Summary

1.   Methods have been given for the convenient calculation of free energies and entropies from spectroscopic data for polyatomic molecules.

2.   Calculations have been made for methane, acetylene and ethylene.

3.   The problem of representing the results of spectroscopic calculations by simple equations has been considered.   It is shown that this can only be done satisfactorily by including in $\Delta F/T$ terms in $1/T^2$ and $1/T^3$.

The Reactions of Atomic Hydrogen with Several Alkyl Halides

BY H. MARSHALL CHADWELL AND TOSHIZO TITANI[1]

The chemical behavior at ordinary temperatures of atomic hydrogen has been the subject of numerous investigations[2] during the past decade. The present investigation deals with the reactions of atomic hydrogen, produced by the Wood discharge tube, upon simple alkyl halide vapors: methyl fluoride, chloride, bromide and iodide, and ethyl chloride and bromide.   The reactions with methane and ethane were also investigated. Boehm and Bonhoeffer[2] found that methyl chloride was attacked, but did not investigate the products.   Of particular interest in connection with our results are the experiments of Hartel and Polanyi[3] on the reaction of sodium vapor with the alkyl halides.

Our experiments have shown that the reactions concerned are complicated, that in the series methyl fluoride, chloride, bromide and iodide, the amount decomposed under the experimental conditions varies from 0 to 100%.   Both methyl and ethyl halides form methane, ethane and a small amount of ethylene.   The chlorides produce only hydrogen chloride, while the bromides and iodides yield both hydrogen halide and free halogen.

Experimental Manipulation

Purification of Materials

Methyl Fluoride.—The methyl fluoride was prepared by the method of Moissan[4]

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(2) For a review of the early literature see Bonhoeffer, *Ergebnisse Exakten Naturwissenschaften*, **6**, 201 (1927), and Taylor, THIS JOURNAL, **48**, 2840 (1926).   For reactions with hydrogen produced by the Wood discharge tube, Bonhoeffer and Boehm, *Z. physik. Chem.*, **119**, 385 (1926); Bonhoeffer and Harteck, *ibid.*, **139**, 64 (1928);   Wartenberg and Schultze, *ibid.*, **B2**, 1 (1929);   Urey and Lavin, THIS JOURNAL, **51**, 3286, 3290 (1929); Geib and Harteck, *Z. physik. Chem.*, Bodenstein Festband, 849 (1931); Dixon, THIS JOURNAL, **54**, 4262 (1932).   See also Smallwood, *ibid.*, **51**, 1985 (1929); Bichowsky and Copeland, *ibid.*, **50**, 1315 (1928); Harteck, *Z. physik. Chem.*, **139**, 98 (1928).

(3) Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1931).

(4) Moissan, *Jahresber. Chem.*, **41**, 931 (1888).

from methyl iodide and silver fluoride[5] in an evacuated all-glass apparatus, the methyl fluoride being condensed with liquid air and subsequently fractionally distilled.

Methyl Chloride, Bromide and Iodide. Ethyl Chloride and Bromide.—These alkyl halides were obtained from a reliable commercial source and purified (in vacuum) by passing the vapor over fresh calcium oxide, followed by very careful fractional distillation. Blank experiments proved the absence of free halogen or halogen acid.

Methane.—Methane, obtained in a cylinder from a commercial source, was condensed with liquid air, and twice fractionally distilled, the final middle fraction being used in the experiments.

Ethane.—Ethane was prepared by the action of a copper–zinc pair on ethyl iodide, the gas being washed with water, fuming sulfuric acid. concentrated potassium hydroxide, and finally condensed with liquid air. It was then fractionally distilled three times, any methane being removed by pumping.

Apparatus

The atomic hydrogen was produced in a discharge tube similar in design to that used by Geib and Harteck.[6] Figure 1 shows the assembly of the apparatus.
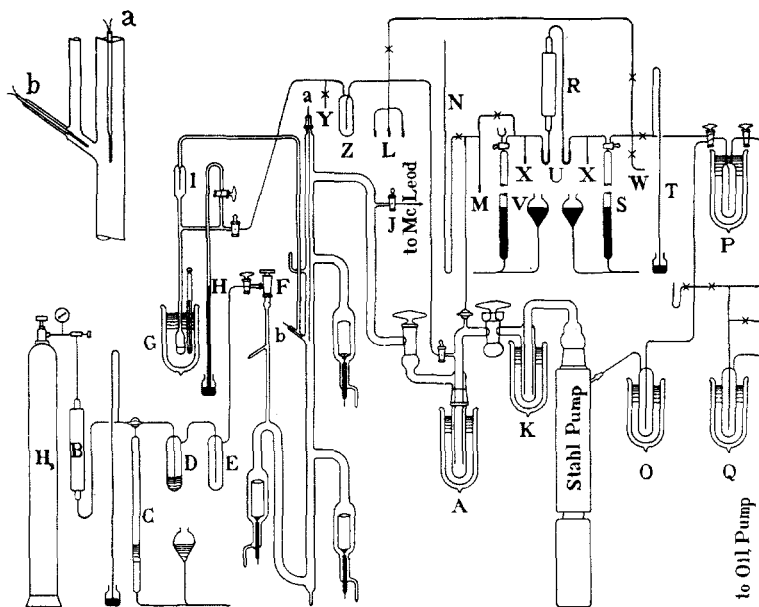

Fig. 1.—Diagram of apparatus.

