[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. III. The Addition of Hydrogen Bromide to Propylene

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Introduction

The addition of halogen acids to propylene has been studied by a number of investigators[1] under a variety of experimental conditions. The effects of the following factors on the ease of addition were evaluated: temperature,[1a,e,f,h,i] concentration of halogen acid in the anhydrous addition mixture,[1f] pressure,[1f,k] concentration of water,[1f] catalysis by metals,[1f] metallic salts in solvents,[1j,l] metallic salts and surfaces in the vapor phase,[1i,l] excess halogen acid,[1f] and air.[1i] In spite of all these variations, the final product of all the reactions was always the isopropyl halide. While Michael[1d] isolated a very small amount of normal propyl iodide from the reaction between aqueous hydriodic acid and gaseous propylene at 0°, his method of analysis of the addition product was far too inexact to justify the great significance that has been attached to his observation. The formation of a hexyl halide as by-product was studied by Maass and collaborators.[1e,f,g]

The Addition of Hydrogen Bromide to Propylene.—Our interest in the addition of hydrogen bromide[2] to propylene was aroused by our observations that the direction of addition of hydrogen bromide to allyl bromide,[3] allyl chloride,[4] vinyl bromide,[5] and butene-1[6] is determined by the peroxide content of the reaction mixture. It has been shown also that the peroxide effect can be overcome by the use of good antioxidants. An investigation was therefore undertaken to determine whether isopropyl bromide is the normal or the peroxide-catalyzed addition product.

Table I is a summary of our results. Briefly, the addition of hydrogen bromide to propylene in the presence or absence of air and the presence or absence of any of a wide selection of (for this type of reaction) excellent antioxidants always resulted in practically quantitative yields of isopropyl

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[1] (a) Berthelot, *Ann.*, **104,** 184 (1857); (b) Erlenmeyer, *ibid.*, **139,** 228 (1866); (c) Butlerow, *ibid.*, **145,** 275 (1868); (d) Michael, *J. prakt. Chem.*, [2] **60,** 445 (1899); (e) Maass and Wright, THIS JOURNAL, **46**, 2664 (1924); (f) Maass and Sievertz, *ibid.*, **47,** 2883 (1925); (g) Sutherland and Maass. *Trans. Roy. Soc. Can.*, **20**, 499 (1926); (h) Sutherland and Maass, *Can. J. Research*, **5**, 48 (1931); (i) Wibaut, Diekmann, and Rutgers, *Proc. Acad. Sci. Amsterdam*, **27,** 671 (1924); *Rec. trav. chim.*, **47**, 477 (1928); (j) Wibaut, *Z. Elektrochem.*, **35**, 602 (1929); (k) United States Patent 1,518,182, Curme, Carbide and Carbon Chemicals Corporation, *Chem. Zentr.*, I, 1129 (1925); (l) Canadian Patent 258,816, English Patent 235,547, French Patent 599,595, Weber, Schrader, and Wiedbrauch, Goldschmidt, A. G., *ibid.*, I, 179 (1927).

[2] An investigation of the addition of other halogen acids to substituted ethylenes is now under way in this Laboratory.

[3] Kharasch and Mayo, THIS JOURNAL, **55,** 2468 (1933).

[4] Kharasch and Shane, unpublished work.

[5] Kharasch, McNab and Mayo, THIS JOURNAL, **55**, 2521 (1933).

[6] Kharasch, Shane and Ryan, unpublished work.

bromide. On the other hand, the presence of benzoyl peroxide or ascaridole modified profoundly the course of the addition and the product of the reaction was largely, if not all, normal propyl bromide.

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO PROPYLENE

The propylene used was obtained in compressed form from a commercial source. Hydrogen bromide was prepared from tetralin and bromine as described by Kharasch and Mayo, Ref. 3. Tertiary butyl isocyanide was the Kahlbaum product. The other organic materials were obtained from the Eastman Kodak Co. and were used without purification.

