H_5)_2$$

These authors concluded that the phenylethynyl group was only weakly bound to silicon since it decomposes on hydrolysis with formation of silica, ethanol and phenylacetylene.

Hexaethynyldisiloxane $[(HC{\equiv}C)_3Si]_2O$ was also prepared by the same investigators by treating ethynylmagnesium bromide with silicon tetrachloride and hydrolyzing the reaction product. Hexaethynyldisiloxane also decomposes in cold water, yielding acetylene and silica, confirming apparently the labile behavior of the carbon–silicon bond in which one of the carbon atoms of the triple bond is linked to silicon.

Boldebuck[2] in a recent patent described the preparation of "esters of ethynyl siliconic acid." Ethoxytriethynylsilane, diethoxydiethynylsilane and triethoxyethynylsilane were described. These compounds were prepared by reaction of sodium

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* Presented at the Atlantic City Meeting of the A. C. S., September. 1952.

[1] Y. N. Volnov and A. Reutt, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1600 (1940).

[2] E. N. Boldebuck, U. S. Patent 2,551,924 (to Pittsburgh Plate Glass Co.) (1951).

acetylide with ethyl chlorosilicates

$$(C_2H_5O)_mSiCl_n + nNaC{\equiv}CH \longrightarrow nNaCl + (C_2H_5O)_mSi(C{\equiv}CH)_n$$

Certain higher substituted ethynyl silicon derivatives, obtained as by-products in the above process, were also isolated and characterized.

The present investigation was undertaken to see whether acetylenic silicon derivatives could be prepared which would be stable toward hydrolysis in water as well as shown sufficient stability to be of use in the compounding of silicone rubber and other silicon polymers.

Acetylenic silicohydrocarbons were prepared by reaction of acetylenic Grignard[4] compounds with trimethylchlorosilane. Bis-(trimethylsilyl)-ethyne was prepared from acetylenedimagnesium dibromide and trimethylchlorosilane

$$BrMgC{\equiv}CMgBr + 2(CH_3)_3SiCl \longrightarrow (CH_3)_3SiC{\equiv}C{-}Si(CH_3)_3$$

1-Pentynyl and 1-hexynyltrimethylsilane were prepared from the appropriate Grignard reagent and trimethylchlorosilane

$$CH_3{-}(CH_2)_n{-}C{\equiv}C{-}MgBr + (CH_3)_3SiCl \longrightarrow CH_3{-}(CH_2)_n{-}C{\equiv}C{-}Si(CH_3)_3$$
$$n = 2 \text{ or } 3$$

The presence of a triple bond in these compounds was confirmed by means of addition products as well as infrared data. Acetylenic chlorosilanes, hitherto unreported, were prepared similarly from acetylenic Grignard compounds and the corresponding chlorosilane. Thus, bis-(dimethylchlorosilyl)-ethyne was prepared as shown

$$BrMgC{\equiv}CMgBr + 2(CH_3)_2SiCl_2 \longrightarrow Cl(CH_3)_2Si{-}C{\equiv}C{-}Si(CH_3)_2Cl$$

The yield of this chlorosilane was considerably smaller than for the other acetylenic chlorosilanes due to the formation of higher substituted products as well as resin formation.

In an analogous manner, 1-pentynylmethyl- and 1-hexynylmethyldichlorosilane were synthesized from methyltrichlorosilane and the appropriate Grignard reagent

$$CH_3{-}(CH_2)_n{-}C{\equiv}C{-}MgBr + CH_3SiCl_3 \longrightarrow CH_3{-}(CH_2)_n{-}C{\equiv}C{-}Si(CH_3)Cl_2$$
$$n = 2 \text{ or } 3$$

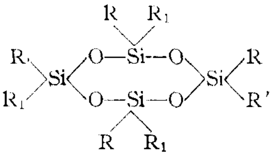
In all of the above reactions it was found that small amounts of cuprous chloride, added to the acetylenic Grignard solution, prior to the addition of the chlorosilane, raised the yield of the acetylenic silicon derivatives considerably. The use of cuprous chloride and similar metallic halides in conjunction with acetylenic Grignard reagents was previously described by Nieuwland and co-workers[3] but has not been applied so far in the silicon field.

The above chlorosilanes can be hydrolyzed in water without rupture of the $\equiv$C—Si bond.

