(a) the complexes are invariably very stable, being exceeded in stability by I_3^- only; (b) the solubility in water as compared with that in carbon tetrachloride is but a fraction of that of any pure halogen, with the possible exception of chlorine. (c) the hydrolysis constants are much larger throughout.

Summary

A method has been devised for determining the equilibrium constants of complexes of interhalogen compounds, the distribution ratios of interhalogen compounds between water and carbon tetrachloride, and the hydrolysis constants of interhalogens.

The equilibria for the complexes studied are: $(IBr)(Br^-)/(IBr_2^-) = 0.0027$; $(IBr)(Cl^-)/(IBrCl^-) = 0.023$; $(ICl)(Cl^-)/(ICl_2^-) = 0.0060$.

The distribution ratios of IBr and ICl between carbon tetrachloride and water are: $(IBr)_c/(IBr) = 3.9$; $(ICl)_c/(ICl) = 0.34$.

By the aid of previously collected data it has been possible to calculate a value for the dissociation of iodine chloride and iodine bromide in aqueous solution: $(I_2)(Br_2)/(IBr)^2 = 1.2 \times 10^{-5}$ and $(I_2)(Br_2)/(IBr)^2 = 1.6 \times 10^{-10}$.

Hydrolysis of interhalogen compounds is commented upon and preliminary values given for equilibria constants of the generally recognized equations.

Attention is drawn to the divergence of these results from the rule that the properties of interhalogen compounds are intermediate between those of the halogens from which they are formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Kinetics of the Thermal Reaction of Gaseous Alkyl Iodides with Hydrogen Iodide

BY RICHARD A. OGG, JR.[1]

There appears to have been very little study of the reactions of organic iodides with hydrogen iodide, although such a reaction is an important step in a process widely used in organic syntheses, namely, the reduction of alcohols to hydrocarbons through the agency of red phosphorus and hydriodic acid. Kekulé[2] observed that iodobenzene on heating in a sealed tube with hydriodic acid yielded benzene and iodine. Butlerow[3] heated methyl and ethyl iodides with hydriodic acid and obtained methane and ethane, respectively. Apparently no study has been made of the reactions in the gas phase. That the presumably reversible reaction of an alkyl or aryl iodide with hydrogen iodide proceeds practically to completion with the formation of iodine and hydrocarbon is indicated by the well-known fact that iodination of saturated hydrocarbons can be accomplished only in the presence of oxidizing agents (iodic and nitric acids, persulfates, etc.) which destroy the hydrogen iodide formed.

It appeared to the author that reactions of alkyl iodides with hydrogen iodide in the vapor phase offered an interesting problem for kinetic study, especially because of their apparent simplicity (bimolecular metatheses involving only univalent atoms and radicals) and the opportunity for observing the effects of increasing radical size on the reaction rate. The present investigation was therefore undertaken with the object of establishing the suitability of such reactions for kinetic study, and of then measuring the rates quantitatively.

Qualitative Study of Alkyl Iodides and Hydrogen Iodide.—The first experiments were made by heating in an air-bath sealed bulbs containing measured quantities of purified hydrogen iodide and alkyl iodide vapor, and judging the extent of the reaction by the depth of iodine color produced. At pressures of the reactants around 50–100 mm., the reactions of methyl, ethyl and *n*-propyl iodides with hydrogen iodide were observed to proceed with convenient rapidity in the temperature range 250–300°. Blank tests with the pure alkyl iodides showed them to be comparatively stable at these temperatures, even *n*-propyl iodide decomposing at a negligible rate. From the work of Bodenstein[4] it is known that the decomposition of hydrogen iodide is exceedingly slow at these temperatures. It therefore appeared that there would be no appreciable side reactions. No trace of tarring was observed.

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(1) National Research Fellow in Chemistry.

(2) Kekulé, *Ann.*, **137**, 163 (1866).

(3) Butlerow, *ibid.*, **144**, 36 (1867).

(4) Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898).

Evidence that the vapor phase reactions of the lower alkyl iodides with hydrogen iodide proceed almost exclusively by the process

$$RI + HI \longrightarrow RH + I_2$$

was obtained with the apparatus used for subsequent studies of the reaction rate. In all cases no appreciable pressure change occurred during the reaction. This eliminates such steps as

$$RI \longrightarrow R{-}H + HI$$

In the case of ethyl and *n*-propyl iodides the reaction products were condensed completely by liquid air, showing that no hydrogen was produced. Since methane is not condensable in liquid air, this test could not be applied to methyl iodide, but it seems safe to infer that the same is true of the reaction of this compound.

The reaction of ethyl iodide with excess of hydrogen iodide was allowed to go to completion and the products were frozen out with liquid air. The liquid air was then replaced by ice. The ethane and hydrogen iodide were volatilized, but the iodine, having a vapor pressure of only 0.03 mm. at 0°, remained practically all condensed. The gas pressure was then measured. In several experiments at various temperatures and with differing concentrations of reactants it was found that the decrease in pressure due to condensation of the iodine corresponded exactly to the initial pressure of ethyl iodide. This fact eliminates such reactions as

$$2C_2H_5I \longrightarrow C_4H_{10} + I_2$$

and also indicates that the reaction with hydrogen iodide goes practically to completion. It was assumed that these results were likewise valid for the other alkyl iodides.

Proof that the vapor phase reaction of ethyl iodide with hydrogen iodide is essentially homogeneous in Pyrex glass was obtained by altering the surface–volume ratio of the reaction vessel. This could not be done conveniently with the apparatus used for the rate measurements, so recourse was had to a different method. Two 100-cc. Pyrex bulbs, one empty, the other filled with bits of tubing, were attached through a three-way stopcock to a system consisting of a high vacuum line, reservoirs of hydrogen iodide and ethyl iodide, and a mercury manometer. After evacuation and baking out the two vessels were filled simultaneously with measured amounts of reactants. The stopcock was then closed and each bulb was sealed off after freezing out the reactants with liquid air. The vessels were heated simultaneously in an oil thermostat at 230–240°. They were then opened and the contents were analyzed for iodine and hydriodic acid by titration with thiosulfate, sodium iodate being added after the iodine end-point was reached. Several such experiments were made, with pressures of reactants around 50 mm., and amounts of reaction from 10 to 60%. In all cases the iodine–hydrogen iodide ratio was practically identical for the packed and empty vessels, indicating the rates to be the same in the two. Since the surface–volume ratios differed eight-fold, this is a satisfactory proof of homogeneity. As all subsequent rate measurements were at higher temperatures and mostly at greater pressures, it appears reasonable to assume that the reaction was homogeneous under these conditions also. It was likewise assumed that the reactions of the other alkyl iodides with hydrogen iodide were homogeneous.

