715. *The Kinetics of Catalytic Polymerisations. Part VI.* Polymerisations catalysed by the Chloroacetic Acids.*

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The reactions of trichloroacetic acid with various vinyl compounds have been investigated. Addition to form the trichloroacetate occurs with hydrocarbons containing unconjugated unsubstituted double bonds. Conjugation with other double bonds and the phenyl group leads to the formation of polymers of relatively low molecular weight. Strong electrophilic substituents inhibit both addition and polymerisation.

MOST detailed studies of cationic polymerisations have been made with Friedel–Crafts catalysts, and the mechanisms by which they function are very complex (see, *e.g.*, Pepper [1]). Strong hydrogen acids such as sulphuric acid (Heiligmann [2]) and hydrochloric acid (Pepper and Somerfield [3]) catalyse the polymerisation of styrene and α-methylstyrene. Many other acids, including acetic, formic, phosphoric, hydrofluoric, nitric, trichloroacetic, sulphuric, and hydrochloric, bring about dimerisation and " conjunct " polymerisation as well as true polymerisation of a wide range of monomers, mostly alkenes, and most of the results are recorded in patents.[4]

Since these hydrogen acids contain readily available protons they may function in a simpler manner than the Friedel–Crafts halides. Also, certain series exist where the acid strength changes in a known, regular way. Such a series is the three chloroacetic acids, a comparison of whose catalytic activities for the same monomer might yield valuable information on the mechanism of the reaction. Furthermore, the fate of an acid catalyst during polymerisation is much more readily determined than that of a Friedel–Crafts halide.

Trichloroacetic acid has been used to convert buta-1 : 3-diene homologues into rubbers [5] and to form dimers and polymers of *cyclo*pentadiene.[6] The chloroacetic acids also co-catalyse Friedel–Crafts polymerisations of *iso*butene; trichloroacetic and dichloroacetic acids titanium tetrachloride-catalysed polymerisation [7] and acetic acid boron trifluoride-catalysed polymerisation.[8] Trichloroacetic acid co-catalyses the titanium tetrachloride-catalysed polymerisation of styrene [9] and stilbene.[10] Russell [11] compared the effect of different co-catalysts on the polymerisation of *iso*butene by stannic chloride in ethyl chloride at −78° and found they are effective in the order $CCl_3{\cdot}CO_2H > Cl{\cdot}CH_2{\cdot}CO_2H \gg Me{\cdot}CO_2H > EtNO_2 > MeNO_2 > PhOH > H_2O$.

RESULTS AND DISCUSSION

Reactions of the Chloroacetic Acids at Carbon–Carbon Double Bonds.—The mechanism of polymerisations catalysed by chloroacetic acids can be more readily understood against

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* Part V, *J.*, 1952, 2363.

[1] Pepper, *Quart. Rev.*, 1954, **8**, 88.

[2] Heiligmann, *J. Polymer Sci.*, 1951, **6**, 155.

[3] Pepper and Somerfield, " Cationic Polymerisation," Heffer, Cambridge, 1953, p. 75; *Chem. and Ind.*, 1954, 42.

[4] *Chem. Abs.*, 1910, **4**, 1909; 1911, **5**, 3519; 1916, **10**, 47; 1920, **14**, 2480; 1927, **21**, 1444; 1928, **22**, 4281; 1930, **24**, 2423; 1932, **26**, 3406; 1933, **27**, 1638, 2572, 2591; 1934, **28**, 4587; 1935, **29**, 526, 1905, 5540.

[5] G.P. 542,647/1930; *Chem. Abs.*, 1932, **26**, 3406.

[6] Eisler, Wassermann, Farnsworth, Kendrick, and Schnurmann, *Nature*, 1951, **168**, 459; Eisler, Farnsworth, Kendrick, Schnurmann, and Wassermann, *J. Polymer Sci.*, 1952, **8**, 157.

[7] Plesch, *Nature*, 1947, **160**, 868.

[8] Evans, Meadows, and Polanyi, *Nature*, 1947, **160**, 869.

[9] Plesch, " Cationic Polymerisation," Heffer, Cambridge, 1953, p. 103.

[10] Brackman and Plesch, *ibid.*, p. 19.

[11] Russell, *ibid.*, p. 114.

the background of the general reactions of these acids with carbon–carbon double bonds. Frequently trichloroacetic acid adds to a double bond,[12-15] rather than polymerising the olefin.

Since the action of the chloroacetic acids on only a few unsaturated compounds has been recorded, we have made a general survey of the effect of these acids on carbon–carbon double bonds. Unsaturated compounds were divided arbitrarily into five groups: (1) hydrocarbons containing "isolated" double bonds; (2) hydrocarbons containing conjugated double bonds; (3) compounds containing phenyl groups and double bonds; (4) compounds containing alkoxyl and carboxyl groups and double bonds; (5) compounds containing heterocyclic oxygen or nitrogen (see Table).

