Kinetics of the Photolysis of Methyl Iodide and the Hydrogen Halides I. Photolysis of Hydrogen Iodide in the Presence of Iodine, Hydrogen Bromide and Hydrogen Chloride

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I. Photolysis of Hydrogen Iodide in the Presence of Iodine, Hydrogen Bromide and Hydrogen Chloride

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The photodissociation of hydrogen iodide by light of λ2537A has been utilized as a source of hydrogen atoms for a study of their subsequent reactions with iodine and the hydrogen halides. The observed rate of hydrogen formation has been used to evaluate the ratio of rate constants for the following reactions:
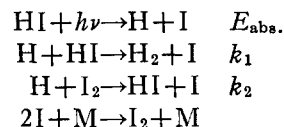
$$H + HX \rightarrow H_2 + X$$
$$H + I_2 \rightarrow HI + I$$
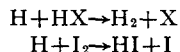
where X represents Cl, Br or I.

INTRODUCTION

HYDROGEN iodide absorbs ultra-violet radiation continuously and with increasing efficiency toward shorter wave-lengths below λ3000A. Absorption of radiation dissociates the molecule into a hydrogen atom and an iodine atom.[1] The photolysis has been investigated by several workers[2,3] and the mechanism of the reaction is analogous to the well known photolysis of hydrogen bromide.[4,5] The accepted mechanism and appropriate rate constants are given as

follows:

$$HI + h\nu \rightarrow H + I \quad E_{abs.}$$
$$H + HI \rightarrow H_2 + I \quad k_1$$
$$H + I_2 \rightarrow HI + I \quad k_2$$
$$2I + M \rightarrow I_2 + M$$

The last reaction is assumed to proceed rapidly enough, in comparison with other possible reactions of iodine atoms, so that the concentration of molecular iodine is equal to the concentration of molecular hydrogen. By use of the "steady state" treatment the following differential rate expression is obtained:

$$\frac{d(H_2)}{dt} = \frac{E_{abs.}}{1 + k_2(I_2)/k_1(HI)}. \tag{1}$$

Integration of this expression gives the following equation, with the indicated substitutions performed:

$$X + \frac{k_2}{k_1}\left[\frac{a+2b}{4}\ln\frac{a}{a-2X} - \frac{X}{2}\right] = E_{abs.}t \tag{2}$$

[1] K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie* (Steinkopf, Dresden and Leipzig, 1933).
[2] E. Warburg, Sitz. Preuss. Akad. Wiss., Physik.-Math. Klasse, 300 (1918).
[3] K. F. Bonhoeffer and L. Farkas, Zeits. f. Physik. Chemie **132**, 235 (1928).
[4] G. K. Rollefson and M. Burton, *Photochemistry* (Prentice-Hall, New York, 1939).
[5] W. A. Noyes and P. A. Leighton, *Photochemistry of Gases* (Reinhold, New York, 1941).
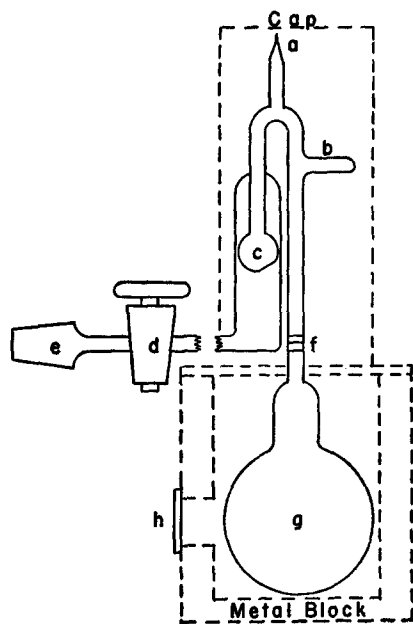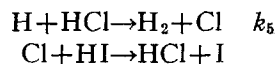
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FIG. 1. Reaction system. (a) Capillary seal-off. (b) Side-arm. (c) Click gauge. (d) Stopcock. (e) Ground joint. (f) Graded seal. (g) Silica bulb. (h) Silica window.

where $X=$ change in (H_2) in time interval $t=\Delta(H_2)$, $a=(HI)$ at beginning of time interval $t=(HI)_0$, and $b=(I_2)$ at beginning of time interval $t=(I_2)_0$. The measurable quantities in this equation are X, a, $E_{abs.}$, and t, leaving the ratio of the rate constants, k_2/k_1, to be evaluated. This reaction was reinvestigated[6] in order that it might be used as an actinometer in other studies.