Experimental Details of Reaction Rate Measurements. Preparation of Materials.—Pure anhydrous hydrogen iodide was prepared by passing hydrogen over molten iodine at around 150°, and then over platinized asbestos at 350°. The issuing gases passed successively through traps cooled with ice and salt (to remove water and iodine), solid carbon dioxide and acetone, and liquid air. The condensed hydrogen iodide was purified by low temperature sublimation. It was stored in a trap cooled with solid carbon dioxide and acetone, provided with a stopcock lubricated with pure vaseline.

Methyl, ethyl and *n*-propyl iodides were prepared in the usual fashion from the alcohols and phosphorus tri-iodide, and were carefully dried and fractionated before use. They were stored in a trap connected to the line through a stopcock, and were freed of dissolved gases by repeated freezing out and evacuation. All three remained colorless during the course of the experiments.

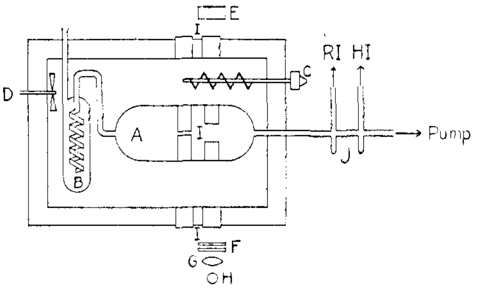

Fig. 1.—The apparatus. A, reaction flask; B, quartz spiral manometer; C, de Khotinsky bimetallic thermoregulator; D, fan; E, photronic cell; F, color filters; G, collimating lens; H, automobile lamp; I, windows; J, traps for freezing out.

Apparatus and Procedure.—Since the reaction involves no pressure change, the rate was followed by colorimetric determination of the iodine concentration. Approximately monochromatic light from a source of constant intensity passed through the reaction vessel, and the intensity of the transmitted beam was measured. By taking the ratio of intensity of the light transmitted by the cell containing iodine vapor to that transmitted by the empty cell the corrections for reflection and absorption losses at the windows were eliminated, and the fraction of light absorbed by the iodine could be measured. Hence by suitable calibration the absorption of light in the reaction vessel could be used to measure the iodine concentration. The essential details of the apparatus are shown in Fig. 1. The light source was a fifty candlepower automobile lamp operated on direct current. Before use the lamp was allowed to burn for several minutes to attain equilibrium. By aid of a rheostat the current was maintained at a fixed value, measured with an accurate ammeter. Since deterioration was very slow, constant intensity during an experiment was assured. Parallel monochromatic light was obtained by means of a collimating lens and color filters. The filters, of Corning glass Nos. 503 and 401, were chosen to transmit a narrow band of maximum intensity at 5000 Å., the maximum in the iodine absorption spectrum.[5] The cylindrical reaction vessel, of Pyrex glass, was provided with two sets of plane parallel windows fused to the ends of tubes projecting into the interior. The optical paths were 20 mm. and 2 mm., for low and high iodine concentrations, respectively. The thermostat was furnished with two corresponding sets of windows. Intensity of the transmitted beam was measured with a Weston Photronic Cell connected to a Leeds–Northrup high sensitivity galvanometer, critically damped. The cell was equipped with a shutter operated by remote control, and a semi-ballistic method of reading the galvanometer was employed to eliminate drift of zero. The response of the system was practically linear. The optical parts were of course shielded from outside light. The light source and photronic cell were mounted on an optical bench which could be so moved as to bring either of the sets of windows in the cell into line.

The remaining apparatus needs little description. The electrically heated air thermostat was provided with an efficient stirrer and a de Khotinsky bimetallic thermoregulator. Temperatures were read with a calibrated thermometer graduated in 0.1°. Regulation was usually good to ±0.1°. Pressure of gas in the cell was measured to 0.1 mm. with a mercury manometer, connected through a quartz spiral manometer as a zero instrument. Connection of the reaction vessel to the stopcocks attached to the vacuum line and alkyl iodide and hydrogen iodide reservoirs was made through long capillary tubing wrapped with heating wire and asbestos. Diffusion through the capillaries was very slow and hence condensation of iodine in the cool portions adjacent to the stopcocks was prevented. This arrangement prevented working at higher partial pressures of alkyl iodide than the vapor pressure of the liquid at room temperature. The two-way stopcock leading to the vacuum line allowed evacuation either directly or through a tube filled with sodium hydroxide pellets. The tube leading to the reaction vessel was provided with two small side arms for freezing out of reactants. When not in use these were covered with tiny auxiliary heaters. The system was evacuated through a cold trap with a two-stage diffusion pump.

Since it appeared from the work of Vogt and Koenigsberger[5] that the absorption coefficient of iodine depends somewhat on the concentration of foreign gases, it was considered desirable to calibrate the optical system under conditions closely approximating those obtaining during subsequent measurements. Hence the calibration was made with the products resulting from the reaction of ethyl iodide and hydrogen iodide, and it was assumed that the results were valid for use with the other alkyl iodides. The reaction cell, at some fixed temperature, was evacuated and the desired quantities of reactants were introduced. When the reaction had gone to completion, the lamp was adjusted to the proper current and the galvanometer deflection was determined. A small amount of the products was then frozen out with liquid air. The liquid air was replaced by ice, causing the volatilization of all constituents except the iodine. The gas pressure and galvanometer deflection were then measured. The process was repeated and continued until all of the iodine had been removed from the vapor phase. The galvanometer deflection corresponding to light through the empty cell was then measured. From the pressure measurements the partial pressures of iodine vapor at the various readings were obtained. These pressures were plotted against the logarithms of the ratios of the corresponding galvanometer deflections to the deflection obtained with the empty cell. Such calibrations were made for both the long and short optical paths at various temperatures and with various concentrations of reactants. There appeared to be no effect of temperature other than the usual gas law correction of pressure, and no appreciable variation with concentration of foreign gases. The calibration plots were slightly curved, indicating some deviation from Beer's law, which is not surprising, since only approximately monochromatic light was employed.

The procedure of a typical measurement of reaction rate is as follows. The cell was thoroughly evacuated and the thermostat was brought to the desired temperature. The lamp was warmed up and adjusted to the proper current, and the galvanometer deflection was determined. The desired amount of alkyl iodide vapor was then admitted and its pressure was accurately measured. It was then condensed with solid carbon dioxide and acetone, and the proper quantity of hydrogen iodide was introduced. The alkyl iodide was quickly vaporized and the stop watch was started. From the total gas pressure that of hydrogen iodide was obtained by difference. At measured time intervals the galvanometer deflection was read. The shortest feasible period between readings was thirty seconds. When it was judged that the reaction had been followed sufficiently far the products were pumped out through the tube filled with sodium hydroxide to absorb iodine and hydrogen iodide. The cell was then directly evacuated. The two-way stopcock to the vacuum line occasionally became plugged with iodine, necessitating cleaning and regreasing. For this purpose the cell was filled with dried nitrogen to avoid possible catalytic effect of oxygen and moisture on the walls.

