$E_2 - {}^1/_2E_3 = 9.5$ kcal./mole and we consider this value to be correct within 1.5 kcal./mole. We note the very good agreement between this value and that reported by Trotman-Dickenson and Steacie[1] (9.7 ± 0.1 kcal./mole). The values of $k_2/k_3{}^{1/2}$ obtained by us are lower by about 25% than those recorded by Trotman-Dickenson and Steacie (see Table III).

The agreement in the estimated activation energy and the observed rates for the processes producing methane in the photolytic system investigated by Trotman-Dickenson and Steacie and in the pyrolytic system investigated by us is particularly gratifying. It assures us that we do indeed measure the activation energy for the radical reaction (2).

MANCHESTER 13, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Kinetics of Hot Hydrogen Atoms in the Photolysis of the Hydrogen Halides[1-3]

BY HAROLD A. SCHWARZ,[4] RUSSELL R. WILLIAMS, JR., AND WILLIAM H. HAMILL

RECEIVED APRIL 29, 1952

The photolyses of hydrogen iodide, deuterium iodide and hydrogen bromide were studied in the presence of added inert gases. The inhibiting effect of the free halogens was found to be a function of the concentration of inert gas, the effect being independent of its nature at large pressure of inert gas. The results are interpreted in terms of hot atom mechanisms. The moderating effect of the inert gas is accounted for semi-quantitatively and the difference of activation energies between the thermal reactions, $E_1 - E_2$: [$H + HI \rightarrow H_2 + I, k_1$; $H + I_2 \rightarrow HI + I, k_2$] is found to be 4.5 ± 0.8 kcal. mole^{-1}.

Introduction

The photodissociation of the hydrogen halides with light of λ 2537 Å. yields hydrogen atoms with considerable kinetic energy, since the bond strength is much less than the quantum energy and this energy difference will be divided in the inverse ratio of the atomic masses. In the case of hydrogen iodide, spectral investigations[5,6] indicate the production of the $^2P_{3/2}$ state of the iodine atom and, therefore, hydrogen atoms of *ca.* 42 kcal. mole^{-1} excess energy should be produced. The inhibitory effect of iodine in this photolysis, represented by the ratio $k_2/k_1 = 3.8$ (independent of temperature) in pure hydrogen iodide[7] increases to a value of 7.0

$$\begin{aligned} H + HI &\longrightarrow H_2 + I \quad k_1 \\ H + I_2 &\longrightarrow HI + I \quad k_2 \end{aligned}$$

at pressures of cyclohexane greater than 300 mm.[8] This effect was attributed to the moderation of the hot hydrogen atoms by cyclohexane and appropriate reactions were added to the classical mechanism

$$\begin{aligned} \mathbf{H} + HI &\longrightarrow H_2 + I \quad k_3 \\ \mathbf{H} + I_2 &\longrightarrow HI + I \quad k_4 \\ \mathbf{H} + M &\longrightarrow H + M \quad k_5 \end{aligned}$$

where **H** is a hot hydrogen atom and M the moderating substance.

In a similar fashion, the photolysis of hydrogen bromide should yield hydrogen atoms of *ca.* 26 kcal. mole^{-1} excess energy. In this case, the inhibition constant k_7/k_6 has not been measured directly, but is expected to have a value of 8.6, independent of temperature, from experiments on the photobromination of hydrogen.[9]

$$\begin{aligned} H + HBr &\longrightarrow H_2 + Br \quad k_6 \\ H + Br_2 &\longrightarrow HBr + Br \quad k_7 \end{aligned}$$

It is the purpose of the present work to investigate more extensively the effect of inert diluents on these photolyses in the light of the hot atom mechanism previously proposed.

Experimental

The extent of photolysis was measured through titration of the halogen produced. The high degree of precision required in the analyses did not permit initial additions of halogen to the reaction mixture, which consisted of the hydrogen halide with various amounts of inert gas. Four photolyses were conducted simultaneously in four quartz cells held in rigid positions with respect to each other and rotated past a light source. In each group one cell, containing only the hydrogen halide, was used as an actinometer for the other three, which contained added moderator. The relative extents of photolysis in the various cells could be repeated with a reproducibility of 1%, but since the quantity of interest, the inhibition constant, is obtained by a difference calculation (see equation 2), the reproducibility of this quantity is approximately 10%.

