

The catalytic reaction of acetylenic magnesium halides with other halogen derivatives is being studied in this Laboratory.

TABLE I
PHYSICAL CONSTANTS OF ALLYL ACETYLENES,
 $\text{CH}_2=\text{CH}-\text{CH}-\text{C}\equiv\text{CR}$

R	B. p., °C.	Mm.	d_{25}^{25}	n_D^{25}	MR _D	
					Calcd.	Found
$\text{CH}_3-\text{CH}-$	109-110	750	0.787	1.4694	31.59	32.60
C_4H_9-	58	22	.777	1.4413	41.30	41.48
$\text{C}_6\text{H}_{11}-$	73-74	22	.785	1.4444	45.92	46.28
C_8H_5-	107-108	22	.932	1.5574	46.93	49.08

Experimental

Reagents.—The monoalkyl acetylenes used in this work were prepared by the modified Picon synthesis.⁸ Monovinyl acetylene was furnished by E. I. du Pont de Nemours and Co. Allyl bromide was prepared by the standard method from allyl alcohol.⁹ All other reagents were c. p. grade.

Preparation of *n*-Butylallylacetylene.—Into a three-necked, one-liter flask equipped with a motor-driven, mercury-sealed stirrer, a reflux condenser and a dropping funnel was added 26.5 g. (1.1 moles) of magnesium turnings, a crystal of iodine and 40-50 ml. of anhydrous ether. To this was added dropwise and with constant stirring 120 g. (1.1 moles) of ethyl bromide diluted with ether. When the reaction had ceased, 82 g. (1 mole) of *n*-butylacetylene diluted with an equal volume of ether was added dropwise. After the addition of all the acetylene, the contents of the flask were refluxed for one hour on a water-bath and 2 g. of anhydrous cuprous chloride was added. After cooling to room temperature, 133 g. (1.1 moles) of allyl bromide diluted with an equal volume of ether was added dropwise. When the addition was complete separation into two layers had occurred and a large amount of

flocculent, yellowish-green solid had precipitated. The mixture was refluxed for one hour and then poured into an ice-dilute hydrochloric acid mixture. The organic layer was separated, washed with water and dried over calcium chloride. Fractionation yielded 23 g. of a mixture of allyl bromide and *n*-butylacetylene and 95 g. of *n*-butylallylacetylene (88% yield based on acetylene used). *Anal.* Calcd. for C_9H_{14} : C, 88.54; H, 11.48. Found: C, 86.3; H, 11.3. The preparation of the other allylacetylenes described is similar except for the substitution of a liquid ammonia condenser¹⁰ for a water-cooled condenser in the preparation of vinylallylacetylene.

The Structure of Vinylallylacetylene.—Analysis for carbon and hydrogen by combustion was found to be impractical for this compound because of its extremely explosive character under the conditions obtaining during the combustion. One fused quartz tube was literally pulverized by a 0.2-g. sample at a moderately low temperature. The compound is readily oxidized by neutral permanganate but the main product of the oxidation is carbon dioxide. Molecular weight (cryoscopic in benzene): calcd. 92; found, 91.

Summary

1. Vinyl, phenyl, *n*-butyl and *n*-amyl allylacetylenes have been prepared in high yields from the corresponding acetylenic Grignard reagent and allyl bromide, using cuprous chloride as a catalyst. Without a catalyst no substituted allylacetylenes could be obtained.

2. Cuprous chloride and bromide used as a catalyst produce the highest yields of substituted allylacetylenes. Cupric halides and cuprous cyanide also catalyze the reaction.

(10) Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

(8) Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

(9) "Organic Syntheses," Vol. I, 1921, p. 3.

