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

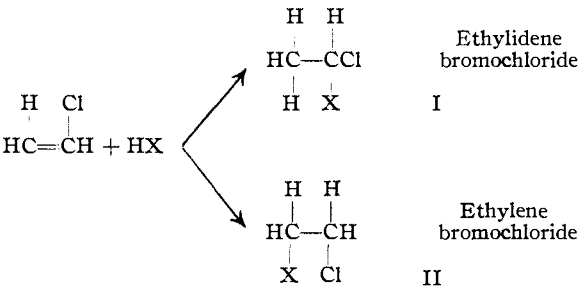
The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. IV. The Addition of Halogen Acids to Vinyl Chloride

BY M. S. KHARASCH AND C. W. HANNUM[1]

Introduction

In previous communications Kharasch and coworkers[2] demonstrated that the most important factor in the addition of hydrogen bromide to certain unsaturated substances was the peroxide content of the reaction mixture. It was shown that the "peroxide" effect could be overcome by good antioxidants in the absence of oxygen. An investigation was undertaken to determine to what extent "peroxides" influenced the addition of halogen acids to vinyl chloride.

The addition of halogen acid can occur according to scheme I or II



Under normal "non-peroxide catalyzed" conditions the formation of ethylidene bromochloride was found to occur exclusively as predicted.[3]

Previous Work on the Addition of Halogen Acids to Vinyl Chloride.—Very little work has been published on the addition of halogen acids to vinyl chloride. Wibaut[4] found no addition between the two in the vapor phase while working with hydrogen chloride except when the reaction was catalyzed by the presence of certain metallic salts.

Factors Influencing the Addition of Hydrogen Bromide to Vinyl Chloride.—The "peroxide" content of the vinyl chloride-hydrogen bromide mixture is the most important single factor governing the direction and velocity of addition of hydrogen bromide to vinyl chloride. This behavior is similar to that of vinyl bromide, except that in our experience vinyl chloride is even more sensitive to "peroxides" than allyl chloride, allyl bromide or vinyl bromide. This view is borne out by examination of Table I.

This table demonstrates that when attempts are made to remove all oxygen and peroxides by distillation and evacuation of the bomb tubes, the results are still the same as those noted with benzoyl peroxide, ascaridole, air, etc. In short, without a solvent or a good antioxidant the addition of hydrogen bromide to vinyl chloride leads to a rapid, nearly quantitative, formation of ethylene bromochloride. In the presence of metal catalysts, however, the peroxide effect is destroyed and nearly quantitative yields of the ethylidene bromochlorides are obtained.

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE IN ABSENCE OF ANTIOXIDANTS AND SOLVENTS AT ROOM TEMPERATURE AND IN THE ABSENCE OF LIGHT

Agent added	Mml.	Air[b]	Reaction time, days	Yield,[d] %	1,1, %
None		+	3	87[a]	1
None			3	77	0
Ascaridole	6.0	+	2	73[a]	3
Benzoyl peroxide	4.1	+	2	79[a]	0
Ferric chloride	1.2		1	76[a]	87
(anhyd.)	1.2	+	1	42[a]	100

[a] Crude yield of isomers before distillation.

[b] Bomb tubes sealed without evacuation and containing air. In all other runs the vacuum technique described by Mayo[2] was used.

[c] All runs in this table were duplicated at least once.

[d] Yields as given, except those labeled *a*, indicate calculated yields of bromochloroethanes after purification. Because of unavoidable and comparatively large losses in working with such small quantities of material (6.3 g. vinyl chloride), many runs credited with yields of 70–80% are undoubtedly quantitative. The column headed 1,1% gives % ethylidene bromochloride as determined by refractive index, the remainder being ethylene bromochloride.

The Effect of Antioxidants.—Table II summarizes the effect of antioxidants on the addition of hydrogen bromide to vinyl chloride *in vacuo* and in the absence of solvents. Good antioxidants in all cases formed mainly the "normal" addition product, ethylidene bromochloride. One weak antioxidant employed, *tert*-butylcarbylamine, was not as effective as the other antioxidants in producing the normal isomer but

---

(1) Du Pont Fellow. Support for part of this work by E. I. du Pont de Nemours & Co. is gratefully acknowledged.

(2) Kharasch and Mayo, THIS JOURNAL, **55**, 2469 (1933); Kharasch, McNab and Mayo, *ibid.*, **55**, 2521, 2531 (1933).

(3) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931).

(4) Wibaut, *Rec. trav. chim.*, **51**, 636 (1932).

in conjunction with *p*-thiocresol or diphenylamine gave a product which was entirely ethylidene bromochloride. *tert*-Butylcarbylamine increases the velocity of the normal addition four- or five-fold.