Apparatus.—Each quartz cell (35 × 75 mm.) was provided with a fused, quartz window (Fig. 1). The other end was constricted to 8–10 mm. and led to a graded seal. A side-arm was provided for freezing the hydrogen iodide while adding the inert gas. The cells were secured permanently in copper tubes soldered to a brass sleeve which could be fastened to a rotating steel shaft. The cells were rotated in a furnace at 140 r.p.m. No attempt was made to stabilize the speed of rotation since only the average value of the product (intensity) × (time) for each cell is significant. The cells passed the light source about 17,000 times during an experiment and even transient variations due to rotation or illumination were effectively averaged out.

The furnace consisted of an aluminum box about 150 mm. on each edge with two nichrome heating elements in opposite sides. A 35-mm. square window in the bottom of the furnace was covered with a quartz plate. Temperature was measured with a 360° thermometer in an aluminum sheath and was regulated within ±1° by manually adjusting a Variac.

The Hanovia Sc2537 lamp employed in this work is stated by the manufacturer to give about 85% of its light as the 2537 Å. resonance line.

Materials.—All reagents, including those used in preparations, were C.P. or analytical grade. Hydrogen iodide

---

(1) From the doctoral dissertation of H. A. Schwarz.

(2) Presented at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952.

(3) Work supported in part under A.E.C. contract At(11-1)-38.

(4) A.E.C. Predoctoral Fellow, 1949–1951.

(5) C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc., London*, **154**, 181 (1936).

(6) J. Romand, *Compt. rend.*, **227**, 117 (1948).

(7) R. R. Williams, Jr., and R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 691 (1947).

(8) R. A. Ogg, Jr., and R. R. Williams, *ibid.*, **13**, 586 (1945).

(9) M. Bodenstein and G. Z. Jung, *Z. physik. Chem.*, **121**, 127 (1926).

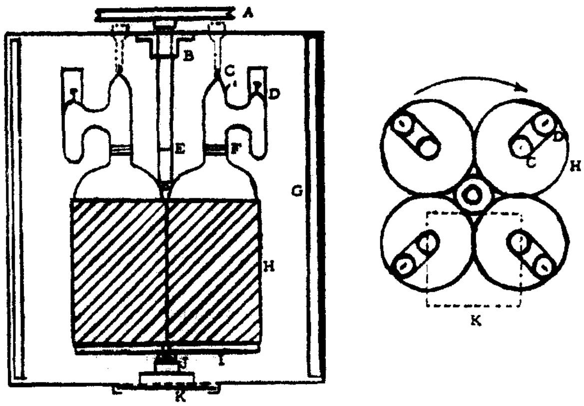

Fig. 1.—Photolysis cells and furnace: A, pulley; B, brass guide; C, capillary seal-off (dotted line represents seal-off while filling); D, break-off for re-entry; E, steel shaft and threaded joint; F, quartz-pyrex graded seal; G, heating element; H, copper tube; I, quartz plate end window; J, brass housing; K, window of furnace and quartz plate.

was prepared by the method of Williams and Ogg.[7] It was distilled twice from Dry Ice to liquid air and stored over Dry Ice.

To prepare deuterium iodide 1 cc. of deuterium oxide, obtained from the Stewart Oxygen Co. by permission of the Atomic Energy Commission, was frozen in the bottom of a tube and a phosphorus pentoxide–potassium iodide mixture was added. Otherwise the procedure was similar to that used for hydrogen iodide. A mass spectrometric analysis of the equilibrium mixture of the hydrogen isotopes released from a sample of the gas by reaction with mercury showed 79 atom per cent. deuterium.

Hydrogen bromide, purchased from the Matheson Chemical Company, was distilled three times from Dry Ice to liquid air; the middle fraction was retained.

Gases used for moderation were purchased from Matheson Chemical Co. and specified to have the following analyses:

Gas	Purity, %	Probable impurities
Helium	99.8	Nitrogen with a small amount of hydrogen
Hydrogen	99.8	Moisture
Argon	99.6	Nitrogen with 0.001% hydrogen and 0.00% oxygen

They were not purified further.

Procedure.—The cells were sealed to a vacuum line, evacuated simultaneously and heated to a glowing red. A mercury manometer was used as a matter of convenience in filling the cells. Hydrogen iodide slowly attacked mercury but no appreciable reaction took place during the time of contact in these experiments.