NOTRE DAME, INDIANA

RECEIVED JANUARY 17, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Radiochemical Synthesis and Decomposition of Hydrogen Bromide

BY S. C. LIND AND ROBERT LIVINGSTON

The radiochemical formation of hydrogen bromide was first studied by Lind,¹ who found that the ion pair yield for a stoichiometric mixture was 0.54 at approximately 25°. Later Gillerot² determined the ion pair yield for synthesis at room temperature, and found that it depended upon the relative concentrations of hydrogen and bromine. He also demonstrated that the ion pair yield for decomposition was approximately 4.3. Working under slightly different conditions and using different values of the molecular ionization,

Lind and Ogg,³ found a value of 2.8. The ion pair yields for most radiochemical reactions which have been studied carefully⁴ are independent of the relative pressures of the reactants. The present unusual behavior combined with the detailed information available for the thermal and photochemical steps in the synthesis of hydrogen bromide made it appear that a careful study of this reaction might yield valuable information on the nature of radiochemical reactions in general.

(1) S. C. Lind, *Le Radium*, **8**, 289 (1911).

(2) R. Gillerot, *Bull. soc. chim. Belg.*, **39**, 503 (1930).

(3) Lind and Ogg, *Bodenstein Festband, Z. physik. Chem.*, 801 (1931).

(4) See Lind, "The Chemical Effects of Alpha Particles and Electrons," p. 101.

Experimental Methods

The hydrogen used in these experiments was prepared by the electrolysis of a potassium hydroxide solution, and was freed from traces of oxygen by being passed over heated palladinized silica gel,⁵ and was dried with anhydrous magnesium perchlorate. The bromine was a carefully purified sample.⁶ The hydrogen bromide was prepared by allowing purified bromine to react with an excess of hydrogen in a heated quartz bulb. Small quantities of bromine were weighed in sealed fragile glass bulbs. The samples of purified radon⁷ were sealed in similar small bulbs. The bromine and radon were introduced simultaneously into the reaction vessel by breaking the bulbs in a side tube with a magnetic glass-enclosed plunger. Before the bulbs were broken, the reaction system was evacuated and the reaction vessel was completely immersed in liquid oxygen. While the bromine and radon were frozen in the reaction vessel, hydrogen was admitted, to the desired pressure, through a stopcock which was separated from the reaction system by a long capillary. The capillary was then sealed off close to the reaction vessel. After allowing three or four hours for RaA and RaC' to accumulate to approximately their equilibrium values, the liquid oxygen was removed, and the reaction vessel was placed in an aluminum block thermostat which was kept at 25°. The total pressure was measured under these conditions with a quartz spiral manometer, which was used as a null instrument. Since the total pressure does not change, the course of the reaction was followed by measuring the pressure of hydrogen when the reaction vessel was immersed (to a definite point on the capillary connection) in liquid oxygen. The quantity of radon present in the reaction vessel was determined with a Lind γ -ray electroscope. Mixtures containing hydrogen bromide were prepared by distilling the hydrogen bromide directly into the reaction vessel before admitting the hydrogen.

Computation Methods

The intensity of ionization (number of ion pairs formed per cc. per second) was computed by Glockler and Heisig's⁸ modification of Mund's⁹

(5) Kindly furnished by L. H. Reyerson; compare Reyerson and Swearingen, *J. Phys. Chem.*, **32**, 113 (1928).

(6) Kindly furnished by A. E. Cameron; compare A. E. Cameron and L. H. Reyerson, *ibid.*, **39**, 173 (1935).

(7) Livingston, *Rev. Sci. Instruments*, **4**, 15 (1933).

(8) G. Glockler and G. B. Heisig, *J. Phys. Chem.*, **36**, 769 (1932).

(9) Mund, *ibid.*, **30**, 890 (1926).

method, using the method of Glockler and Livingston¹⁰ to obtain the molecular ionization of the mixed gases. The hydrogen pressure at 0° was computed from the manometric measurements at liquid oxygen temperatures, allowance being made for the volume (about 2% of the total) of the spiral manometer and capillary connection, which were at room temperature. The hydrogen pressure was plotted against time, and the slope obtained from a smoothed curve with a Bausch & Lomb "tangentmeter." The rate, in molecules reacting per hour, was computed from the slope by the use of the perfect gas laws. The ion pair yield, M/N , was obtained, for any time, by dividing the rate dM/dt , by the total ionization, dN/dt , expressed as ion pairs formed per hour. This involves a slight extension of the usual definition of M/N . Since in this case $(M/N) = f(t)$, the usual definition, $(M/N) = \Delta M/\Delta N$ is not appropriate. Perhaps the simplest definition, and the one which we have adopted, is $(M/N)_t = \left(\frac{dM}{dN}\right)_t / \left(\frac{dN}{dt}\right)_t$, or in other words $(M/N)_t$ is the instantaneous value of $f(t)$.

