

certainty of equation (10) is $\pm 0.5\%$ in a 3 molar solution. The uncertainty decreases considerably as we approach pure water.

Apparent and Partial Molal Expansibilities.—The apparent molal expansibility has been defined¹ like the apparent molal volume as

$$\Phi E_2 = \alpha V - \alpha_1 V_1 \quad (11)$$

where V is the number of ml. of solution which contains one mole of solute, and V_1 is the volume of solvent used in making the solution. The apparent molal expansibility is the temperature derivative of the apparent molal volume. A more convenient equation for calculating the apparent molal expansibility¹ is

$$\Phi E_2 = \frac{1000}{c} (\alpha - \alpha_1) + \alpha_1 \Phi V_2 \quad (12)$$

The mean of the values³ at 25 and 30° gives for the apparent molal volume at 27.5°

$$\Phi V_2 = 44.385 + 0.1203c \quad (13)$$

Substituting the coefficients from (10) and (13) gives the apparent molal expansibility as

$$\bar{E}_2 = 0.0645 - 0.00468c \quad (14)$$

The partial molal expansibilities of solute and solvent, which are the temperature coefficients of the corresponding partial molal volumes, may be calculated conveniently from the equations for the apparent molal expansibility and volume by means of formulas already derived^{3,4} or closely analogous to them. For numerical calculations they may be put in the form

$$\begin{aligned} \bar{E}_2 &= 0.0645 - 0.00936c + 0.00208c^2 \\ \bar{E}_1 &= 0.00508c + 0.0000846c^2 - 1 \times 10^{-8}c^4 \end{aligned}$$

Discussion.—We have shown previously³ that the apparent molal volume of urea is very nearly the same as the molal volume of the solid, and that it changes between 0 and 1 molar only about 4% as much as a typical 1-1 electrolyte. It is rather surprising to find that its apparent molal expansibility is much larger in proportion. The limiting value at zero concentration is about that of a typical 1-1 electrolyte and the change between 0 and 1 molar is about a quarter as great as for such a polar compound. Thus we see that, although the solute-solvent forces are much less in solutions of urea than in electrolytic ones, the temperature coefficient is much more nearly the same in the two different environments. In the case of the volume properties, at least, we have shown a definite linearity with the first power of the concentration in the case of urea, which differentiates it clearly from electrolytes.

Summary

We have developed a method of calculating the coefficient of expansibility of any solution for which the density is known as a function of the molarity at two different temperatures. We have applied the method to urea solutions at 27.5° and give equations for the coefficient of expansibility, apparent and partial molal expansibilities. The apparent molal expansibility of urea is about as great as that of a 1-1 electrolyte, although it is a linear function of the first power and not the square root of the molarity.

EVANSTON, ILLINOIS

RECEIVED MARCH 13, 1939

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

The Addition of Hydrogen Halides to *cis*- and *trans*-2-Pentene

BY M. S. KHARASCH, CHEVES WALLING¹ AND FRANK R. MAYO

Introduction

Over ten years have elapsed since Kharasch and Darkis² published their interpretation of the addition of hydrogen bromide to 2-pentene. At that time, and for some time thereafter, the results of various workers²⁻⁴ seemed to indicate different ratios of products depending upon the conditions of addition and the source and previous

treatment of the pentene employed. To account for this phenomenon, Kharasch and Darkis² postulated the existence of two isomeric 2-pentenes (electromers) differing in their electronic configurations, of which one added hydrogen bromide to give 2-bromopentane, and the other, 3-bromopentane.

More recently the matter has been investigated by Lauer and Stodola⁵ and Lucas and Prater.⁶ The latter authors isolated the *cis* and *trans* isomers of 2-pentene, and claim, on the

(1) Du Pont Fellow, 1938-1939.

(2) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

(3) Lucas and Moyses, *This Journal*, **47**, 1459 (1925); Lucas, Simpson, and Carter, *ibid.*, **47**, 1462 (1925).

(4) Sherrill, Otto, and Pickett, *ibid.*, **51**, 3023 (1929); Sherrill, Baldwin, and Haas, *ibid.*, **51**, 3034 (1929).