No.	Moles HBr[a]	Antioxidant or peroxide	Moles	Air[b]	Temp., °C.	Reaction time	Yield, %[c]	%[d] iso-	Remarks
1	1.23	Diphenylamine	0.024	Absent	Room	3 hours	70	100	
2	1.23	Diphenylamine	.024	Absent	Room	18 hours	95	100	
3	1.23	Tertiary butyl isocyanide	.028	Absent	Room	18 hours	95	100	
4	1.23	Tertiary butyl isocyanide	.070	Absent	Room	18 hours	95	100	
5	1.23	Thiocresol + $MnCl_2$	.032 .0001	Absent	Room	18 hours	95	100	
6	1.23	Thiocresol + $MnCl_2$	.048 .0001	Absent	Room	18 hours	95	100	
7	1.23	Thiocresol + $MnCl_2$	.08 .0001	Absent	Room	18 hours	95	100	0.15 mole propionitrile also present
8	1.23	Thiocresol + $MnCl_2$	.08 .0001	Absent	0	18 hours	95	100	
9	1.23	None		Absent	Room	18 hours	95	100	
10	1.23	Thiocresol + $MnCl_2$	.16 .0001	Absent	Room	18 hours	95	100	
11	1.23	Benzoyl peroxide	.041	Absent	Room	18 hours	90	13	
12	1.23	Benzoyl peroxide	.062	Absent	−78	40 hours	90	70	
13	1.23	(Oxygen)		Present	Room	18 hours	95	79	Oxygen passed through liquid propylene at −78° for ten minutes before solution of hydrogen bromide in propylene
31	1.25	Benzoyl peroxide	.074	Present	Room	17 hours	25	13	HBr passed in very slowly
32	1.30	Ascaridole	.11	Present	Room	17 hours	17	2	
33	0.96	Benzoyl peroxide	.074	Present	−78	15 minutes	41	4	HBr passed in rapidly
34	1.23	Ascaridole	.13	Present	−78	32 minutes	48	0	

[a] For runs Nos. 1–13, 4.2 g., for Nos. 31–34, 3.5 g., of propylene was used. The quantities of hydrogen bromide, antioxidants, and peroxides are calculated on the basis that 1 mole of propylene was used.

[b] In those runs in which air was absent, the propylene was condensed in a bomb tube with the antioxidant or peroxide. Hydrogen bromide was then condensed in a second bomb tube at the temperature of boiling nitrogen. The hydrogen bromide was then distilled *in vacuo* into the first bomb tube according to the technique of Kharasch and Mayo, Ref. 3. In those runs in which air was present, hydrogen bromide was dissolved at −78° in liquid propylene to which the peroxide (if any) had already been added. The bomb tube was then sealed off without taking any precautions to exclude air or moisture.

[c] The yields as given in this column represent the final weights of propyl bromides recovered. In runs 31–32, an attempt was made to remove the peroxides by washing with concentrated sulfuric acid. Difficulties in separation of layers and formation of emulsions caused large losses of addition product. In Nos. 33–34 the peroxides did not dissolve in the cold reaction mixture to any considerable extent, and the mixture was

therefore poured off the undissolved peroxides at low temperatures. Considerable quantities of addition product were lost with the rejected mass of peroxides. These circumstances explain the low apparent yields in the runs. The actual degree of completeness of these four reactions was probably of the order of 80% or more.

[d] The composition of the purified addition product was determined by its index of refraction. We assumed the composition of the mixture to be a linear function of its composition. In the column designated "% iso-" is given the fraction of isopropyl bromide in the purified addition product. The remainder of the addition product was normal propyl bromide. The boiling ranges of the addition products were consistent with their compositions as calculated by their indices of refraction.

These facts indicate either that the rate of the normal reaction of propylene with hydrogen bromide is sufficiently rapid to overcome the effect of minute traces of peroxides, or that propylene does not form peroxides very readily in air. This latter hypothesis finds some substantiation in the run in which oxygen was first bubbled through the propylene at −78° for ten minutes. The addition product in this experiment consisted of 21% normal propyl bromide. It is possible, therefore, that the failure of earlier investigators to obtain the normal halide is to be attributed to the fact that propylene is a gas and that under the experimental conditions of work with it, the gas displaces most of the oxygen from the system before sufficient quantities of peroxides can be formed. It is possible, also, that there may be little tendency toward peroxide formation in the gaseous phase.

It is of interest to note that lowering of temperature has the same apparent result in decreasing the peroxide effect as it has in the case of the other substituted ethylene compounds. The yield of the peroxide catalyzed product, *i. e.*, normal propyl bromide, is only 30% at −78° and 87% at room temperature in the absence of air.

A more thorough investigation to include the effects of solvents, temperature and light was not undertaken because we have previously demonstrated that these factors have no effect by themselves, but only an indirect effect through their action on peroxides. Therefore, probably little more could be learned than what we have already discussed in our previous publications.

Summary

1. The addition of hydrogen bromide to propylene in air and in the presence of antioxidants leads to the formation of pure isopropyl bromide.

2. In the presence of added peroxides, *e. g.*, benzoyl peroxide or ascaridole, hydrogen bromide may add to propylene to give practically quantitative yields of normal propyl bromide.

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