The effects of added hydrogen bromide or hydrogen chloride have also been studied under conditions where they do not themselves absorb light.[1] They add the following reactions to the mechanism given for hydrogen iodide:

$$H+HBr \rightarrow H_2+Br \quad k_3$$
$$Br+HI \rightarrow HBr+I$$
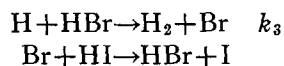
or, in the case of hydrogen chloride:

$$H+HCl \rightarrow H_2+Cl \quad k_5$$
$$Cl+HI \rightarrow HCl+I$$

The second reaction in each case is assumed to take place at virtually every collision, since it is highly exothermic and since the concentration of hydrogen iodide is quite large. Therefore, we treat the concentration of the added hydrogen

6 R. A. Ogg, Jr. and R. R. Williams, Jr., J. Chem. Phys. 11, 214 (1943).

halide as remaining constant during the reaction and assume that no appreciable concentration of molecular bromine or chlorine is built up.

The differential rate expression is modified as follows:

$$\frac{d(H_2)}{dt} = \frac{E_{abs.}}{1+k_2(I_2)/[k_1(HI)+k_3(HBr)]}. \quad (3)$$

A similar expression holds for the case of added hydrogen chloride, and $k_3(HBr)$ or $k_5(HCl)$ are constant additive factors for a given experiment. The integrated rate expression is similarly modified, although not so simply.

Experimentally, the mixtures were treated as pure hydrogen iodide, and from the values of $E_{abs.}$, t, and $\Delta(H_2)$ an "effective $(HI)_0$" was found by trial in Eq. 2. This effective $(HI)_0$ represents the actual $(HI)_0$ plus whatever contribution is made to the rate by HBr or HCl molecules and in the case of HBr may be represented as follows:

$$\text{effective } (HI)_0 = (HI)_0 + \frac{k_3}{k_1}(HBr). \quad (4)$$

A similar expression holds for the case of added hydrogen chloride. Iodine was added initially to furnish the basis for comparison of pure hydrogen iodide with the mixtures. The quantities obtained, then, are relative reaction rate constants for the reactions of hydrogen atoms with iodine and various hydrogen halide molecules.

EXPERIMENTAL DETAILS

Hydrogen iodide, hydrogen bromide and hydrogen chloride were all prepared in essentially the same way, with minor variations according to the nature of the individual substances. The method consisted simply of dropping a concentrated solution of phosphoric acid onto the potassium or sodium salt of the halogen contained in a distilling flask. This vessel was connected by glass-to-glass seals to successive traps cooled in ice water, dry ice, and liquid air. Heat applied to the distilling flask caused the hydrogen halide to condense in the two coldest traps. After most of the product had distilled into the liquid air trap, this section of the system was sealed off, together with a fourth trap and stopcock, as yet unused. The fourth trap was used for a final

distillation under vacuum from a dry ice bath to liquid air. The products were always water white and were kept in small reservoirs at dry ice temperatures. Some discoloration in the grease of the stopcocks over these reservoirs was noticed, but the samples themselves remained colorless for long periods of time.

The iodine used was Baker's reagent grade, resublimed.

The reactions and actinometer runs were performed in a spherical flask of fused silica about sixty millimeters in diameter, with filling and pressure measuring devices attached through a graded seal to Pyrex tubing (see Fig. 1). Reactants were introduced through a capillary seal-off at a, and their pressures measured through the click gauge c. Progress of the reaction was determined at various times by measuring, through the click gauge, the pressure of gases not condensible in liquid air (hydrogen). The cold bath was applied at side-arm b, so that the effective temperature of the main body of gas was that of the surrounding air. Pressure measurements were reproducible within 0.05 millimeters of mercury. Frequently some iodine vapor, in equilibrium with solid iodine at room temperature, would remain in the warm part of the system when a minimum pressure had been reached. This was due to the low vapor pressure (0.2–0.3 millimeters of mercury) of iodine at room temperature, and the consequent slowness of its transfer to the cold trap. This vapor pressure was subtracted from the total pressure and the pressure of non-condensable gas corrected to 25°C.

