[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

# Free Radical Addition and Transfer Reactions of Hydrogen Chloride with Unsaturated Compounds

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The telomerizations of hydrogen chloride with allyl chloride and with styrene in the presence of benzoyl peroxide, reported by Ford, Hanford, Harmon and Lipscomb,[2b] have been re-investigated. It has been found that hydrogen chloride, aqueous or anhydrous, does indeed reduce the molecular weight of polymerizing allyl chloride at 100°. While the dichloropropanes are mostly 1,2-dichloropropane formed by normal addition of hydrogen chloride, 1,3-dichloropropane, formed by the peroxide-initiated abnormal addition also has been found. Calculations of transfer constants indicate that chain transfer with hydrogen chloride is more probable for the trichlorohexyl than for the 1,3-dichloro-2-propyl radical. An abnormal addition of hydrogen chloride to propylene has also been observed, but indications are that such additions to most 1-alkenes will be difficult. Reactions of hydrogen chloride with styrene at 100° in the presence and absence of benzoyl peroxide show that the free radical polymerization to high polymer is little affected by hydrogen chloride but that simultaneous ionic reaction lead to large quantities of α-phenethyl chloride and low polymer containing much chlorine. No β-phenethyl chloride was detected in the α-isomer. There is no evidence of a free radical reaction of hydrogen chloride with styrene.

Previous to 1940, all attempts to obtain an abnormal addition of hydrogen chloride to alkenes had failed.[1] This result was accounted for on the basis that the energy requirement for step (2) of the free radical chain mechanism was too high

$$\mathrm{Cl\cdot + H_2C{=}CHR \longrightarrow ClCH_2{-}\dot{C}HR} \qquad (1)$$

$$\mathrm{ClCH_2{-}\dot{C}HR + HCl \longrightarrow ClCH_2{-}CH_2R + Cl\cdot} \qquad (2)$$

the difference in C–H and H–Cl bond dissociation energies being 15–20 kcal./mole. Subsequently, evidence of free radical reactions of hydrogen chloride with unsaturated compounds has been presented from these laboratories. Hanford and Harmon[2a] obtained a free radical telomerization of hydrogen chloride with ethylene. Raley, Rust and Vaughan[3a] obtained a photochemical addition of hydrogen chloride to ethylene in the vapor phase to give ethyl chloride at both 26 and 155°. The estimated chain length, at least 30, and the inhibition by oxygen and isobutylene indicated a free radical chain mechanism. A peroxide-catalyzed vapor phase addition was also realized above 140° with ethylene, but with propylene the reaction was very slow, and only small, unstated quantities of *n*- and *i*-propyl chloride were obtained. These results indicated that the primary chloroethyl radical might be able to effect reaction (2) although the secondary or tertiary alkyl radicals from other alkenes encounter more difficulty.[3b] Another possible explanation for the difficulty of abnormal addition to other alkenes was that these could react with chlorine atoms to yield unreactive allyl radicals which could not continue reaction.[3a] This suggestion receives support from the work of Ecke, Cook and Whitmore,[4] who obtained 24% primary chloride (abnormal addition product) from *t*-butylethylene, hydrogen chloride, and benzoyl peroxide at room temperature, but only in the presence of considerable excess alkene. Their results show that 7 moles of hydrogen chloride added abnormally per mole of benzoyl peroxide initially present. Apparently, when the normal addition is retarded by drying and dilution of hydrogen chloride with excess monomer,[5] and when formation of unreactive allyl radicals is impossible, then short chains can propagate at room temperature with alkenes other than ethylene. The recent report of Ford, Hanford, Harmon and Lipscomb[2b], that benzoyl peroxide effected a reaction of aqueous chloride with ethylene at 100° to give a mixture of primary alkyl chlorides, is therefore consistent with previous work since neither normal nor abnormal addition occurred in the absence of peroxide. However, their supposed benzoyl peroxide-initiated telomerization reactions of hydrogen chloride with allyl chloride and styrene, particularly in the absence of controls without peroxide, warranted re-investigation.

It has now been found that a small amount of abnormal addition of hydrogen chloride to allyl chloride to give 1,3-dichloropropane occurs, and therefore that 2:1 and 3:1 products may also be expected to arise through a free radical mechanism. The supposition of Ford, *et al.*, on the telomerization of hydrogen chloride with allyl chloride is thus substantiated although their theoretical discussion is unsatisfactory. However, essentially all of the reaction of hydrogen chloride with styrene occurs by an ionic mechanism which accompanies the free radical polymerization. Tests with propylene and hydrogen chloride have given low but measurable yields of the abnormal addition product, *n*-propyl chloride, and throw some light on the scope of abnormal additions of hydrogen chloride.