The cells were calibrated against each other by simultaneous photolysis of the pure hydrogen halide. The ratio of the amount of halogen produced in a cell to the amount produced in the actinometer cell is its "actinometer factor." Every fourth run was a calibrating run.

Where hydrogen halide was photolyzed without added moderating gas, the run was interrupted midway for titration of iodine in the actinometer cell. This cell was then refilled and photolysis of all cells continued. The actinometer was thus kept at the initial stage of photolysis. At the end of illumination all cells were analyzed. When moderating gases were used the actinometer cell contained hydrogen halide without moderator. In this case it was not necessary to interrupt photolysis as the production of halogen from a large energy input in pure hydrogen halide had already been determined.

After photolysis a cylindrical funnel was sealed to each cell above the break-off, the cell was immersed in liquid nitrogen and a dilute solution of potassium iodide was introduced through the funnel. The solution with combined rinsings was titrated with standard sodium thiosulfate solution using starch indicator. The cells were washed with distilled water, rinsed with acetone and air-dried before reuse.

Results

The simple reaction mechanism for the photolysis of hydrogen iodide, which neglects the hot atom effect, leads to the rate equation

$$\frac{d(I_2)}{dt} = \frac{E_{abs}}{1 + R\frac{(I_2)}{(HI)}} \qquad (1)$$

where $R = k_2/k_1$. Considering R constant, integration leads to

$$E_{abs} \times t - (I_2)_f = R\left[\frac{(HI)_i}{4}\ln\frac{(HI)_i}{(HI)_i - 2(I_2)_f} - \frac{(I_2)_f}{2}\right] \qquad (2)$$

where $(I_2)_f$ is the final concentration of iodine, $(HI)_i$ is the initial concentration of hydrogen iodide and $E_{abs} \times t$ is the total quantity of light absorbed, measured actinometrically. Initial amounts of hydrogen halide were calculated by the perfect gas law. For hydrogen iodide, the extinction coefficient is so large at 2537 Å. that variation in absorption due to pressure decrease during the experiments may be disregarded. At the usual working pressure (160 mm.) of hydrogen iodide, 90% of the incident light was absorbed in the first centimeter of path.

The results of Williams and Ogg[7] indicate that R is experimentally constant at a value of 3.8 ± 0.3 over a range of iodine concentrations. It has also been found in this work that R is constant in eleven experiments covering the range 12–30% photolysis and a value of 4.2 ± 0.2 for this ratio is obtained in pure hydrogen iodide.

In experiments conducted with added inert gas the results have also been expressed in terms of the quantity R in equation (2), and at a given inert gas pressure no dependence of R on $(I_2)/(HI)$ is observed. The value of R is, however, a function of the inert gas pressure as is shown in Figs. 2 and 3 where it is plotted against the ratio of pressures of hydrogen iodide (average for the experiment) to inert gas (helium and hydrogen). The data for two experiments using argon as the inert gas are given in Table I. The value of R at infinite inert gas pressure (R_∞) can be estimated by extrapolation. The curves drawn in these figures accomplish this by a method outlined in the Discussion. Figure 3 indicates that the extrapolated values of R_∞ are 13.5 ± 1 at 114°, 9.0 ± 0.8 at 154°, and 4.7 ± 0.5 at 198°. These three values fit a straight line on an Arrhenius plot, with a slope and intercept corresponding to

$$k_2/k_1 = 4 \times 10^{-2} \exp(4500/RT)$$

In experiments on the photolysis of deuterium iodide in the presence of inert gases, hydrogen iodide was used as the actinometer. Although deuterium iodide has a smaller extinction coefficient than hydrogen iodide at long wave lengths, at 2537 Å. the value should be nearly as large as that for hydrogen iodide. Figure 4 shows the values of R found in the photolysis of deuterium iodide with added helium. The results are not as precise as with hydrogen iodide, because of the larger values of R encountered, and extrapolation is unwarranted.

Hydrogen bromide was briefly studied in the same manner as hydrogen iodide, using the pure

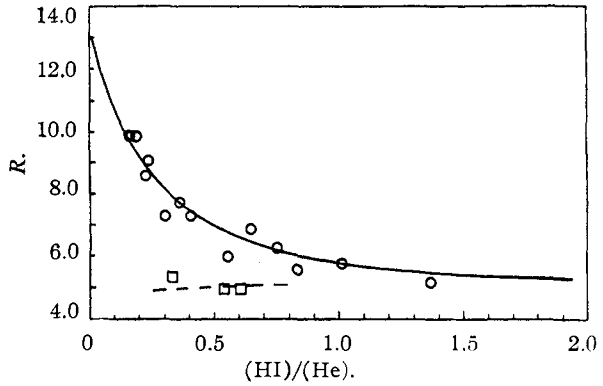

Fig. 2.—Helium dependence of inhibition constant R in hydrogen iodide photolysis: ⊙, 114°; ⊡, 198°.