Analysis for iodine was made, if necessary, at the end of a series of exposures only, since this necessitated opening the system. The seal-off constriction was broken and air admitted slowly while the reactants were cooled in liquid air. After reaching atmospheric pressure, aqueous potassium iodide was added to dissolve the iodine. The dissolved iodine was titrated in the reaction flask, using standard sodium thiosulfate solution. In this way the hydrogen analyses could be checked, or, if iodine was added initially, subtraction of the quantity of iodine produced during the experiment gave the initial iodine concentration.

A metal block thermostat was used to maintain the reaction cell at the desired temperatures. The general outline of this thermostat is indicated by the broken lines in Fig. 1. A heated cap in the indicated position kept the reactants from condensing in the upper portion of the reaction vessel, while the stopcock remained outside the heated zone. Diffusion of the reactants to this cold portion was prevented by the glass membrane of the click gauge. Cap and metal block were wound with resistance wire, and the temperature controlled by a thermoregulator and appropriate resistances. Temperature control, as measured by a thermometer inserted in the metal block, was good to ±0.5° variation from the average temperature.

Light was admitted to the reaction vessel through a hole twenty-three millimeters in diameter in the metal block, covered with a fused-silica plate. A crystal-quartz lens focussed the light from the illuminating lamp in such a manner as to give a nearly cylindrical beam of light within the reaction cell. This was necessary in order to insure a thick absorbing layer of gas.

Ultra-violet radiation of $\lambda 2537A$ was supplied by a "Life-Lite" mercury resonance lamp in conjunction with a "Sola" constant-voltage transformer. This lamp contains argon gas at a low pressure and liquid mercury in equilibrium with its vapor. The operating temperature is only a little above room temperature and therefore its intensity depends markedly upon such factors as room temperature and air circulation. These variations were a serious drawback in certain phases of the work, as will be explained later.

TABLE I. Photolysis of hydrogen iodide.

Exposure	Temp. °C	$(HI)_0$* mm Hg	$(I_2)_0$* mm Hg	E_{abs}.**	Time hrs.	$\Delta(H_2)$* mm Hg	k_2/k_1
17a	189.0	166.40	12.20	0.930	6.00	4.30	3.4
17b	189.0			0.930	6.00	3.95	3.5
17c	189.0			0.930	6.00	3.75	3.3
18a	189.0	189.40	11.23	0.920	6.00	4.30	3.9
18b	189.0			0.920	6.00	4.10	3.5
22a	189.0	202.80	6.55	0.915	5.12	4.10	3.3
22b	189.0			0.915	5.28	3.95	3.4
22c	189.0			0.915	5.13	3.70	3.0
24a	102.0	195.70	10.15	0.915	5.33	3.90	3.9
24b	102.0			0.915	5.38	3.65	3.9
24c	102.0			0.915	5.88	3.75	3.9
27a	102.0	174.00	8.45	0.860	5.13	3.85	2.4
27b	102.0			0.860	6.13	3.95	3.8
27c	102.0			0.860	7.08	4.35	3.3

* All pressures of reactants were measured at room temperature and corrected to 25°C.
** E_{abs}. was measured in an independent run with no iodine added initially and is given in millimeters of hydrogen per hour for the system used.