In runs in which iodine was added initially to the reaction mixture a somewhat different procedure was followed. Reaction between the proper quantities of alkyl iodide and hydrogen iodide was allowed to go to completion and the products were frozen out in one of the small side-arms with liquid air. This was replaced by ice and the volatile constituents were pumped off, leaving the iodine. The alkyl iodide vapor was admitted to a measured pressure and then condensed in the other side-arm. Hydrogen iodide was introduced. The alkyl iodide was vaporized and the pressure was quickly read. The iodine was then volatilized, and the pressure again determined. The partial pressures of iodine and hydrogen iodide were thus obtained by difference.

With the longer optical path iodine pressures up to 10 mm. could be measured with sufficient accuracy. The shorter path sufficed for pressures up to some 80 mm. The accuracy of this optical method is at best inferior to that of direct pressure measurement, since the calibration was based on the latter, and there are various sources of possible error. In addition there were occasional fluctuations of light intensity during the course of a measurement. Runs in which this occurred too frequently were discarded.

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(5) Vogt and Koenigsberger, *Z. Physik*, **13**, 292 (1923).

The random fluctuations in individual measurements made it advisable to take these frequently and to use averaging methods in calculating velocity constants (*vide infra*). Despite these drawbacks, the accuracy was sufficient for the purposes of this investigation, and it appears doubtful that any other method would be as satisfactory.

Experimental Results

Study was made of the rate of reaction of gaseous methyl, ethyl and *n*-propyl iodides with hydrogen iodide at various concentrations and temperatures. The reactions of all three iodides appeared to be very similar. During a given run it was found that the rates agreed well with the simple bimolecular expression

$$\frac{d(I_2)}{dt} = K(RI)(HI)$$

The differential form could be used, but it was usually more convenient and accurate to calculate the velocity constants by the integrated form

$$K = \frac{1}{(t_2 - t_1)(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

where a and b are the concentrations of reactants at time t_1 and x is the amount reacting during the interval $(t_2 - t_1)$. At the very start the reaction was usually abnormally slow. This effect was most marked in runs in which the hydrogen iodide was in large excess, and was doubtless caused by delay in mixing of the reactants through diffusion. For this reason the initial time t_1 was usually chosen when the reaction had proceeded some 10% toward completion. This was ordinarily sufficient time to ensure complete mixing. In Table I are given data for typical runs with the three alkyl iodides. In each case the first time given is the initial point for all of the time intervals used in calculating rate constants. It will be observed that there is no drift in the constants over a very considerable percentage of reaction, and that the fluctuations are not serious—of the order of a few per cent. Reactions were nearly always followed until at least one-half of the reactant present in smaller concentration was consumed.

TABLE I

DATA FOR RUNS

Methyl iodide: Run No. 40a; temp. 280.0°; init. press. CH_3I, 263.6 mm.; HI, 120.4 mm.

t, sec.	Press. I_2, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$
480	8.2	
840	16.4	3.07
1320	26.5	2.99
1800	35.0	3.00
2400	44.0	2.94
3360	56.6	2.98
4800	67.6	2.74
5640	78.6	3.12
		Av. 2.98

Ethyl iodide: Run No. 6b; temp., 260.0°; init. press. C_2H_5I, 84.6 mm.; HI, 57.2 mm.

t, sec.	Press. I_2, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$
600	3.3	
1800	12.1	6.38
3000	18.9	6.60
4200	23.5	6.20
6000	29.2	6.09
8400	35.5	6.34
		Av. 6.32

n-Propyl iodide: Run No. 9c; temp., 290.0°; init. press. C_3H_7I. 42.2 mm.; HI, 172.6 mm.

t, sec.	Press. I_2, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$
420	11.4	
600	16.7	23.1
840	21.2	20.6
1200	28.0	23.0
1680	32.6	22.0
		Av. 22.1

Despite the good bimolecular constants obtained during a given run, it was observed that they varied widely in different experiments. When sufficient data were examined it was found that this variation was systematic and reproducible. At high total pressures, the velocity constant was independent of alkyl iodide concentration but was an inverse function of that of hydrogen iodide. This behavior is best represented by the kinetic expression

$$\frac{d(I_2)}{dt} = K_1(RI)(HI) + K_2 \frac{(RI)(HI)}{(HI) + (I_2)} \qquad (I)$$

During the course of a given run the sum of hydrogen iodide and iodine concentrations is constant and equal to $(HI)_0$, the initial hydrogen iodide concentration. Hence the above expression reduces to the simple bimolecular form, but the velocity constant K is now equal to $(K_1 + (K_2/(HI)_0))$, which is independent of concentration of alkyl iodide and an inverse function of that of hydrogen iodide. This formulation was found to agree with the experimentally observed variation of the velocity constant. If the constant K be plotted against the reciprocal of hydrogen iodide concentration, there should result a straight line of intercept K_1 and slope K_2. At each temperature several experiments with widely differing hydrogen iodide pressures were made and the velocity constants were found in all cases to be fitted satisfactorily by such a straight line.

Still further proof of the validity of Equation I was obtained from the experiments with ethyl iodide and hydrogen iodide in which iodine was added initially. The results show conclusively that iodine does give the expected retardation of the reaction. The data appear in Table II. The velocity constants were calculated by the simple bimolecular expression, and were found to be satisfactorily constant during the course of each run. The quantities K_1 and K_2 used in computing the theoretical values of K were obtained from experiments at the same temperature, but with no added iodine (see Table IV). In column 6 are given the values of $(K_1 + K_2/[(HI)_0 + (I_2)_0])$, which should be the rate constants according to Equation I. In column 7 are given $(K_1 + (K_2/(HI)_0))$, which would be equal to K if iodine exerted no retarding influence. The close agreement of the observed values of K with the figures of column 6 is strong evidence for the validity of Equation I.

