860. *The Pyrolysis of Poly-*(sec.*-butyl α-Chloroacrylate*).

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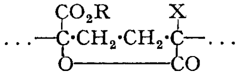
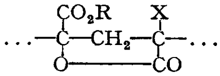
When poly-[(+)-*sec.*-butyl α-chloroacrylate] is pyrolysed, *sec.*-butyl chloride is formed as the result of a lactonization reaction. The configuration of the chloride is inverted, with about 40% racemization. Mechanisms for the lactonization reaction have been considered, and it is concluded that a "unimolecular" process involving the formation of butyl ions occurs at least to the extent of the racemization of the butyl chloride.

(+)-*sec.*-Butyl γ-chlorobutyrate, used as a model for the reactive units of the chloroacrylate polymer, forms, with inversion, *sec.*-butyl chloride of rotatory power similar to that obtained from the chloroacrylate polymer, but only when heated in presence of zinc chloride or similar catalyst.

During an investigation of the polymers of methyl α-chloro- and α-bromo-acrylates, Marvel and Cowan (*J. Amer. Chem. Soc.*, 1939, **61**, 3156) observed that, when pyrolysed, the bromoacrylate polymer evolved methyl bromide as well as hydrogen bromide. Polymerization of the methyl esters, or of other esters (*ibid.*, 1940, **62**, 3495), led on occasion to products which were low in halogen; they suggested that this might also be due to loss of alkyl halide. Loss of halide would result in formation in the polymers of lactone structures (I) or (II), according as the polymer had a head-to-head or head-to-tail structure. The head-to-head structure yielding the six-membered lactone ring (I) was preferred by the above authors on grounds of chemical behaviour of the polymers. The head-to-tail structure seems to be that more generally met with in ethenoid polymers.



(I)



(II)

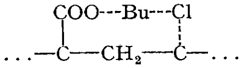
Poly-[(+)-*sec.*-butyl α-chloroacrylate], derived from (+)-*sec.*-butanol, has been pyrolysed. Heated *in vacuo* at 190°, the polymer decomposed, yielding as volatile products butene, hydrogen chloride, *sec.*-butyl chloride, and probably some monomer formed by depolymerization. The butyl chloride was lævorotatory. Rotatory powers of the materials involved in the series of reactions are given below:

	$[\alpha]_D^t$	Temp.
(+)-*sec.*-Butanol	+15·1°	20°
(+)-*sec.*-Butyl α-chloroacrylate	+34·2	22
Poly-[(+)-*sec.*-butyl α-chloroacrylate] (solid)	+ 8·0	21·5
(−)-*sec.*-Butyl chloride	−22·2	21

Since *sec.*-butyl chloride of the same configuration as (+)-*sec.*-butanol is dextrorotatory (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1268), it follows that in the series of reactions leading from butanol to butyl chloride, inversion occurred of the configuration of the butyl radical. The monomeric ester was prepared by esterification of (+)-*sec.*-butanol with α-chloroacrylic acid; the configuration of the butyl radical would be preserved in this reaction, apart from the possibility of very slight racemization. Polymerization of the monomeric butyl α-chloroacrylate would not affect the configuration of the butyl radical. The inversion must therefore have occurred during the pyrolysis, in the formation of butyl chloride by the lactonization reaction.

The possibility has been considered that butyl chloride might alternatively have been formed by reaction of the carbobutoxy-groups in the polymer with hydrogen chloride. The latter is formed in the pyrolysis of poly(methyl α-chloroacrylate), and can therefore arise by dehydrochlorination of the main polymer chain, with formation of ethylenic unsaturation in this. In the case of the pyrolysis of poly-(*sec.*-butyl α-chloroacrylate), hydrogen chloride could additionally arise from lactonization of the chloroacrylic acid units left in the polymer when butylene was evolved. Experiment indicated that butyl chloride was unlikely to be formed in this way; *sec.*-butyl hexanoate, α-chloropropionate, and γ-chlorobutyrate, esters which might in some degree simulate the reactive units in the butyl chloroacrylate polymer, gave no butyl chloride (or butene) when heated with hydrogen chloride.