The pumping system consisted of a large all-metallic three-stage mercury vapor Gaede pump electrically heated, with a rotary oil pump producing the forevacuum. A linear velocity of hydrogen of 7 meters per second was obtained when the hydrogen was admitted at the rate of 50 cc. (atmospheric conditions) per minute. The pressure of hydrogen in the apparatus was about 0.3 mm.

Electrolytic hydrogen from a cylinder, purified by heated platinized asbestos, was saturated with water vapor in the trap (D) or dried when desired by placing liquid air

(5) Gmelin–Kraut, "Handbuch der anorganischen Chemie," Band V, Abt. 2, 87 (1914).

(6) Geib and Harteck, *Z. physik. Chem., Bodenstein Festband*, 849 (1931).

about the second trap (E). The rate of flow measured by the buret (C) was controlled by a very fine metallic needle valve (F).

The alkyl halide, stored as a liquid in a bulb sealed to the apparatus at (G), was introduced in various amounts by surrounding (G) with baths of different temperatures, the resulting vapor pressures being read on the mànometer (H). The vapor then passed through the fine capillary (I). Blank experiments established the velocity of halide (moles per minute) for different vapor pressures.

In all of the experiments reported the alkyl halide entered the hydrogen from the discharge tube through the lower side tube (30 cm. above the discharge). That no diffusion of vapor into the discharge took place was predicted from a calculation of this back-diffusion, and proved experimentally by no spectroscopic change in the discharge. A transformer delivering approximately 3000 volts and producing a current of 300 m.a. was used to excite the discharge. Two copper–constantan thermocouples inclosed in small glass tubes were mounted within the reaction zone as shown in Fig. 1. This section of the vertical tube was surrounded by a mantle and cooled by a blast of air.

The products of the reactions passed through the large trap (A) immersed in liquid air. The second large trap (K), also cooled by liquid air, prevented the diffusion of mercury vapor from the pump. Materials caught in the first trap could be fractionally distilled, either into one of the small tubes (L) for subsequent weighing and analysis or into the tube (M) for vapor pressure measurements with the manometer (N), or could be removed directly for analysis.

Method of Analyzing the Hydrocarbons

Because of the relatively small partial pressures of methane, ethane and ethylene, and possibly acetylene, in the gas mixture, all of these gases passed through the traps (A) and (K). They were caught by activated coconut charcoal, cooled with liquid air, before the gas passed to the oil pump.

The gases leaving the mercury-vapor pump passed through a trap (O), cooled to $-80°$ and then through the tube of charcoal (P). The oil pump, protected by its liquid-air trap (Q), could be used independently of the charcoal by a suitable manipulation of the stopcocks, as is evident from Fig. 1. This use of charcoal proved very effective in holding the hydrocarbons and in decreasing the amount of hydrogen in the gas mixture. After an experiment the contents of the charcoal tube were pumped into the copper oxide tube (R) by means of the leveling bulb (filled with mercury) connected to the first buret (S). Here the remaining hydrogen was burned at $240°$ by circulating the gas over the copper oxide by means of the leveling bulbs and burets (V) and (S). The small traps (U), cooled with liquid air, were attached to both ends of the copper oxide tube to condense ethane, ethylene, acetylene, most of the methane and water.

The methane, contaminated with a small amount of inert gas which was probably oxygen from the decomposition of water in the discharge tube, was pumped out of the apparatus, by means of buret (S) and its leveling bulb, into a buret connected at (W). This gas was analyzed by combustion with oxygen and usually showed 95% methane.

The higher hydrocarbons, carbon dioxide and water, were distilled from the traps (U) into one of the small tubes (X), cooled with liquid air, sealed off and analyzed. The gas in the tube (X) was collected over mercury in a 25-cc. buret by breaking its capillary end in an evacuated rubber tube connected to the buret. During this operation the tube was cooled to $-20°$, so that the water remained as ice. The volume of gas remaining in the tube was later measured and a correction applied. The gas in the buret was analyzed for carbon dioxide by absorption with potassium hydroxide, for acetylene with alkaline mercuric cyanide,[7] for ethylene with half-saturated bromine water followed by potassium hydroxide, and for ethane by combustion with oxygen. The total quan-

(7) Treadwell, *Helv. Chim. Acta.* **2**, 60 (1919).

tity of hydrocarbon found agreed very well with that calculated from the extent of the reaction as determined by the amount of inorganic substances produced.

Method of Analysis for Halogen and Halogen Hydride

The extent of the reaction (percentage decomposed) could be determined by two methods: first, the relation of unreacted halide to the amount entering the apparatus, and, second, the amount of free halogen and halogen hydride formed. It was found that both methods gave the same reproducible results.

Fluoride.—No measurable reaction took place with methyl fluoride.