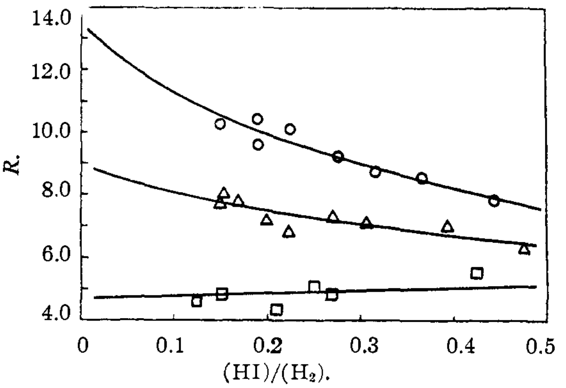

Fig. 3.—Hydrogen dependence of inhibition constant R in hydrogen iodide photolysis: ⊙, 114°; △, 154°; ⊡, 198°.

gas as an actinometer for experiments with added hydrogen. The small value of the extinction coefficient of this substance results in only partial absorption of the light in the reaction vessels and necessitates a correction in the computation of light absorbed due to the decrease in hydrogen bromide pressure in the course of photolysis. This effect and the longer illumination periods required for this substance decrease the precision of the results, which are indicated in Fig. 5.

TABLE I

PHOTOLYSIS OF HYDROGEN IODIDE IN THE PRESENCE OF ARGON

Run No.	Moles HI × 10^6	(HI)/(A) (average)	Temp., °C.	E_{abs} Einst. × 10^6	Moles I$_2$ produced × 10^6	R
39a	59.94	0.234	114	6.374	4.994	5.85
39b	60.75	.254	114	6.374	5.030	5.74

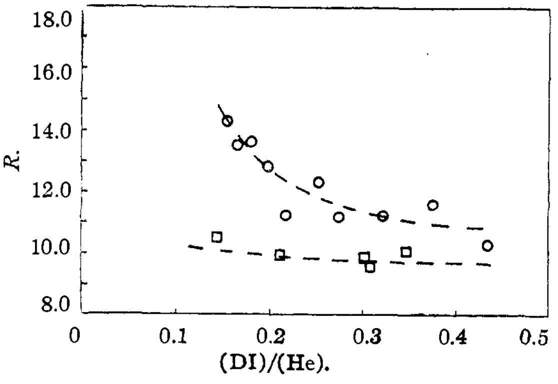

Fig. 4.—Helium dependence of inhibition constant R in deuterium iodide photolysis: ⊙, 114°; ⊡, 198°. In pure DI, two experiments gave R_0 = 5.7, 6.6 at 198°.

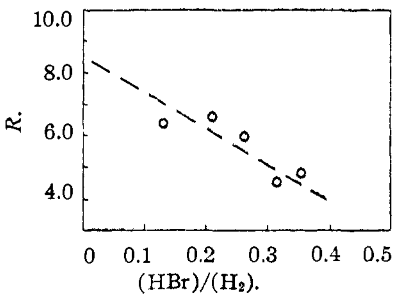

Fig. 5.—Hydrogen dependence of the inhibition constant R in the hydrogen bromide photolysis at 30°: in pure HBr three experiments gave R_0 = 0.55, 0.75, 0.69.

Discussion

The Mechanism of the Photolysis of Hydrogen Iodide.—The remarkable effects of helium and hydrogen upon the course of the photolysis of hydrogen iodide are apparently not compatible with the classical mechanism for this reaction and seem to confirm the hot atom mechanism proposed by Ogg and Williams.[4] Serious consideration has been given to possible alternate mechanisms, two of which are worthy of mention. The diluents used could conceivably lead to formation of reaction intermediates such as HeH or H_3 and in this case the retardation constant R would involve reactions of these intermediates with hydrogen iodide and iodine. It seems an unlikely coincidence that the ratios of rate constants would be identical for the two hypothetical intermediates and therefore this explanation is set aside.[10] Secondly, possible deactivation of excited hydrogen iodide molecules by the diluents should be considered. However, since there is no structure reported in the hydrogen iodide spectrum, dissociation should occur much more rapidly than gas collisions. Also, the greater de-excitation efficiency of diatomic *versus* monatomic gases ought to lead to a difference between hydrogen and helium much greater than that observed. Finally, this hypothesis predicts no temperature coefficient for R_∞, contrary to observation.