**Results with Allyl Chloride.**—Experiments with allyl chloride are summarized in Table I. Reaction times were chosen so that essentially all the initiator could decompose. Experiment 1 shows that 18% yield of propylene chloride (b.p. <100°) is the main product of reaction of allyl chloride with aqueous hydrogen chloride in the absence of peroxide. This product arises from the normal ionic addition mechanism[6] and very little polymeric material is formed. Experiment 2, in the presence of peroxide and absence of aqueous hydrogen chloride, gave 28% yield of polymer, mostly distillable. Experiment 3, with both peroxide and aqueous hydrogen chloride, like the recorded experiment of

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[1] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] (a) W. E. Hanford and J. Harmon, U. S. Patents 2,418,832 (1947), 2,440,801 (1948); (b) T. A. Ford, W. E. Hanford, J. Harmon and J. D. Lipscomb, THIS JOURNAL, **74**, 4323 (1952).

[3] (a) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 2767 (1948); (b) K. Nozaki, *Discs. Faraday Soc.*, **2**, 337 (1947).

[4] G. G. Ecke, N. C. Cook and F. C. Whitmore, THIS JOURNAL, **72**, 1511 (1950).

[5] F. R. Mayo and J. J. Katz, *ibid.*, **69**, 1339 (1947); F. R. Mayo and M. G. Savoy, *ibid.*, **69**, 1348 (1947).

[6] Kharasch, Kleiger and Mayo, *J. Org. Chem.*, **4**, 428 (1939).

TABLE I

REACTION OF HYDROGEN CHLORIDE WITH ALLYL CHLORIDE[a]

| Expt. no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Charge (g.) | | | | | | | | |
| Allyl chloride | 28.0 | 27.4 | 28.0 | 17.5 | 28.0 | 42.0 | 41.7 | 15.1 |
| Hydrogen chloride | 40.0[b] | ... | 40.0[b] | ... | 7.2 | 9.7 | 9.1 | 7.3 |
| Benzoyl peroxide | ... | 0.40 | 0.40 | 0.39 | 0.40 | 0.60 | 0.59 | 0.24 |
| Other | ... | ... | ... | 9.33[c] Dichloropropanes | | | Dried[d] | 21.3 *n*-Hexane |
| Reaction | | | | | | | | |
| Time, hr. | 11 | 16 | 11 | 16 | 16 | 233 | 336 | 15 |
| Temp., °C. | 100 | 100 | 100 | 100 | 100 | 50 | 50 | 80 |
| Products (g.) | | | | | | | | |
| Dichloropropanes[e] 1,2- | 7.61 | ... | 6.26 | 8.25 | 5.16 | 3.94 | 5.08 | 2.62[n] |
| Dichloropropanes[e] 1,3- | | | | | 2.15 | 1.64 | 1.95 | 1.62 |
| "Dimer"[f] | 0.38[j] | 1.20 | 7.57[k] | 4.08[l] | 5.13[m] | .72 | 0.90 | 0.36 |
| Dimer hydrochloride[g] | | | | | | 1.97 | 2.78 | 1.04 |
| Higher boiling[h] | | 3.85 | | | | 1.82 | 2.05 | 0.63 |
| Highest b.p. (°C., mm.) | 100, 12 | 190, 0.3 | 120, 0.2 | 190, 0.3 | 110, 11 | 134, 17 | 165, 65 | 150, 3 |
| Distln. residue[i] | 0.52 | 2.84 | 1.63 | 2.01 | 1.44 | 1.27 | 0.85 | 0.13 |

