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

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. II. The Addition of Hydrogen Bromide to Vinyl Bromide

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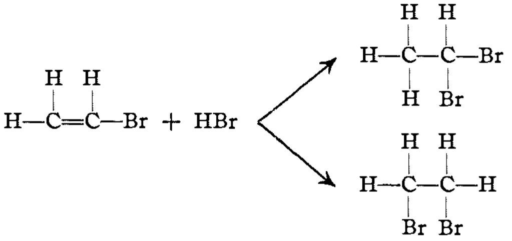
Introduction

In a previous communication, Kharasch and Mayo[2] proved conclusively that the most important factor in the addition of hydrogen bromide to allyl bromide is the peroxide content of the latter material. Peroxide-free conditions in that case were attained either by preparing and working with materials under carefully controlled conditions or by the addition to the reaction mixture of antioxidants. It was shown that once peroxide-free conditions were attained, temperature, infra-red and possibly all other radiation, and solvents played very minor roles in directing the addition of the halogen acid except in so far as these factors influenced the peroxide effect. It became important to ascertain, therefore, to what extent other unsaturated compounds are affected by peroxides ordinarily present in these materials as impurities.

In the case of vinyl bromide it is particularly important to know whether the normal reaction proceeds according to scheme (1) or (2)



(1)

(2)

The formation of ethylene dibromide (2) is predicted by the Lewis–Lucas[3] hypothesis, while the hypothesis of Kharasch and collaborators[4] predicts the formation of ethylidene bromide (1). Both hypotheses predict the exclusive formation of one product. A rigorous test of the merit of the two concepts is thus made possible by the study of the compounds formed under normal and under catalyzed conditions. The peroxide effect was entirely overlooked in previous studies of the addition of halogen acids to unsaturated compounds.

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[1] Eli Lilly and Co. Fellow. Appreciation of support for part of this work by Eli Lilly and Co. of Indianapolis is gratefully acknowledged.

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

[3] Lewis, "Valence and the Structure of Atoms and Molecules" (A. C. S. Monograph Series), Chemical Catalog Co., New York City, 1923, p. 89; Lucas and Jameson, THIS JOURNAL, **46**, 2475 (1924).

[4] For a summary of references, see Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).

Previous Work on the Addition of Hydrogen Bromide to Vinyl Bromide.—Previous work on the addition of hydrogen bromide to vinyl bromide is adequately summarized by Wibaut[5] in a recent paper. Two papers[6] along the same line have appeared since, but they contribute little more to the theoretical explanation of the course of the reaction. Briefly both possible addition products, 1,1-dibromoethane and 1,2-dibromoethane, have been obtained pure and in varying proportions. The literature is distinguished by unexplained lack of agreement in supposedly identical experiments and much is made of the relation between the concentration of reacting substances and the addition products obtained. A more complete survey and discussion of the earlier work is not justified because the previous workers were entirely unaware of the peroxide effect which we find to be the dominating factor in the addition. Therefore, the previous investigators were seldom investigating one single factor at a time, and any agreement between their data and ours is to be looked upon as a fortuitous coincidence.

Factors Influencing the Addition of Hydrogen Bromide to Vinyl Bromide

The Effect of Peroxides.—As already mentioned, the peroxide content of the vinyl bromide is the most important single factor governing the direction and velocity of addition of hydrogen bromide to that substance. We have found that the peroxide content of a lot of vinyl bromide increases regularly from day to day after its preparation, even when the sample is kept at −78° in the presence of antioxidants. Since even our best antioxidants are incapable of overcoming completely the effects of comparatively large quantities of peroxides, it is obvious that the properties of the vinyl bromide in any addition experiment will depend upon a constantly varying factor, and it is not surprising that exact duplication of results has been attained only with great difficulty.

Tables II, III and IV, to be discussed later, will show that 1,1-dibromoethane is the product of the "normal" addition taking place under peroxide-free conditions. On the other hand, Table I demonstrates that the addition of hydrogen bromide to vinyl bromide leads to a rapid formation of 1,2-dibromoethane if no special precautions are taken to remove peroxides. Furthermore, temperature, light and solvent (except acetic acid) have no effect on the direction, although they presumably modify the velocity of this peroxide-catalyzed addition. The same result is obtained whether the addition is carried out in air or whether air is excluded. This was not the case with allyl bromide and therefore these results indicate an apparently greater sensitivity of vinyl bromide than of allyl bromide to traces of peroxides. Thus, while a very low concentration of peroxides in allyl bromide would cause only a minor variation from

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(5) Wibaut and co-workers, *Rec. trav. chim.*, **50**, 313 (1931).