In order to isolate the intermediate hydrolysis products the acetylenic chlorosilanes were converted into the acetoxysilanes and the latter hydrolyzed in saturated salt solution, yielding the corresponding silanediols or disiloxanediols. In the case of 1-pentynyl- and 1-hexynyl-methyldichlorosilane this process can be represented as

$$CH_3{-}(CH_2)_n{-}C{\equiv}C{-}Si(CH_3)Cl_2 \xrightarrow{Ac_2O} CH_3{-}(CH_2)_n{-}C{\equiv}C{-}Si(CH_3)(OAc)_2 \xrightarrow{H_2O}$$
$$CH_3{-}(CH_2)_n{-}C{\equiv}C{-}Si(CH_3)(OH)_2 \text{ or } [CH_3{-}(CH_2)_nC{\equiv}C{-}Si(CH_3)(OH)]_2O$$

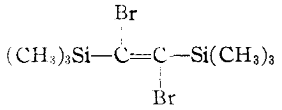
The question of whether the silanediol or the disiloxanediol has been formed was decided by means of molecular weight determinations carried out cryoscopically in dioxane. Additional evidence was obtained by infrared data and hydroxyl determinations. Distillation of these products was very difficult and led in one instance to the isolation of the cyclic tetramer which probably possesses the structure



$R = CH_3$
$R_1 = CH_3{-}(CH_2)_3{-}C{\equiv}C{-}$

Tests were carried out to determine the stability of these acetylenic derivatives toward acids and alkali. These tests indicate, as had been evident from the hydrolysis of the chlorosilanes derived from acetylene, 1-hexyne and 1-pentyne, that these derivatives are stable in dilute acid solutions. Higher homologs of acetylene show a reduced stability toward acids as well as alkali. Silicon derivatives from acetylene itself were stable toward dilute alkali.

Several addition reactions were carried out with silicon-containing acetylenic hydrocarbons. Addition of bromine to bis-(trimethylsilyl)-ethyne resulted in the formation of the dibromide, even when an excess of bromine was used in conjunction with prolonged heating. This dibromide is in all probability the *trans* form which would be expected from stereochemical considerations.



$$(CH_3)_3Si{-}\overset{Br}{C}{=}\underset{Br}{C}{-}Si(CH_3)_3$$

Catalytic hydrogenation of 1-pentynyltrimethylsilane, using palladium black as catalyst led to the formation of the corresponding olefinic derivative

$$CH_3{-}(CH_2)_2{-}C{\equiv}C{-}Si(CH_3)_3 \xrightarrow{H_2} CH_3{-}(CH_2)_2{-}CH{=}CH{-}Si(CH_3)_3$$

Prolonged hydrogenation with additional fresh catalyst did not bring about a conversion to the saturated compound. Platinum oxide failed to reduce this compound altogether.

Experimental

The yields reported in this section are based upon the amount of the substituted acetylene compound used and, in the case of derivatives from acetylene, the ethyl bromide used in the preparation of the acetylenedimagnesium dibromide was taken as basis for the calculations.

The procedure used for the preparation of acetylenic Grignard reagents was essentially that of Iotsitch,[4] in which

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(3) J. P. Danehy, D. B. Killian and J. A. Nieuwland, THIS JOURNAL, **58**, 611 (1936).

(4) I. Iotsitch, *J. Russ. Phys. Chem. Soc.*, **34**, 241 (1902); *Bull. soc. chim.*, **28**, 922 (1902); **30**, 209 (1903).

ethylmagnesium bromide is reacted with acetylene or a substituted acetylene.

Bis-(trimethylsilyl)-ethyne.—Eight grams of powdered cuprous chloride was added to the ethereal solution of acetylenedimagnesium dibromide (prepared from 436 g. (4 moles) of ethyl bromide). This addition proceeded with some heat evolution and the mixture had to be cooled.

The resulting mixture was added to 434 g. (4 moles) of trimethylchlorosilane. A voluminous, white precipitate formed which became so dense that it had to be broken up and more ether added to permit stirring. The mixture was stirred overnight at room temperature and then refluxed for 4.5 hours. The precipitate was filtered off and washed with several portions of ether. The solvent was removed from the filtrate and the residual liquid fractionally distilled. The product, a colorless liquid, distilled at 133–135°. The yield was 30%; n^{25}_{D} 1.4259, d^{25}_{4} 0.763; M_{R} (calcd.) 56.82, M_{R} (found) 57.07. *Anal.* Calcd. for $C_8H_{18}Si_2$: Si, 32.9; mol. wt., 170. Found: Si, 32.8; mol. wt., 173.