If the formation of butyl chloride in the pyrolysis of poly-(*sec.*-butyl α-chloroacrylate) proceeded solely by a "bimolecular" mechanism through the transition state (III) the butyl radical would undergo complete inversion of configuration, to yield fully active butyl chloride. One might suppose, as an alternative, that the butyl chloride could arise by formation of butyl ion from the carbobutoxy-group, followed by reaction of the ion with chlorine. The butyl chloride produced in this "unimolecular" reaction would be expected to be racemized, or partially racemized with inversion (owing to screening of the butyl by the carboxyl ion). From the indications given by Letsinger, Maury, and Burwell (*J. Amer. Chem. Soc.*, 1951, **73**, 2373), fully active *sec.*-butyl chloride (from fully active *sec.*-butanol of $[\alpha]_D^{20}$ 15·1°, $[\alpha]_D^{25}$ 14·9°) would have $[\alpha]_D^{25}$ about 36·8°. On this basis, the *sec.*-butyl chloride produced in the pyrolysis was about 40% racemized, indicating that the "unimolecular" reaction occurred to at least this extent.



$$\ldots-\overset{\displaystyle\text{COO}---\text{Bu}---\text{Cl}}{\text{C}-\text{CH}_2-\text{C}}-\ldots$$

(III)

sec.-Butyl γ-chlorobutyrate, which might provide a model for the lactonization behaviour of poly-(*sec.*-butyl α-chloroacrylate), was stable when boiled by itself or in presence of hydrogen chloride, but readily evolved butene, hydrogen chloride, and *sec.*-butyl chloride when heated with very small amounts of zinc chloride, stannic chloride, or sulphuric acid. The *sec.*-butyl chloride produced from active *sec.*-butyl γ-chlorobutyrate was inverted in configuration, and showed activity (when corrected to initial *sec.*-butanol of the same rotatory power) similar to that produced in the pyrolysis of poly-[(+)-*sec.*-butyl α-chloroacrylate]. The kind of catalyst effective in bringing about the decomposition of the chlorobutyrate suggests that this was facilitated by formation at the carbobutoxy-group of an oxonium adduct with the catalyst. The formation of such an adduct would not of necessity imply the subsequent formation of free butyl ion.

If the chlorobutyrate is a model for the polychloroacrylate in its pyrolytic behaviour, hydrogen chloride is not a catalyst for the decomposition of the latter. Since no other possible catalyst is known to have been present in the polychloroacrylate, its decomposition may have been purely thermally induced.

EXPERIMENTAL

(+)-sec.-*Butyl α-Chloroacrylate*.—Technical (±)-*sec.*-butanol was purified by fractional distillation and resolved by Pickard and Kenyon's method (*J.*, 1913, **103**, 1937); the active alcohol had b. p. 98—99°, d_4^{20} 0·8079, $[\alpha]_D^{20}$ +15·1°.

α-Chloroacrylic acid was prepared from trichloroethylene by Crawford and McLeish's method (B.P. 514,619); it was purified by recrystallization from hot light petroleum, the solution being cooled to −15° before the crystals of acid were filtered off. These were freed from residual solvent *in vacuo* over calcium chloride and active charcoal.

Butanol (47 g.), chloroacrylic acid (80 g., 1·14 mol.), benzene (150 g.), 98% sulphuric acid (1 g.), and technical *tert.*-butylcatechol (1 g.) were mixed with shaking in the order named, and esterification carried out in an apparatus with automatic separation of water of reaction from the condensed reflux of benzene–water azeotrope. The reaction was complete in 6¼ hours. The reaction mixture was cooled and made alkaline with potassium carbonate solution, and the organic layer washed twice with water and dried (Na_2SO_4), to give 227 g. of liquid. This was distilled under reduced pressure through a 9″ Vigreux column. 69 G. of ester were obtained, of b. p. 56—59·5°/13 mm., n_D^{20} 1·4368. Redistilled in the same apparatus, 61·5 g. (59·6%) of ester were collected between 56·5° and 57°/13 mm. This had n_D^{20} 1·4368, d_4^{20} 1·0488, d_4^{25} 1·0424, $[R_L]_D$ 40·57 (Calc.: 40·58), $[\alpha]_D^{22}$ +34·2° (Found: Cl, 21·8. Calc. for $C_7H_{11}O_2Cl$: Cl, 21·8%).

Poly-[(+)-sec.-*butyl α-Chloroacrylate*].—The monomeric ester had been prepared some 15 hours previously, and had been stored in the dark at −15° to minimize autoxidation. Benzoyl peroxide (0·0125 g.) was dissolved in the ester (50 g.), and the solution poured into a casting cell, made of two sheets of glass separated by a flexible gasket round the edges. The size of the glass plates and thickness of the gasket were chosen to provide a sheet of the polymer of

3 mm. thickness. The cell was sealed up by replacing the gasket where it had been pulled out to allow of filling, and heated at 50° for 64 hours, by which time the ester had polymerized to a solid. A further 24 hours' heating at 100° was given to complete polymerization to equilibrium. On removal of the gasket and cooling, the resin separated from the glass plates. The polymer was glassy, clear, and colourless, and had n_D^{20} 1·4961, d_4^{20} 1·231, d_4^{26} 1·228, $[\alpha]_D^{21\cdot5}$ (solid) +8·0°, $[\alpha]_D^{21}$ (in chloroform, $c = 2\cdot290$) +14·4°, (in methylene dichloride, $c = 1\cdot933$) +13·7° (Found: Cl, 21·7%).