TABLE II

REACTION OF ETHYL IODIDE WITH HYDROGEN IODIDE IN PRESENCE OF IODINE

Temperature, 270.0°

Run	$P_{C_2H_5I}$, mm.	P_{HI}, mm.	P_{I_2}, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Obs.	Calcd.	Calcd.
37b	81.1	46.0	16.0	12.5	12.3	14.4
40b	80.8	43.2	16.1	13.0	12.5	14.8
38b	74.9	29.8	10.5	15.3	15.5	18.9
36b	80.4	28.0	12.9	15.9	15.4	19.7
39b	88.1	18.9	14.1	18.1	17.6	26.4

When experiments were made at very low partial pressures of alkyl iodide and hydrogen iodide it was found that good bimolecular constants were obtained for each run, but that they were smaller than the values calculated from K_1 and K_2 obtained from experiments at higher pressures. It will be observed that in Equation I, K_1 has the dimensions of a second order rate constant, K_2 those of a first order constant. In the discussion of the reaction mechanism (*vide infra*) K_1 is interpreted as the velocity constant for a simple bimolecular reaction of alkyl iodide and hydrogen iodide and hence should be independent of pressure. K_2 is interpreted as the constant for a unimolecular decomposition of the alkyl iodide, and might be expected to fall off at low pressures in the same fashion as do the constants for unimolecular reactions of other simple molecules. Hence it seems justified to assume that the decrease in K at low pressures is due to decrease of K_2, and to calculate the value of the latter as $(K-K_1)(HI)_0$, using the value of K_1 from the high pressure experiments. Even if K_1 were not strictly constant this would introduce no serious error, since at the lowest pressures employed K_1 was usually only a few per cent. of K. This pressure dependence made it advisable to work at as high pressures as possible to get the true values of K_1 and K_2. Fortunately, methyl iodide, which shows the greatest falling off of K_2, also has the highest vapor pressure, and so no difficulty was experienced in attaining the high pressure rate.

The results of experiments on the reaction of methyl, ethyl and *n*-propyl iodides with hydrogen iodide are given in Tables III, IV and V. At

TABLE III

REACTION OF METHYL IODIDE WITH HYDROGEN IODIDE

Run	T, °C.	P_{CH_3I}, mm.	P_{HI}, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Obs.	Calcd.	$K_1 \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$	$K_2 \times 10^5$ sec.$^{-1}$
27a	320.0	195.0	235.1	21.6	22.2	11.40	70.0
28a		241.1	164.1	28.4	27.0		
29a		292.7	103.8	36.8	36.2		
26a		312.8	49.6	61.8	63.4		
35a		66.1	109.3	32.8			63.8
34a		85.2	47.0	52.0			51.6
32a		15.2	30.8	80.5			57.5
33a		32.4	15.8	96.5			36.3
31a		5.9	10.0	142.0			37.3
30a		10.4	5.9	161.0			23.8
24a	310.0	194.5	216.4	13.0	13.2	7.18	35.8
23a		249.7	148.6	16.4	16.0		
25a		256.7	120.7	18.2	18.0		
22a		298.7	55.5	29.2	30.7		
11a	300.0	300.0	265.0	7.18	7.11	4.43	20.0
10a		202.4	219.4	7.90	7.71		
8a		302.9	72.4	14.1	14.3		
12a		363.7	54.1	17.5	17.7		
7a		101.8	219.7	7.65			19.8
6a		48.7	116.2	8.37			12.8
5a		52.6	62.6	10.16			10.00
9a		199.3	85.9	11.35			16.6
14a		21.8	68.8	11.35			13.3
2a		124.0	51.0	11.95			10.54
1a		136.3	50.2	13.15			12.2
18a		11.1	41.4	14.9			12.1
3a		227.5	56.4	14.9			16.5
21a		36.6	13.4	33.2			10.35
20a		3.0	5.1	53.8			7.01
16a		11.6	5.5	65.8			9.42
19a		4.6	2.4	71.7			4.50
17a		11.0	3.3	95.6			8.38
37a	290.0	187.5	206.8	4.17	4.28	2.52	10.32
38a		238.9	151.8	4.99	4.93		
39a		278.0	103.6	6.46	6.05		
36a		326.9	48.5	10.28	10.00		
42a	280.0	185.7	239.0	2.25	2.25	1.50	5.17
43a		218.2	208.5	2.31	2.37		
40a		263.6	120.4	2.98	3.00		
41a		317.3	56.6	4.73	4.68		
45a	270.0	167.3	254.9	1.08	1.15	0.80	2.66
47a		243.0	202.8	1.19	1.30		
46a		261.1	111.9	1.59	1.60		
44a		311.7	57.5	2.44	2.43		

TABLE IV

REACTION OF ETHYL IODIDE WITH HYDROGEN IODIDE

Run	T, °C.	$P_{C_2H_5I}$, mm.	P_{HI}, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Obs.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Calcd.	$K_1 \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$	$K_2 \times 10^5$ sec.$^{-1}$
31b	300.0	53.1	158.2	46.0	47.0	26.3	91.7
27b		43.6	151.5	47.8	48.0		
32b		33.8	127.6	53.8	52.8		
26b		89.4	92.9	65.8	61.7		
30b		102.7	59.3	77.7	81.6		
28b		82.8	52.3	92.6	89.0		
29b		101.5	31.9	119.6	130.0		
58b		15.9	38.0	112.4			91.2
59b		36.7	16.2	197.0			77.3
56b		4.3	11.8	227.0			66.0
53b		4.0	9.0	269.0			60.8
57b		4.7	6.9	323.0			57.0
52b		7.7	5.3	335.0			56.5
51b		4.5	6.1	359.0			45.3
24b	290.0	27.0	153.5	26.4	27.1	16.5	46.6
17b		48.1	152.9	27.6	27.2		
23b		92.9	146.0	28.2	27.7		
19b		70.4	109.0	32.3	31.4		
18b		109.1	47.5	52.9	51.1		
22b		24.3	27.7	76.4	75.8		
21b		41.3	19.9	100.0	98.1		
65b		4.7	4.3	246.0			28.0
66b		6.8	4.1	252.0			27.5
14b	280.0	78.9	177.7	15.0	14.9	10.20	23.4
15b		48.7	148.5	15.6	15.8		
13b		76.6	68.3	21.9	22.2		
12b		79.5	46.9	28.3	27.6		
16b		115.1	41.1	31.2	30.0		
63b		14.1	38.9	31.2			23.4
64b		21.8	27.6	39.2			23.0
62b		31.9	19.0	48.5			20.9
60b		3.7	5.3	75.0			9.90
61b		4.8	3.7	98.0			9.37
43b	270.0	75.6	170.4	8.15	8.20	5.95	11.32
9b		80.3	100.6	9.34	9.80		
11b		78.8	64.4	11.6	11.9		
41b		78.0	60.1	12.4	12.3		
10b		82.9	57.2	12.2	12.7		
42b		76.5	31.2	17.5	18.3		
8b	260.0	35.9	166.3	4.29	4.43	3.70	5.50
5b		45.9	118.7	5.00	4.88		
4b		90.5	87.8	5.29	5.43		
6b		84.6	57.2	6.32	6.55		
7b		84.2	48.1	6.95	7.15		
44b	250.0	92.1	178.9	2.64	2.64	2.18	2.50
46b		82.9	135.1	2.77	2.79		
45b		101.0	55.8	3.66	3.65		