(6) Burkhardt and Cocker, *ibid.*, **50**, 837 (1931); Wibaut and Van Dalfsen, *ibid.*, **51**, 636 (1932).

the normal addition, a similar concentration in vinyl bromide causes the occurrence of the peroxide-catalyzed reaction to the exclusion of the normal addition. However, because the normal addition to vinyl bromide is only about one-tenth as fast as to allyl bromide, the same concentration of

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE WHEN NO PRECAUTIONS WERE TAKEN TO REMOVE PEROXIDES

No.	Moles HBr	Solvent	Moles solvent	Air[b]	Temp., °C.	Light (lamp size)	Reaction time	% yield[c]	% 1,1-[c]	Remarks
5	1.51	None		X	Room	None	31 hours	70	0	
29[a]	1.50	None		X	Room	None	3 days	89	0	
1[a]	1.52	None		X	Room	100W	4 days	70	0	
6	1.57	None		X	Room	100W	28.5 hours	70	0	Tube 25 cm. from lamp
32	1.45	(Water)		X	Room	500W	42.5 hours	85	0	Vinyl bromide saturated with water at 0°
132[a]	1.58	None			Room	None	2 days	98	0	
28	1.58	None			76	None	12 hours	72	0	
97[a]	1.58	None			76	None	18 hours	92	0	
10	2.60	Water	37.3	X	Room	None	18 days	1	0	Equivalent of 24% aqueous HBr used
22	1.50	Water	1.69	X	−75	None	1 day			
					then 0	None	11 days	64	0	80% aqueous HBr
7	1.32	HAc	10.3	X	7	None	7 days	<10	..	
13	1.64	HAc	1.59	X	Room	None	7 days	73	1	
21	1.53	HAc	1.68	X	−75	None	1 day			
					then 0	None	11 days	60	2	
91[a]	2.00	HAc	1.50		Room	None	1 day	90	17	Peroxide test 0[d]
81	2.00	HAc	1.50		Room	500W	16 hours	90	10	Tube 8 cm. from lamp
153	4.00	HAc Containing 5% by weight of water	1.50		Room	None	7 days	96	10	
3	1.49	Chloroform	1.62	X	Room	100W	4 days	70	0	
8[a]	1.50	Chloroform	1.89	X	7	None	7 days	70	0	
24	1.49	Carbon disulfide	1.54	X	−75	None	1 day			
					then 0	None	11 days	62	0	
26	1.49		1.50		Room	None	6 days	60	0	
60	1.58	Nitrobenzene	0.029	X	Room	None	1 day	94	0	

[a] One to several duplicate runs giving essentially the same results are omitted to conserve space.

[b] In runs marked "X" the bomb tubes were sealed off without evacuation and therefore contained air. In all other runs, the reaction mixtures (except acetic acid and nitrobenzene) were dried and distilled and air was excluded.

[c] Yields as given represent the fraction of the theoretical yields of dibromoethanes recovered after washing, drying, and distillation. Because of unavoidable and comparatively large losses in working with small quantities of material, many runs in which theoretical yields were undoubtedly obtained are credited with yields of 70–98%. The column headed "% 1,1-" gives the % of 1,1-dibromoethane in the pure addition product, the remainder being 1,2-dibromoethane.

[d] Just before starting many runs, a few drops of the stock vinyl bromide were tested qualitatively for peroxides with a few crystals of ferrous ammonium sulfate and about 1 cc. of 10% ammonium thiocyanate solution. "0" indicates no immediate color change and the absence of peroxides within the sensitivity of the test. "4" indicates the presence of comparatively large quantities of peroxides as shown by the immediate development of a strong red coloration. "1", "2" and "3" indicate intermediate stages.

peroxide may exert a proportionally greater effect on vinyl bromide by virtue of the slowness of the competing normal reaction. Hence, while we may not say rigorously that vinyl bromide is more susceptible to the oxygen effect than allyl bromide, the effect obviously shows up to a greater extent.

The sensitivity of vinyl bromide to the peroxide effect is such that none of the normal addition product is obtained under any circumstances except in the presence of antioxidants or acetic acid or ferric chloride. However, the amount of 1,1-dibromoethane formed in acetic acid solution never exceeds 20% in the absence of antioxidants. Such an effect of acetic acid for this exceedingly peroxide-sensitive system could have been anticipated from the much more pronounced effect of this solvent in the case of the less peroxide-sensitive allyl bromide.