Chlorides.—No free halogen was found. Because of its relatively high vapor pressure, hydrogen chloride could not be caught quantitatively in Trap A, either by a frozen layer of water, of ammonia hydroxide, or potassium hydroxide solution, or by solid potassium hydroxide. Consequently the percentage of methyl and ethyl chlorides decomposed was obtained by distilling at −50° the unreacted halide from Trap A into a small tube (L, Fig. 1), sealing and weighing. Vapor pressure measurements showed the material to be pure halide.

Bromides.—Bromine and hydrogen bromide were products of the reaction of the alkyl bromides with atomic hydrogen, and were caught in Trap A. The unreacted alkyl halide was distilled from Trap A (ethyl bromide at −40°, methyl bromide at −60°, for four to five hours), into a small tube (L). This was weighed and analyzed for the trace of hydrogen bromide and bromine which it contained. The residue in Trap A was also analyzed for bromine by titrating with 0.01 N sodium thiosulfate and for total bromide with 0.01 N silver nitrate after heating with dilute ammonium hydroxide.[8] Knowing the velocity of the entering alkyl halide, the percentage which reacted could be calculated from the unreacted alkyl halide and from the inorganic products formed.

Iodide.—The reaction of ethyl iodide with atomic hydrogen was not studied because of the relative ease of thermal decomposition. With methyl iodide, both hydrogen iodide and free iodine were obtained. No unreacted methyl iodide could be found, showing complete reaction of the alkyl halide.

The content of Trap A was analyzed by repeatedly extracting with small amounts of chloroform, titrating the water layer with 0.01 N sodium hydroxide and the chloroform layer with 0.01 N sodium thiosulfate in the presence of potassium iodide and starch.[9]

The Concentration of Atomic Hydrogen

The concentration of atomic hydrogen, present in the reaction zone under conditions similar to those before the alkyl halide was admitted, was measured by the method of Wrede and of Harteck[10] with the modification of substituting for the fine capillary a sintered glass plug, similar to that used by Dr. W. G. Leighton.[11] The results are given in Table I.

TABLE I

CONCENTRATION OF ATOMIC HYDROGEN

Per cent. H at different currents (m. a.) and velocities of H_2 (cc./min.)

Velocity \ Current	100	100	200	200	300
50	44	48	52	55	56
60	50	58	64	68	70

(8) Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, New York, fourth ed., Vol. II, p. 324.

(9) Beckmann, Ann., **367**, 289 (1909).

(10) Harteck, Z. physik. Chem., **139**, 98 (1928); Wrede, Z. Instrumentenk., **48**, 201 (1928); Geib and Harteck, Z. physik. Chem., Bodenstein Festband, 849 (1931).

(11) Leighton, unpublished investigation. This method is being confirmed in this Laboratory by Dr. H. Cordes. We are indebted to Dr. Cordes for calibrating the Wrede gage and for suggestions concerning the mechanism of the reactions.

Experimental Results

Light and Heat Produced by the Reactions.—The production of a yellowish-green light by the reaction of atomic hydrogen with organic compounds has been reported by many investigators.[12] We have observed this same light in the reactions with the alkyl bromides, stronger in the case of the methyl compound than with the ethyl.

The reactions produced a considerable quantity of heat, the position of maximum heating being very dependent upon the velocity of the alkyl halide entering the stream of hydrogen. In all cases the highest temperatures were obtained in the experiments with the greatest amount of alkyl halide. These temperatures were: for methyl chloride $105°$ ($RX/H = 0.122$), ethyl chloride $125°$ ($RX/H = 0.135$), methyl bromide $135°$ ($RX/H = 0.058$), ethyl bromide $140°$ ($RX/H = 0.113$), methyl iodide $125°$ ($RX/H = 0.043$). It is highly improbable that these results represent accurately the maximum temperature existing in the reaction zone. From the measurements of temperature with the two thermocouples, it could be concluded that the length of the reaction zone in the tube was greater for methyl chloride than for methyl bromide, which in turn was greater than for methyl iodide. In the case of the methyl chloride not all of the atomic hydrogen was used up by the reactions.

Since methyl iodide was the most easily decomposed by heat of any of our materials, we made blank experiments with a heating jacket about the reaction zone, and using only molecular hydrogen. No halide decomposed at $295°$. We therefore concluded that it was improbable that thermal reactions taking place on the walls played a part in determining the products of the reactions.

Hydrocarbon Products.—The results of the examination of the hydrocarbon products of the reactions are given in Table II.

TABLE II

HYDROCARBON PRODUCTS

Velocity of hydrogen 50 cc./min. Current through discharge 300 m.a.