The polymer was coarsely powdered for pyrolysis experiments. This was done by chilling it in liquid nitrogen, which embrittled it so that it could readily be pulverized in a mortar whilst cold. The powder was dried *in vacuo* over phosphoric oxide.

Pyrolysis of Poly-[(+)-sec.*-butyl α-Chloroacrylate*].—The polymer was pyrolysed *in vacuo* (10^{-4} mm.) at 190°. The pyrolysis vessel was similar in construction to a " drying pistol " and the pyrolysis chamber was heated by the vapour of boiling ethylene glycol in the surrounding jacket. The polymer was contained in a glass tray of semicircular cross-section, fitting closely to the walls of the pyrolysis chamber, and measuring 13 cm. long by 2 cm. external diameter of cross-section. Each charge of polymer weighed approximately 10 g.; four pyrolyses were carried out.

The pyrolysis chamber was connected with a receiver which could be cooled in liquid nitrogen. The products of pyrolysis condensed here at any time could be distilled into a second receiver, also cooled in nitrogen, and graduated so that the volume of condensate could be measured. This second receiver could be isolated from the evacuated pyrolysis system, and the contents distilled at atmospheric pressure from baths of appropriate temperatures. It was proposed by this means to estimate the contents of the distillate in hydrogen chloride, butene, and crude butyl chloride, the last being the residue left when the condensate had reached room temperature. The method failed mainly because hydrogen chloride was retained by the condensate far above the b. p. of the former. Data obtained in the four pyrolyses are given below:

Polymer, g.	Pyrolysis residue, g.	$\frac{\text{Residue}}{\text{Polymer}}$, %	Cl content of residue, %	Crude butyl chloride (g.), after heating for (hours):				
				0—½	½—1	1—1½	1½—3½	Total
10·044	5·230	52·10	10·7	—	—	—	—	2·43
9·368	5·081	54·24	11·2	—	0·37	0·05	0·0	
8·899	4·864	54·67	11·4	0·29	0·47	0·13	0·01	0·90
8·756	4·769	54·46	11·4	0·51	0·34	0·07	0·10	1·02
38·077	19·944							4·35

Distillation of Crude sec.*-Butyl Chloride.*—The crude chloride (3·87 g.) was distilled from a small bulb sealed to a Vigreux column 15 cm. long and of 0·7-cm. bore. Butene and hydrogen chloride were at first evolved; condensation of slightly moist butyl chloride (0·39 g.) commenced at 55°; pure butyl chloride passed over at 68° (0·85 g.). A high-boiling residue remained (1·52 g.). The butyl chloride fraction had d_4^{20} 0·8693, d_4^{25} 0·8690, $[\alpha]_D^{21}$ −22·2°, $[\alpha]_D^{25}$ (in *n*-heptane, $c = 2\cdot802$), −20° (Found: Cl, 37·7, 38·2. Calc. for C_4H_9Cl: Cl, 38·3%). (In these and other micro-Carius determinations of chlorine in butyl chloride, difficulty was found in sealing up the volatile chloride without loss.) The high-boiling residue had d_4^{20} 1·0128, d_4^{25} 1·0103, $[\alpha]_D^{21\cdot5}$ +15·4° (Found: Cl, 24·4%).

Properties of Pyrolysis Residue.—The sintered, light brown residue was insoluble in hot or cold water. It dissolved in cold dilute sodium hydroxide to a yellow, viscous solution; it did not dissolve in epichlorohydrin, tetrahydrofuran, acetone, dioxan, ethanol, methylene dichloride, or chloroform.

sec.*-Butyl γ-Chlorobutyrate.*—*γ-Chlorobutyric acid.* Tetramethylene chlorohydrin was prepared from tetrahydrofuran and hydrogen chloride (*Org. Synth.*, Coll. Vol. II, p. 571) and oxidized with nitric acid in the same way as described (*op. cit.*, Coll. Vol. I, 2nd Edn., p. 168) for oxidation of trimethylene chlorohydrin to β-chloropropionic acid, with molar substitution of tetramethylene chlorohydrin. The temperature of the oxidation mixture was allowed to rise to 50—55°. Tetramethylene chlorohydrin (505 g.) gave distilled γ-chlorobutyric acid (392 g.), b. p. 68—74°/0·8 mm.; on redistillation this gave 373 g. (65·5%) of acid, b. p. 67°/0·5 mm., m. p. 14°, n_D^{20} 1·4540, d_4^{20} 1·2373, $[R_L]_D$ 26·84 (Calc.: 27·08) (Found: Cl, 29·2. Calc. for $C_4H_7O_2Cl$: Cl, 28·95%).