Experimental Results

Tables I and II give the averaged results (read

TABLE I

Synthesis: $P_{\text{H}_2}^0 = 169.0$ mm., $P_{\text{Br}_2}^0 = 122.0$ mm., $P_{\text{HBr}}^0 = 0$ mm., $E^0 = 123.5$ mc., $V = 105$ cc.

Time, hrs.	$P_{\text{H}_2}^0 - P_{\text{H}_2}$	$\frac{dM_{\text{HBr}}/dt}{\times 10^{-17}}$	$\frac{dN/dt}{\times 10^{17}}$	$(M_{\text{HBr}}/N)_t$
0	0
10	1.5	9.84	16.98	0.58
30	4.2	8.44	14.60	.58
50	6.4	6.83	12.58	.54
70	8.1	5.23	10.82	.48
90	9.4	4.05	9.31	.43
110	10.5	3.49	8.02	.44
130	11.5	3.07	6.90	.45
150	12.3	2.79	5.95	.47

TABLE II

Decomposition: $P_{\text{H}_2}^0 = P_{\text{Br}_2}^0 = 0$ mm., $P_{\text{HBr}}^0 = 169.5$ mm., $E^0 = 180.0$ mc., $V = 105$ cc.

Time, hrs.	$P_{\text{H}_2}^0 - P_{\text{H}_2}$	$\frac{dM_{\text{HBr}}/dt}{\times 10^{-17}}$	$\frac{dN/dt}{\times 10^{17}}$	$(M_{\text{HBr}}/N)_t$
0	0
10	-10.6	-55.78	15.58	-3.57
30	-20.8	-25.35	13.41	-1.89
50	-26.8	-17.43	11.54	-1.51
70	-31.1	-12.69	10.08	-1.26
90	-34.2	-9.20	8.55	-1.08
110	-36.6	-7.39	7.36	-1.01
130	-38.4	-5.58	6.33	-0.88
150	-39.8	-4.45	5.45	-.82
170	-40.9	-3.53	4.69	-.75

(10) G. Glockler and R. S. Livingston, *ibid.*, **38**, 655 (1934).

from the curve) for experiments 3 and 14, and serve to illustrate the course of typical synthesis and decomposition experiments.

Table III includes a summary of all of the experiments. The values of the change in hydrogen pressure, ΔP_{H_2} , and of the ion pair yield, M/N , are for a time ten hours after the start of the reaction. The last two columns will be discussed later.

TABLE III
SUMMARY OF EXPERIMENTS

Expt.	Initial pressure at 0°			E^0 , mc.	$P_{H_2}^0 - P_{H_2}$	$(M+HB_r/N)$ at 10 hours	
	$P_{H_2}^0$, mm.	$P_{Br_2}^0$, mm.	$P_{HB_r}^0$, mm.			Found	Calcd.
1	85.5	128.4	0	110.4	0.6	0.24	0.27
2	126.5	115.7	0	51.4	.3	.42	.42
3	169.0	122.0	0	123.5	1.5	.58	.51
4	251.6	96.7	0	89.7	1.2	.88	.86
5	414.0	59.3	0	121.4	2.7	1.90	1.81
6	470.5	59.6	0	52.6	1.2	1.76	2.02
7	460.0	43.9	0	134.2	3.9	2.67	2.16
8	426.5	28.3	0	91.5	1.9	2.76	2.64
9	516.8	31.4	0	69.4	1.7	2.85	2.77
10	505.4	28.3	0	126.2	3.2	2.85	2.70
11	512.6	20.2	0	121.3	2.3	2.89	2.91
12	0	135.1	73.9	82.3	-1.0	-0.89	-0.19
13	0	0	171.3	71.3	-4.5	-3.98	-4.03
14	0	0	169.5	180.0	-10.6	-3.57	-3.42
15	574.0	0	116.7	146.9	-5.5	-2.57	-2.00
16	572.4	0	87.1	40.6	-1.3	-5.07	-2.18