The Effect of Antioxidants.—Table II shows the effect of various antioxidants on the addition of hydrogen bromide to vinyl bromide in the absence of solvents and air. It is shown that antioxidants are unable to overcome completely the effect of peroxides in many cases and the amount of normal product obtained depends on both the concentration of peroxides and the nature of the antioxidant used. However, with vinyl bromide of very low peroxide content and in the presence of good antioxidants, the product is always 1,1-dibromoethane. Diphenylamine, thiophenol and thiocresol are shown to be satisfactory antioxidants, the first being the least effective of the three. Phenyl-β-naphthylamine, dimethylaniline, hydroquinone and an isocyanide are found to be less effective and ammonium bromide and diphenyl ether, as anticipated, are without effect. We are satisfied that the weak effect exerted by some nitriles is due to the presence of isomeric isocyanides in the materials.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE ABSENCE OF SOLVENTS AND AIR[b] AND THE PRESENCE OF ANTIOXIDANTS

No.	Antioxidant	Mole	Temp., °C.	Reaction time	%[c] Yield	% 1,1-[c]	Peroxide test[d]	Remarks
33	Diphenylamine	0.02	Room	3 days	<5	...		
38	Diphenylamine	.01	Room	16 days	35	100		
68	Diphenylamine	.02	Room	68 days	79	100		
95[a]	Phenyl-β-naphthylamine	.024	Room	48 days	84	78	1	
146	Dimethylaniline	.013	Room	10 days	50	96	0	
53	Ammonium bromide	.036	Room	4 days	98	2		
125[a]	Propionitrile	.097	Room	3 days	94	5	2	
147	Propionitrile +	.097						
	dimethylaniline	.013	Room	2.5 days	35	100	0	
123	Propionitrile	.097						
	+ diphenylamine	.01	Room	2.5 days	62	100	1	
148	Propionitrile + phenyl-	.097						
	β-naphthylamine	.016	Room	2.5 days	34	100	0	

TABLE II (*Concluded*)

No.	Antioxidant	Mole	Temp., °C.	Recttion time	%[c] Yield	% 1,1-[c]	Peroxide test[d]	Remarks
149	Propionitrile	0.097						
	+ thiocresol	.028	Room	2.5 days	32	100	0	
92	Benzonitrile	.054	Room	2.5 days	88	25	0	
93	Phenylacetonitrile	.046	Room	2.5 days	82	28	0	
120[a]	*t*-Butyl isocyanide	.069	Room	2.5 days	90	100	0	
136[a]	*t*-Butyl isocyanide	.069	Room	4 days	92	63	2	
113[a]	*t*-Butyl isocyanide	.047	Room	4 days	97	2	4	
124	*t*-Butyl isocyanide	.047						
	+ diphenylamine	.021	Room	2.5 days	82	100	1	
58	Butyl mercaptan	.045	Room	18 days	<10	...		
55	Thiophenol	.032	Room	29 days	<10	...		
66	Thiophenol + manganese chloride	.032 .0002	Room	70 days	70	100		
52	Hydroquinone	.032	Room	3 days	20	...		Large quantity of tar obtained
89	Hydroquinone	.032	Room	53 days	50	30		
56	Diphenyl ether	.021	Room	1 day	96	0		
128	Nitric oxide (tube filled with gas)		Room	3 days	45	100		Large quantity of polymerized products
43	Diphenylamine	.021	100	1 day	82	32		
47[a]	Diphenylamine	.021	76	2 days	92	1		
51	Diphenylamine	.042	76	2 days	93	24		
85	Phenyl-β-naphthylamine	.024	76	2 days	86	0		
86	Thiophenol	.032	76	2 days	80	17		
105[a]	Diphenylamine	.021	56	4 days	81	17	1	
99	Thiophenol	.032						
	+ manganese chloride	.0002	56	2 days	48	78	0	
109	Thiophenol	.041						
	+ manganese chloride	.0002	56	4 days	72	78	0	
122	Diphenylamine	.021	46	5 days	92	7	4	
134	Phenyl-β-naphthylamine	.024	46	5 days	92	4	1	
121[a]	Thiophenol +	.04	46	5 days	86	77	0	
143	manganese chloride	.0002			90	32	3	
	Runs made 8 cm. from 500W lamp							
49	Diphenylamine	.021	Room	16 hours	90	0		
77	Phenyl-β-naphthylamine	.024	Room	16 hours	92	0		
78	Thiophenol +	.032						
	manganese chloride	.0002	Room	16 hours	84	0		
101	Diphenylamine	.021	5	16 hours	78	12	0	
137	Thiophenol +	.032						
	manganese chloride	.0002	5	16 hours	49	83	0	
140	Thiocresol +	.028						
	manganese chloride	.0002	5	16 hours	64	79	0	

1.51 moles of hydrogen bromide was used in the first experiment listed, and 1.58 moles in all of the others.