Expt.		Time, min.	Vel. RX mole, ×10⁶/ min.	RX/H	CH₄	Volume (cc.) of gas found				C₃Hₓ	CH₄ equiv., cc.		% RX found as		
						CO₂	C₂H₂	C₂H₄	C₂H₆		Found	Calcd.	CH₄	C₂Hₓ	CO₂
CH₃Cl	A	60	140	0.086	9.0	9.0				$\leqq$0.5	19	18	50	$\leqq$6	50
	B	140	74	.046	13.5	20.5				$\leqq$0.3	34	25	54	$\leqq$2	82
CH₃Br	A	80	87	.054	33.8	14.4	0.5	3.0	7.0	10.5	69	63	54	33	23
CH₃I	A	40	70	.043	32.6	6.8	0.3	1.2	6.6	8.1	56	67	49	24	10
	B	30	64	.040	21.8	9.5				6.9	45	46	47	30	21
	C	30	65	.040		4.8	0.2	0.7	6.5	7.4		47		32	10
	D	60	29	.018	25.1	14.2				5.8	51	42	60	28	34
	E	60	29	.018	25.8	4.2				5.0	40	42	61	24	10
C₂H₅Cl	A	60	148	.091	47.0	15.2	0.5	1.5	4.6	6.6	75	81	58	16	19
	B	60	148	.091	44.5	19.9	0.7	2.1	4.3	7.1	79	81	55	18	25
C₂H₅Br	A	80	113	.070	58.0	16.9	1.2	9.2	21.0	31.4	138	134	43	47	13
	B	40	114	.070		3.2	0.9	5.3	9.9	16.1		74		44	4

(12) See, for example, Bonhoeffer and Harteck, *Z. physik. Chem.*, **139**, 64 (1928).

The table is self-explanatory. All ratios of concentrations are molal. The theoretical yield (cc. CH_4 or its equivalent) was calculated from the percentage decomposition determined from the inorganic products (next section), with the exception of the bromides, where the bromine and hydrogen bromide formed were titrated directly. In experiments CH_3I C and C_2H_5Br B, the copper oxide was not used.

When the difficulties of the analyses are considered, for instance in experiment CH_3Cl B the products from 25 cc. of reacted alkyl halide had to be found in 7000 cc. of hydrogen, the results are satisfactory.

An examination of the table shows that both methyl and ethyl halides produced methane, ethane, and perhaps a trace of ethylene. The composition of the hydrocarbon product was not very dependent upon the relative concentration of atomic hydrogen. At the same relative concentration of alkyl halide to atomic hydrogen, the different methyl halides produced the same quantity of methane. Methyl chloride produced practically no ethane, while the bromide and iodide gave the same amount. With an increase of atomic hydrogen concentration, the concentration of methane increased. Ethyl bromide produced less methane and more ethane than did ethyl chloride.

If any hydrocarbons of greater molecular weight than ethane, or any quantity of acetylene, were produced, they would have been caught in Trap A. No evidence, either from distillation and subsequent vapor pressure measurements or from analysis, could be obtained for such products.

The continual formation of such a relatively large quantity of carbon dioxide was rather surprising. Blank experiments proved that only small quantities could have resulted from oxidation of hydrocarbon by the copper oxide or from oxidation in the tube of absorbent charcoal. We consequently concluded that at least the major portion of carbon dioxide arose from a reaction above the discharge tube between either O or OH, formed by the presence of water vapor and alkyl halide or hydrocarbon. These reactions must have produced carbon monoxide which was subsequently oxidized. This conclusion is supported by the fact that the amount of carbon dioxide found is very dependent upon the duration of the experiment, about 0.16 cc. being formed each minute for methyl compounds, and 0.26 cc./min. for ethyl compounds. Harteck and Kopsch[13] have shown that atomic oxygen produced in a discharge tube from oxygen gas reacts very slightly (0–2%) with methane, but to a greater extent (2–5%) with ethane and alkyl halides. In our experiments, the greater velocity of oxidation of ethane (than methane) would have resulted in a relatively larger change in the ethane concentration, because the ethane was present in smaller quantities. Consequently the methane concentration found

(13) Harteck and Kopsch, Z. physik. Chem., **B12**, 327 (1931).

more nearly represents that produced by the reaction of atomic hydrogen on the alkyl halide.

In order better to understand the mechanism of these reactions, experiments on the reaction of atomic hydrogen with methane and ethane were also performed. With methane no reaction could be obtained, confirming the observations of previous investigators. Two experiments with ethane were made. In the first (25 cc. of ethane was used), 5% of the ethane was found as methane, 1.4% as carbon dioxide and 1.6% as ethylene; in the second (150 cc. ethane), 3% of the ethane as methane, 3% as carbon dioxide and 1.7% as ethylene. No acetylene or higher hydrocarbons were obtained. The heat generated by the reaction (or catalysis of recombination of atomic hydrogen) was large.[14] We concluded that the greater portion of the methane produced from the alkyl halides under our conditions was not formed by intermediate ethane.

Inorganic Products and Extent of the Reaction of the Alkyl Halides with Atomic Hydrogen.—When methyl fluoride was introduced into the stream of atomic hydrogen, no heating effect could be observed and no etching of the glass by hydrogen fluoride formed by the reaction could be seen. Consequently we concluded that there was no reaction.