***trans*(?)-1,2-Dibromo-1,2-bis-(trimethylsilyl)-ethene.**—In a beaker was placed 20 g. of bis-(trimethylsilyl)-ethyne and 50 cc. of carbon tetrachloride. Nineteen grams of bromine was added slowly to the solution while cooling the mixture in an ice-bath. The uptake of bromine was relatively slow as indicated by the discoloration of the solution. The reaction mixture was heated for one hour on the steam-bath when a colorless liquid resulted. The solvent was removed and the residual material vacuum distilled. The product distilled at 167–168° (77 mm.) in form of a colorless liquid which solidified on standing. Recrystallized from alcohol, colorless plates, m.p. 41–42° (uncor.), resulted. The dibromide probably occurs in the pure *trans* form.

Anal. Calcd. for $C_8H_{18}Br_2Si_2$: Br, 48.5; Si, 16.97. Found: Br, 49.4; Si, 17.01.

1-Hexynyltrimethylsilane.—The preparation of this compound was carried out in a similar manner to that of bis-(trimethylsilyl)-ethyne using equimolecular amounts of the acetylenic Grignard compound and trimethylchlorosilane in the presence of cuprous chloride (2.5 g. per mole of Grignard compound).

1-Hexynyltrimethylsilane, a colorless liquid, distilled at 155°. The yield was 46%; n^{25}_{D} 1.4318, d^{25}_{4} 0.768; M_{R}(calcd.) 51.82, M_{R}(found) 51.25.

Anal. Calcd. for $C_9H_{18}Si$: Si, 18.18; mol. wt., 154. Found: Si, 18.09; mol. wt., 162.

1-Pentynyltrimethylsilane.—This preparation was carried out in an analogous manner to that of 1-hexynyltrimethylsilane.

1-Pentynyltrimethylsilane, a colorless liquid, distilled at 133–134°. The yield was 52%; n^{25}_{D} 1.4272, d^{25}_{4} 0.765, M_{R}(calcd.) 47.19, M_{R}(found) 47.01.

Anal. Calcd. for $C_8H_{16}Si$: Si, 20.0; mol. wt., 140. Found: Si, 19.57; mol. wt., 146.

1-Pentenyltrimethylsilane.—In a citrate bottle was placed 10 g. of 1-pentynyltrimethylsilane, 0.25 g. of palladium black and 200 cc. of decalin (b.p. 194.6°).

The reduction was carried out in a Parr hydrogenation apparatus at room temperature. The hydrogenation was allowed to run for a considerable length of time to see whether complete reduction to the saturated compound would occur. The solution was filtered and the filtrate distilled.

The product, a colorless liquid, distilled at 133–135°; n^{28}_{D} 1.4200, d^{28}_{4} 0.734; M_{R}(calcd.) 48.33, M_{R}(found) 48.9.

Anal. Calcd. for $C_8H_{22}Si_2$: Si, 19.7. Found: Si, 19.1.

An unsaturation test was run, using the Benham–Klee method but omitting mercuric acetate. The unsaturation was 94.4%. In view of the above analytical results it seems fairly certain that the reduction stops at the olefinic stage.

The preparation of the acetylenic chlorosilanes was carried out in a similar fashion to that of the acetylenic silicohydrocarbons. However, in the coupling of the acetylenic Grignard reagents an excess (3 moles) of the appropriate chlorosilane was used in order to obtain high yields of the desired dichlorosilanes.

1-Pentynylmethyldichlorosilane.—1-Pentynylmethyldichlorosilane, a colorless liquid, distilled at 168–169°. The yield was 52.5%.

Anal. Calcd. for $C_6H_{10}SiCl_2$: Si, 15.47. Found: Si, 14.93.

1-Hexynylmethyldichlorosilane.—The preparation of this compound was carried out in an analogous manner to that of 1-pentynylmethyldichlorosilane. 1-Hexynylmethyldichlorosilane distilled at 187–188° in form of a colorless liquid. The yield was 55.5%.

Anal. Calcd. for $C_7H_{12}Cl_2Si$: Si, 14.36. Found: Si, 13.91.

In addition to the above product, a smaller amount of a product, distilling at 148–150° at 8 mm., was obtained, which was found to be **di-(1-hexynyl)-methylchlorosilane**, $[CH_3—(CH_2)_3—C{\equiv}C\text{-}]_2—Si(CH_3)Cl$.

Anal. Calcd. for $C_{13}H_{21}ClSi$: Si, 11.7. Found: Si, 12.4.

Bis-dimethylchlorosilylethyne.—Bis-(dimethylchlorosilyl)-ethyne, a colorless liquid, distilled at 113° at 65 mm. The yield was low due to the formation of higher substitution products.