[a] All experiments were carried out in sealed, evacuated Pyrex tubes. Products 1–5 were distilled in a short Vigreux column, 6–8 in a 20-cm. column with a platinum spiral for packing. [b] Concentrated aqueous hydrochloric acid, sp. gr. 1.19. These reaction tubes were rocked during heating. [c] Recovered from experiments 1 and 3, b.p. 92–98°. [d] Reactants dried over $P_2O_5$ and distilled *in vacuo* through glass wool into peroxide. [e] B.p. 90–125° (750 mm.). [f] B.p. mostly near 100° (50 mm.), contained unsaturation and peroxide residues (carbonyl groups); fractions from 6 and 7 contained 44.6% and 47.3% Cl (theoretical for polyallyl chloride, 46.35%). [g] B.p. 130–135° (50 mm.), b.p. 92° (5 mm.), the fractions from 6, 7 and 8 contained 54.8, 54.0 and 54.8% Cl (theoretical, 56.1%), also carbonyl groups and therefore a small proportion of peroxide residues. [h] Upper limit of boiling range for this fraction given on next line. Fraction from 8, molecular weight in benzene, 192. [i] Residues from 1, 5 and 6 contained 17.9, 47.4 and 39.1% Cl, indicating that least volatile material contains the most peroxide residues. Molecular weight for 5, 263. [j] 29.5% Cl. [k] 5.69 g. b.p. 50–130° (12 mm.), 41.4% C, 6.5% H, 52.3% Cl; 1.88 g. higher boiling distillate. [l] 1.45 g. b.p. below 130° at 13 mm., 2.63 g. above. [m] 52.6% Cl, molecular weight, 181. [n] About 0.5 g. of unidentified material, probably coming from the solvent, was found in dichloride fractions.

Ford, *et al.*, gave a little less dichloropropane (15%) than expt. 1 and about the same yield of polymer as expt. 2, after allowance is made for incorporation of hydrogen chloride in the polymer of expt. 3. The dichloropropane fraction was not analyzed but is presumably mostly 1,2- with a little 1,3-dichloropropane, as in expts. 5–8. The distillate was mostly the 2:1 allyl chloride–hydrogen chloride reaction product. In expt. 2, 60–70 moles of allyl chloride polymerized per mole of benzoyl peroxide, so that most polymer molecules were terminated by chain transfer with the monomer. Some unsaturated dimer presumably is formed mostly by this route. Some reaction of dimer with hydrogen chloride by a non-radical mechanism has been neglected but not excluded in other experiments. However, comparison of fractions in expts. 2 and 3 shows that the average molecular weight of the polymers is lower in the presence of hydrogen chloride and therefore that hydrogen chloride may react by chain transfer. Experiment 4 shows that the decrease in molecular weight is not due to the regulating action of dichloropropanes which may be formed before or during polymerization.

It was concluded that hydrogen chloride must be undergoing chain transfer with polymerizing allyl chloride, and so expt. 5 was carried out with peroxide and anhydrous hydrogen chloride so that the concentration of hydrogen chloride in the allyl chloride phase would be better known. The results correspond to those obtained with aqueous hydrogen chloride: the principal product was the 2:1 allyl chloride–hydrogen chloride reaction product. The dichloride fraction was found to contain 29% (±2%) 1,3-dichloropropane and 71% 1,2-dichloropropane.[7] The formation of 1,3-dichloropropane proves an abnormal addition of hydrogen chloride to allyl chloride.

Experiments 6–8 were carried out to obtain more information on the abnormal addition reaction, and the products were investigated more carefully by use of a 20-cm. platinum spiral column. Most of the information obtained on the "dimer" and higher-boiling fractions is summarized in footnotes *f*-*i* in Table I. Experiment 6 shows that abnormal addition can be obtained at 50° as well as at 100°. Experiment 7 shows that drying of the reaction mixture did not reduce the amount of normal addition. In expt. 8, the reaction mixture was diluted with hexane so that the ratio of hydrogen chloride to allyl chloride could be increased without increasing the rate of normal addition.[5] The proportion of higher-boiling products was thereby decreased.

The analyses of the fractions from 8, along with some reasonable estimates, permit calculation of transfer constants for hydrogen chloride with some free radicals in polymerizing allyl chloride.[8] The average mole ratio of unreacted allyl chloride to hydrogen chloride during reaction was 1.00, and the following amounts of chain transfer products are estimated to have been formed: 0.0143 mole of 1,3-dichloropropane, 0.0065 mole of 2:1 addition product, presumably 1,5-dichloro-2-(chloromethyl)-pentane and 0.0012 mole of higher addition prod-

[7] Analysis by infrared absorption and comparison with known mixtures of Eastman dichloropropanes. 1,3-Dichloropropane has absorption bands at 10.36 and 12.67 μ where 1,2-dichloropropane has none. Dichlorides 6–8 were analyzed by the same method.