TABLE V

REACTION OF *n*-PROPYL IODIDE WITH HYDROGEN IODIDE

Run	T, °C.	$P_{C_3H_7I}$, mm.	P_{HI}, mm.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Obs.	$K \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$ Calcd.	$K_1 \times 10^{-2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$	$K_2 \times 10^5$ sec.$^{-1}$
24c	300.0	44.5	168.4	40.7	41.2	11.36	140.0
15c		44.6	131.4	50.3	49.6		
16c		42.3	89.5	68.8	68.0		
17c		42.0	66.0	83.8	87.5		
9c	290.0	42.2	172.6	22.1	22.4	7.64	75.0
10c		44.4	110.8	31.7	31.5		
11c		43.5	77.7	40.5	41.6		
12c		46.2	46.0	61.7	65.1		
5c	280.0	47.7	169.1	12.2	12.1	4.66	36.7
6c		46.1	115.1	16.2	15.6		
7c		46.5	71.0	21.9	22.5		
8c		43.4	31.3	43.9	45.2		
2c	270.0	50.6	181.7	6.23	6.23	2.84	18.3
3c		43.9	127.6	7.65	7.70		
1c		49.3	73.6	10.88	11.28		
4c		45.3	44.1	17.6	17.0		
18c	260.0	43.1	176.5	3.12	3.24	1.67	8.33
20c		39.6	166.8	3.34	3.34		
19c		49.2	122.6	3.95	3.94		
21c		43.6	68.7	6.12	5.71		
22c		46.1	42.6	8.35	8.18		
23c		42.5	30.1	10.58	10.91		

each temperature the values of K_1 and K_2 have been chosen to give the best fit of the variation of K with hydrogen iodide concentration for the high pressure experiments. Column 6 gives the calculated values of $(K_1 + (K_2/(\mathrm{HI})_0))$. The close agreement with the observed values of K indicates the essential validity of Equation I. For the low pressure experiments the values of K_2 are calculated as above.

The plots of log K_1 and log K_2 (*i. e.*, of the high pressure values of K_2) against $1/T$ are shown in Fig. 2. Satisfactory straight lines are obtained, indicating that the Arrhenius equation is obeyed. From the slopes of the lines the computed activation energies for the bimolecular reactions corresponding to K_1 are 33,400, 29,800 and 29,200 calories per mole for methyl, ethyl and *n*-propyl iodides, respectively. The observed values of K_1 for the three iodides may then be represented as $5.22 \times 10^{13} T^{1/2} e^{-(33{,}400 - {}^1/_2 RT)/RT}$, 1.34

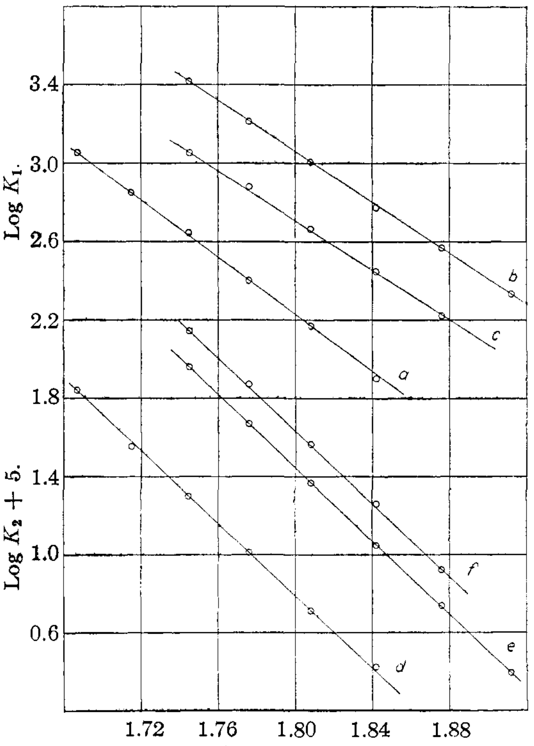

Fig. 2.—Plots of log K_1 and log K_2 against $1/T$: a, K_1 for CH_3I; b, K_1 for C_2H_5I; c, K_1 for *n*-C_3H_7I; d, K_2 for CH_3I; e, K_2 for C_2H_5I; f, K_2 for *n*-C_3H_7I.

$\times\ 10^{13}T^{1/2}e^{-(29{,}800-1/2RT)/RT}$ and $3.43 \times 10^{12}T^{1/2}e^{-(29{,}200-1/2RT)/RT}$ (mole/cc.)$^{-1}$ sec.$^{-1}$.

From the slopes of the lines for K_2 the activation energy of the corresponding unimolecular reaction is found to be 43,000 calories per mole for all three alkyl iodides. Hence the high pressure values of K_2 for methyl, ethyl and *n*-propyl iodides may be represented, respectively, as $3.93 \times 10^{12}e^{-43{,}000/RT}$, $1.82 \times 10^{13}e^{-43{,}000/RT}$ and $2.80 \times 10^{13}e^{-43{,}000/RT}$ sec.$^{-1}$. Incidentally it should be pointed out that the high pressure values of K_2 employed may all be slightly lower than the true limiting values. This difference is probably insufficient to affect the activation energy appreciably.

Discussion

The following mechanism is adduced to account for the observed rate expression (Equation I)

$$\mathrm{RI} + \mathrm{HI} \longrightarrow \mathrm{RH} + \mathrm{I_2} + 16 \text{ kilocalories} \quad (1)$$
$$\mathrm{RI} \longrightarrow \mathrm{R} + \mathrm{I} - 43 \text{ kilocalories} \quad (2)$$
$$\mathrm{R} + \mathrm{HI} \longrightarrow \mathrm{RH} + \mathrm{I} + 24 \text{ kilocalories} \quad (3)$$
$$\mathrm{R} + \mathrm{I_2} \longrightarrow \mathrm{RI} + \mathrm{I} + 8 \text{ kilocalories} \quad (4)$$
$$2\mathrm{I} + \mathrm{M} \longrightarrow \mathrm{I_2} + \mathrm{M} \quad (5)$$

The given thermal changes accompanying the various reactions are calculated from the accepted values of the dissociation energy of hydrogen iodide and iodine and from the value of 94.5 kc. given by Kistiakowsky and Gershinowitz[6] for the heat of dissociation of the carbon-hydrogen linkage in organic compounds. The value of 43 kc. for the carbon-iodine linkage is discussed below.

The simple bimolecular metathesis (1) appears entirely plausible and accounts for the first term on the right-hand side of Equation I, its rate constant being K_1. Reactions (2), (3), (4) and (5) account for the second term, if it is assumed that (2) is much slower than the subsequent reactions and hence is rate controlling, and that the concurrent steps (3) and (4) have equal rate constants. K_2 is then the velocity constant for the unimolecular dissociation (2).