TABLE II. Photolysis of hydrogen halide mixtures.

a. Hydrogen iodide and hydrogen chloride

Expo-sure	Temp. °C	$(HI)_0^*$ mm Hg	$(HCl)_0^*$ mm Hg	$(I_2)_0^*$ mm Hg	$E_{abs.}^{**}$	Time hrs.	$(H_2)^*$ mm Hg	Eff. $(HI)_0^*$ mm Hg	k_1/k_3
15	102.0	173.00	417.00	11.70	0.895	10.63	7.20	175	
16	102.0	163.50	292.50	10.35	0.895	10.92	7.40	165	
17	102.0	142.30	272.70	10.40	0.895	12.33	7.80	140	
19	154.5	185.00	420.00	13.15	1.170	10.53	9.50	220	12
20	154.5	139.50	439.50	10.20	1.170	11.40	9.70	155	30
9	189.0	136.30	274.20	0.00	0.932	7.67	6.71	190	5.1
10	189.0	129.50	270.00	9.35	0.932	6.72	5.00	170	6.6
11	189.0	148.50	283.50	11.20	0.927	8.70	6.20	180	6.8

b. Hydrogen iodide and hydrogen bromide

Expo-sure	Temp. °C	$(HI)_0^*$ mm Hg	$(HBr)_0^*$ mm Hg	$(I_2)_0^*$ mm Hg	$E_{abs.}^{**}$	Time hrs.	$(H_2)^*$ mm Hg	Eff. $(HI)_0^*$ mm Hg	k_1/k_2
15	102.0	159.25	120.25	10.50	0.865	11.87	8.20	210	2.4
16	102.0	162.00	173.00	12.05	0.865	10.98	8.15	220	3.0
17	154.5	152.30	156.70	11.00	0.865	11.42	8.10	240	1.8
19	154.5	140.50	240.50	12.75	1.130	9.93	9.15	275	1.8
20	154.5	182.70	180.80	11.00	1.130	11.12	10.35	270	2.0
11	189.0	158.90	75.60	13.72	0.925	6.83	4.85	190	2.4
12	189.0	152.30	167.30	11.37	0.955	6.80	5.50	260	1.7
13	189.0	160.60	121.30	11.85	0.920	8.00	6.10	250	1.4

* All pressures of reactants were measured at room temperature and corrected to 25°C.
** $E_{abs.}$ was measured in an independent run with no iodine added initially and is given in millimeters of hydrogen per hour for the system used.

Protection of the lamp from drafts and undue temperature changes helped to minimize this difficulty, but it still gave an uncertainty of up to five percent in the actinometer values. Approximately ninety percent of the radiant energy of this lamp is furnished at λ2537A, and therefore it can be considered essentially a monochromatic source. The position of the reaction cell was reproducible, and therefore reflection losses were constant and required no correction factor.

Our experimental procedures were such as to permit mercury in the reaction system to the extent of its vapor pressure at room temperature, as a *maximum*. While this may seem undesirable, due to the high absorption coefficient of mercury for the radiation used, this contamination should disappear in the earliest stages of the reaction, through reactions with iodine atoms, if not hydrogen iodide and iodine. The removal of iodine atoms by silver foil, an analagous reaction, is well known.[7]

[7] W. West and L. Schlesinger, J. Am. Chem. Soc. 60, 961 (1938).

EXPERIMENTAL RESULTS

Hydrogen Iodide

Earlier experiments performed with somewhat lower pressures of hydrogen iodide than those reported below were inaccurate due to incomplete absorption of the incident radiation, and gave a spuriously high value of k_2/k_1.[6] It was later found that a pressure of 150 mm of hydrogen iodide was sufficient for complete absorption. When such quantities of reactant are used, and only a few millimeters pressure of hydrogen produced, the value of $E_{abs.}$ obtained by use of Eq. (2) is very insensitive to errors in k_2/k_1. This is due to the fact that the ratio $(I_2)/(HI)$ is very small at all times during the run, and consequently there is very little retardation. Using only an approximate value of k_2/k_1 it is possible, therefore, to get a good value of $E_{abs.}$. This was done in the second determination of k_2/k_1.

In these experiments an actinometer run, to get $E_{abs.}$ in the manner indicated above, was followed by runs with iodine added initially. Using the value of $E_{abs.}$ previously obtained, an accurate value of k_2/k_1 was obtained in these runs by virtue of the fact that there was sufficient iodine to cause considerable retardation. It was necessary, however, to keep the iodine concentration as low as about one-tenth the concentration of hydrogen iodide lest it compete in absorption of ultra-violet light.[8]

Table I presents the data obtained on the photolysis of hydrogen iodide with iodine initially added. An interval method was used, employing successive exposures and measurements with the same initial mixture. These showed that there was no variation of the ratio of rate constants over a range of concentrations of the reactants. The extreme cases are experiments $17c((HI) = 142$ mm, $(I_2) = 24$ mm) and $22a((HI) = 202$ mm, $(I_2) = 6$ mm).