The results for the chlorides, bromides and iodide are given in Tables III, IV and V. The percentages of alkyl halide decomposed at different

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TABLE III

METHYL AND ETHYL CHLORIDE

Velocity of hydrogen 50 cc./min. Current through discharge 300 m. a.
</div>

No.	Time, min.	Put in	Moles RX × 10⁶ Unreacted	Reacted	RX/H	% RX Reacted
			Methyl Chloride			
1	40	2700	2440	260	0.042	9.6
2	20	3940	3625	315	.122	8.0
3	40	1044	954	90	.016	8.6
4	40	1444	1297	147	.022	10.2
5	60	1566	1414	152	.016	9.7
			Ethyl Chloride			
1	40	2230	1410	820	0.034	37
2	40	1188	724	464	.018	39
3	20	4392	3760	632	.135	14
4	20	1439	970	469	.044	33
5	60	1581	986	595	.016	38
6	40	1424	884	540	.022	38
7	40	1074	687	387	.016	36
8	40	1205	792	413	.019	34

(14) Wartenberg and Schultze, Ref. 2, concluded that ethane largely catalyzed the recombination of atomic hydrogen while Bonhoeffer and Harteck, Ref. 2, found that about 25% of the ethane reacted Under their experimental conditions 480 cc. of gas was condensed in the liquid-air trap, from 640 cc. of ethane introduced. They concluded that the loss (25%) was probably methane and ethylene. The difference between their results and ours may have been caused by a loss of ethane passing through their liquid-air trap or by a difference in relative concentrations.

Table IV

Methyl and Ethyl Bromides

Current through the discharge 300 m.a. for methyl bromide, 250 m.a. for ethyl bromide

No.	Time, min.	Vel. H_2, cc./min.	Moles RX × 10⁶ Put in	Unre- acted	Re- acted	G. equiv. × 10⁶ Br	HBr	HBr/ Br	RX/H	% RX reacted RX	Br + HBr
			Methyl Bromide								
1	40	60	916	295	621	24	619	26	0.009	68	70
2	40	60	3096	1811	1285	99	1139	12	.029	42	40
3	40	50	3744			65	1096	17	.058		31
4	40	50	1384	620	764	48	726	15	.021	55	56
5	40	50	921	295	626	29	571	19	.014	68	62
			Ethyl Bromide								
1	40	39	1320	690	630	39	648	17	0.039[b]	48	52
2	20	60	2202	1376	826	75	752	10	.043	37	38
3	40	51	1290			28	778	28	.020		63
4	30	50	5350	4400	950	62	936	15	.113	18	19
5	30	50	1635	872	763	45	690	15	.035	47	45
6[a]	40	50	920	250	670	24	616	26	.014	73	70

[a] Current through discharge 300 m.a. 　[b] Calculated from a value for the % atomic hydrogen obtained by extrapolating the data in Table I.

Table V

Methyl Iodide

Velocity of hydrogen 50 cc./min.　Current through discharge 300 m.a.

No.	Time	Moles RX × 10⁶ put in	G. equiv. × 10⁶ I	HI	HI/I	RX/H	% RX reacted
1	20	1386	300	1020	3.4	0.043	95
2	20	612	63	529	8.4	.019	97
3	10	462	110	360	3.3	.029	102
4	10	449	85	358	4.2	.028	99
5	10	372	40	334	8.4	.023	101
6	10	478	115	362	3.2	.030	100
7	10	332	28	311	11.0	.021	102
8	10	676	210	457	2.2	.042	99
9	20	364	21	351	16.7	.011	104
10	10	346	40	317	7.9	.021	103

values of the ratio RX/H are plotted in Fig. 2. It should be noted that the curve for ethyl bromide was determined not only by varying the amount of alkyl halide introduced, but also by varying the concentration of atomic hydrogen.

An examination of the data for the methyl halides shows that the percentage of halide reacted varied from 0 to 100 (from fluoride to iodide). The extent of the reaction of ethyl bromide was about the same as that of methyl bromide, but the behavior of ethyl chloride was quite different from that of the methyl compound. The methyl chloride was little affected by a change in the relative concentration of atomic hydrogen. The gradual sequence in the order of the methyl halides suggests a change in the heats of activation from a low value for the iodide to such a large value for the fluoride that no perceptible reaction took place.

Figure 3 shows the variation of the relative amounts of hydrogen halide

(HX) and free halogen (X) produced by different concentrations of atomic hydrogen. As the concentration of atomic hydrogen increased, the relative amount of hydrogen bromide and iodide increased. Ethyl bromide produced more hydrogen bromide than did methyl bromide, for a given ratio of RX/H. And, finally, the products of the reaction of methyl iodide were richest in free halogen.

From the experiments of Boehm and Bonhoeffer on the action of atomic hydrogen on bromine, we can conclude that the quantity of bromine changed to hydrogen bromide decreased with an increase in the value of Br_2/H. The shape of the curve, when HBr/Br_2 is plotted against Br_2/H, is the same as when HX/X is plotted against CH_3X/H. This dependence of HX/X upon CH_3X/H is believed to be the result of the action of atomic hydrogen upon the hydrogen halide and halogen formed during the decomposition of CH_3X and producing a condition of equilibrium. As a consequence, Fig. 3 cannot be used in deciding whether free halogen or hydrogen halide is the product of the primary reaction.
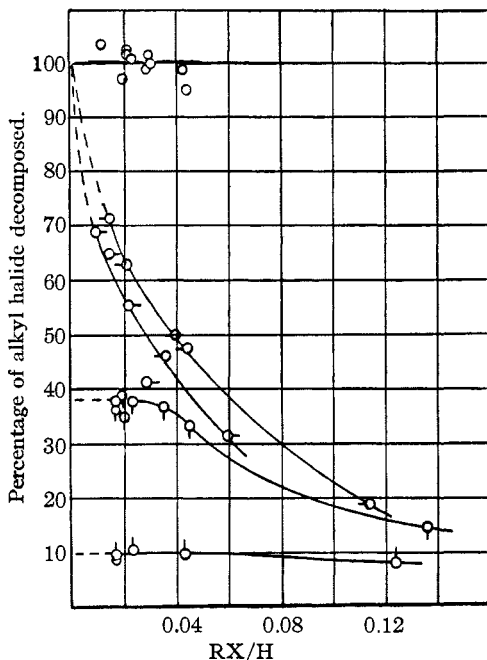