Anal. Calcd. for $C_6H_{12}Cl_2Si_2$: Si, 26.54. Found: Si, 27.29.

Procedure for the Preparation of Acetylenic Acetoxysilanes.—The acetylenic chlorosilane was treated with the equivalent amount of acetic anhydride in the presence of a small amount of a solution of triethanolamine in acetic anhydride as a catalyst. The reaction mixture was refluxed for 1.5 hours. Low-boiling material was then removed and the residual product vacuum distilled.

1-Pentynylmethyldiacetoxysilane.—The product, a colorless liquid, distilled at 96–102° at 0.3 mm.; the yield was 85%.

Anal. Calcd. for $C_{10}H_{16}O_4Si$: sapn. equiv., 114. Found: sapn. equiv., 116.

1-Hexynylmethyldiacetoxysilane.—This product distilled at 102–106° at 0.3 mm. in form of a colorless liquid. The yield was 83%.

Anal. Calcd. for $C_{11}H_{18}O_4Si$: sapn. equiv., 121. Found: sapn. equiv., 124.

Procedure for the Preparation of Acetylenic Silanediols and Disiloxanediols.—The chlorosilanes or acetoxysilanes, prepared above, were hydrolyzed by adding them slowly to a saturated salt solution with constant stirring. Two layers formed. The organic layer was removed in a separatory funnel, the product dried over anhydrous calcium sulfate, and then centrifuged to give a clear, colorless liquid.

1,3-Dimethyl-1,3-di-(1-pentynyl)-disiloxane-1,3-diol.—*Anal.* Calcd. for $C_{12}H_{22}O_3Si_2$: Si, 20.74; mol. wt., 270; OH, 12.6. Found: Si, 20.68; mol. wt., 261; OH, 12.3.

1,3-Di-(1-hexynyl)-1,3-dimethyldisiloxane-1,3-diol.—*Anal.* Calcd. for $C_{14}H_{26}O_3Si_2$: Si, 18.79, mol. wt., 298. Found: Si, 18.74, mol. wt., 302.

An attempt was made to distil the above product. A major portion of the product, which distilled only with difficulty, came over at 167° at 0.5 mm. in form of a colorless, slightly viscous oil. The molecular weight determination indicated that the cyclic tetramer 2,4,6,8-tetra-(1-hexynyl)-2,4,6,8-tetramethylcyclotetrasiloxane, had probably formed during the distillation.

Anal. Calcd. for $C_{28}H_{48}O_4Si_4$: mol. wt., 560. Found: mol. wt., 583.

Bis-dimethylhydroxysilylethyne.—This product was obtained by direct hydrolysis of the corresponding chlorosilane in a saturated salt solution. The product was a colorless liquid, possessing a pleasant odor.

Anal. Calcd. for $C_6H_{14}O_2Si_2$: Si, 32.2; mol. wt., 174. Found: Si, 32.3; mol. wt., 180.

The infrared spectra of 1,3-dimethyl-1,3-di-(1-pentynyl)-disiloxane-1,3-diol and the corresponding 1-hexynyl compound were determined and show the following characteristic absorption bands

Wave length, microns	Assignment
2.9–3.1	O—H
3.4–3.5	C—H
4.6	C≡C
7.95	Si—(CH_3)
8.8–9.8	Si—O

Acknowledgment.—The authors wish to express their appreciation to Mr. Robert E. Scott for infrared determinations, to Mrs. Richard McC. Ross 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 1

DECHLORINATION OF DICHLOROETHYLENE COPOLYMER

Expt. No.	Copolymer concentration, g./l.	Zinc dust, g./25 ml.	$\frac{-\log(1-x) \times 10^3}{t}$
1-A	24.478	1.000	2.2 ± 0.2
1-B	14.914	1.000	2.1 ± .1
1-C	14.914	2.000	4.1 ± .3
1-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.	$x^{1/2}/t$
11-A	11.776	1.000	0.16 ± 0.01
11-B	13.537	1.000	.17 ± .01
11-C	13.537	2.000	.15 ± .01
11-D	6.761	0.500	.11 ± .01
11-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

$$[\mathrm{ZnCl^+}][\mathrm{ZnCl_3^-}]/[\mathrm{ZnCl_2}]^2 = K_1 \quad (1)$$

$$[\mathrm{RCl^+}][\mathrm{ZnCl_3^-}]/[\mathrm{RCl_2}][\mathrm{ZnCl_2}] = K_2 \quad (2)$$

Finally it is postulated that the rate-determining reaction is

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

and therefore

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

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

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

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).