The hot atom mechanism taken here for detailed consideration predicts that R_∞ will be the same for all inert gases; this was observed for hydrogen and helium. It accounts for the lack of a temperature dependence of R_0 (in pure hydrogen iodide) and permits a temperature dependence in the presence of inert gas. It predicts that hydrogen will be a slightly better moderator than helium, which should be much better than argon. In general, the mechanism is compatible with all of the facts and the interpretation of data based upon this mechanism is very reasonable. The remainder of this discussion of the photolysis of hydrogen iodide is based upon this mechanism or models suggested by it.

---

(10) Ogg and Williams[4] found R_∞ = 7.0 ± 0.4 at 155°, using cyclohexane diluent. The present value for hydrogen at 154° is 9.0, an approximate agreement for a third diluent.

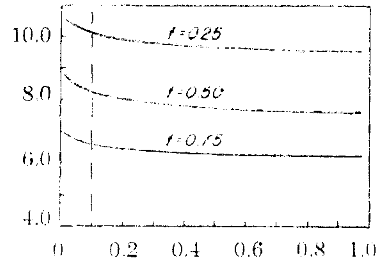

Fig. 6.—Expected dependence of inhibition constant, *R*, on the iodine concentration for various fractions of hot reaction.

Kinetic Treatment of the Mechanism.—Since the products of the hot reactions and the thermal reactions in the photolysis of hydrogen iodide are chemically identical, a detailed kinetic analysis of the system is needed in order to treat the hot atom reactions.

By steady state treatment, assuming one steady state for hot hydrogen atoms and another for thermal hydrogen atoms, one obtains

$$\frac{d(\mathrm{I_2})}{dt} = \frac{k_3(\mathrm{HI})E_{\mathrm{abs}}}{k_3(\mathrm{HI}) + k_4(\mathrm{I_2}) + k_5(\mathrm{M})} + \frac{k_5(\mathrm{M})}{k_3(\mathrm{HI}) + k_4(\mathrm{I_2}) + k_5(\mathrm{M})}\,\frac{E_{\mathrm{abs}}}{1 + \dfrac{k_2}{k_1}\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}}$$

Multiplying the first term of the right-hand side by $(k_3(\mathrm{HI}) + k_4(\mathrm{I_2}))/(k_3(\mathrm{HI}) + k_4(\mathrm{I_2}))$ one obtains

$$\frac{d(\mathrm{I_2})}{dt} = f\left[\frac{E_{\mathrm{abs}}}{1 + R_0\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}}\right] + (1 - f)\left[\frac{E_{\mathrm{abs}}}{1 + R_\infty\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}}\right] \qquad (3)$$

where R_0 is k_4/k_3, the ratio of the rate constants for the hot reaction; R_∞ is k_2/k_1, the ratio of the thermal rate constants; and f is identified with the fraction of hydrogen atoms that undergo hot atom reactions. This expression can be integrated when f is constant but it is difficult to interpret the integrated equation, particularly since the results of a given experiment must be expressed in terms of several parameters.

It can be seen that if all of the atoms reacted hot, f would become unity and equation (3) would reduce to the first term. With an infinite amount of moderator present there would be no hot atom reactions, f would be zero and (3) would reduce to the second term. Both of these limiting equations are of the form of (2), which suggests that an adequate evaluation of the parameters of (3) can be found by interpreting the results in terms of R in equation (2), provided that R is not strongly composition dependent. This has been found to be the case within the limited range of values of $(\mathrm{I_2})/(\mathrm{HI})$ encountered in the experiments and may be further justified by the following consideration: Equating the right-hand sides of equations (2) and (3) we find

$$R = \frac{f(R_0 - R_\infty) + R_0 + R_0R_\infty\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}}{f(R_0 - R_\infty)\dfrac{(\mathrm{I_2})}{(\mathrm{HI})} + R_0\dfrac{(\mathrm{I_2})}{(\mathrm{HI})} + 1} \qquad (4)$$

If R_0 and R_∞ have the values 5.2 and 13.5, respectively, the dependence of R on $(\mathrm{I_2})/(\mathrm{HI})$ for various values of f may be described by the curves in Fig. 6. It is seen that in the range of relative concentrations encountered in the experiments (indicated by the region to the left of the dotted line) the dependence of R on $(\mathrm{I_2})/(\mathrm{HI})$ is indeed expected to be minor.