[8] F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948), equation 10.

ucts. The last value is least reliable but is probably accurate to ±30%. From these data, and the assumption that all the 2:1 and higher products arise by a free radical mechanism, the transfer constant of the $(ClCH_2)_2CH\cdot$ radical with hydrogen chloride is 1.8, of the $Cl{-}CH_2{-}CH(CH_2Cl){-}CH_2{-}\dot{C}H{-}CH_2Cl$ radical, 5.4. Similar calculations on expts. 6 and 7 give less reliable but similar values, 1.4 and 5. These results show that hydrogen chloride (at 80°) is 20–100 times as reactive as carbon tetrachloride[9] (at 100°) in chain transfer with allyl chloride. Furthermore, as with carbon tetrachloride, transfer with the longer radical is more probable than with the 1,3-dichloro-2-propyl radical. This may be why the molecular weight regulating properties of hydrogen chloride in the polymerization of allyl chloride were observed before the simple abnormal addition.

The data for expt. 8 show that 14 moles of 1,3-dichloropropane and about 8 moles of higher hydrogen chloride addition products were obtained per mole of benzoyl peroxide. Similar calculations on expts. 5–7 gave 15–30 molecules of hydrogen chloride reacting by a radical mechanism per initial molecule of benzoyl peroxide. These yields of chain transfer products are about half those found in the comparable carbon tetrachloride addition at 100°, even though the hydrogen chloride reaction has the advantage of a lower temperature.[9]

In order to account for a free radical transfer reaction of hydrogen chloride and allyl chloride without reversal of addition of hydrogen chloride, Ford, *et al.*,[2b] have proposed a chain mechanism for addition of hydrogen chloride in which the alkyl radical abstracts a chlorine atom instead of a hydrogen atom from hydrogen chloride. Such a step will be 10–20 kcal. more endothermic than reaction 2, the slow step in the accepted mechanism, because the chlorine–carbon bond is that much weaker than the carbon–hydrogen bond.[10] A similar proposal for hydrogen bromide was rejected long ago on the same grounds.[1] Further, 1,3-dichloropropane has now been shown to result from free radical addition, and 1,2-dichloropropane results from the competing normal addition. There is no reason to suspect that the 2:1 allyl chloride-hydrogen chloride reaction product formed by a free radical mechanism has an unusual structure. However, isomers may arise from a carbonium ion type polymerization or addition of hydrogen chloride to unsaturated dimer.

**Results with Propylene.**—The discovery of an abnormal addition of hydrogen chloride to allyl chloride suggested that the abnormal addition of hydrogen chloride to propylene, as a representative 1-alkene, should be re-investigated.

Previous efforts to obtain an abnormal reaction had failed.[1] They employed ascaridole as initiator in the presence of air, or a mercury arc and quartz apparatus to illuminate the reactants, in the presence of ascaridole or benzoyl peroxide. The only hydrogen chloride addition product identified was isopropyl chloride. In the present work, 0.100 mole each of propylene and hydrogen chloride, both from cylinders supplied by the Matheson Company, and 0.002 mole of recrystallized benzoyl peroxide were dissolved in 30 g. of *n*-hexane and heated in a sealed, evacuated Pyrex tube for 113 hours at 70°. Distillation through the platinum spiral column and analysis of fractions by infrared absorption[11] showed that the products consisted of 0.027 mole of isopropyl chloride, the normal non-radical, addition product, 0.0038 mole of *n*-propyl chloride, the abnormal addition product, 0.11 g., 0.00090 mole, of benzoic acid, 0.23 g. of viscous brown oil with the odor of a benzoic ester, and the hexane fraction. Only 1.9 moles of *n*-propyl chloride were found per initial mole of benzoyl peroxide.

This experiment demonstrates that abnormal addition of hydrogen chloride to a 1-alkene is possible, but difficult. All abnormal additions of hydrogen chloride suffer from the high energy requirement of reaction 2. In addition, most 1-alkenes give much poorer yields than *t*-butylethylene[4] because they react easily with free radicals to give unreactive allyl radicals, which are unable to continue the chain. At least one such reaction leads to inefficient use of initiator, since 24% of the peroxide was found as benzoic acid. Possibly an induced chain decomposition of the peroxide occurs.[12,13] With allyl chloride, some of these factors are more favorable for the chain reaction with hydrogen chloride. Although 1-alkenes have not been successfully polymerized by a free radical mechanism, over a hundred molecules of allyl chloride have been polymerized per molecule of benzoyl peroxide.[9] In view of the easy reaction of alkyl radicals with oxygen and their difficult reaction with hydrogen chloride, the presence of oxygen should be avoided in attempts to obtain abnormal additions of hydrogen chloride.