Trichloroacetic acid was added at 20° to the olefin either pure or, if reaction was slow, in ethylene dichloride or nitromethane. Up to 20% of the acid was added if necessary to achieve a positive result. Several methods were used conjointly to determine, when reaction occurred, whether it was addition or polymerisation or both, namely, observation of change of temperature and increase in viscosity, alcohol precipitation of polymers, acid titration, titration of residual double bonds, and microchemical analysis and molecular weights of products. The results are summarised in the Table.

Summary of reactions of trichloroacetic acid at double bonds.

				Polymer		
Class	Compound	Reaction *	D.P.	C (%)	H (%)	Cl (%)
1	3-Methylbut-2-ene	Addn.				
	Pent-2-ene	,,				
	*cyclo*Hexene	,,				
	Pinene	,,				
	Limonene	,,				
2	Isoprene	Conj. Polyn.	5—6	66·2	8·41	17·9
	Phellandrene	Polyn.	9—10	78·1	9·42	7·48
	*cyclo*Pentadiene	,,	18			
3	Styrene	Polyn.	10—20			3·25—9·51
	p-Chlorostyrene	,,				
	α-Methylstyrene	,,	2—15			6·7—24·8
	Anethole	,,	9—10			
	*iso*Safrole	,,	?			nil
	*iso*Eugenol	,,	?			nil
	Indene	,,	20			nil
	Safrole	None				
	Eugenol	,,				
	Stilbene	,,				
4	*n*-Butyl vinyl ether	A(P)				
	Ethyl vinyl ether	,,				
	2-Chloroethyl vinyl ether	,,				
	Phenyl vinyl ether	,,	7—9	64·6	7·35	9·86
	Methyl acrylate	None				
	Ethyl acrylate	,,				
	Methyl methacrylate	,,				
	Coumarin	,,				
	Cinnamic acid	,,				
5	2 : 3-Dihydropyran	Polyn.	7—8			18·3
	Pyrrole	,,		Insoluble resin		
	Coumaranone	,,				
	Indole	,,	2—3	N, 8·6		26·4
	β-Methylindole	None				

* Addn., Addition; Polyn., Polymerisation; A(P) Addition with a little polymerisation.
? Not certain.

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[12] Scovill, Burk, and Herman, *J. Amer. Chem. Soc.*, 1944, **66**, 1039.
[13] Nernst and Hohmann, *Z. phys. Chem.*, 1893, **11**, 352.
[14] Timotheev, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 838.
[15] Dorris, Sowa, and Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2689.

The reactions of trichloroacetic acid at isolated double bonds are similar to those of the hydrogen halides, addition generally taking place in accordance with Markownikov's rule, *e.g.*, with 3-methylbut-2-ene:

$$Me_2C = CHMe + CCl_3{\cdot}CO_2H \longrightarrow CCl_3{\cdot}CO_2{\cdot}CMe_2{\cdot}CH_2Me$$

These addition products tend to be unstable, and with water yield the alcohol in some cases even at room temperature. For instance, the reaction

$$MeHC = CHEt + CCl_3{\cdot}CO_2H \longrightarrow CCl_3{\cdot}CO_2{\cdot}CHMe{\cdot}CH_2Et$$

is endothermic and on addition of water evolution of heat is accompanied by the formation of the corresponding alcohol, $HO{\cdot}CHMe{\cdot}CH_2Et$. The product of dimerisation of α-methylstyrene with trichloroacetic acid loses the acid radical similarly, and this is reasonably true for all the polymers.

With compounds containing conjugated double bonds both addition and polymerisation can occur. With isoprene, both proceed simultaneously; in absence of solvent about 10% of the isoprene is polymerised; in nitromethane the reaction is very rapid and more polymer is formed (20—30%). Phellandrene in absence of solvent is over 90% polymerised. The chlorine content of these two polymers indicates that there is one trichloroacetate end-group per polymer molecule.

Styrene and α-methylstyrene are readily and quantitatively polymerised by trichloroacetic acid in the absence of solvent and in solution; α-methylstyrene yields a large proportion of dimer. Both polymers contain one trichloroacetate group per polymer molecule. Anethole gives mainly the dimer in absence of solvent but polymers of D.P. 9—10 in ethylene dichloride. *iso*Eugenol and *iso*safrole react readily in ethylene dichloride, giving polymers containing a chlorine-free fraction insoluble in ethylene dichloride, benzene, or ether, and a soluble fraction of molecular weight 1000—1200. Solutions of eugenol and safrole become bottle-green in the presence of trichloroacetic acid but no reaction can be detected. An approximate study of the relative rates of polymerisation in this class of monomer showed the sequence anethole > α-methylstyrene > *iso*eugenol = *iso*safrole > styrene. Indene yields a chlorine-free high polymer with trichloroacetic acid, both without solvent and in ethylene dichloride.