Equation (4) may now be rearranged to a form which gives f the fraction of atoms reacting hot in terms of quantities determined directly and indirectly by experiment

$$f = \frac{(R_\infty - R)\left(1 + R_0\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}\right)}{(R_\infty - R_0)\left(1 + R\dfrac{(\mathrm{I_2})}{(\mathrm{HI})}\right)} \qquad (5)$$

It is to be noted that this expression for f is valid at constant $(\mathrm{I_2})/(\mathrm{HI})$ but must be applied to experimental results for which $(\mathrm{I_2})$ increases during the photolysis. The arbitrary choice has been made that the weighted mean value of the concentration ratio is 0.8 of the final ratio. The relative magnitudes of the terms in the equation make the values of f so derived rather insensitive to this choice.

A good estimate of the proper value for R_0 in these relations may be obtained by inspection of the data given in Figs. 2 and 3. At 114°, both hydrogen and helium moderation produce little change in R, and values in the region of 5.0 are obtained at larger values of $(\mathrm{HI})/(\mathrm{M})$. At higher temperatures the values of R decrease with increasing $(\mathrm{HI})/(\mathrm{M})$ and with helium at 198°, the lowest value attained is 5.3. A value of 5.2 is chosen for use in equation 5. The disagreement of this value with the value of R found in pure HI (4.2) is discussed later.

The proper value of R_∞ is more difficult to evaluate, but from Figs. 2 and 3 it is seen that the value cannot be less than 12 at 114°, corresponding to a linear extrapolation, and is probably somewhat greater. A method will not be presented which serves as a plausible guide for extrapolation of the curves in Figs. 2 and 3 and which is interesting in itself as a model for the moderation of the hot hydrogen atoms.

Moderation in the Photolysis of Hydrogen Iodide.—As an approximate description of the moderation let it first be assumed that significant moderation occurs only in collisions with the inert gas. The large mass disparity between H and HI justifies this, which is further borne out by the experimental data indicating little change in R with small additions of inert gas. Secondly, let it be assumed that hot hydrogen atoms react principally with hydrogen iodide. The experimental fact that the quantum yields are close to two in these experiments permits this approximation.

The fraction of collisions that take place with the moderating gas is therefore

$$\frac{\sigma_{\mathrm{M}}^2(\mathrm{M})}{\sigma_{\mathrm{M}}^2(\mathrm{M}) + \sigma_{\mathrm{R}}^2(\mathrm{HI})} = \frac{1}{1 + (\sigma_{\mathrm{R}}^2(\mathrm{HI})/\sigma_{\mathrm{M}}^2(\mathrm{M}))}$$

where σ_{M}^2 and σ_{R}^2 are the cross-sections for moderation and for reaction. If an atom makes N moderating collisions before it is thermalized, then the probability that it will do so without reacting is

$$1 - f = \left[\frac{1}{1 + (\sigma_{\mathrm{R}}^2(\mathrm{HI})/\sigma_{\mathrm{M}}^2(\mathrm{M}))}\right]^N \qquad (6)$$

To estimate N one needs to know (i) the average energy lost per collision, given by

$$\overline{\Delta E}/E = 2m_{\mathrm{A}}/m_{\mathrm{B}}/(m_{\mathrm{A}}/m_{\mathrm{B}} + 1)^2$$

where m_{A} and m_{B} are the masses of the collision partners, (ii) the initial energy of the hot atom (42 kcal. mole^{-1}) and (iii) the minimum energy of hot atoms. The last quantity may be identified with the activation energy of k_1 and may be estimated by straight line extrapolation of the data in Fig. 3. This yields $E_1 - E_2 = 4$ kcal. and if E_2 is zero, $E_1 = 4$ kcal. Hirschfelder's rule for this reaction also gives 4 kcal. and in any event the subsequent treatment is not sensitive to reasonable variations in this value. It will therefore require, on the average, six collisions with helium to moderate hydrogen atoms from 42 to 4 kcal.