**Results with Styrene.**—Two experiments were run, one with 0.50 g. of benzoyl peroxide, one with no peroxide. In each experiment, 100 g. each of freshly distilled styrene and concentrated aqueous hydrochloric acid were stirred under gentle reflux for 10 hours. Considerable hydrogen chloride gas was lost during the first half hour. The organic products were washed with water and most of the styrene and phenethyl chloride were separated by distillation at reduced pressures. The higher polymer (H fraction) was then precipitated with methanol[14] and freed from solvent by the frozen benzene

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[9] F. M. Lewis and F. R. Mayo, THIS JOURNAL, **76**, 457 (1954).

[10] See *e.g.*, K. S. Pitzer, *ibid.*, **70**, 2140 (1948); C. T. Mortimer, H. O. Pritchard and H. A. Skinner, *Trans. Faraday Soc.*, **48**, 220 (1952).

[11] *n*-Propyl chloride has strong absorption bands at 11.69, 12.69 and 13.77 μ, while isopropyl chloride has no bands in this region.

[12] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1686 (1946); W. E. Cass, *ibid.*, **69**, 500 (1947).

[13] A very similar experiment with an equivalent quantity of α-azobisisobutyronitrile gave only 0.4 mole of *n*-propyl chloride per initiator molecule. However, formation of 0.5–1 ml. of a heavier immiscible liquid layer, soluble in water, makes the experiment of doubtful significance.

[14] The product was dissolved in about its own volume of benzene and methanol was added until no more polymer precipitated. The precipitate was washed repeatedly with methanol, then precipitated twice more from benzene solution as before. The methanol-soluble material was concentrated at reduced pressure, but some intermediate polymer was insoluble in pure methanol. The residue was therefore precipitated three times more by the procedure above: the methanol insoluble material thus obtained was combined with the first (main) lot of higher polymer as fraction H. The methanol solution was concentrated at reduced pressure, finally heating to about 150° at 0.3 mm. pressure to remove styrene and phenethyl chloride. The residue is designated fraction L.

TABLE II

REACTION OF STYRENE WITH AQUEOUS HYDROGEN CHLORIDE AT 100°

| Run with no $Bz_2O_2$ | | Run with 0.5 g. $Bz_2O_2$ |
|---|---|---|
| 23.56 g. | Frac. L-MeOH-soluble | 12.76 g. |
| 84.1, 7.4, 7 3 (1.2) | C, H, Cl (O by difference), % | 84.4, 7.5, 7.1 (1.0) |
| 234, 1330 | Mol. wt.,[a] bromine equiv.[b] | 308, 1340 |
| $(C_8H_8)_{2.07}(HCl)_{.481}$ | Av. composition (O neglected) | $(C_8H_8)_{2.74}(HCl)_{.617}$ |
| 0.176, 0.343 | Av. C=C, ring per molecule[c] | 0.230, 0.153 |
| 7.54 g. | Frac. H-MeOH-insoluble | 51.44 g. |
| 1.448, 277,000 | Intrinsic viscosity, $M_n$[d] | 0.283, 29600 |
| 1.3, 100 | % Cl, "Cl/molecule"[e] | 0.5, 4.2 |
| 35.0 g. | α-Phenethyl chloride | 9.7 g. |
| 68.5, 6.6, 24.2 (0.7) | C, H, Cl(O by difference), % | (*f*) |
| 26.8 g. (81.9 g.) | Styrene recovered (accounted for[g]) | 11.44 g. (81.7 g.) |
| 11.0 g. | HCl found in products | 3.67 g. |

[a] By freezing point in benzene. [b] Grams sample required to add one mole of bromine. [c] Linear pure polystyrenes average one double bond/molecule; a cyclic structure is assumed to account for each double bond not found or accounted for by reaction of hydrogen chloride. [d] Number average molecular weight calculated from the relation,[17] $\bar{M}_n = 167000[\eta]^{1.37}$. [e] Based on molecular weight in (*d*). [f] Infrared absorption spectrum was essentially identical with corresponding fraction prepared in the absence of peroxide, which is presumed to contain only the α-isomer of the phenethyl chlorides. The two spectra were indistinguishable at 14.0 μ, where known β-phenethyl chloride has a strong absorption band and where 5% known β-isomer showed up clearly in α-isomer. [g] Loss in washing and removal of methanol and benzene.

technique. Styrene and phenethyl chloride were separated from the methanol-soluble polymer (L fraction) by vacuum distillation and the combined styrene–phenethyl chloride fractions were analyzed in a Piros–Glover spinning band column at reduced pressure.