The chloroacetic acids react exothermically with the alkyl vinyl ethers, but very little polymer is formed. The product from butyl vinyl ether has a molecular weight of 203 (Found: C, 65·5; H, 12·8%) and contains only a trace of chlorine. It is probably largely butyl alcohol with condensation products and a trace of polymer. Phenyl vinyl ether in nitromethane reacts readily with trichloroacetic acid giving 10—15% of polymerisation, the remainder undergoing the alternative reaction. The acrylates are more readily polymerised by anionic catalysts and it is not surprising that the chloroacetic acids are without effect. No reaction was detected even when the monomer was kept in dichloroacetic acid for several days. Pfeiffer *et al.*[16] have described an addition compound between trichloroacetic acid and cinnamic acid.

2 : 3-Dihydropyran is readily polymerised by trichloroacetic acid and the polymers contain one trichloroacetate group per polymer molecule. An insoluble polymer is obtained from pyrrole with trichloroacetic acid. Indole gives a polymer which is more readily soluble in alcohol than in benzene, ether, or acetone. Both the poly-2 : 3-dihydropyran and the polyindole contain one trichloroacetate end-group per polymer molecule.

Conclusions.—It is clear that, for polymerisation to occur, there must be some degree of resonance between the double bond and other double bonds or a phenyl group. Addition occurs readily with unsubstituted isolated double bonds (class 1), conjugation leads to polymerisation together with addition (isoprene), and resonance with a phenyl group leads to polymerisation alone (class 3). Comparison of eugenol and safrole with *iso*eugenol and *iso*safrole is interesting; in eugenol and safrole resonance with the phenyl

[16] Pfeiffer, *Ber.*, 1914, **47**, 1580.

group is prevented by the insertion of a methylene group between the double bond and the phenyl group, and no polymerisation takes place. Steric hindrance may be responsible for the inability of these catalysts to polymerise stilbene. Strongly electronegative groups on the carbon atoms of the ethylenic double bond tend to deactivate it towards both addition and polymerisation. Where the double bond is adjacent to an ether linkage reaction with the oxygen atom predominates, but again the presence of a phenyl group enhances polymerisation. The cyclic compounds of this type show a greater tendency to polymerise.

The Polymers.—The polymers formed can be divided into two groups, with or without trichloroacetate end-groups; in the former there is always one end-group per polymer molecule. The interpretation of the chlorine content of the polymers in terms of trichloroacetate end-groups has been justified, for styrene and α-methylstyrene, by infrared analysis and a test for ester-linkages.[17] This difference in the constitution of the polymers suggests a significant difference in the mechanism of their formation; styrene and indene could be representative of either class and so the kinetics and mechanism of the polymerisation of both compounds were investigated in detail. The results for styrene and α-methylstyrene are reported in the following papers.

EXPERIMENTAL

Materials.—The chloroacetic acids were recrystallised from benzene and fractionated at reduced pressure, the middle fraction of constant b. p. being retained. They were then distilled from $MgSO_4$ to remove water and stored in an atmosphere of dry nitrogen. Styrene and α-methylstyrene were shaken with aqueous potassium hydroxide, washed with water, and fractionated thrice under reduced pressure. After a final distillation from barium monoxide to remove water they were stored in the dark in an atmosphere of dry nitrogen. The other vinyl compounds were washed with aqueous sodium hydroxide and water, then fractionated under reduced pressure. They were distilled from calcium chloride to remove water and stored under dry nitrogen. Nitromethane was refluxed for several hours in a current of dry nitrogen, then fractionated from calcium chloride. Ethylene dichloride was washed with aqueous sodium hydroxide, then water, and fractionated from calcium chloride.

Extraction of Polymers.—Polymers insoluble in methanol were dissolved in benzene, reprecipitated, and redissolved. The solution was frozen as a film inside a tube with solid CO_2–methanol, and the tube was evacuated for several hours to remove all remaining monomer and solvent. This process was repeated to constant weight. Polymers soluble in methanol were extracted by shaking the solution several times with water to remove excess of catalyst and evaporating the solution under reduced pressure at room temperature to remove most of the solvent and unchanged monomer. The extract, consisting of polymer of low molecular weight contaminated with solvent and unchanged monomer, was subjected to a horizontal temperature gradient for several hours, whereupon the various fractions collected along different sections of the evacuated tube.

Titration of Residual Monomer and Acid.—Solutions of 0·1—0·2N-bromine in glacial acetic acid were added to known amounts of the reaction solution and excess of bromine was estimated with potassium iodide and thiosulphate. To estimate acid, known fractions of the solutions were extracted with water, and excess of sodium hydroxide was added and back-titrated with hydrochloric acid. This was not possible for nitromethane solutions.

Viscosities.—Ostwald viscometers were used.

Molecular Weights.—These were determined cryoscopically in benzene by the Beckmann method.

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[17] Brown and Mathieson, *J.*, 1957, 3620.