(5) Lauer and Stodola, *ibid.*, **56**, 1216 (1934).

(6) Lucas and Prater, *ibid.*, **59**, 1682 (1937).

TABLE I
 PHYSICAL CONSTANTS OF 2-PENTENES AND THEIR ADDITION PRODUCTS

Compound	This paper			Other workers			Ref.
	B. p., °C.	Pressure, mm.	n_{20D}	B. p., °C.	Mm.	n_{20D}	
2-Bromopentane	58.4-58.8	100	1.4412			1.4412	4
						1.4416	3
3-Bromopentane	59.0-59.5	100	1.4444			1.4443	4
						1.4443	3
2-Chloropentane	95.5-96.0	755	1.4068	96.84-86	760	1.4069	9
3-Chloropentane	96.8-97.2	755	1.4103	97.76-82	760	1.4104	9
<i>cis</i> -2-Pentene	36.5	755	1.3825	37.0		1.3822	8
				36.5		1.3817	7
				36.2		1.3817	6
<i>trans</i> -2-Pentene	36.0	755	1.3798	36.25		1.3790	8
	35.9	740	1.3798	36.2		1.3799	6
				35.7 - .9		1.3797	5

basis of rather meager experimental evidence, that the two isomers add hydrogen bromide to give different proportions of 2- and 3-bromopentane.

It should be noted that, with the exception of Lauer and Stodola, all investigators have used the index of refraction to determine the composition of the reaction mixture, and have obtained a variety of results. Lauer and Stodola converted the mixture of bromides into anilides and found that their addition products contained approximately equal quantities of the two bromides.

To account for the lack of agreement between various groups of workers, and because of the far-reaching advances which have been made in recent years in our knowledge of the factors influencing the rate and direction of addition of hydrogen bromide to a large number of unsaturated compounds, a careful reinvestigation of the addition of hydrogen bromide and hydrogen chloride to both *cis*- and *trans*-2-pentene appeared desirable.

The present paper confirms the results of Lauer and Stodola on the addition of hydrogen bromide to *trans*-2-pentene. Furthermore, it shows that the addition of hydrogen chloride as well as hydrogen bromide to both *cis*- and *trans*-2-pentene results in an equimolecular mixture of 2- and 3-halopentanes regardless of the conditions of addition.

Preparation of 2-Pentene

Three methods of preparing 2-pentene were selected to give products of definite composition in sufficient amounts for study. 2-Pentene was prepared by the elimination of hydrogen bromide from (I) 2-bromopentane and (II) 3-bromopentane, and (III) by the partial hydrogenation of 3-pentyne. A fourth method, the treatment of a

carefully purified sample of one of the two isomeric 2,3-dibromopentanes with zinc, was investigated, but the amount of pentene obtained was too small to permit more than an investigation of its physical properties.

The pentenes from 2- and 3-bromopentanes were found, after repeated fractionations through a 1.5-m. column of both the pure hydrocarbons and their azeotropic mixtures with methyl alcohol, to be identical. Their physical constants show that both are either the *trans* modification^{5,6} or a mixture of *cis* and *trans* rich in the latter.⁷ Our data support the view of Lucas and Prater⁶ that previous preparations⁴ differed in their content of 1-pentene.

The pentene from the partial hydrogenation of 2-pentyne had physical constants in good agreement with those recorded by Sherrill and Launsbach⁸ for a similar preparation. This, together with its manner of preparation, indicates it to be largely or entirely the *cis* isomer.⁷

The pentene from the higher-melting 2,3-dibromopentane had similar properties, so that it, too, is apparently the *cis* isomer.

The constants which we and others have obtained for the *cis*- and *trans*-2-pentenes and for the 2- and 3-halopentanes are summarized in Table I.

Experimental

2-Pentanol was prepared via the Grignard reagent from *n*-propyl bromide and acetaldehyde according to the directions of Wood and Scarf.¹⁰ The constants for the product were: n_{20D} 1.4063-7; b. p. 117-118.5°.

2-Bromopentane was prepared by saturation of the alcohol with hydrogen bromide at 10° and warming to 60° on a

(7) Sherrill and Matlack, *THIS JOURNAL*, **59**, 2134 (1937).