Reaction (2) appears reasonable in view of the considerable evidence accumulated regarding the production of free hydrocarbon radicals in the gas phase by thermal decomposition of organic compounds, from the original work of Paneth[7] with lead tetra-alkyls to the recent results of Rice[8] and his collaborators with hydrocarbons, acetone, etc. Further, the energy of activation for (2) was found to be the same for methyl, ethyl and *n*-propyl iodides, 43 kc. For the energy of the carbon-iodine linkage in aliphatic iodides Eucken[9] gives some 44 kc., a value also obtained from data on the heats of combustion of aliphatic iodides[10] and the values of Kistiakowsky and Gershinowitz[6] for the strength of the carbon-carbon bond (77 kc.) and the carbon-hydrogen bond (94.5 kc.). Also, the heat of dissociation of cyanogen iodide into iodine atoms and cyanide radicals may be calculated from the results of Lewis and Keyes[11] and of Yost and Stone[12] on the heat of the reaction $\mathrm{ICN} \longrightarrow 1/2\, \mathrm{I_2} + 1/2(\mathrm{CN})_2$ and from the heat of dissociation of cyanogen.[6] The value so found for the carbon-iodine linkage in cyanogen iodide is 40 kc. The close agreement of these thermal values with the observed activation energy lends additional evidence for reaction (2). It appears that the activation energy is almost exactly equal to the dissociation energy of the carbon-iodine linkage, and that 43 kc. may be taken as the best value for this quantity. The fact that the activation energy is the same for methyl, ethyl and *n*-propyl iodides lends direct evidence in support of the hypothesis of constancy of bonding energies in organic compounds.

The work of Chadwell and Titani[13] on the reaction of hydrogen atoms with methyl iodide indicates that reaction (3) occurs in the case of methyl radicals. Evidence that methyl radicals undergo reaction (4) with great rapidity is found in the work of Bates and Spence[14] on the photo-oxidation of methyl iodide. It seems justifiable to infer that other alkyl radicals behave in similar fashion. Both (3) and (4) are exothermic elementary reactions and probably require no activation energy, taking place at every collision except for a steric factor. This would account for the observed fact that their rates are practically identical for a given alkyl radical. One would expect a smaller steric factor for (3) than for (4), but this might well be balanced by the greater collision rate of the former reaction. Reaction (5), the trimolecular recombination of iodine atoms, is well known.

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(6) Kistiakowsky and Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).

(7) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(8) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932), etc.

(9) Eucken, "Lehrbuch der chemischen Physik," Akademische Verlagsgesellschaft, Leipzig, 1930.

(10) Thomsen, "Thermochemistry," Longmans, Green and Co., N. Y., 1920.

(11) Lewis and Keyes, THIS JOURNAL, **40**, 472 (1918).

(12) Yost and Stone, *ibid.*, **55**, 1889 (1933).

(13) Chadwell and Titani, *ibid.*, **55**, 1363 (1933).

(14) Bates and Spence, *ibid.*, **53**, 1681 (1931).

It is interesting to compare the above mechanism with that commonly proposed for the chlorination and bromination of saturated hydrocarbons. Whereas in the case of iodine and hydrocarbons equilibrium is shifted far toward the halogen and hydrocarbon, with bromine and chlorine it is largely toward the hydrogen halide and alkyl halide. However, the reaction mechanism is essentially the same for all three halogens. The reactions given to explain the chlorination and bromination of saturated hydrocarbons, either photochemical[15] or induced by alkyl radicals or halogen atoms,[16] are as follows.

$$RH + X \longrightarrow R + HX \qquad (6)$$

$$R + X_2 \longrightarrow RX + X \qquad (7)$$

$$2X + M \longrightarrow X_2 + M \qquad (8)$$

$$R + X \longrightarrow RX \qquad (9)$$

X indicates the bromine or chlorine atom. (6) and (7) yield reaction chains, broken by (8) and (9). (Reaction (9) is ordinarily given as trimolecular, but in light of the present work is probably a bimolecular association.) This mechanism is seen to be analogous to that given for the reaction of alkyl iodides and hydrogen iodide, with the exception of reaction (1). With bromine and chlorine the reaction analogous to the reverse of (1) may occur, but at low temperatures is probably negligible in rate as compared to the chain reactions involving atoms and radicals. (6) is seen to be merely the reverse of reaction (3). In the case of chlorine atoms (6) is exothermic to the extent of some 7 kc.; with bromine and iodine atoms it is endothermic by 8 and 24 kc., respectively. Correspondingly, with chlorine atoms (6) is rapid and produces long chains, of the order of 10^4. With bromine atoms (6) is much slower, and the reverse reaction is doubtless important. As a result, very short chains, around 2 members, are produced. With iodine atoms (6) does not occur appreciably, the reverse reaction greatly predominating. Reaction (7) is exothermic for all three halogens, and probably occurs at nearly every collision.

Reaction (2) should occur even in the absence of hydrogen iodide. Experimentally it was observed that the alkyl iodides themselves were comparatively stable at the temperature of these experiments. This would seem to indicate that the reverse of (2), *i. e.*, a bimolecular association of alkyl radicals and iodine atoms, must take place, and that a dissociation equilibrium is reached. Such an association reaction would be analogous to those studied by Pease[17] and by Vaughan.[18] Since the activation energy of reaction (2) is apparently equal to the heat of the reaction, the reverse reaction has a zero activation energy. Direct evidence that the reverse of (2) does take place is found in the observation of Bates and Spence[14] that the quantum efficiency for the photodecomposition of pure gaseous methyl iodide is only some 0.02. These authors suggest that the recombination of methyl radicals with iodine atoms is a three-body process. However, since the dissociation is unimolecular, thermodynamically the association must be bimolecular. The considerable number of degrees of freedom and resultant long life of the association complex make this possible at high pressures. At lower pressures, where the unimolecular constant has become pressure dependent (this was observed in the case of methyl and ethyl iodides), the association must be in part trimolecular and hence likewise pressure dependent. Reactions (3) and (4) are doubtless much more rapid than this association reaction, and so in the presence of hydrogen iodide the latter plays no appreciable part.

It appears that at the temperatures employed the recombination of iodine atoms with alkyl radicals must be considerably more rapid than other reactions which would compete for the radicals, as

$$2R \longrightarrow R_2 \qquad (10)$$

$$2R \longrightarrow RH + R{-}H \qquad (11)$$

$$R + RI \longrightarrow R_2 + I \qquad (12)$$

(The trimolecular recombination of iodine atoms would of course be much slower than their bimolecular association with alkyl radicals.) It seems probable that these side reactions are attended with considerable activation energy. At higher temperatures the pure alkyl iodides themselves undergo decomposition, probably as a result of the increasing importance of such reactions. The well-known fact that the stability of alkyl iodides decreases markedly in the order primary, secondary, tertiary suggests that with branched chain radicals such side reactions may be rapid. Glass and Hinshelwood[19] have studied qualitatively the decomposition of gaseous isopropyl iodide, which is rapid around 300°.