Under influence of sun or artificial light, at room temperatures or near 0°, the effect of *p*-thiocresol and other antioxidants is almost completely destroyed. Strong illumination, particularly sunlight, increases tremendously the velocity of the "abnormal" reaction. Kharasch and his collaborators[2] have found that lowering the temperature during illumination decreases the magnitude of the peroxide effect in case of some substances. Due, however, to the greater susceptibility of vinyl chloride to peroxides we were unable to duplicate this effect at 0°. Lower temperatures were not investigated.

The addition of hydrogen bromide at elevated temperatures in the dark proceeds at an increased velocity but decreases the yield of "normal" product, showing the "peroxide" effect to be increased under these conditions. Manganese chloride *in vacuo* was found to have no effect on the course of the addition.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE IN VACUO IN ABSENCE OF SOLVENTS AT ROOM TEMPERATURE AND IN THE ABSENCE OF LIGHT (EXCEPT AS NOTED IN REMARKS)

Added agent	Mml.	Reaction time, days	Yield, %	1,1, %	Remarks
p-Thiocresol	2.4	14	62	97	Washed vinyl chloride
p-Thiocresol	2.4	17	71	100	Unwashed vinyl chloride
p-Thiocresol*	1.6	5	50[a]	19	
Thiophenol	3.6	14	54	93	
Diphenylamine	3.0	17	59	100	
t-Butylcarbylamine	2.1	4	93	80	
t-Butylcarbylamine and *p*-thiocresol	2.1 2.4	7	57	100	
t-Butylcarbylamine and diphenylamine	2.1 3.0	7	81	100	
Pyrogallol*	1.6	2	0	..	Red solid
p-Thiocresol	2.4	1	50	3	8 cm. from 500-watt lamp, 5°
p-Thiocresol	2.4	1.5	19	7	
p-Thiocresol	2.4	5	78	2	Sunlight
p-Thiocresol	2.4	0.75	61	2	0° and sunlight
p-Thiocresol	2.4	3	77	19	76°
Diphenylamine	3.0	3	70	43	76°
Manganese chloride	1.0	2.5	70	2	

[a] All materials must be freshly distilled *in vacuo* to be able to duplicate results consistently. It was found that a sample of *p*-thiocresol which was old and impure was rather ineffective as an antioxidant (*) but after purification by distillation *in vacuo* it behaved as an excellent antioxidant.

The Effect of Solvents.—Three solvents were used with and without antioxidants, namely, glacial acetic acid, nitrobenzene and mesitylene. We were able to form some 1,1 isomer, without the use of antioxidants, by causing the addition to proceed *in vacuo* in solvents such as nitrobenzene and particularly mesitylene. The addition of antioxidants to the solvents greatly increases the percentage of "normal" product, ethylidene bromochloride. In the presence of air, however, the solvent effect is of minor importance since the "peroxide catalyzed reaction" proceeds so fast that it obliterates quite effectively any antioxidant effect of the solvent.

The "peroxide" effect is accelerated by light to a tremendous extent, and only in the presence of good antioxidants may one obtain any appreciable yields of the "normal" addition product.

TABLE III

THE ADDITION OF HYDROGEN BROMIDE TO VINYL CHLORIDE IN THE PRESENCE OF SOLVENTS AT ROOM TEMPERATURE

All solvents in vacuum bombs distilled *in vacuo* before use; 5 cc. of solvent used per run.

Agent added	Mml.	Solvent	Air	Light	Reaction time, days	Yield, %	1,1, %
None		HAc		None	12	83	3
p-Thiocresol	2.4	HAc		None	12	56	77
Diphenylamine	3.0	HAc		None	15	65	44
None		HAc		500W	1	74	5
p-Thiocresol	2.4	HAc		500W	1	46	35
None		Nitrobenzene		None	32	71	29
p-Thiocresol	2.4	Nitrobenzene		None	12	54	77
Diphenylamine	3.0	Nitrobenzene		None	15	59	81
None		Nitrobenzene	+	None	6	84	2
None		Mesitylene		None	32	31	95
p-Thiocresol	2.4	Mesitylene		None	14	31	100
Diphenylamine	3.0	Mesitylene		None	18	38	97
None		Mesitylene	+	None	6	76	2

Factors Influencing the Addition of Hydrogen Chloride to Vinyl Chloride.—We find that no appreciable addition of hydrogen chloride to vinyl chloride occurs under peroxide-containing or peroxide-free conditions or upon illumination with light. We found, as did Wibaut,[4] that addition occurs only under the influence of metallic salt catalysts such as ferric chloride and then ethylidene chloride was formed exclusively.