Fig. 2.—The percentage of alkyl halide decomposed by atomic hydrogen The molar percentages of alkyl halide are plotted as ordinates, the values of the ratio RX/H as abscissas. The data for methyl chloride are represented by ϕ, for ethyl chloride by φ, for methyl bromide by O-, and for ethyl bromide by -O. Methyl iodide was completely decomposed at all values of RX/H investigated. Methyl fluoride did not react.

Discussion of Results

Because of the relatively small probability of three-body collisions, and because of the experimental fact that our reactions took place in a very limited space, we believe that the primary reactions which occurred were due to two-body collisions.

There are three possible primary reactions to explain the results for methyl halides.

$$(I) \quad CH_3X + H = CH_3 + HX$$
$$(II) \quad CH_3X + H = CH_4 + X$$
$$(III) \quad CH_3X + H = CH_2X + H_2$$
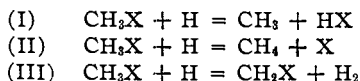
The heats of reaction[15] (kilogram calories per gram mole) for these three changes and for the different methyl halides are given in Table VI.
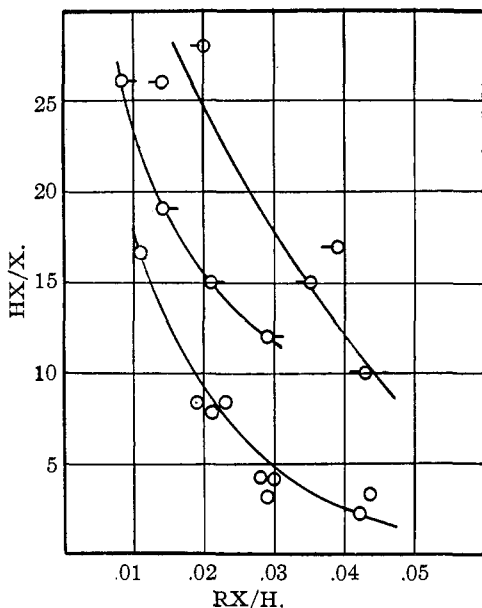

Fig. 3.—The relative concentrations of hydrogen halide to free halogen found in the reaction products. The values of the ratio of the gram equivalents of hydrogen halide (HX) to free halogen (X) are plotted as ordinates, while the values of RX/H are plotted as abscissas. The data for methyl iodide are represented by O, those for methyl bromide by O-, and those for ethyl bromide by -O. The alkyl chlorides produced only hydrogen chloride.

A reaction similar to I has been used by Hartel and Polanyi[3] to explain the reaction of sodium vapor upon the methyl halides. They have concluded from their experimental results as well as from theoretical considerations that the heats of activation (kg. cal.) increase from methyl iodide to methyl fluoride (CH₃I = 0, CH₃Br = 3.2, CH₃Cl = 8.8, CH₃F = 25). From the similarity of the reactions we can suppose that reaction I is the primary reaction and, furthermore, because of the comparable values of the H–X and Na–X bonds (H–Cl = 101 kg. cal., Na–Cl = 96, H–Br = 85, Na–Br = 89, H–I = 67, Na–I = 72), it is safe to conclude that the heats of activation for our reactions are of the same order of magnitude as those for the reactions with sodium vapor.

That reaction II is the only primary reaction is very improbable. First, this reaction cannot come into the consideration of the chlorine compound because we know from photochemical data[16] that methane reacts with chlorine atoms, formed from molecular chlorine by

(15) The heats of reaction were calculated from the following data: ¹/₂(H₂) + ¹/₂(X₂) = (HX) + a, X + X = (X₂) + b, heats of combustion of CH₃X = c.

X =	H	F	Cl	Br	I
a		64.2[a]	21.9[b]	12.3[c]	1.4[a,d]
b	101.9[a]	64.6[a]	56.9[a]	45.2[a]	35.4[a]
c	212.8[e]		164.8[e]	184.7[e]	201.3[e]

[a] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Second Supplement, 1931, pp. 1498, 1615. [b] Wartenberg and Hanisch, Z. physik. Chem., A161, 463 (1932). [c] Gmelin, "Handbuch der anorg. Chem.," 7, 191 (1931). [d] [I] = (I) − 7.5 kg. cal., Gmelin, ibid., 8, 81 (1931). [e] Landolt-Börnstein, Vol. II, 1923, or Second Supplement, 1931. The data for CH₃F were calculated from the above, together with CH₃F + H₂ = CH₄ + HF + 20.0; Grimm, "Handbuch der Physik," 24, 536 (1927). The values for the binding forces (kg. cal.) are C–H = 92, C–F = 118, C–Cl = 71, C–Br = 58, C–I = 44. See Hartel and Polanyi, Ref. 3.