These data indicate that while the ion pair yield is independent of the intensity of ionization, it is a complicated function of the relative pressures of hydrogen, bromine and hydrogen bromide. This conclusion is in contradiction to the statement of Lind and Ogg³ that they had "some evidence. . . that the velocity of the reaction varies with the square root of the intensity of alpha radiation." It appears probable that their statement was based upon insufficient evidence. Furthermore, as these authors realized³ (p. 803) it would be difficult to reconcile a square root law, at ordinary temperatures, with the photochemical data.

Theoretical Considerations

The simple cluster theory does not offer an adequate explanation of these results, even when the possibility of back reaction and of ionic sensitization is taken into account. The hypothesis that atoms are formed by the alpha particles and that they undergo the several reactions which are known to occur in the photochemical and thermal reactions is likewise inadequate. Furthermore, it does not seem to be possible to explain the experimental results by any simple combination of cluster formation, dissociation and the known atomic reactions.

A consistent, though in some respects rather indefinite, view of all radiochemical reactions, including the experiments presented here, may be outlined as follows. The primary act consists of the ionization of a molecule by an alpha particle. Each ion tends to cluster or attract a number of molecules around it. If there are several different types of molecules present, they will not all have the same tendency to be clustered. Under the usual experimental conditions, the average cluster will attain dynamic equilibrium with the surrounding gas before it is neutralized.¹¹ Upon recombination of the positive and negative ions the energy of ionization is taken up by the molecules of the (combined) cluster as thermal energy. Immediately after recombination, the cluster may be thought of as a small isolated volume of gas which is momentarily at a high temperature. In general there is no obvious way of predicting the course of the reactions occurring in these small high temperature volumes. In cases where chain reactions occur (*e. g.*, hydrogen chloride and phosgene formation) this lack of knowledge is of relatively little importance, since the total effect of the reactions occurring in the clusters is small compared to the effect of the chains which are initiated by the clusters but then spread throughout the "cold" gas. In all non-chain reactions the total chemical change is the sum of the reactions in these small isolated volumes of gas at high temperatures. It may be expected that the temperature coefficient of such reactions will be small, and the rate will be directly proportional to the intensity of ionization. Reactions with high negative free energies (*e. g.*, the oxidation of hydrogen and carbon monoxide) will be practically unidirectional. However, in the case of non-chain reactions where the free energy is not too large and where the thermal reaction is known to be relatively rapid at moderate temperatures, it is not unreasonable to assume that the changes which occur correspond to the realization of equilibrium in isolated gas volumes at high temperatures.¹² It is to be expected that the hydrogen bromide and hydrogen iodide reactions will fall into this latter class. In the following discussion this hypothesis is applied to the hydrogen bromide reaction.

(11) This assumption is not necessary for the further development of the theory and is quite possibly incorrect. It is introduced here only for the sake of simplicity.

(12) The application of these ideas to radiochemical reactions in general, and their relation to other theories of radiochemistry, will be discussed in greater detail elsewhere.

Due to the different tendencies to be clustered which the various gases exhibit, the mole fractions of the reaction components will not be the same in the clusters as they are in the bulk of the gas. Immediately before recombination, the mole fractions in an average cluster (X_{H_2} , X_{Br_2} and X_{HBr}) will be

$$\begin{aligned} X_{H_2} &= \frac{P_{H_2}}{P_{H_2} + \alpha P_{Br_2} + \beta P_{HBr}} \\ X_{Br_2} &= \frac{\alpha P_{Br_2}}{P_{H_2} + \alpha P_{Br_2} + \beta P_{HBr}} \\ X_{HBr} &= \frac{\beta P_{HBr}}{P_{H_2} + \alpha P_{Br_2} + \beta P_{HBr}} \end{aligned} \quad (1)$$