The best value of k_2/k_1 obtained from these measurements is taken as 3.5 ± 0.3. This ratio of constants is apparently independent of temperature.

Hydrogen Halide Mixtures

The absorption coefficients of hydrogen bromide and hydrogen chloride at λ2537A are such

[8] A. Coehn and Stuckardt, Zeits. f. physik. Chemie 91, 722 (1916).

that considerable amounts of these gases may be added to hydrogen iodide without appreciable change in the primary absorption process. Since pressures of hydrogen iodide above 150 mm are needed to insure complete light absorption, the effect of added HX on the observed rate of reaction is sometimes rather small, and the light intensity difficulties mentioned previously become rather serious. Consequently, the results of this section of the work can only be regarded as good approximations.

The data for hydrogen halide mixtures is given in Table II, with the value of the effective $(HI)_0$ calculated as indicated in the Introduction. Also given are the ratios of constants k_1/k_3 and k_1/k_5, which are seen to be the relative effectiveness of two halides in reacting with hydrogen atoms. The E_{abs}. given for each run is the result of an independent hydrogen iodide actinometer run, with no iodine initially added, which immediately preceeded or followed the experiment in question.

The value of k_1/k_5 for hydrogen iodide-hydrogen chloride mixtures is seen to be strongly temperature dependent. The mixtures studied at the lowest temperature (Nos. 15, 16, and 17) were experimentally indistinguishable from pure hydrogen iodide. At 154.5°C the precision is obviously poor, but for purposes of approximate calculation we have taken the value 12 for k_1/k_5 since it represents the greatest difference in the effective and actual $(HI)_0$. Combining this with the values for 189.0°C, we see that k_1/k_5 may be approximately given as:
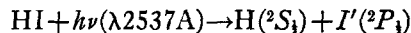
$$2\times10^{-3}\exp(7500/RT).$$

The value of k_1/k_3 for hydrogen iodide-hydrogen bromide mixtures is much less dependent on temperature. Figure 2 is a plot of $\log k_1/k_3$ against $1/T$. The slope and intercept of the indicated line correspond to

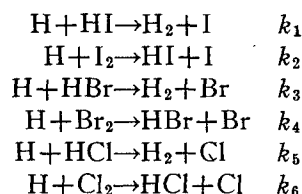$$k_1/k_3=0.54\exp(1000/RT).$$

DISCUSSION

Subsequent work[9] has indicated that the rate constants evaluated here probably refer to high velocity hydrogen atoms produced in the primary

[9] R. A. Ogg, Jr. and R. R. Williams, Jr., J. Chem. Phys. 13, 586 (1945).

process:

$$HI+h\nu(\lambda2537A)\rightarrow H(^2S_i)+I'(^2P_i)$$

which is exothermic by some 20 kilocalories per mole. In the absence of inert molecules to slow down the hydrogen atoms, the reaction rates observed are probably those of thermally "hot" hydrogen atoms. Thus the effective temperature may be much higher than the reported values and activation energy effects may be quite unpredictable or too small to be observed.

The ratios of rate constants obtained in this work may be summarized in terms of the following equations:

$$\begin{array}{ll} H+HI\rightarrow H_2+I & k_1 \\ H+I_2\rightarrow HI+I & k_2 \\ H+HBr\rightarrow H_2+Br & k_3 \\ H+Br_2\rightarrow HBr+Br & k_4 \\ H+HCl\rightarrow H_2+Cl & k_5 \\ H+Cl_2\rightarrow HCl+Cl & k_6 \end{array}$$