(8) Sherrill and Launsbach, *ibid.*, **60**, 2562 (1938).

(9) Whitmore and Karnatz, *ibid.*, **60**, 2538 (1938).

(10) Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

water-bath. This process was repeated until no more hydrogen bromide was absorbed. A product was obtained in 90% yield upon working up in the usual manner; n_{20}^D 1.4412.

2-Pentene (method I) was prepared from 2-bromopentane by the method of Sherrill, Baldwin and Haas.⁴ After repeated fractionations of the azeotropic mixture with methyl alcohol (b. p. at 739 mm., 30.8–31.1°) through a 1.5-m. packed column, 2-pentene having the constants, b. p. (740 mm.) 35.9°, n_{20}^D 1.3798, was obtained in 32% yield.

3-Pentanol was obtained from two sources: (a) a sample of "synthetic diethyl carbinol" from the Eastman Kodak Company, b. p. 110–115°, n_{20}^D 1.4095–1.4106, and (b) a material obtained in 75% yield via the Grignard reaction between methyl formate and ethylmagnesium bromide, b. p. 114–114.5°.

3-Bromopentane was prepared in the same manner as its isomer, in yields of about 80%. The indices of products from three preparations varied between n_{20}^D 1.4443 and 1.4445. We have taken 1.4444 as being the probable index for the pure substance.

2-Pentene (method II) was prepared from 3-bromopentane in the same manner as from 2-bromopentane, and the yield of pure product on a representative preparation was 60%. The products, whether purified by distillation of their azeotropic mixtures (b. p. 749 mm., 31.0–31.1) with methyl alcohol through a 1.5-m. packed column, or by distillation of the pure hydrocarbon alone through a Podbielniak column¹¹ were identical with each other and with pentene prepared by method I. Constants were b. p. (755 mm.) 36.0°, n_{20}^D 1.3798.

2-Pentene (method III).—2-Pentyne was prepared from acetylene via ethylacetylene, as this seemed the most practical method for obtaining large quantities of the material.

Ethylacetylene was prepared from acetylene, sodium, and diethyl sulfate in liquid ammonia.¹² A specially constructed three-necked cylindrical flask with stirrer was used which fitted into a gallon (4-liter) dewar vessel. The latter was filled with an acetone–solid carbon dioxide mixture, as it was found that cooling both prevented loss of liquid ammonia and aided in controlling the reaction during the addition of diethyl sulfate. This last was added at such a rate that no product came off until the reaction was complete. The product was fractionated once through an 8-bulb column to remove acetylene, b. p. 10–20°. Yields as high as 172 g. (64%) were obtained from 5 moles of sodium.

2-Pentyne was prepared from the magnesium bromide derivative of ethylacetylene (prepared from ethylacetylene and ethylmagnesium bromide) and dimethyl sulfate.¹³ After the addition of dimethyl sulfate and before hydrolysis, the product and ether were removed from the reaction vessel by distillation. A further amount of product was obtained following the addition of water by collecting all material volatile at the temperature of a steam-bath.

The 2-pentyne was separated from ether by distillation through a 1.5-m. packed column, to give a fraction boiling 54.5–56.5°. Continued refractionation of this portion

through a Podbielniak column gave the pure acetylene, b. p. (755 mm.) 55.6–55.9°, n_{20}^D 1.4035. From 294 g., of ethylacetylene, 580 g. of ethyl bromide, 1500 g. of diethyl sulfate, and excess magnesium, 153 g. (41%) of pure 2-pentyne were obtained.

Preparation of 2-Pentene.—The 2-pentyne was hydrogenated at 0° and atmospheric pressure in methyl alcohol solution. The vessel employed was a 200-cc. flask fitted with inlet and outlet tubes for gas and a mercury seal stirrer. Eighteen grams of pentyne was treated at a time. The progress of the reaction, which was allowed to proceed until 0.7 to 0.9 mole of hydrogen per mole of pentyne had been absorbed, was followed by measuring the volume of hydrogen consumed. One to three hours were required for reaction, depending upon the effectiveness of stirring and the activity of the catalyst, 5% palladium on barium sulfate prepared according to Schmidt.¹⁴ The product was distilled from solution, washed with water to remove alcohol, dried over barium oxide, and distilled through a Podbielniak column. A fraction boiling over not more than 0.4° was collected, the yields approximating 50%. The index of refraction of the pure pentene was n_{20}^D 1.3823–5.

