Haloacyloxylation. II. Addition of Bromine or Chlorine to Propylene in the Presence of Peracetic Acid[1]

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Received July 11, 1966

It has been found that the ratio of 1-halo-2-acetoxypropane to 1,2-dihalopropane increases when the addition of bromine or chlorine to propylene in an acetic acid solution is conducted in the presence of peracetic acid. The ratio is further increased by employing halide ion instead of molecular halogen. These facts suggest that the oxidation ot halide ion by peracetic acid competes with the addition of halide ion to cyclic halonium ion in the two-step halogen addition mechanism *via* a cyclic halonium ion intermediate. The ease of oxidation of halide ion in acetic acid by peracetic acid is in the decreasing order iodide > bromide > chloride.

In the previous paper[2] it has been reported that the addition of iodine to propylene in acetic acid produces 1,2-diiodopropane, but the presence of peracetic acid results in the exclusive formation of 1-iodo-2-acetoxypropane and a mechanism *via* a π complex between olefin and molecular iodine has been suggested. The present report is an extension of the study to the haloacyloxylation of olefin using bromine and chlorine.

The addition of bromine to olefin in an acetic acid solution is in most cases expressed by a rate equation: $v = k[\text{olefin}][Br_2]^2$, which is interpreted by a mechanism *via* a cyclic bromonium ion followed by an attack of tribromide ion to form *vic*-dibromo compound.[3–7] Other anions present in the solution, *e.g.*, acetate ion,[8] can compete in the second step with tribromide ion and can give other bromo compounds,[9–14] *e.g.*, *vic*-bromoacetoxy compound,[8] besides the dibromo compounds. These additions which generally afford *trans* products have been considered to be an evidence for the two-step addition mechanism described above.[3–7]

Although the chlorination of olefins in nonpolar solvents seems to have both ionic and free-radical features,[15] the addition in acetic acid is ionic and its rate is expressed as $v = k[\text{olefin}][Cl_2]$, where a considerable amount of *vic*-choroacetate[16–18] is formed in addition to *vic*-dichloride. In general, the chlorine addition in acetic acid gives *trans* adduct,[16] which supports the intermediary formation of cyclic chloronium ion, but the fact that the minor amounts of *cis* adduct are also formed in some cases leaves open the possibility of the open carbonium ion intermediate.[16]

In order to obtain more information concerning the mechanism with respect to several halogenating agents, the reaction of propylene with a mixture of peracetic acid and bromine or chlorine was studied.

Experimental Section

Materials.—Acetic acid of 99.5% was used without further purification. Propylene was 99.5% pure. Bromine, potassium bromide, 47% hydrobromic acid (*d* 1.48), and 35% hydrochloric acid (*d* 1.190) were all reagent grade.

An *ca.* 3.5–3.2 *M* peracetic acid solution was prepared by adding dropwise acetic anhydride (407 g, 3.99 moles) to a stirred solution of 60% hydrogen peroxide (100 g, 1.77 moles; H_2O, 2.22 moles) and concentrated sulfuric acid (1 ml) as catalyst at 30–45° over a period of 2 hr.[19,20] The solution contained a small amount (0.05–0.2 *M*) of diacetyl peroxide.

Analyses of Reaction Products.—The infrared spectra were determined by a Perkin-Elmer Model 333 spectrophotometer; the nmr spectra were determined for neat liquid samples on a Varian Model A-60 instrument using tetramethylsilane as an internal standard. The reaction products were analyzed by means of gas chromatography employing a Yanagimoto Model GCG-220 operated with a 3 m × 4 mm column packed with silicone DC 550 (30 wt %) on Celite 545 of 80–100 mesh using hydrogen as a carrier gas (60 ml/min) at 150°. The retention times of 1,2-dibromopropane, 1-bromo-2-acetoxypropane, 1,2-dichloropropane, and 1-chloro-2-acetoxypropane were 5, 7, 2.3, and 4.7 min, respectively. Toluene was used as an internal standard and the ratios of products were calculated by weighing cut peak area of the gas chromatograms. Blank tests with a mixture of authentic samples confirmed the reliability of this analysis.