where P_{H_2} , P_{Br_2} and P_{HBr} are the pressures of the reactants, and α and β are constants, which specify the enrichment of bromine and hydrogen bromide relative to hydrogen. If we let Δn be the change in the number of hydrogen bromide molecules in an average cluster (due to the attainment of equilibrium after recombination), and n_Σ be the total number of molecules of all kinds in an average cluster,¹³ then the mole fractions in the clusters immediately after the attainment of equilibrium (at some high temperature) are

$$\begin{aligned} X'_{H_2} &= \frac{n_{H_2} - \frac{\Delta n}{2}}{n_\Sigma} = X_{H_2} - \frac{\Delta n}{2n_\Sigma} \\ X'_{Br_2} &= \frac{n_{Br_2} - \frac{\Delta n}{2}}{n_\Sigma} = X_{Br_2} - \frac{\Delta n}{2n_\Sigma} \\ X'_{HBr} &= \frac{n_{HBr} + \Delta n}{n_\Sigma} = X_{HBr} + \frac{\Delta n}{n_\Sigma} \end{aligned} \quad (2)$$

where n_{H_2} , n_{Br_2} and n_{HBr} are the numbers of molecules of each species (indicated by the subscript) present in the average cluster immediately before recombination. Introducing the mass action equation

$$X'_{HBr}/X'_{H_2} \cdot X'_{Br_2} = K \quad (3)$$

we may write

$$\frac{\left(X_{HBr} + \frac{\Delta n}{n_\Sigma}\right)^2}{\left(X_{H_2} - \frac{\Delta n}{2n_\Sigma}\right)\left(X_{Br_2} - \frac{\Delta n}{2n_\Sigma}\right)} = K \quad (4)$$

where K is the equilibrium constant at some undetermined high temperature. Since Δn is the

(13) It should be pointed out that the term "cluster" is used in an unusual sense in the present discussion. It does not refer specifically to either the cluster around the positive ion or around the negative ion (or electron), but rather to the group of molecules surrounding both ions at the instant before they recombine. The description of the cluster (number of molecules, composition, and temperature) applies exactly only to that hypothetical isolated small volume of gas, the reactions in which are postulated to be equivalent to the reactions which occur upon the recombination of an average pair of ions. For instance, if the positive and negative clustered ions contain equal numbers of molecules, that number will be not n_Σ but $n_\Sigma/2$.

number of hydrogen bromide molecules formed per average ion pair, it is identical with the ion pair yield, $(M/N)_t$, at any time, t , and therefore we may rewrite equation (4) as follows

$$\begin{aligned} \left(\frac{M}{N}\right)_t &= \frac{n_\Sigma}{4-K} [K^2 X_{H_2}^2 + K^2 X_{Br_2}^2 + 4K X_{HBr}^2 + \\ &8K X_{HBr} (X_{H_2} + X_{Br_2}) - 2K(K-8)X_{H_2}X_{Br_2}]^{1/2} - \\ &\frac{n_\Sigma}{4-K} (4X_{HBr} + KX_{H_2} + KX_{Br_2}) \end{aligned} \quad (5)$$

The values of the constants of this equation (5) were adjusted by trial to bring the computed values of the ion pair yield at ten hours, $(M/N)_{10 \text{ hours}}$, into agreement with the experimental values. The process of trial was quite laborious and we feel no certainty that the values of the constants ($\alpha = 38$, $\beta = 15$, $K = 2.2$, and $n_\Sigma = 8$) are the best possible values. The experimental and computed values of $(M/N)_{10 \text{ hours}}$ are given in the last two columns of Table III. Although in a few cases, notably experiments 12 and 16, the discrepancy appears to be greater than the magnitude of the experimental error, it is evident that equation 5 does represent satisfactorily the ion pair yield (in the early part of the reaction) as a function of the initial pressures of the reactants and (indirectly) of the initial amount of ra-