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[15] Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930); Jost, *ibid.*, Bodenstein Festband, 291 (1931).

[16] Polanyi and Style, *Naturwissenschaften*, May, 1932, p. 402.

[17] Pease, THIS JOURNAL, **54**, 1876 (1932).

[18] Vaughan, *ibid.*, **54**, 3863 (1932).

[19] Glass and Hinshelwood, *J. Chem. Soc.*, 1815 (1929).

They find that the reaction proceeds almost quantitatively

$$2C_3H_7I \longrightarrow C_3H_8 + C_3H_6 + I_2$$

This suggests that (11) may be the predominant reaction for the consumption of alkyl radicals.

For the simple bimolecular reactions of hydrogen iodide with methyl, ethyl and *n*-propyl iodides the activation energies were found to be, respectively, 33,400, 29,800 and 29,200 calories per mole. That is, the activation energies for ethyl and *n*-propyl iodides are nearly identical, but some ten per cent. lower than that for methyl iodide. A similar relation is to be found among the Raman frequencies interpreted as due essentially to longitudinal vibration of the carbon-halogen bond in homologous normal alkyl halides.[20] It is found that the vibration frequency for the carbon–halogen bond in methyl halides is some 10% greater than that for the corresponding ethyl halides, whereas it is nearly identical for ethyl and higher normal halides. This correlation between vibration frequency of the carbon–iodine bond and activation energy of the reaction with hydrogen iodide suggests that in bimolecular reactions a decrease in vibration frequency of the reacting molecules lowers the intramolecular repulsion and hence the activation energy. A similar suggestion, based on different evidence, was offered by Polanyi and Cremer.[21] It should be pointed out that the energy of the carbon–iodine bond is the same in all three iodides. The difference in vibration frequencies is due to a different relation between binding energy and internuclear separation of the carbon and iodine atoms.

From the expressions given above for the bimolecular rate constant K_1 of the reaction of methyl, ethyl and *n*-propyl iodide with hydrogen iodide the simple kinetic theory (*i. e.*, assuming that the activation energy is confined to relative translational energy and that the steric factor is unity) would demand that the rates at which alkyl iodide molecules collide with those of hydrogen iodide are, respectively, $5.22 \times 10^{13}T^{1/2}$, $1.34 \times 10^{13}T^{1/2}$ and $3.43 \times 10^{12}T^{1/2}$ (mole/cc.)$^{-1}$ sec.$^{-1}$. These correspond to average molecular diameters of 12.4, 6.37 and 3.07×10^{-8} cm., respectively. If the diameter of the hydrogen iodide molecule is taken as 3.5×10^{-8} cm. the diameters of the methyl, ethyl and *n*-propyl iodide molecules are found to be, respectively, 21.3, 9.2 and 2.6×10^{-8} cm. This set of values suggests that the simple theory is not adequate. In the first place, the order of the collision diameters is the reverse of that which would be expected; *i. e.*, the larger molecule appears to have the smaller diameter. This may be explained by assuming that the steric factor is not unity, but decreases in the order methyl, ethyl and *n*-propyl. This decrease appears plausible from spatial considerations. The larger alkyl radical probably exerts a greater shielding influence on the carbon–iodine linkage, and renders proper orientation at collision more critical. These effects would tend to reduce the collision efficiency.

Another difficulty with the simple theory is that the diameter found for the methyl iodide molecule appears improbably large, and if the above steric factor correction is assumed the same applies to the ethyl and *n*-propyl iodide molecules. This suggests that other degrees of freedom (vibrational and rotational) also contribute to the energy of activation at collision. Since one of the molecules is polyatomic, a large number of degrees of freedom are available. This effect would lead to too large an apparent diameter if the activation energy were assumed to be all translational. To be sure, the over-large diameters might be due in part to error in the activation energies, but it is doubtful that this is sufficient to explain the discrepancy.

When the high pressure values of the unimolecular constant K_2 are expressed in the form $Ae^{-Q/RT}$, where Q is the activation energy, the values of A for methyl, ethyl and *n*-propyl iodides, respectively, are 3.93×10^{12}, 1.82×10^{13} and 2.80×10^{13} sec.$^{-1}$. These are of a reasonable order of magnitude, A for other known unimolecular reactions being usually from 10^{12} to 10^{16}. It is interesting to observe that in the above series A increases with the size of the molecule, the increase being considerably larger in going from methyl to ethyl than from ethyl to *n*-propyl iodide. It appears possible that this effect is related to the above mentioned variation in fundamental vibration frequency of the carbon–iodine bond. Since the larger iodide has the lower vibration frequency, the energy levels of the carbon–iodine bond are more closely spaced. This may result in an increased probability of flow

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[20] Harkins and Bowers, *Phys. Rev.*, **38**, 1852 (1931).

[21] Polanyi and Cremer, *Z. physik. Chem.*, Bodenstein Festband, 770 (1931).

of energy into this bond and hence in an increased intrinsic rate of dissociation, reflected in a larger value of A.

The unimolecular constant K_2 for the dissociation of methyl and ethyl iodides is seen to be approximately independent of pressure at large concentrations of reactants, but to fall off at low pressures (the reaction of *n*-propyl iodide was not studied at low pressures). It is interesting to consider this falling off in the light of current theories of unimolecular reactions. Only the simplest of these, the so-called Theory I,[22] will be considered here. Experimental irregularities in the falling off of the rate constants and the complex nature of the reaction mixtures render useless the application of more refined theories. According to Theory I the rate at pressure p is given by

$$k = k_\infty/(1 + \beta_1/p)$$

where k_∞ is the limiting high pressure rate and β_1 is defined by Equation 5 of Rice and Ramsperger's paper. If $1/k$ is plotted against $1/p$ a straight line should result of intercept $1/k_\infty$ and slope β_1/k_∞. As nearly as can be judged this expression fits satisfactorily the plots of $1/K_2$ against the reciprocal of total gas pressure for methyl and ethyl iodides at the temperatures studied. For methyl iodide the best fit was obtained with a model having seven classical oscillators and a collision diameter of 6×10^{-8} cm. The values of $(K_2)_\infty$ at 320 and 300° were taken, respectively, as 7.2×10^{-4} and 2.1×10^{-4} sec.$^{-1}$. The corresponding values of β_1 are 35 mm. and 25 mm. For ethyl iodide a model having nine oscillators and a diameter of 7.5×10^{-8} cm. was used. $(K_2)_\infty$ at 300, 290 and 280° was taken, respectively, as 9.4×10^{-4}, 4.8×10^{-4} and 2.4×10^{-4} sec.$^{-1}$. Corresponding values of β_1 are 11.4, 9.8 and 8.5 mm. . . It will be observed that the experimental variation with temperature of the falling off of the rate constants is in agreement with theory; *i. e.*, the falling off is greater at higher temperatures.