1,2-Dibromopropane was prepared by the reaction of propylene with bromine in carbon tetrachloride: bp 141–142°, n^{21}_{D} 1.5208, d^{20}_{20} 1.9417 (lit.[21] bp 141.5–141.9°, n^{20}_{D} 1.5200, d^{20}_{4} 1.93326).

The Reaction of Propylene with a Mixture of Bromine and Peracetic Acid. 1,2-Dibromopropane and 1-Bromo-2-acetoxypropane.—A typical procedure was as follows. An acetic acid solution (100 ml) of bromine (24 g, 0.15 mole) was added dropwise to an acetic acid solution (200 ml) of 1.35 *M* peracetic acid at 25–40° over a period of 120 min, and at the same time propylene was passed into the solution. After standing at room temperature for 3 days, the mixture was diluted with water and extracted by ether. The ethereal layer was washed with aqueous sodium hydroxide or sodium bicarbonate to remove acetic acid, dried over anhydrous sodium sulfate, and removed of solvent. The residual liquid was analyzed by gas chromatography to estimate the ratio of 1,2-dibromopropane to 1-bromo-2-acetoxypropane. Table I lists the results under various conditions. The combined products from several runs were rectified, giving the following fraction: colorless liquid, bp 75.5° (31 mm), redistilled at bp 166–169° (760 mm), $n^{19.5}_{\mathrm{D}}$ 1.4510, d^{20}_{20} 1.4107

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(1) Contribution No. 96.

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TABLE I

THE REACTION OF PROPYLENE WITH BROMINE IN ACETIC ACID WITH OR WITHOUT PERACETIC ACID

Solvent CH_3CO_2H, ml	Material added	Bromine,[a] mole	CH_3CO_3H, mole	Temp, °C	Time, min	Yield,[e] %	CH_3CHBr-CH_2Br, %	$CH_3CH(OAc)$-CH_2Br, %	
100	Et_2O (200 ml)	0.15	0[b]	23–30	60	62	95	5	Av 8
30	None[f]	0.01[c]	0	25–63	20	61	94	6	
50	None	0.01[c]	0	24–30	3	58	92	8	
200	None	0.15	0	27–33	240	57	88	12	
40	H_2O (20 ml)	0.01	0	23–28	3	20	83	17	
200	AcOK (0.15 mole)	0.15	0	39–42	44	73	77	23	
20	Et_2O (50 ml)	0.01[c]	0.032	−40–−32	10	74	78	22	Av 26
106	None	0.065[c]	0.10	35–75	10	33	77	23	
30	None[f]	0.01	0.032	25–75	21	56	76	24	
74	None	0.085	0.17	40–42	180	45	74	26	
50	None	0.01[c]	0.032	25–33	3	67	74	26	
300	None	0.15	0.27	25–40	150	61	61	39	
100	H_2O (1.5 mole)	HBr (0.30)[d]	0.33	30–37	45	65	56	44	
300	None	KBr (0.30)	0.32	34–39	45	81	50	50	

[a] An acetic acid solution of bromine was added to peracetic acid in acetic acid with simultaneous passage of propylene. [b] Peracetic acid (0.15 mole) was added after most of the bromine had been consumed by propylene in ether. [c] Solutions of bromine and peracetic acid were mixed quickly and propylene was passed into the mixture. [d] A 47% HBr solution (35 ml) containing water (1.5 moles) was added to the peracetic acid solution with simultaneous passage of propylene. [e] The yield is a sum of dibromide and bromoacetate based on used bromine. [f] Irradiated by a 200-w tungsten lamp at a distance of 10 cm.

[lit.[22] bp 161–165° (750 mm), bp 64.5–65.3° (18–19 mm), d^{18}_4 1.413].

Anal. Calcd for $C_5H_9BrO_2$: Br, 44.14. Found: Br, 44.13.