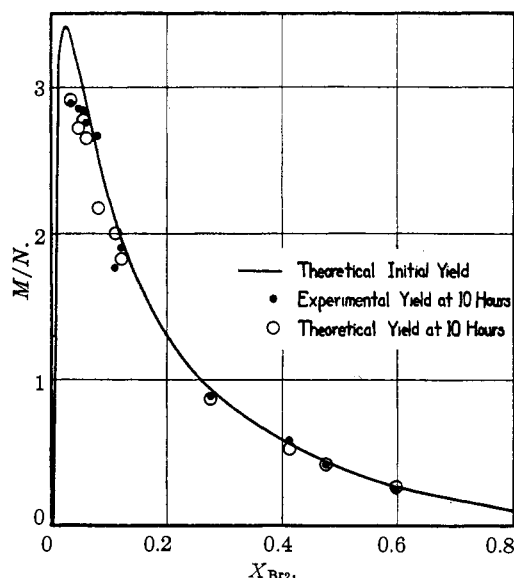


Fig. 1.—A comparison of the theoretical and experimental values for the ion pair yield in the synthesis of hydrogen bromide.

don. This is shown more clearly in Fig. 1 where the experimental and computed values of $(M/N)_{10 \text{ hours}}$ (for synthesis only) are plotted as a function of the mole fraction of bromine, in the

bulk of the gas; and in addition a plot of equation 5, for the special case when P_{HBr} equals zero, is represented by a smooth line. All of the ten-hour points should lie below this curve, which represents the initial ion pair yield. Neither the theoretical nor the experimental ten-hour points should be expected to lie on any smooth curve, since their values are (indirectly) functions of E^0 .

To avoid the necessity of graphical differentiation and to make it possible to apply the theory to other experiments, such as those of Gillerot,² where only the initial and final compositions were measured, it is convenient to convert equation 5 into an expression of, $P = P_{\text{H}_2} - P_{\text{H}_2}^0$, the change in pressure of hydrogen as an explicit function of time and the initial conditions ($P_{\text{H}_2}^0$, $P_{\text{Br}_2}^0$, P_{HBr}^0 and E^0). The rate of formation of ion pairs is given by the relation

$$dN/dt = c'F'E^0 e^{-\lambda t} \quad (6)$$

where λ is the radioactive decay constant, F' is the modified Mund factor,^{8,9} and c' is a coefficient which is in part a function of the pressure and composition of the gas.¹⁰ Combining equation 6 with the definition of $(M/N)_t$ and the assumption that the reactants follow the perfect gas laws, it follows that

$$\frac{dP}{dt} = \frac{RTc'F'E^0}{2Av} \left(\frac{M}{N}\right)_t e^{-\lambda t} \quad (7)$$

where R is the gas constant, T is the absolute temperature, v is the volume of the reaction system, and A is Avogadro's number. Eliminating $(M/N)_t$ between equations 5 and 7, rearranging, and combining some of the constants

$$\frac{(B - Cp)dp}{\sqrt{I - Jp - Op^2 - (Q + Sp)}} = We^{-\lambda t} dt \quad (8)$$

where the several coefficients are the following functions of the initial pressures $P_{\text{H}_2}^0$, $P_{\text{Br}_2}^0$ and P_{HBr}^0 .

$$B = P_{\text{H}_2}^0 + \alpha P_{\text{Br}_2}^0 + \beta P_{\text{HBr}}^0$$

$$C = 1 + \alpha - 2\beta$$

$$I = K[KP_{\text{H}_2}^0 + \alpha^2 KP_{\text{Br}_2}^0 + 4\beta^2 P_{\text{HBr}}^0 + 8\beta P_{\text{H}_2}^0 P_{\text{HBr}}^0 + 8\alpha\beta P_{\text{Br}_2}^0 P_{\text{HBr}}^0 - 2(K - 8)\alpha P_{\text{H}_2}^0 P_{\text{Br}_2}^0]$$

$$J = 2K[(8\beta + \alpha K - 8\alpha - K)P_{\text{H}_2}^0 + (8\alpha\beta + \alpha K - 8\alpha - \alpha^2 K)P_{\text{Br}_2}^0 + 4(2\beta^2 - \beta - \alpha\beta)P_{\text{HBr}}^0]$$

$$O = 16(\beta + \alpha\beta - \alpha - \beta^2)K - (1 - 2\alpha + \alpha^2)K^2$$