For large extents of moderation equation 6 may be written

$$\log (1 - f) = -(N\sigma_{\mathrm{R}}^2(\mathrm{HI})/\sigma_{\mathrm{M}}^2(\mathrm{M})) \qquad (7)$$

and in this form it is seen that N and $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2$ constitute a single parameter. By a method of trial and error, the two equations for f (5 and 6 or 7 where appropriate) have been solved for the best values of R_∞ and $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2$. The agreement between f's calculated from equations 5 and 6 in helium at 114° is indicated in Fig. 7 for the values $R_\infty = 13.5$ and $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2 = 0.49$ (for $N = 6$). This is translated into a "theoretical" curve for R (the solid line) in Fig. 2.

The ratio of cross-sections found for reaction with hydrogen iodide to moderation by helium is the size expected if the reaction to form hydrogen occurred on every sterically favorable collision of the hot hydrogen atom with the hydrogen atom of the hydrogen iodide molecule. The cross-section of a hydrogen atom is about the same as that of a helium atom and it is half shielded by its iodine atom bond partner.

For moderation by hydrogen, N is estimated to be 5 if the H_2 molecule is regarded as a rigid sphere of mass 2. Although the data are not sufficiently extensive for careful test, the curve drawn through the data at 114° (see Fig. 3) corresponds to $R_\infty = 13.5$ and $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2 = 0.44$ indicating that the hydrogen molecule has a slightly larger cross-section for moderation than helium. The moderation equation 6 should not be temperature dependent and therefore equation 6 may be used for extrapolation of the data for hydrogen moderation at 154°, using the same values of N and $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2$. Best fit of the data to this relation yields R_∞ equal to 9.0. The use of equation 6 is superfluous in the case of the data at 198° since the variation in R is so small. The best value of R_∞ at this temperature appears to be 4.7.

The two values of R observed for argon (see Table I) may be compared with the prediction of equation 6 as follows: The average energy loss in collision of a hot hydrogen atom with argon is 80/1681 and therefore N will be approximately 50. Using gas viscosity diameters to estimate the relative cross-sections of the rare gases, $\sigma_{\mathrm{R}}^2/\sigma_{\mathrm{M}}^2$ for this case is 0.21. Computing f from equation 6 and using this value to estimate R from equation 4, we find 5.7 at the experimental ratio (HI)/(A) = 0.244. The average of two experiments is 5.8. This degree of agreement is certainly fortuitous, but represents at least a satisfactory qualitative test of the moderation hypothesis.

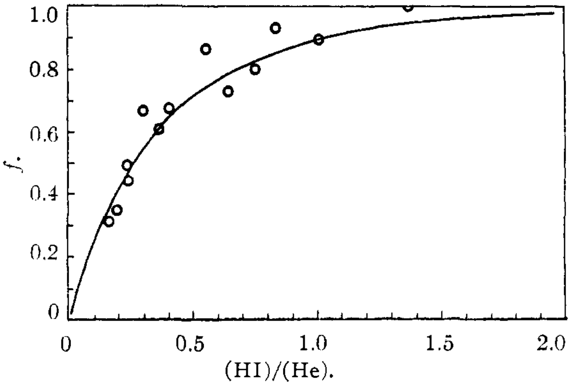

Fig. 7.—Helium dependence of fraction, f, of atoms reacting while hot: solid line, equation 6: O, experimental data. equation 5.

Reaction Rate Constants.—The preceding discussion has indicated our method of treating the experimental results in order to obtain R_∞, the ratio of rate constants for thermal reaction and R_0, the corresponding ratio for hot atom reaction. The values of R_∞ for hydrogen iodide have been given in the section on Results and the exponential factor corresponds to

$$E_1 - E_2 = 4.5 \pm 0.8 \text{ kcal. mole}^{-1}$$ [11]