The value of k_2/k_1 was found in this work to be 3.5 ± 0.3 and was independent of temperature. This may be compared to a value of 7.0 ± 0.4 at 155°C obtained in the presence of a deactivating agent.[9] The difference may be due to a small difference in activation energies of the first two reactions. The value 3.5, then, probably is the ratio of frequency factors. Both values are in marked disagreement with the value obtained by Bonhoeffer and Farkas,[3] who report that fifteen
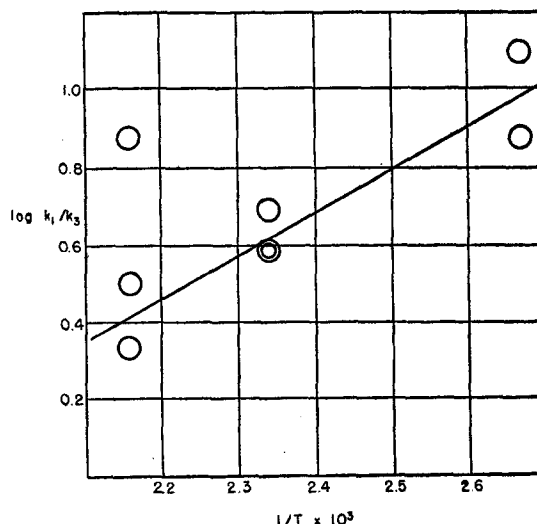

FIG. 2. $\log k_1/k_3$ as a function of $1/T$.

percent of iodine "completely inhibits" the photolysis of hydrogen iodide. On this observation they base their estimate of k_2/k_1 as greater than 100. Their experiments were conducted at extremely low gas pressures, and the secondary reactions probably occurred principally on the walls of the vessel. The value reported in this work certainly corresponds to the true homogeneous reactions.

The value of k_4/k_3 has been accurately determined by other workers[10] as 8.4 and is also independent of temperature. The value of k_6/k_5 has been estimated to be greater than 100.[11] The new values for k_2/k_1 therefore fall into a more logical sequence with the other halogens and hydrogen halides.

The value of k_1/k_3 obtained in this work was $0.54 \exp(1000/RT)$. In view of the "hot atom"

hypothesis proposed above, this representation of the data can be regarded only as tentative, until further experiments with deactivating agent present have been performed. However, the activation energy given is not in conflict with other information, such as an estimate by Morris and Pease[11] that reaction 3 has an activation energy of about 1 Kilocalorie/mole. This would give reactions 1 and 2 small and nearly equal activation energies.

Note: The ratio of rate constants k_1/k_5 obtained in this work corresponds to the form

$$0.002 \exp(7500/RT).$$

The approximate nature of this portion of the work and the extremely small ratio of frequency factors obtained leave this result open to grave doubt. Further experiments in the presence of a deactivating agent have given significantly different results, which may contribute to a better understanding of this value.

[10] M. Bodenstein and G. Jung, Zeits. f. physik. Chemie 121, 127 (1926).
[11] J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).

# Kinetics of the Photolysis of Methyl Iodide and the Hydrogen Halides*

II. Photolysis of Methyl Iodide in the Presence of Iodine and the Hydrogen Halides

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The photodissociation of methyl iodide by light of λ2537A has been utilized as a source of methyl radicals for a study of their subsequent reactions with iodine and the hydrogen halides. The observed rate of methane formation has been used to evaluate the ratio of rate constants for the following reactions:

$$CH_3 + HX \rightarrow CH_4 + X$$
$$CH_3 + I_2 \rightarrow CH_3I + I$$
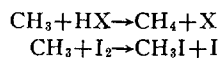
where X represents Cl, Br or I. The reaction with hydrogen chloride has been found to be complicated by the unequal yield of methane and iodine, and possible explanations of this phenomenon have been considered.

INTRODUCTION

GASEOUS methyl iodide absorbs ultra-violet radiation below λ3650A with an absorption maximum occurring at λ2632A.[1] The reactions resulting when pure methyl iodide vapor is irradiated with light of λ2537A have been carefully studied[2] with the conclusion that the primary process of light absorption results in the formation of a methyl radical and an iodine atom. The very low quantum yield obtained with pure

[1] G. K. Rollefson and M. Burton, *Photochemistry* (Prentice-Hall, New York), 1939.
[2] W. West and L. Schlesinger, J. Am. Chem. Soc. 60, 961 (1938).