Esterification with sec.*-butanol.* *sec.*-Butanol (37 g.), γ-chlorobutyric acid (65 g., 1·05 mol.), benzene (150 g.), and toluene-*p*-sulphonic acid hydrate (1·0 g.) were mixed and heated under reflux in an apparatus provided with an automatic separator of water of esterification, until no more water was rejected. The reaction mixture was washed with water, made alkaline with 20% aqueous sodium hydroxide, washed again with water, and dried (Na_2SO_4). Solvent was removed, and the ester fractionated under reduced pressure, with use of a 9-in. Vigreux column. From (+)-*sec.*-butanol, d_4^{20} 0·8084, $[\alpha]_D^{20}$ +12·2°, the ester (34 g., 38%) was collected at 85—86°/10 mm., and had n_D^{20} 1·4323, d_4^{20} 1·0210, d_4^{25} 1·0156, $[R_L]_D$ 45·40 (Calc.: 45·67), $[\alpha]_D^{20}$ +17·9° (Found: Cl, 20·2. Calc. for $C_8H_{15}O_2Cl$: Cl, 19·85%). From (±)-*sec.*-butanol, the ester (30 g., 33·6%) had b. p. 84·5—85°/10 mm., n_D^{20} 1·4323, d_4^{20} 1·0207, $[R_L]_D$ 45·42 (Found: Cl, 20·4%).

(±)-sec.-*Butyl α-Chloropropionate.*—This was prepared similarly to the γ-chlorobutyrate. α-Chloropropionic acid (108·5 g.) gave redistilled ester (116·5 g., 70·8%), with b. p. 61·5°/15 mm., n_D^{20} 1·4201, d_4^{20} 1·0190, $[R_L]_D$ 40·88 (Calc.: 41·05) (Found: Cl, 21·8. Calc. for $C_7H_{13}O_2Cl$: Cl, 21·6%).

Pyrolysis of sec.-*Butyl γ-Chlorobutyrate.*—(*a*) The ester was contained in a 150-c.c. flask, provided with a thermometer reaching into the liquid, a narrow inlet tube for hydrogen chloride, and a 6-in. Vigreux column connected directly to a trap cooled to −80° in solid carbon dioxide–methanol. The flask was heated by a metal-bath. The ester (22 g.) was distilled at atmospheric pressure for 30 minutes without producing low-boiling material or evolving hydrogen chloride; the temperature of the boiling liquid was in the range 200—211°. A stream of dry hydrogen chloride was passed through for 45 minutes, the temperature of the boiling liquid being in the same range. It was estimated that about 5 molar proportions of hydrogen chloride passed through the boiling ester. On conclusion of this treatment, the trap contained only a drop of liquid, smelling of the ester.

(*b*) The above treatment of ester with hydrogen chloride at the b. p. was carried out with (±)-*sec.*-butyl hexanoate and α-chloropropionate. The temperatures of the liquid esters, and times of treatment were respectively 185—190°, 4 hours; and 173°, 2 hours. In both cases the sole condensate was a drop of liquid smelling of ester.

(*c*) Samples of ester containing in solution small amounts of zinc chloride, stannic chloride, or sulphuric acid began to evolve hydrogen chloride and butene at about 132°. Trimethylamine hydrochloride and aniline hydrochloride were not catalysts for this decomposition. Aluminium chloride caused more profound decomposition, with blackening.

(*d*) (+)-*sec.*-Butyl γ-chlorobutyrate (20 g.), containing in solution fused zinc chloride (0·05 g.), was heated in the apparatus used in (*a*). At ester temperature 130°, decomposition commenced, with evolution of hydrogen chloride. Between 142° and 169°, distillation occurred, with a vapour temperature at the column top ranging between 39° and 60°, the temperature falling with time. The pyrolysis occupied 55 minutes, after which distillation practically ceased. The residue weighed 11·5 g. (Found: Cl, 10·9%). The distillate (9 g. at −80°) weighed 6·5 g. when warmed to room temperature, the loss in weight being due to evolution of hydrogen chloride and butene. It was distilled through a 6-in. Vigreux column. Distillation commenced at 68°. After neglect of a small forerun (0·2 g.), the butyl chloride (3·4 g.) was collected at 68°. The residue (<0·5 g.) was mainly column drainings. The butyl chloride had d_4^{20} 0·866, $[\alpha]_D^{20}$ −16·0° (Found: Cl, 38·0. Calc. for C_4H_9Cl: Cl, 38·3%).

The pyrolysis residue was treated with an equal volume of water, to extract butyrolactone, and the extract evaporated on the water-bath. This residue was converted into γ-hydroxybutyrophenylhydrazide by heating it at 100° with phenylhydrazine. The solid product, crystallized from chloroform, and recrystallized from benzene, had m. p. 93—93·5°. Seib (*Ber.*, 1927, **60**, 1399) gives 93·7—94° for the m. p. of this compound.

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