$$Q = KP_{\text{H}_2}^0 + \alpha KP_{\text{Br}_2}^0 + 4\beta P_{\text{HBr}}^0$$

$$S = 8\beta - \alpha K - K$$

$$W = \frac{RT_{\text{H}_2}c'F'E^0}{2Av(4 - K)}$$

The integration of equation 8 is facilitated by the introduction of the parameter¹⁴

$$z = \sqrt{\frac{p-b}{a-p}} \quad (9)$$

where a and b are defined by the equation

$$(p-b)(a-p) = \frac{I}{O} + \frac{J}{O}p - p^2$$

In terms of this parameter, equation 8 may be written as

$$\frac{W(Sa + Q)}{2(b-a)(Ca-B)} \int_0^t e^{-\lambda t} dt = \int_{P=0}^{P=P_t} \frac{z^2 + jz}{(1+z^2)^2(z^2 + lz + m)} dz \quad (10)$$

where

$$j = (Cb - B)/(Ca - B)$$

$$l = ((b-a)\sqrt{O})/(Sa + Q)$$

$$m = (Sb + Q)/(Sa + Q)$$

The left-hand member of equation 10 may be integrated directly and the right-hand member after expansion into partial fractions. The resulting integral between the limits 0 and t and between ϵ and z , where $\epsilon = \sqrt{-b/a}$ and corresponds to $p = 0$, may be written as

$$\begin{aligned} \frac{W(Sa + Q)}{2(b-a)(Ca-B)} (1 - e^{-\lambda t}) &= \frac{\lambda z - \kappa}{2(1 - z^2)} - \\ &\frac{\lambda \epsilon - \kappa}{2(1 + \epsilon^2)} + \left(\mu + \frac{l}{2}\right) (\tan^{-1} z - \tan^{-1} \epsilon) + \\ &\frac{\nu}{2} \ln \frac{1 + z^2}{1 + \epsilon^2} + \frac{\tau}{2} \ln \frac{z^2 + lz + m}{\epsilon^2 + l\epsilon + m} + \\ &\frac{2\rho - l\tau}{2\sqrt{l^2 - 4m}} \ln \frac{2z + l - \sqrt{l^2 - 4m}}{2z + l + \sqrt{l^2 - 4m}} \times \\ &\frac{2\epsilon + l + \sqrt{l^2 - 4m}}{2\epsilon + l - \sqrt{l^2 - 4m}} \quad (11) \end{aligned}$$

where the coefficients of the partial fractions (ι , κ , μ , ν , ρ , τ) are defined by the following simultaneous equations

$$\begin{aligned} \nu + \tau &= 0 \\ \mu + l\nu + \rho &= 0 \\ \kappa + l\mu + (1 + m)\nu + 2\tau &= 1 \\ \iota + l\kappa + (1 + m)\mu + l\nu + 2\rho &= 0 \\ l\iota + m\kappa + l\mu + m\nu + \tau &= j \\ m\iota + m\mu + \rho &= 0 \end{aligned}$$

Equation 11 was compared to the experimental data as follows. The several coefficients were evaluated for a given experiment in terms of the initial pressures of the reactants and the initial amount of radon. A value of p slightly greater than any attained in the experiment was assumed and the corresponding value of z computed by means of equation 9. This value of z was substituted and the corresponding value of $e^{-\lambda t}$, and finally t , computed. Several smaller values of p were then assumed and the corresponding values of t computed in the same way. In this way a curve of p vs. t was constructed corresponding to

(14) We wish to express our appreciation to Professor R. W. Brink of the Department of Mathematics for suggesting this method of integration.

the initial conditions (leading to either synthesis or decomposition) by means of equations 9 and 11.

Since these computations are time consuming and laborious they have been completed only for certain typical experiments; synthesis being represented by experiments 1, 2, 4, 6 and 11, and decomposition by experiments 12, 14, 15 and 16 of Table III. These comparisons are plotted on Fig. 2. The smooth curves are drawn through the computed points, while the experimental determinations are represented by circles. In judging the agreement between experimental and theoretical values it should be remembered that the constants (α , β , K and n_2) were adjusted to the ten-hour values of $(M/N)_t$ only. While the agreement is far from perfect and there are some obvious trends, equation 11 does represent the course of these reactions closely enough to offer strong support for the theory of ionic reactions suggested here.