The Addition of Hydrogen Iodide to Vinyl Chloride.—The addition of anhydrous hydrogen iodide to vinyl chloride occurs rapidly in peroxide-containing or peroxide-free mixtures to give pure ethylidene chloroiodide as indicated by the sharp boiling point of the addition product corresponding to that given in the literature for the 1,1 isomer. The refractive indices of all runs were identical which, together with a common boiling point (114–115°), indicates a common product. The same products are obtained at −40° in the dark although addition at this temperature is quite slow. The strongly reducing hydriodic acid[5] destroys all peroxides even at −40°, giving the "normal" addition product, ethylidene chloroiodide.

TABLE IV

THE ADDITION OF HYDRIODIC ACID TO VINYL CHLORIDE

Added agent	Mml.	Air	Reaction time, days	Yield,[b] %	1,1, %
None		+	0.5	31	100
None[a]		+	2	15	100
None[a]			3	1	..
Benzoyl peroxide	0.8	+	0.5	100	100
Ascaridole	3.0	+	2	91	100
Benzoyl peroxide[a]	0.8	+	30	77	100
p-Thiocresol	2.4		4	84	100
p-Thiocresol[a]	4.8		30	10	100

[a] Tubes stored in liquid ammonia (−40°) during addition.

[b] Yield data rather inaccurate due to method of loading bomb tubes at liquid air temperatures.

Experimental Part

The vinyl chloride used was distilled as needed from a tank of the material kindly furnished through the courtesy of the Union Carbide and Chemical Co. It was sufficiently free from peroxides as indicated by the test with ferrous ammonium sulfate–ammonium thiocyanate as previously described.[2] To ensure uniform results, however, it was passed through a wash tower of dilute acetic acid and ferrous iron (to decompose any small amount of peroxides contained in the material), and then dried by passing through a large tube filled with calcium chloride and condensed in the bomb tube. The technique of addition was identical with that used by Kharasch and Mayo.[2]

Hydrogen bromide was prepared by the method described in previous articles.[2] The bomb tubes used were of Pyrex glass of 21 mm. o. d. and 2 mm. wall. A trace of manganese chloride was added to all mercaptans used as antioxidants due to the action of this salt in catalyzing the oxidation of organic sulfur compounds. The bomb tube system was evacuated with a 3-stage mercury pump. The pressures obtained were 10^{-4} mm. or less. In all of the experiments 0.1 mole of vinyl chloride and 0.15 mole of hydrogen bromide were used. In the case of hydrogen iodide we used 0.12 mole of the halogen hydride.

In working up the crude reaction product the bomb was chilled at −80°, the top cracked off with a hot wire, the contents drowned in water, washed with weak alkali and water, vacuum distilled, dried, distilled at atmospheric pressure and the refractive index taken at 20°. As the index of refraction of the two isomers was found to be a linear function of composition, the amount of each isomer in the addition product was easily obtained. The refractive index of the bromochlorides and chloroiodides of ethane are not given in the literature, but by fractionation of a mixture of the two bromochloro isomers through a Hempel column we obtained each isomer in a pure state. The fractions were refractionated and the refractive index of the largest portion taken as the refractive index of the pure isomer. The following constants were obtained.

	B. p. (735 mm.), °C.	n^{20}_{D}
Ethylene bromochloride	104–105	1.4908
Ethylidene bromochloride	80.5–81.5	1.4660

The ethylene bromochloride was identified by refluxing, with aniline to form the N,N′-diphenylethylenediamine m. p. 63.5–64°. The ethylidene bromochloride was decomposed by heating with moist silver oxide in a bomb tube for five hours at 100° and identifying the acetaldehyde formed as the 4-nitrophenylhydrazone of m. p. 127°.

Summary and Conclusions

1. It has been shown that under well-defined conditions hydrogen bromide can be added to vinyl chloride to give either 100% ethylidene bromochloride or 100% ethylene bromochloride.
2. It has been demonstrated that an oxygen or "peroxide" effect is responsible for the formation of ethylene bromochloride.
3. The addition of hydrogen iodide to vinyl chloride under peroxide-containing or peroxide-free conditions forms only ethylidene chloroiodide.
4. The addition of hydrogen chloride to vinyl chloride in the absence of metal salt catalysts does not proceed at a sufficiently rapid rate to be studied conveniently.
5. The effects of solvents, light, temperature, antioxidants, metallic salts, and different halogen acids on the velocity and direction of the addition have been evaluated.

CHICAGO, ILL. RECEIVED NOVEMBER 28, 1933

---

(5) The addition of hydrogen iodide to many unsaturated substances is under way in this Laboratory to determine the extent and validity of this assumption.