Occasional hydrogenations, particularly with new catalyst, gave products with a lower index (approximately n_{20}^D 1.3810). We have no adequate explanation to advance for this phenomenon, but such products were not used in our addition experiments.

2-Pentene from 2,3-Dibromopentane.—Samples of *cis*-2-pentene of low refractive index (as indicated just above) were combined and brominated at –78° in the absence of a solvent. After washing with cold, concentrated sulfuric acid and distilling, 121 g. of dibromide was obtained, which was then crystallized repeatedly from 90–98% aqueous methanol at –78°. After six recrystallizations, the melting point became constant at –33°. Thirty-three grams of this pure dibromopentane was treated with zinc in ethyl alcohol and the resulting pentene (6.7 g.) was distilled through a Podbielniak column. The fraction of b. p. (750 mm.) 36.0–36.4° had an index n_{20}^D 1.3825, indicating it to be pure *cis*-2-pentene.

Addition of Hydrogen Bromide and Hydrogen Chloride and Analysis of Addition Products.

Hydrogen bromide was added to the pentenes from three sources under a variety of conditions as indicated in Table II. The index of refraction of the products varied between n_{20}^D 1.4429 and 1.4434, corresponding to a product containing 52–69% 3-bromopentane. As this whole range in index is covered by the addition products to the pentene of source II with which most of the experiments were made, and as the nine additions in acetic acid cover almost as large a range (n_{20}^D 1.4429–33), we conclude that the ratio of addition products is independent of both the isomer of 2-pentene employed and the conditions of addition.

As all our determinations of the proportions of the two bromides had been made by index of re-

(11) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

(12) Vaughn, Hennon, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

(13) Thorn, Hennon and Nieuwland, *THIS JOURNAL*, **58**, 796 (1936).

(14) E. Schmidt, *Ber.*, **52**, 409 (1919).

TABLE II
 THE ADDITION OF HYDROGEN BROMIDE TO 2-PENTENE

Source of pentene ^a	Moles HBr ^b	Substance added	Moles ^b	Reaction Time, hours	Temp., °C.	Method of isolation ^c	Yield, ^b %	<i>n</i> ²⁰ _D ^d	Remarks
I	1.8	Acetic acid	3.6	2	0	1	90	1.4431	
				40	20				
II	1.8	Acetic acid	3.6	2	0				
				40	20	1	90	1.4431	
II	1.8	Acetic acid	3.6	2	5	1	80	1.4433	Pentene heated and illuminated in xylene (24 hrs.)
I	1.7	Acetic acid	1.5	2	0	1	74	1.4431	
II	1.8	Acetic acid	4.2	0.5	20	2	60	1.4429	
III	2.0	Acetic acid	4.0	48	20	2	..	1.4431	
III	2.0	Acetic acid	2	12	20	2	70	1.4431	
III	1.6	Acetic acid	2	0.75	20	1	85	1.4429	15 g. pentene used ^e
						2	1.4429		
II	1.6	Acetic acid	2	0.75	20	1	85	1.4429	15 g. pentene used ^e
						2	1.4430		
III	1.7	Diphenylamine	0.04	1	78	2	60	1.4430	Vacuum
I	1.5	Thiophenol	.03	1	80	1	88	1.4433	Vacuum
				20	5				
II	1.5	Thiophenol	.03	1	80	1	88	1.4432	Vacuum
				20	5				
II	1.5	Thiophenol	.03	1	80	1	75	1.4433	Vacuum
				20	5				
II	1.5	Thiocresol	.04	1	80	1	82	1.4433	Vacuum
				20	5				
I	1.5	None		2	75	1	65	1.4434	Some polymerization
				1	0				
II	1.3	FeBr ₃	.005	2	78	2	50	1.4430	
III	1.3	FeBr ₃	.005	2	78	2	60	1.4429	
III	1.2	Ascaridole	.05	0.75	0	2	..	1.4430	
II	1.5	Benzoyl peroxide	.01	2	0	1	36	1.4434	