The maximum possible number of oscillators in the molecule of methyl iodide is 9. That for ethyl iodide is 18. These are to be compared with the experimental values of 7 and 9, respectively. It may be pointed out that for each molecule the apparent effective number of oscillators is approximately three times the number of heavy atoms—a relation observed also for several other unimolecular reactions.[23] For *n*-propyl iodide a still larger number of oscillators would probably be required, and the falling off of the rate constant would occur at lower pressures.

In the low pressure experiments K and hence K_2 remained constant during a given run. This indicates that the reaction products (iodine and hydrocarbon) are about as effective as the reactants in maintaining the rate of unimolecular dissociation of methyl and ethyl iodides. Scrutiny of the data in Tables III and IV shows that hydrogen iodide is more effective in maintaining the rate of unimolecular dissociation of methyl and ethyl iodides than these substances themselves. The fact that collisions of hydrogen iodide molecules with those of alkyl iodides are effective in activating the latter for unimolecular reaction is especially interesting because of the bimolecular reaction that can also take place between these molecules. Further, the activation energy of the unimolecular reaction is considerably greater than that of the bimolecular process. The entire independence of the two reactions is doubtless a result of the difference in localization of their respective activation energies. That for the unimolecular process is contained in vibrational degrees of freedom, while that for the bimolecular reaction is essentially relative kinetic energy of the two molecules. Energy transfer between these two types does not take place readily, and so the two reactions are not coupled.

In conclusion, it may be pointed out that the reactions of alkyl iodides with hydrogen iodide constitute further examples of chemical reactions in which two entirely independent mechanisms leading to the same products occur with substantially equal rates in the same temperature range. In this respect the reactions studied here resemble the thermal decomposition of ethylene iodide investigated by Arnold and Kistiakowsky.[24]

The author wishes to express to Professor G. B. Kistiakowsky sincere appreciation of his interest and advice, which greatly aided this research.

Summary

1. The thermal reactions of methyl, ethyl and *n*-propyl iodides with hydrogen iodide have been investigated in the temperature range 250–320° and at pressures from a few mm. to some half an atmosphere.

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[22] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

[23] Leermakers, THIS JOURNAL, **55**, 3098 (1933).

[24] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

2. The reactions have been found to be homogeneous and free from appreciable side reactions, proceeding almost to completion by the process $RI + HI \longrightarrow RH + I_2$.

3. The order of the reactions was found to be complex, the rates being best represented by the kinetic expression

$$\frac{d(I_2)}{dt} = K_1(RI)(HI) + K_2(RI)\,\frac{(HI)}{(HI) + (I_2)}$$

This is interpreted as being due to two concurrent mechanisms. The rate controlling steps are, respectively, a bimolecular reaction of alkyl iodide and hydrogen iodide, and a unimolecular dissociation of the alkyl iodide into alkyl radical and iodine atom. The constants for the two are, respectively, K_1 and K_2.

4. For methyl, ethyl and *n*-propyl iodides, respectively, the values of K_1 were found to be $5.22 \times 10^{13}T^{1/2}\, e^{-(33,400 - {1/2}RT)/RT}$, $1.34 \times 10^{13} T^{1/2}e^{-(29,800 - {1/2}RT)/KT}$ and $3.43 \times 10^{12}T^{1/2} e^{-(29,200 - {1/2}RT)/RT}$ (mole/cc.)$^{-1}$ sec.$^{-1}$. The corresponding values of K_2 are 3.93×10^{12}-$e^{-43,000/RT}$, $1.82 \times 10^{13}e^{-43,000/RT}$ and $2.80 \times 10^{13}e^{-43,000/RT}$ sec.$^{-1}$.

5. The unimolecular constant K_2 for methyl and ethyl iodides was found to fall off at low pressures in the manner demanded by collision theories of unimolecular reactions.

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[FROM THE DEPARTMENT OF ZOÖLOGY, HARVARD UNIVERSITY]

Dielectric Constants of Polar Solutions

BY JEFFRIES WYMAN, JR.

There has been a considerable amount of recent work[1] on the dielectric constant of aqueous solutions of amino acids and related compounds, underlying which has been the idea that the abnormally large values of the dielectric constant encountered in the case of nearly all these ampholytes are due to their existence as zwitter ions. For the dielectric constant must reflect the magnitude of the polarization of the solutions, and, taking account of molecular dimensions, it is easy to calculate that the electric moment (polarization) of such zwitter ions should be far greater than that of ordinary un-ionized compounds. On the other hand, increasing evidence from quite other sources of itself places the zwitter ion hypothesis almost beyond doubt.[2] The presentation of the results of these dielectric studies and their correlation with the zwitter ionic properties of the ampholytes in question have been greatly facilitated by the fact that in all the cases investigated the dielectric constant has been found to increase linearly with the concentration of the ampholyte, expressed in moles (or grams) per liter, up to the highest concentrations studied, *i. e.*, about 2.5 moles per liter in the case of the more soluble amino acids. On account of this, the results may all be expressed in terms of the increase of dielectric constant per mole of ampholyte, a quantity to which we will refer hereafter by δ. It has been shown for aqueous solutions that δ is very nearly the same for all amino acids of a given type, *e. g.*, the α-amino aliphatic acids, and that it increases in a very regular way with the separation between the acid and basic groups in the molecule.[3] Since the electric moment, or polarization, of these substances in water must be primarily determined by their properties as zwitter ions, these facts lead to the concept that in general the δ value of a substance in aqueous solution is a measure of its electric moment, or perhaps polarization, and may be used to estimate, at least qualitatively, the magnitude of this on a relative basis.

The situation revealed by the study of aqueous solutions raises a number of questions. For one thing, are the characteristic δ values of these ampholytes the same in other polar solvents where the zwitter ionic form may also be supposed to predominate and where consequently the electric moments, or polarizations, may be supposed to be the same? In general this would not be expected; but the matter can obviously be settled only empirically, for theoretical considerations break down in the case of these

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(1) See Blüh, *Z. physik. Chem.*, **106**, 341 (1923); Devoto, *Gazz. chim. ital.*, **60**, 520 (1930); *ibid.*, **61**, 897 (1932); *ibid.*, **63**, 50 (1933); Fürth, *Ann. Physik*, **70**, 63 (1923); Frankenthal, *Z. physik. Chem.*, **19**, 328 (1932); *ibid.*, **21**, 310 (1933); Hedestrand, *ibid.*, **135**, 36 (1928); Walden and Werner, *ibid.*, **129**, 389 (1927); Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933); *ibid.*, **55**, 915 (1933).

(2) See Cohn, *Ergebnisse der Physiologie*, **33**, 781 (1931).

(3) Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).