(16) Coehn and Cordes. Z. physik. Chem., B9, 1 (1930).

TABLE VI

HEATS OF REACTION

Alkyl halide	Heat of reaction (cal.) for reaction number		
	I	II	III
CH_3F	30	−26	10
CH_3Cl	30	21	10
CH_3Br	28	34	10
CH_3I	27	48	10

the action of suitable light, to form methyl chloride and hydrogen chloride. Second, the formation of ethane is not possible since methane is not reacted upon by atomic hydrogen. Further, it is certain that methane cannot react with any of the possible intermediate products of our reactions with the exception of atomic chlorine.
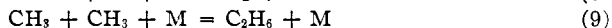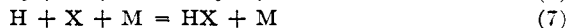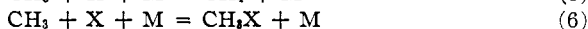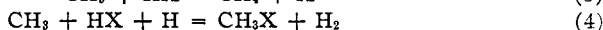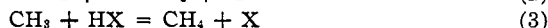
That reaction III is the primary reaction is also improbable. It is evident from our experimental results that the reaction of methyl fluoride involves a large heat of activation, and that as we proceed through the series to the iodide, the heat of activation must decrease. If III was the primary reaction, similar rather than very different heats of activation would be expected, because the primary process, according to this mechanism, is the same for all the methyl halides, namely, the removal of a hydrogen atom from the methyl group by a free hydrogen atom. From a study of band spectra[17] it has been concluded that the distances between the carbon and hydrogen atoms in the different methyl halides are practically the same. Consequently we can believe that the strength of the C–H bond is not very greatly affected by the change of halogen. Very different heats of activation for the different methyl halides are quite improbable.

The constant relationship between the amount of methane formed to the amount of methyl halide reacted, in the case of all of the methyl halides, makes it improbable that two of the three or all three reactions take place concurrently and to a similar extent for the different halides. The results of our experiments can all be explained by assuming that only reaction I is the primary process. That the other reactions take place to a very small degree cannot be excluded because of possible experimental error.

In the reaction of methyl chloride a maximum amount of 10% of the material reacted. This amount was not appreciably increased by an increase of atomic hydrogen concentration. It is possible that a portion of this decomposition of halide was due to oxidation by either O or OH formed in the discharge tube. This oxidation process could not change the character of the curve, because it was taking place to the same degree in all of the experiments.

To explain the experimental facts for all of the methyl halides, we must consider the following reactions

(17) Mecke, Leipziger Vorträge, "Molekulstruktur," 1931.

$$CH_3X + H = CH_3 + HX \qquad (1)$$
$$HX + H = H_2 + X \qquad (2)$$
$$CH_3 + HX = CH_4 + X \qquad (3)$$
$$CH_3 + HX + H = CH_3X + H_2 \qquad (4)$$
$$CH_3 + H + M = CH_4 + M \qquad (5)$$
$$CH_3 + X + M = CH_3X + M \qquad (6)$$
$$H + X + M = HX + M \qquad (7)$$
$$X + X + M = X_2 + M \qquad (8)$$
$$CH_3 + CH_3 + M = C_2H_6 + M \qquad (9)$$

M represents a third body or the wall. From the photochemical investigation[16] of the chlorination of methane we know that reaction 3 is very improbable in the case of methyl chloride. Free methyl (CH_3) formed by 1 can react according to 4 and 5, and to a lesser degree according to 6 and 9. The reactions 4 and 6 produce a reformation of methyl halide. The fact that a maximum value of 10% of methyl chloride reacted, not increasing with an increase of atomic hydrogen concentration, must be explained by such a mechanism leading to the reformation of the alkyl halide. The small value for this decomposition is quite understandable when the relatively high heat of activation is considered. From previous experiments by Boehm and Bonhoeffer we know that the hydrogen halides act as catalysts for the recombination of atomic hydrogen according to the mechanism of reaction 2 and 8 followed by the reaction $X_2 + H = HX + X$.

In the case of methyl bromide and iodide reaction 3 must be considered. It takes place with reaction 2 in the formation of free halogen. That we found free bromine and iodine, but no free chlorine, is also in accord with Boehm and Bonhoeffer's experiments with the hydrogen halides. The reformation of these methyl halides, taking place by reactions 4 and 6, both three-body collisions, must be slower than the formation of methane by the two-body collision-reaction 3. Furthermore, these reactions (4 and 6) must increase more rapidly than linearly with the CH_3 concentration. Consequently the percentage of methyl bromide found decomposed decreased when its concentration was increased.

The relatively high concentration of methane is to be expected from the above mechanism. Because ethane was obtained in a considerable amount, one can assume perhaps that the life period of the CH_3 radical is sufficiently great so that the number of successful three-body collisions, according to reaction 9, is comparable to the number of collisions which produce methane.

The constant quantity of methane produced by the bromide and iodide is understood since the two-body reaction 3 takes place more rapidly than reactions 4, 5, 6 and 9, all three-body reactions which remove CH_3. In order to explain the same amount of methane from methyl chloride, one must make the further assumption that reaction 5 is much faster than reaction 6. This is plausible because the concentration of atomic hydrogen must have been much greater than that of chlorine.