The infrared spectrum (liquid film) has strong absorption at 1740 and 1240 cm^{-1} characteristic for an acetoxyl group. Other bands were at 2980 (m), 2930 (w), 1455 (m), 1430 (m), 1375 (s), 1143 (m), 1132 (m), 1060 (s), 1035 (s), 956 (m), 665 (w), 632 (w), 605 (m), and 510 (w) cm^{-1}. The nmr spectrum (no solvent, standard TMS) shows signals at τ 8.69 (doublet $J = 6.2$ cps), 7.99 (singlet), 6.51 (doublet $J = 5.2$ cps), and 4.97 (multiplet $J = 6.0$ cps). In addition, rather weak signals at τ 8.32 (doublet $J = 6.2$ cps), 7.95 (singlet), and 5.76 (doublet $J = 2.2$ cps) are observed. These data agree with the calculated values[23] and indicate that the principal product is 1-bromo-2-acetoxypropane contaminated probably with a small amount of isomeric 2-bromo-1-acetoxypropane.

The Addition of Bromine to Propylene in Pure Acetic Acid.—An acetic acid solution (100 ml) of bromine (24 g, 0.15 mole) was added dropwise to acetic acid (200 ml) with simultaneous passage of propylene into the solution at 27–33° over a period of 240 min. The products were worked up as above and analyzed by glpc. (See Table I.)

The Reaction of Propylene with a Mixture of Hydrobromic and Peracetic Acids.—Propylene was passed into a stirred acetic acid solution (100 ml) of 3.3 *M* peracetic acid with simultaneous dropwise addition of 47% aqueous hydrogen bromide (*d* 1.48, 35 ml, 0.3 mole; H_2O, 1.52 mole) at 30–37° over a period of 45 min. After being worked up as above, the product was analyzed by glpc. (See Table I.)

The Reaction of Propylene with a Mixture of Potassium Bromide and Peracetic Acid.—Propylene was passed into a stirred mixture of acetic acid (200 ml) and a suspension of powdered potassium bromide (36 g, 0.3 mole) with simultaneous addition of an acetic acid solution (100 ml) of 3.2 *M* peracetic acid at 34–39° over a period of 75 min and then worked up similarly.

The Reaction of Propylene with a Mixture of Chlorine and Peracetic Acid. 1-Chloro-2-acetoxypropane and 1,2-Dichloropropane.—Propylene and chlorine (0.008–0.88 mole) were passed into a stirred acetic acid solution (30–200 ml) of peracetic acid (0.032–0.28 mole) with the molar ratio of peracetic acid *vs.* chlorine of 0.3–4 at 18–52° over a period of 2–300 min. The mixture was diluted with water and extracted with ether. After being washed with aqueous sodium hydroxide or sodium bicarbonate to remove acetic acid, the extract was dried over anhydrous sodium sulfate and evaporated for the analysis by gas chromatography. The molar ratio of $CH_3CHClCH_2Cl$ *vs.* $CH_3CH(OAc)CH_2Cl$ was 47:53 in average. The combined products from several runs were rectified, giving fractions described below.

1,2-Dichloropropane had bp 95.2–95.8°, $n^{19.5}_D$ 1.4389, d^{20}_{20} 1.1558 (lit.[24] bp 96.20°, n^{20}_D 1.4390, d^{14} 1.1656).

1-Chloro-2-acetoxypropane had bp 150.2°, $n^{19.5}_D$ 1.4246, d^{20}_{20} 1.1024 (lit.[25,17] bp 149–150°, n^{20}_D 1.4270, d_{20} 1.1012).

Anal. Calcd for $C_5H_9ClO_2$: Cl, 25.96. Found: Cl, 25.94.

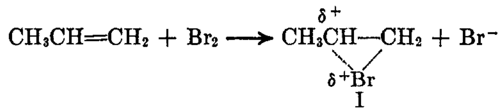
The infrared spectrum shows strong absorption at 1740 and 1240 cm^{-1} characteristic for acetoxyl group. The nmr spectrum shows signals at τ 8.72 (doublet $J = 6.5$ cps), 8.00 (singlet), 6.40 (doublet $J = 5.0$ cps), and 4.96 (multiplet $J = 5.9$ cps), and confirms the presence of an 2-acetoxyl group in propane.