^a Numeral indicates source of pentene. Sources I and II yield *trans*-2-pentene; source III, *cis*-2-pentene. ^b Expressed in moles per mole of pentene. ^c (1) Product vacuum distilled (100 mm.), all volatile products which condensed at room temperature collected. (2) Product distilled through 40-cm. column at atmospheric pressure, 1° fraction collected. ^d *n*²⁰_D 1.4428 corresponds to a mixture of equal proportions of 2- and 3-bromopentane. An increase of 0.0001 corresponds to an increase of 3% in the proportion of 3-bromopentane. ^e A portion of product isolated by each method, remainder fractionated (see experimental part).

fraction measurements, and as this method is inaccurate if a third substance is present, it seemed advisable to prepare larger quantities of the mixed bromides from both *cis*- and *trans*-2-pentene and to submit these to a careful fractionation which might be presumed to remove all impurities of higher and lower boiling point than the 2- and 3-bromopentanes. The mid-fractions from this purification were then analyzed both by index of refraction and by the mixed anilide method of Lauer and Stodola,⁵ using their melting point curves. Both results agreed within the limit of error (3%) and indicated an equimolar mixture of 2- and 3-bromopentanes for the entire addition product. From these data, given in detail in the experimental part, we conclude that analysis by index of refraction, as ordinarily employed, gives results which indicate the propor-

tion of 3-bromopentane to be too high by 2-28%.

Hydrogen chloride was added to the isomers of 2-pentene in the presence of acetic acid as solvent or ferric chloride as catalyst. The results are given in Table III. In order to obtain constant indices of refraction, it was found necessary to fractionate the products through a Podbielniak column. They were then analyzed both by index of refraction and by the melting points of their anilide derivatives. Neither method gives results differing from an equimolar mixture of 2- and 3-chloropentane by more than the probable experimental error; but, due to the difficulty in obtaining reproducible indices, we believe the anilide method to be the more reliable.

Experimental

Addition of hydrogen bromide was carried out as indicated in Table II, 5 g. of pentene usually being employed.

TABLE III
 ADDITION OF HCl TO 2-PENTENE

Run	Pentene ^a	Moles ^b HCl	Substance added	Moles ^b	Reaction		<i>n</i> ²⁰ _D ^c	M. p. of anilide, °C.	3%-chloro- pentane
					Time, hours	Temp., °C.			
1 ^d	II	2.0	FeCl ₃	0.005	12	20	1.4082	84.1	45-48%
2 ^e	III	2.0	FeCl ₃	.005	12	20	1.4081		
3	II	2.2	FeCl ₃	.005	12	20	1.4082		
4	III	2.2	FeCl ₃	.005	12	20	1.4081		
5	II	1.2	Acetic acid	2	96	20	1.4082	84.1	45-48%
6	III	1.2	Acetic acid	2	96	20	1.4083	83.3	47%

^{a, b} Have the same significance as in Table II. ^c Taking the index of refraction as a linear function of composition 1.4081, 1.4082, and 1.4083 correspond, respectively, to 37, 40, and 43% of 3-chloropentane. ^d As two experiments on *trans*-pentene fractionated on a short column failed to give reproducible indices, they were combined to make (1), fractionated on a Podbielniak column and analyzed. ^e Same as *d* for two experiments of *cis*-pentene.

In the cases marked "vacuum" the usual vacuum technique developed in this Laboratory was used.¹⁵ All products were washed successively with cold, concd. sulfuric acid, water, and sodium carbonate solution, and dried over either calcium chloride or potassium carbonate.

Two methods of distilling the products were used, as explained in Table II. Due to the elimination of some high- and low-boiling fractions, yields by method (2) were lower than by method (1) (40-60%), and it will also be noted that the average index by this method is nearer to what we consider to be the most probable value, 1.4428, that of an equimolecular mixture.