Any suggested reaction mechanism for the decomposition of ethyl bromide and iodide is very complex and uncertain. If we accept the following values for the energies of binding (kg. cal.) namely, $C-C^{18} = 71$, $C-H = 92$, $C-Cl = 71$, $C-Br = 58$, we should conclude that the $C-Br$ bond is more easily attacked than the $C-Cl$ bond and that the $C-H$ bond is probably not attacked at all. The attack of hydrogen atoms on the $C-C$ linkage would produce methane and should be about the same in the case of bromide as of chloride. Therefore the relative quantity of ethane to methane should be greater for ethyl bromide than for ethyl chloride, which is in accordance with the experimental facts.

We wish to thank Professor K. F. Bonhoeffer, Director of the Institute of Physical Chemistry of the University of Frankfort, for making available to us the facilities of the Institute, and for his kindly interest in this investigation.

Summary

The reactions of atomic hydrogen, produced by a Wood discharge tube, on methyl fluoride, chloride, bromide, iodide and ethyl chloride and bromide have been investigated. Incidental experiments were also made with methane and ethane.

The organic and inorganic products of the reactions have been determined quantitatively. This required the development of a method for analyzing hydrocarbons in a large excess of hydrogen.

The extent of the decomposition of the alkyl halides caused by different relative concentrations of atomic hydrogen has also been investigated, as well as the variation in composition of the various products.

The methyl halides varied in reactivity toward atomic hydrogen under the conditions of our experiments from no reaction in the case of the fluoride to 100% reaction in the case of the iodide. About the same amount of ethyl bromide was decomposed as methyl bromide, but the decomposition of ethyl chloride was three-fold as great as methyl chloride.

The reaction of atomic hydrogen on the methyl halides produced methane, ethane, and possibly a trace of ethylene. The ethyl halides formed the same products but in different concentration.

The halogen of the alkyl halide appeared only as hydrogen halide in the case of the chlorides, but as free halogen and hydrogen halide in the experiments with the bromides and chlorides. The ratio of hydrogen halide to free halogen increased with an increase in atomic hydrogen concentration.

A possible mechanism to explain these results has been proposed and the heats of reaction for each of the possible primary reactions have been calculated.

The experimental results show that the heat of activation for the reaction of atomic hydrogen with the methyl halides must decrease rapidly from the fluoride to the iodide.

(18) Grimm, *Handbuch Phys.*, **24**, 536 (1927).

All of the experimental results for the methyl halides can be explained by assuming that the primary reaction is $CH_3X + H = CH_3 + HX$.

The reactions with the ethyl halides were too complicated to warrant the proposal of a definite mechanism.

Gaseous Thermal Diffusion—The Principal Cause of Discrepancies among Equilibrium Measurements on the Systems Fe₃O₄–H₂–Fe–H₂O, Fe₃O₄–H₂–FeO–H₂O and FeO–H₂–Fe–H₂O

BY P. H. EMMETT AND J. F. SHULTZ

When Sainte-Claire Deville[1] in 1870 first determined the ratio of water vapor to hydrogen in equilibrium with Fe–FeO, he pioneered the investigation of a system that up to the present has yielded puzzling and widely varying results. Although the apparatus devised by him and illustrated in principle in Fig. 1B has been used by practically all of the later workers, the experimental equilibrium water vapor–hydrogen ratios for a given temperature cover a considerable range of values, some being as much as 40% higher than others. Recently,[2] using a dynamic rather than a static type apparatus, we obtained experimental results for the equilibrium constants K_1 and K_2 of the reactions

$$FeO + H_2 = Fe + H_2O \qquad K_1 = H_2O/H_2 \qquad (1)$$

and

$$Fe_3O_4 + H_2 = 3FeO + H_2O \qquad K_2 = H_2O/H \qquad (2)$$

that were consistent among themselves and agreed with the values calculated indirectly from the Fe–C–O system[3] and the equilibrium constant[4] for the reaction

$$CO_2 + H_2 = CO + H_2O \qquad K_3 = (H_2O)(CO)/(CO_2)(H_2) \qquad (3)$$
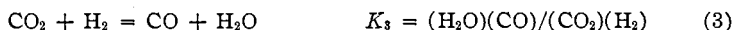
Although there seemed to be little doubt that the flow experiments were correct, no entirely satisfactory explanation could be given for the 40% discrepancy between them and some of the carefully performed static experiments. Inasmuch as the source of error causing this gross uncertainty might be affecting the equilibrium constants not only for the Fe–H–O system but also for other equally important heterogeneous systems, a careful study was undertaken of the static types of apparatus and procedure used in previous experimental studies of the Fe–H–O system.

(1) Sainte-Claire Deville, Compt. rend., 70, 1105, 1201 (1870); 71, 30 (1871).
(2) Emmett and Shultz, THIS JOURNAL, 52, 4268 (1930).
(3) E. D. Eastman, Bur. of Mines Circular 6125 (1929).
(4) Equation 38 from paper of Bryant, Ind. Eng. Chem., 23, 1019 (1931).