The Reaction of Propylene with Chlorine in Pure Acetic Acid.—Propylene and chlorine (0.008–1.5 moles) were passed into acetic acid (30–200 ml) at 23–40° over a period of 2–120 min. The product was worked up as above, being analyzed by glpc. The molar ratio of $CH_3CHClCH_2Cl$ *vs.* $CH_3CH(OAc)CH_2Cl$ was 50:50 in average.

The Reaction of Propylene with a Mixture of Hydrochloric and Peracetic Acids in Acetic Acid.—An acetic acid solution (100 ml) of 2.8 *M* peracetic acid was added dropwise to a mixture of 35% aqueous hydrogen chloride (*d* 1.19, 30 ml, 0.342 mole; H_2O, 1.29 moles) and acetic acid (170 ml) with simultaneous passage of propylene at 20–30° over a period of 50 min. The products were analyzed by glpc. The molar ratio of $CH_3CHClCH_2Cl$ *vs.* $CH_3CH(OCOCH_3)CH_2Cl$ was 36:64.

Results and Discussion

It was found that the addition of bromine to propylene in acetic acid forms a small amount of 1-bromo-2-acetoxypropane together with 1,2-dibromopropane in a molar ratio of 8:92. This fact implies the competitive reaction of bromide and acetate ions with cyclic bromonium ion (I).



$$CH_3CH{=}CH_2 + Br_2 \longrightarrow \underset{\delta^+Br}{\overset{\delta^+}{CH_3CH{-}CH_2}} + Br^- \quad (1)$$

I

$$I + Br^- \longrightarrow CH_3CHBrCH_2Br \quad (2)$$

$$I + CH_3COO^- \longrightarrow CH_3CH(OCOCH_3)CH_2Br \quad (3)$$

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When the reaction is carried out in the presence of peracetic acid with molar ratio of peracetic acid *vs.* bromine of 1.5–3.2 under similar conditions, the ratio of 1-bromo-2-acetoxypropane to 1,2-dibromopropane increases to 26:74 (Table I). The rates of the reaction and related reactions are too fast to be measured; hence the accurate mechanistic discussion is difficult. However, the result is explicable by the oxidation of bromide ion by peracetic acid, forming acetyl hypobromite which is effective for bromoacetoxylation of propylene.

$$Br^- + CH_3CO_3H + CH_3CO_2H \longrightarrow CH_3CO_2Br + CH_3CO_2^- + H_2O \quad (4)$$

$$CH_3CO_2Br + CH_3CH{=}CH_2 \longrightarrow CH_3CH(OCOCH_3)CH_2Br \quad (5)$$

The oxidation of bromide ion by peracetic acid resulting in the haloacyloxylation of olefin was confirmed by our independent experiments. Thus, the peracetic acid oxidation of hydrogen bromide in acetic acid can give a higher yield of the haloacyloxylation product of propylene (1-bromo-2-acetoxypropane) together with 1,2-dibromopropane in a molar ratio of 44:56. Similarly, the higher ratio (50:50) of bromoacetate to dibromide was obtained, when potassium bromide was used instead of molecular bromine (Table I). Although the reaction of hydrogen bromide or potassium bromide with peracetic acid can give molecular bromine, the present reaction does not seem to go only by way of free bromine, but also probably *via* acetyl hypobromite because of the higher yield of bromoacetate (eq 4 and 5).

The reaction of 1,2-dibromopropane with peracetic acid did not give 1-bromo-2-acetoxypropane; hence, the present reaction does not go by way of acetolysis of dibromopropane.

It has been reported that the rate of bromination of benzene by a mixture of bromine and peracetic acid is determined by the reaction of bromine with peracetic acid.[26] The reaction of bromine with peracetic acid forming acetyl hypobromite is slow compared to the addition of bromine to propylene. Therefore, the mechanism *via* the preliminary formation of acetyl hypobromite is less important for the bromoacetoxylation using molecular bromine.