The experiment in the absence of peroxide will be considered first. Table II shows that a large amount of very low molecular weight product and a moderate amount of very high molecular weight product are obtained. Such a molecular weight distribution is incompatible with a single mechanism of polymerization, and the following discussion will show that two reactions are occurring in the absence of peroxide, a thermal polymerization to *high* polymer by a free radical mechanism, not sensitive to hydrogen chloride, and a hydrogen chloride-catalyzed and regulated polymerization to *low* polymer by a carbonium ion mechanism.[15] α-Phenethyl chloride, which may be considered the 1:1 ionic chain transfer product, is the major product of the ionic reaction. The methanol-soluble fraction includes most of the remaining ionic polymerization product. Since the thermal polymerization of styrene at 100° in the absence of hydrogen chloride[16] yields only 1–2% of methanol-soluble material, the large methanol-soluble fraction in the presence of hydrochloric acid must represent mainly ionic reaction products. The methanol-insoluble fraction must be largely the result of free radical polymerization because the molecular weight is much higher than those obtained in other carbonium ion polymerizations, even at lower temperatures, and because it corresponds fairly well to the 380,000 obtained[16a] in the absence of hydrogen chloride. If we calculate the number of chlorine atoms per molecule on a 277,000 molecular weight, the result is 100 chlorine atoms per molecule. This absurd result shows that this fraction contains much more low-molecular weight polymer than a polymer of the same intrinsic viscosity prepared exclusively by a free radical mechanism.[17] This low polymer must be high in chlorine, arise from ionic polymerization, and be closely related to the methanol-soluble material. When allowance is made for this low molecular weight material, the remainder of the methanol-insoluble material will have a higher intrinsic viscosity, therefore a higher number average molecular weight, and will correspond even more closely to the polymer made without hydrogen chloride. It then follows that hydrogen chloride has had little or no discernible effect on the molecular weight of the thermally initiated high polymer formed by the free radical mechanisms and that the telomerization of hydrogen chloride occurred by an ionic mechanism. A real regulating effect of hydrogen chloride on a radical polymerization would be even less discernible in the presence of an initiator, which tends to depress the molecular weight, as in the next experiment, and in that of Ford, *et al.*

In comparison with the above results, all the fractions obtained from polymerization in the presence of benzoyl peroxide show some reasonable changes. First, much more methanol-insoluble polymer is formed and its molecular weight is much lower. Since the half-life of the peroxide at 100° is about half an hour, both changes would result from a rapid decomposition of benzoyl peroxide. Since hydrogen chloride had little or no regulating effect on radical polymerization in the absence of peroxide, it can have no more effect here. From its chlorine content, this methanol-insoluble polymer must also be a mixture of peroxide-initiated polymer of molecular weight more than 30,000 and of low molecular weight, relatively high chlorine, carbonium ion polymer. Second, the lower yields of phenethyl chloride, methanol-soluble polymer, and total bound chlorine in the presence of peroxide are con-

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(15) This mechanism is the aqueous counterpart of the reaction studied by G. Williams and H. Bardsley, *J. Chem. Soc.*, **1707** (1952); *cf.* C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950), for a distinction between three mechanisms of vinyl polymerization.

(16) (a) R. A. Gregg and F. R. Mayo, *Discs. Faraday Soc.*, **2**, 328 (1947); (b) F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953); (a) provides data on rates and molecular weights at 100°; (b) measures the proportion of methanol-soluble material at both 60° and 155°.

(17) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951).

clusive evidence that the principal chlorine-binding reaction is not a free radical reaction associated with the peroxide-catalyzed polymerization of styrene, but is competing with it. Finally the $\alpha$-phenethyl chloride formed in the presence of peroxide contains no more $\beta$-phenethyl chloride than that made in the absence of peroxide (see Table II, note *f*), a proportion too low to have been detected.[18]

The two polymer fractions from the peroxide run average 1.8% chlorine as compared with 4.75% reported by Ford, *et al.*, on their whole product (after assumed removal of phenethyl chloride, b.p. about 195°, by steam distillation). They gave no data on yields.