[a,b,c,d] See corresponding notes to Table I.

The relationship between the effectiveness of the antioxidants and the peroxide content of the vinyl bromide is brought out in a most striking manner with tertiary butyl isocyanide. When a sample of vinyl bromide freshly distilled and containing only the merest trace of peroxides, is treated with hydrogen bromide in the presence of this antioxidant, the product is invariably pure 1,1-dibromoethane. The same lot of vinyl bromide, upon standing for one or two days, definitely shows an increase in peroxide content, and the proportion of the "normal" product formed upon the addition of hydrogen bromide under the same conditions may vary from 50–90%. After three or four days' standing, the vinyl bromide gives a fairly strong peroxide test and adds hydrogen bromide to give practically quantitative yields of 1,2-dibromoethane. This isocyanide is thus only a sufficiently powerful antioxidant to exert an effect when the peroxide content of the vinyl bromide is extremely low. The validity of this statement has been substantiated by thirty experimental runs in which the peroxide content varied in the manner indicated above and absolutely concordant results were obtained.

There is no evidence that any antioxidant has any retarding effect on the normal addition if we assume that the velocity of the normal addition is that found in the presence of diphenylamine and mercaptans. However, it should be noted that an isocyanide, nitriles (including hydrogen cyanide from potassium cyanide) and nitrobenzene cause a tremendous acceleration of the normal addition even when various antioxidants are also added to counteract the peroxide effect. The usual interpretation of such results on the basis of the dielectric constant of the medium is, in our estimation, inadequate. There seems also to be some variation in velocity with different antioxidants in the absence of solvents. In the presence of substances which we term antioxidants, we have obtained both very rapid and very slow additions to give 1,1-dibromoethane, and we have also experienced the formation of 1,2-dibromoethane in the presence of the weaker antioxidants and comparatively large amounts of peroxides. Our conclusion is that antioxidants have no effect on the direction of addition of hydrogen bromide except that they tend to overcome the peroxide effect.

The Effect of Temperature.—In the case of other ethylene compounds studied by us, increased temperature exaggerates the peroxide effect, and with a system as sensitive to peroxides as vinyl bromide, the increased peroxide effect might easily become the dominating factor in the reaction, even in the presence of antioxidants. The initial peroxide content of the system would thereby produce an effect far greater than under lower temperature conditions and the ability to duplicate experiments would resolve itself into our ability to prepare lots of vinyl bromide of the same peroxide content.

We attribute the formation of the 1,2-isomer at 100 and 76° (Table II) in the presence of antioxidants to the effect of the peroxides as exaggerated by temperature rather than as a temperature effect *per se*. Thus when the vinyl bromide contains only a minute trace of peroxide, thiophenol is capable of overcoming its effect and the product is about 70–80% of 1,1-dibromoethane at 56°. On the other hand, diphenylamine, a weaker antioxidant, is unable to overcome the peroxide effect as exaggerated at this temperature and also at 46°. However, even thiophenol is unable to overcome the effect of an increase in the peroxide content of the vinyl bromide at this temperature, and the addition product contains only 32% of 1,1-dibromoethane.

The Effect of Light.—The last results in Table II show that at room temperature under strong illumination, the addition product is 1,2-dibromoethane, even in the presence of good antioxidants. Under similar conditions at 5°, up to 80% of the normal product is formed. Since it was shown in the previous section as well as in the paper on allyl bromide that temperature lowering greatly decreases the peroxide effect, the experiments mentioned above indicate that light has no effect on the direction of addition of hydrogen bromide to vinyl bromide except that it increases the magnitude of the peroxide effect. Note also that strong illumination increases tremendously the velocity of both the "normal" and "peroxide-catalyzed" additions.