The addition of chlorine to propylene in pure acetic acid affords a fairly large amount of 1-chloro-2-acetoxypropane together with 1,2-dichloropropane (in a ratio of 50:50) and hydrogen chloride, the amount of hydrogen chloride corresponding to that of 1-chloro-2-acetoxypropane, which suggests the following stoichiometry.

$$CH_3CH{=}CH_2 + Cl_2 + CH_3COOH \longrightarrow CH_3CH(OCOCH_3)CH_2Cl + HCl \quad (6)$$

The addition of peracetic acid in this system resulted in only a small increase in the molar ratio of 1-chloro-2-acetoxypropane to 1,2-dichloropropane as 53:47. At the same time, the amount of formed hydrogen chloride was decreased, which implied the oxidation of hydrogen chloride by peracetic acid. This presumption was verified by a rather favorable chloroacetoxylation of propylene by a mixture of peracetic and hydrochloric acids in a molar ratio of 1-chloro-2-acetoxypropane to 1,2-dichloropropane of 64:36.

$$HCl + CH_3CO_3H \longrightarrow CH_3CO_2Cl + H_2O \quad (7)$$

$$CH_3CO_2Cl + CH_3CH{=}CH_2 \longrightarrow CH_3CH(OCOCH_3)CH_2Cl \quad (8)$$

The reaction of olefin with a mixture of peracetic acid and halide ion derived from hydrogen chloride, hydrogen bromide, or potassium bromide is of interest as a synthetic procedure for haloacyloxylation of olefin, because of the higher yield of haloacetate compared with the reaction using molecular halogen and peracetic acid.

It was observed that the percentage of haloacetate in the product mixtures containing haloacetates and dihalides obtained by the reaction of halogen and propylene in pure acetic acid were in the order iodine (0%), bromine (8%), chlorine (50%). This order is reverse to the nucleophilicity of halide ions relative to acetate ion as a competing anion which attacks on the cyclic halonium ion, *e.g.*, 1.

On the other hand, in view of our results on the bromination and chlorination of propylene in acetic acid in the presence of peracetic acid, these reactions seem to proceed mainly by ionic pathway, peracetic acid operating as an oxidizing reagent for bromide or chloride ion, which is then converted to the haloacyloxylating agent. The rates of oxidation of halide ions in acetic acid or water are in the order of their nucleophilicities or reactivities for electrophilic (oxidizing) agent, $Cl^- < Br^- < I^-$.[27] Therefore, the higher nucleophilicity of iodide means the more facile attack of iodide ion on the cyclic halonium ion complex and easier oxidation of iodide ion to form hypoiodous acid; these opposite effects are competing. The effect of addition of peracetic acid is most remarkable in the iodoacetoxylation, and the percentage of haloacetate in the product mixtures was raised to 100% for the iodine reaction, but it was 26% for the bromine reaction and 53% for the chlorine reaction. Hence, the nucleophilicity of iodide ion is more effective on the halide oxidation. On the other hand, in the addition of bromine to propylene, the rate of bromide ion addition to cyclic bromonium ion (I) is comparable to the rate of oxidation of bromide ion by peracetic acid.[27]

The rate of addition of a halide ion to general cyclic halonium ions may be estimated by using this three-component reactions.

These findings present an additional evidence for the two-step mechanism of halogen addition *via* halide ion and cyclic halonium ion.

Acknowledgment.—The authors wish to thank Nissan Chemical Industries Company, Daicel Company, Toyo Rayon Company, and Yanagimoto Company, for their aid in performing these experiments.

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[26] The second-order rate constant for the reaction of bromine with peracetic acid was reported to be $k_2 = 1.60 \times 10^{-3}$ l. mole^{-1} sec^{-1} (at 60°): Y. Ogata, Y. Furuya, and K. Okano, *Bull. Chem. Soc. Japan*, **37**, 960 (1964).

[27] The rate of bromide ion oxidation by peracetic acid in an aqueous solution is expressed as: $v = k[Br^-][CH_3CO_3H]$ and $k = 0.258$ l. mole^{-1} sec^{-1} (at 25.0°): D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 778 (1960).