The low reactivity of styrene in chain transfer with hydrogen chloride is to be expected. The substituted benzyl radical involved should be less reactive than any saturated aliphatic radical in the crucial reaction 2.

**Conclusions.**—Table III permits comparison of factors which limit free radical additions of hydrogen chloride to unsaturated compounds. The reaction with ethylene is limited mostly by the endothermic nature of reaction (2). The result with styrene shows how the reactivity of the radical in reaction (2) further restricts reaction. Comparison of propylene and *t*-butylethylene shows that chain termination by transfer with allylic hydrogen atoms may be an equally critical factor when radicals sufficiently reactive to undergo reaction (2) are involved. The results with allyl chloride support the same conclusion and suggest that the ability of an unsaturated compound to polymerize with peroxides is a measure of the importance of the allyl termination mechanism in hydrogen chloride additions.

TABLE III

ABNORMAL ADDITION OF HYDROGEN CHLORIDE TO DOUBLE BONDS

| Unsaturated compound | Chain length[a] | Reference |
|---|---|---|
| Ethylene | ≥30 at 26° | 3a |
| Propylene | 2 at 70° | |
| *t*-Butylethylene | >7 at 25° | 4 |
| Allyl chloride | 22 at 80° | |
| Styrene | 0 at 100° | |

[a] Quantum yield of ethyl chloride from ethylene in vapor phase, moles of hydrogen chloride reacting by a free radical mechanism per mole of peroxide initially present in other instances. The decomposition of benzoyl peroxide was probably complete except with *t*-butylethylene.

**Acknowledgment.**—Mrs. D. K. Ladd, Miss Bess Rickman, and several members of the Analytical Chemistry Unit have contributed much of the experimental work.

SCHENECTADY, N. Y.

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[18] J. Schramm, *Ber.*, **26**, 1709 (1893).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

# Oxidation of Bicyclo[2.2.2]octene-2 and Bicyclo[2.2.1]heptene-2[1]

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Bicyclo[2.2.2]octene-2 has been synthesized by a Diels–Alder condensation between ethylene and 1,3-cyclohexadiene. The olefin was oxidized to the epoxide and the *cis* and *trans* vicinal glycols. The anomalous behavior of bicyclo[2.2.1]-heptene-2 toward oxidation is discussed.

## Introduction

Birch and Oldham[2] reported that the oxidation of bicyclo[2.2.1]heptene-2 by potassium permanganate gave the normal product, *cis*-cyclopentanedicarboxylic acid. However, when the olefin was oxidized by peracetic acid and the resulting glycol oxidized by chromic acid, 1,2,4-butanetricarboxylic acid and succinic acid were obtained. To account for the unpredicted result obtained by the chromic acid oxidation, the authors postulated a mechanism which involved the use of an intermediate with a double bond at the bridge-head.

The use of such an intermediate is questionable since this would represent a molecule of high energy as a result of the violation of Bredt's rule.[3] It was therefore of interest to repeat Birch's oxidation and to investigate the oxidation of bicyclo[2.2.2]octene-2 to determine whether or not this olefin would behave in an analogous anomalous manner.

## Results and Discussion

Bicyclo[2.2.2]octene-2 was prepared in *cà.* 50% yield by the condensation of ethylene and 1,3-cyclohexadiene[4] in a high pressure vessel at 250°.[5] This method is a distinct improvement over the previously reported methods[6,7] which entailed seven to ten step procedures. The olefin was reduced catalytically to yield the saturated hydrocarbon, bicyclo[2.2.2]octane.

The oxidation of bicyclo[2.2.2]octene-2 (I) was carried out in the manner

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[1] This was presented in part before the 5th Southeast Regional Meeting of the American Chemical Society in New Orleans, La., December 10, 1953.

[2] S. Birch, W. Oldham and E. Johnson, *J. Chem. Soc.*, 818 (1947).

[3] J. Bredt, *Ann.*, **437**, 1 (1924).

[4] This procedure is a modification of the method of Tom (T. B. Tom with C. Boord and K. Greenlee, The Ohio State University Ph.D. Thesis, 1948). P. Wilder, Ph.D. Thesis (January, 1950) at Harvard with R. Woodward, report a similar preparation.

[5] The procedure described in this paper was developed in the laboratories of Dr. M. S. Newman at The Ohio State University.

[6] R. Seka and O. Tramposch, *Ber.*, **75B**, 1379 (1942).

[7] G. Komppa, *ibid.*, **68B**, 1267 (1935).