In Table IV, the number of molecules of hydrogen bromide formed during the course of the experiments of Gillerot² (p. 511) are compared to the corresponding values based upon equation 11.

The agreement between the computed and measured quantities is much less satisfactory for these experiments than for the experiments presented in this paper. The disagreement seems to be chiefly between the two sets of experimental values. It is difficult to determine what is responsible for this difference. Entirely different methods and technique were used in the two series of experiments, and either of the methods may have involved unsuspected systematic errors. Furthermore, there is some uncertainty in the application of equation 11 to the data of Table

IV, since only the average value (160 cc.) of the volumes of the reaction vessels is available, and

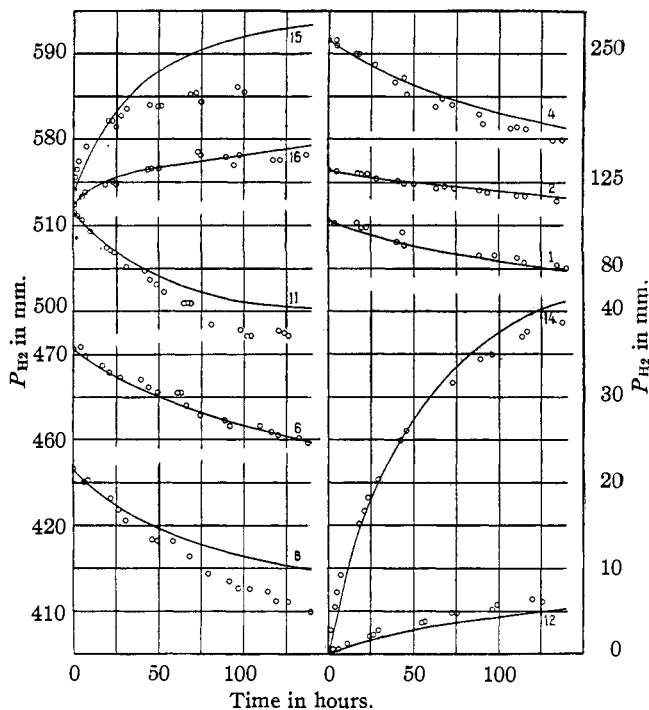


Fig. 2.—A comparison of the experimental and computed changes of pressure of hydrogen in the radiochemical synthesis and decomposition of hydrogen bromide.

since the reaction temperature is not definitely stated and has been assumed to be 25°.

Summary

1. The rate of the radiochemical synthesis and decomposition of hydrogen bromide has been determined for various mixtures of hydrogen, bromine and hydrogen bromide.

2. Since none of the existing theories of radiochemical reactions appear to be compatible with the data presented here, a modified cluster theory is proposed which is consistent with the measurements.

3. A relation between the ion pair yield and the initial pressures of the reactants has been developed on the basis of the proposed theory. An integrated equation relating the change in pressure to the duration of the experiment and its initial conditions has been derived. It has been shown that the experimental data are in satisfactory agreement with the equations.

4. The earlier experiments of Gillerot² are discussed in the light of the new theory.

TABLE IV

COMPARISON OF EXPERIMENTS OF GILLEROT WITH EQUATION 11

Expt.	E^0 millieuries	$P_{H_2}^0$ atm.	P_{HBr}^0 atm.	t , hours	$M \times 10^{-20}$ Found	$M \times 10^{-20}$ Calcd.
1	36.6	0.697	0.093	144	1.06	0.95
2	45.1	.661	.119	137	1.6	1.13
3	38.5	.492	.148	113	0.95	0.47
4	45.4	.163	.091	162	.41	.22
5	31.2	.134	.116	72	.127	.13
6	20.4	.071	.117	90	.043 ^a	.03
7	43.8	.052	.121	93	.11	.06
8	33.3	.677	.099	66	.654	.54

^a There is an obvious typographical error in the table of reference 2 which is corrected in the present table.