In order to investigate this difference and to determine as accurately as possible the actual ratio of the two bromides, 15-g. samples of both *cis*- and *trans*-2-pentene were treated with hydrogen bromide in acetic acid, and the product washed and dried in the usual manner. A yield of 85% was obtained before distillation.

Five grams of each product was now distilled by methods (1) and (2) and analyzed by index of refraction. Results are indicated in Table II. The remaining portions of the addition products were now carefully fractionated through a Podbielniak column with the results shown in Table IV. The small spread in indices indicates that no appreciable error is introduced into the determination by neglecting the first and last fractions. The mean index of fractions II-V corresponds in each case to a mixture containing 50-52% 3-bromopentane.

 TABLE IV
 FRACTIONATION OF HYDROGEN BROMIDE ADDITION PRODUCTS OF 2-PENTENE

Fraction	<i>Trans</i>		<i>Cis</i>	
	Wt., g.	<i>n</i> ²⁰ _D	Wt., g.	<i>n</i> ²⁰ _D
I	1.0	1.4425	1.1	1.4425
II	1.7	1.4427-8	1.9	1.4427-8
III	3.5	1.4428	4.0	1.4428
IV	3.3	1.4429	3.2	1.4429
V	2.4	1.4430	1.8	1.4430
VI	0.8	1.4434	1.0	1.4432
VII ^a	2.3	..	3.0	..

^a VII.—Mechanical loss and non-volatile material.

A portion of the combined fractions II-V of each addition product was converted to the mixed anilide derivative

(15) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2468 (1933). For several years the vacuum employed in such work has been 10⁻⁴ to 10⁻⁵ mm. rather than 1 mm. as indicated in this paper.

by the method of Lauer and Stodola. Using their melting point curve, the m. p. of the anilides (94.3-4.4°) corresponds to a mixture containing 50-51% 3-bromopentane.

Addition of hydrogen chloride was carried out by two methods: (a) the pentene (5-7 g.) to which 0.2 g. of ferric chloride had been added, was placed in a Pyrex bomb-tube and cooled in liquid nitrogen. Hydrogen chloride (7-10 g. depending upon the amount of pentene used) was then passed in and the tube sealed. After one-half hour at -80° and four to twelve hours at 20°, the tube was again cooled and opened. The product was washed and dried in the same manner as the hydrogen bromide addition products and fractionated through a Podbielniak column.

(b) A mixture of 5 g. of pentene and 10 cc. of acetic acid was cooled to -80° in a Pyrex bomb-tube and saturated with about 3.5 g. of hydrogen chloride. The tube was sealed and allowed to stand at room temperature for four days. It was then cooled to -80°, opened, and the product washed and distilled as above.

In order to investigate further the composition of the mixed chlorides, the products of runs 1-4 were combined and refractionated through the same column. The index of the middle two-thirds, cut into three fractions, varied from *n*²⁰_D 1.4082 to 1.4084. The mean value (1.4083) corresponds to a mixture containing 44% 3-chloropentane.

To check the results obtained above, two portions of the mid-fraction above were converted to their anilides, as were portions of experiments 5 and 6. Since the melting point curve of Lauer and Stodola indicates the melting points of anilides from known mixtures of 2- and 3-bromopentanes, it was necessary to construct a new curve for anilides prepared from known mixtures of the pure 2- and 3-chloropentanes. This curve, while similar to theirs, is shifted to one side (Fig. 1) and was used in all our analyses of the hydrogen chloride addition products. Unfortunately, the melting points of the anilides from the mixed chlorides lie so near the eutectic point of the curve that a greater error is introduced than in the case of the bromides.

Preparation of Pure Halides.—Pure samples of 2- and 3-bromopentane were prepared as already described and were distilled to constant index through a Podbielniak column (Table I).

Pure chloropentanes were prepared according to Whitmore and Karnatz⁹ and similarly purified by distillation. Our constants are in good agreement with theirs (Table I).