The Effect of Solvents.—Although fewer solvents (Table III) were used by us than in the case of allyl bromide, the results are as unmistakable as in that case that the effect of the solvent on the order of addition is negligible, except as it may influence the peroxide effect. The effect of various materials in accelerating the rate of the reaction is without doubt related to the dielectric constant of the solvent but in no case does that effect outweigh that of the peroxides. The difficulties in duplicating runs are directly connected with the day-to-day variation in the peroxide content of the vinyl bromide. On the whole, it can be readily noted that in glacial acetic acid the yield of the 1,1-dibromoethane seldom exceeds 20–25% in the absence of an antioxidant (Table I). This result is in accord with the great susceptibility of vinyl bromide to traces of peroxides and the fact that glacial acetic acid is a poor antioxidant. In the presence, however, of better antioxidants, the yield of the normal product is increased and may vary between 65 and 100%, depending upon the antioxidant and the age of the vinyl bromide, as shown in Table III. Other solvents, such as acetic acid containing 5% water, acetyl bromide, and nitrobenzene show the same trend, and fair yields of the 1,1-isomer may be obtained by the use of good antioxidants.

The Effect of Metal and Surface Catalysts.—As previously stated, the effect of antioxidants is to eliminate the peroxide effect. This, of course, may be accomplished in a variety of ways, and hence the variety of reagents that may be employed is large. Ferric chloride acts as an anti-

TABLE III

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE PRESENCE OF SOLVENTS AND ANTIOXIDANTS

Except as otherwise noted, the runs in this table were made at room temperature, in the dark, and in the absence of air.[a] 2.0 moles of hydrogen bromide was used in all of these experiments except in No. 152 where 4.0 moles was used. 1.5 moles of solvent was used in all cases except that in the last four experiments listed, 1.0 mole of nitrobenzene was used.

No.	Solvent	Antioxidant	Mole	Reaction time	Yield, %[c]	% 1,1-[c]	Remarks
44	Glacial acetic acid	Diphenylamine	0.01	10 days	40	100	
71		Diphenylamine	.021	66 days	85	70	
62		Phenyl-β-naphthylamine	.018	26 days	70	63	
67		Thiophenol + manganese chloride	.032 .0002	32 days	48	100	
72				63 days	70	86	
63		Thiophenol	.032	26 days	80	84	
152		Thiocresol	.028	11 days	48	96	HBr only, not vinyl bromide, dried and distilled *in vacuo*
40	Glacial acetic acid	Diphenylamine	.01	16 hours	79	13	Run 8 cm. from 500-watt lamp
79		Phenyl-β-naphthylamine	.032	16 hours	90	28	
80		Thiophenol + manganese chloride	.064 .0002	16 hours	90	20	
84	Acetic acid (Mixture of acid and water used, containing 5% by weight of water)	Phenyl-β-naphthylamine	.016	56 days	92	61	
83		Thiophenol	.032	55 days	73	85	
154		Thiocresol	.028	11 days	80	89	HBr only, not vinyl bromide, dried and distilled *in vacuo*
65	Acetyl bromide	Phenyl-β-naphthylamine	.016	69 days	92	92	
74	Acetyl bromide	Thiophenol	.033	63 days	90	63	Peroxide test 2
73	Acetyl bromide	Thiophenol + manganese chloride	.033 .0002	64 days	64	69	Peroxide test 2
114	Nitrobenzene	Diphenylamine	.032	2 days	38	50	
119	Nitrobenzene	*t*-Butyl isocyanide	.069	5 days	71	96	Peroxide[d] test 0
88	Nitrobenzene	Thiophenol	.065	4 days	34	54	
117	Nitrobenzene	Thiophenol + manganese chloride	.065 .0002	20 days	62	70	Peroxide test 1

[a,b,c,d] See notes [a,b,c] and [d] to Table I.

oxidant, but it also accelerates tremendously the rate of formation of the normal product, 1,1-dibromoethane. Furthermore, light apparently has no effect upon the order of addition in the presence of the iron salt. These facts may be accounted for also on the basis that the iron-catalyzed addition is fast enough to obscure even the peroxide-catalyzed addition (Table IV).

Of the other metallic salts used, mercuric bromide,[7] manganese chloride,[8] and potassium cyanide, none appears to have any effect on the addition in the liquid phase. Note, for instance, that when a sample of vinyl bromide of moderate peroxide content is treated with hydrogen

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(7) Wibaut, Ref. 5, claims that this material acts as a catalyst for the vapor-phase addition.

(8) Manganese salts have been found to catalyze the oxidation of sulfur compounds. Since manganese chloride was used in conjunction with some of the antioxidants, its effect by itself was also tested.