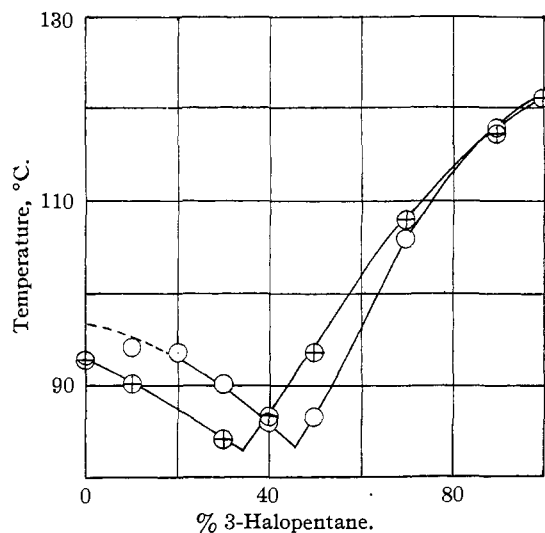


Fig. 1.—Melting points of anilides from mixtures of 2- and 3-halopentanes: ⊕—⊕, bromopentanes (Lauer and Stodola); ○—○, chloropentanes (this paper).

Discussion

Several years ago one of us and Reinmuth pointed out that the cases where two products were to be expected in the (normal) addition of halogen acids to an ethylenic bond were those where the ethylene was symmetrically substituted by groups of about equal electronegativity.¹⁶ Essentially the same rule recently has been advanced by Smith¹⁷ for hydrocarbons of the type $\text{CH}_3-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{CH}_2\text{R}$. At that time 2-pentene furnished the only instance of addition to a double bond to give two products, except for those in which a peroxide effect has since been shown to be involved. However, several compounds have since been shown clearly to give rise to two products upon normal addition of halogen acids: Δ^9 -undecenoic acid,¹⁸ Δ^9 -undecenol-1,¹⁸ Δ^3 -pentenoic acid,¹⁹ 1-bromopropene,²⁰ and *p*-chlorostilbene.²¹ It is to be noted that all the above compounds are ethylenes symmetrically substituted with radicals of similar electronegativity. The possible exception is 1-bromopropene; here one of the substituents is bromine and halogens do not seem to fall within our classification of electronegativity.²²

(16) Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).

(17) J. C. Smith, *Chemistry and Industry*, **15**, 833 (1937).

(18) Abraham, Mowat and Smith, *J. Chem. Soc.*, 948 (1937).

(19) Boorman, Linstead and Rydon, *ibid.*, 568 (1933).

(20) Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(21) Bloodgood, Ph.D. dissertation, The University of Chicago, 1931.

(22) Kharasch and Flenner, *This Journal*, **54**, 674 (1932).

In a recent paper,²⁰ two of us and Engelmann discussed the significance of the formation of two products by normal addition of halogen acids and it was pointed out that this phenomenon might arise in either of two ways: (1) the ethylene may exist in two forms, each giving rise to only one product; (2) the ethylene may exist in only one form. The double bond, however, is so slightly polar that the activation energies for the alternative reactions are very nearly the same.

The first alternative, that the ethylene may exist in two forms, admits of two possibilities: (a) the two forms differ in atomic configuration; (b) the two forms differ in electronic configuration. For ethylenic compounds of the type investigated, only one type of isomerism involving atomic configuration has ever been demonstrated: *cis-trans* isomerism. In all cases investigated (1-bromopropene²⁰ and 2-pentene), both geometrical isomers have been shown to give identical mixtures of products. The second type of isomerism, namely, differences in electronic configuration, we believe can now be dismissed. Not only is conclusive chemical evidence for such isomerism lacking, but the point of view of present-day physics leads to the conclusion that isomers of this type would appear as a resonance hybrid, here a non-polar or slightly polar double bond.

We are left, therefore, with the second alternative, that two products from the normal addition of halogen acids to ethylenic bonds are the result of the nearly identical activation energies of the two reactions, and that this would occur only when the two groups are about equal in electronegativity. This seems to be as far as we can go in the light of present-day experimental knowledge.

Summary

1. The addition of hydrogen chloride and hydrogen bromide to *cis*- and *trans*-2-pentene has been reinvestigated.

2. The ratio of products has been found to be independent of the conditions of addition and the isomer of 2-pentene employed.

3. The conditions under which two products are obtained upon normal addition of hydrogen halides to an ethylene bond and their theoretical implications are discussed.