TABLE IV

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE PRESENCE OF METALLIC SALTS AND SURFACE CATALYSTS

Except as otherwise noted, the runs in this table were made at room temperature, in the dark, and in the absence of air.[a] 1.58 moles of hydrogen bromide was used in all runs except No. 64, where 2.0 moles was used.

No.	Catalyst	Mole catalyst	Reaction time	Yield, %[c]	% 1,1-[c]	Peroxide test[d]	Remarks
48	Anhydrous $AlCl_3$	0.019	1 day	0	0		Only tar obtained
39	Anhydrous $FeCl_3$	.022	1 day	88	100		
41	Anhydrous $FeCl_3$	.022	6 hours	38	100		Run 8 cm. from 500-watt lamp. Tar formation accounts for low yield in No. 41
50	Anhydrous $FeCl_3$	.022	2 hours	72	100		
144	Mercuric bromide	.04	3 days	95	0	1	
59	Manganese chloride	.0002	1 day	97	0		
64	Manganese chloride	.0002	26 days	90	24		1.5 moles of glacial HAc used as solvent
145	Potassium cyanide	.023	3 days	96	0	1	
156	Potassium cyanide	.023	4 days	88	48	1	0.01 mole diphenylamine added
155	Asbestos[e]		3 days	92	0	0	
156	Glass wool[e]		3 days	91	0	0	

[a,b,c,d] See notes [a,b,c] and [d] to Table I.

[e] 2–3 cm. of the bomb tubes was filled loosely with these materials. The asbestos, commercially acid-washed and ignited material, was further washed with acid to remove remaining traces of iron salts. *Cf.* Kharasch and Mayo, Ref. 2.

bromide in the presence of hydrogen cyanide, none of the 1,1-dibromoethane is formed. However, under the same conditions in the presence of diphenylamine, 48% of this product is readily obtained. Anhydrous aluminum chloride caused so much polymerization of the vinyl bromide that no addition product was isolated.

As was to be expected, pure asbestos and glass wool have no apparent effect on the order of addition, and the results of the addition do not differ in any way from those obtained in their absence with samples of vinyl bromide of the same peroxide content.

Experimental Part

Vinyl bromide was prepared by dropping ethylene dibromide (Eastman) into an excess of a 20% solution of potassium hydroxide in 95% ethyl alcohol. The vapors were passed upward through a reflux condenser kept at 20°. The crude product was condensed directly, washed at 0° with water, dried over calcium chloride, and distilled. About 0.5% of diphenylamine was then added and the mixture was kept at −75°. This diphenylamine had little effect on decreasing the formation of peroxides (for possible explanation, consult Ref. 2). The vinyl bromide for those runs made in the presence of air was not kept with diphenylamine, while in the rest of the runs this antioxidant was removed in the vacuum distillation involved in the technique of addition which has been fully described by Kharasch and Mayo.[2] The following changes from the technique described for allyl bromide were made: 6.0 g. of vinyl bromide was used for most of the runs. The quantities of other materials used are given in the tables on the basis that the quantity of vinyl bromide used was one mole. Solvents, antioxidants, and catalysts were usually put into the receiver bomb tube and the hydrogen bromide and vinyl bromide were distilled into them. The unreacted vinyl bromide and solvents not removed by washing were easily removed from the addition product by fractional distillation. The calculation of the yields is described in Note *c* of Table I. The composition of the addition product was determined from the index of refraction of the mixture of purified dibromoethanes and was always checked qualitatively by the boiling range. Our determinations of the indices of refraction of the two dibromoethanes were: n_D^{20} 1,1-, 1.5123; 1,2-, 1.5380. Wibaut[5] has shown that the index of refraction of mixtures of these two compounds is a straight line function of composition.

Summary and Conclusions

1. It has been shown that under well-defined conditions, hydrogen bromide can be added to vinyl bromide to give either 100% of ethylidene bromide or 100% of ethylene dibromide.
2. It has been demonstrated that the formation of ethylidene bromide is the "normal" addition.
3. It has been demonstrated that peroxides in the vinyl bromide are responsible for the formation of 1,2-dibromoethane.
4. The effects of solvents, temperature, light, antioxidants, and different surfaces and salts upon the velocity and direction of addition have been studied. The general conclusion has been reached that the peroxides are probably the most important single factor governing the direction of addition, and that all other agents exert their specific effects not upon the organic unsaturated molecule itself, as assumed in the literature, but either upon the peroxide molecules or in activating oxygen liberated by the decomposition of peroxides.

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