Taking $\sigma_{\mathrm{I_2}}^2/\sigma_{\mathrm{HI}}^2 = 3$, the pre-exponential factor yields *ca.* 10^{-2} for the ratio of steric factors S_2/S_1. This value is not unexpected, since from the absolute reaction rate theory the steric factor for a reaction of the type

$$\mathrm{A} + \mathrm{BC} \longrightarrow \mathrm{AB} + \mathrm{C}$$

is predicted to be inversely proportional to the moment of inertia of B–C and this quantity for iodine is approximately 100 times as great as for hydrogen iodide. It might be presumed that the ratio of hot atom reaction rate constants k_4/k_3 should be equal to the pre-exponential factor of k_2/k_1. Since this is evidently not the case we must conclude that the ratio of steric factors is energy-dependent to a sufficient degree to be observed over the large range of energies involved. This is further evidenced by the fact that the value of R_0 taken for use in equation 5 (found by noting the convergence of R values at different temperatures in Figs. 2 and 3) is not the same as R_0 found in pure hydrogen iodide. We conclude that practically all atoms are reacting hot in mixtures containing as much as 50% hydrogen or helium and

---

[11] This result places a lower limit of 4.5 kcal. mole^{-1} on the activation energy of reaction 1, which is to be contrasted with the accepted activation energy of less than one kcal. mole^{-1} for the corresponding reaction of hydrogen atoms with hydrogen bromide (ref. 9).

that the slow change in R going toward pure hydrogen iodide is due to an energy dependence of the type proposed above. These considerations indicate that the simple moderation equations proposed do not adequately describe the details of the processes involved, but the experimental data do not justify further refinements.

In the case of deuterium iodide (Fig. 4) the data do not justify an attempt to extrapolate for values of R_∞. It is apparent that all quantities, R_0, R_∞ and $E_1 - E_2$, are larger than for hydrogen iodide.

In the photolysis of hydrogen bromide (Fig. 5), the value of R_0 (0.66) stands in contrast to the value of $k_6/k_7 = 8.6$ obtained in the bromination of hydrogen.[9] In the latter case, no hot atom effect is to be expected, and we conclude that our value of the retardation constant in pure hydrogen bromide refers to the ratio of rate constants of the hot atom reactions

$$H + HBr \longrightarrow H_2 + Br \quad k_8$$
$$H + Br_2 \longrightarrow HBr + Br \quad k_9$$

A linear extrapolation of the points obtained with added hydrogen (the more elaborate treatment is not justified) indicates that $R_\infty = 9.5 \pm 1$. This value which we take as a proper measure of k_6/k_7 is in satisfactory agreement with previous results.[9] This transition from a hot atom value for the retardation constant to a previously observed thermal value seems to be an excellent confirmation of the hypothesis.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Participation of f Orbitals in Bonding in Uranium and the Transuranium Elements[1]

BY ROBERT E. CONNICK AND Z Z. HUGUS, JR.

RECEIVED MAY 19, 1952

On the basis of chemical and X-ray evidence it is suggested that f orbitals participate in the metal–oxygen bonding in the oxygenated ions MO_2^{++} and MO_2^+ of the uranides. The electronic structures and the small coördination number are discussed. The uranium–oxygen bonding in the infinite chains of . . . U—O—U—O . . . in UO_3 is compared with that in uranyl ion. It is shown that the entropy of uranyl ion can be accounted for by a charge distribution of +4 on the uranium and −1 on each oxygen. The conclusion is drawn that plutonyl ion should hydrolyze less readily than uranyl ion in spite of the actinide contraction.

Recently Glueckauf and McKay[2] have suggested that f orbitals are involved in the bonding of uranyl ion to other groups such as nitrate ion, water or ether molecules. Katzin[3] has given convincing evidence that the experimental data do not support this conclusion. We might add that the comparison which Glueckauf and McKay made between UO_2^{++} and such doubly charged ions as Mn^{++}, Co^{++} and Cu^{++}, can at best be only qualitative, as shown by the more negative entropy of uranyl ion. As is discussed below the charge on each of the oxygens may approximate −1 and that on the uranium +4. It is not surprising that such a divalent ion behaves differently from Co^{++}, etc.

More recently Street and Seaborg, and Diamond[4] have interpreted some aspects of the complexing behavior of the +3 ions of uranium and the transuranium elements as being due to the participation of f orbitals in the bonding. The observed effects are small but apparently real. We believe that much more striking evidence of f-orbital bonding is to be found in the metal–oxygen bonds of the ions of the +5 and +6 oxidation states of the actinide elements (except protactinium).

Chemical Evidence.—The oxide of uranium(VI), UO_3, readily dissolves in acidic solutions to form uranyl ion, UO_2^{++}. This is in sharp contrast to the behavior of MoO_3 and WO_3 which are the antecedents of uranium in the sixth group. These substances show little tendency to dissolve in acids unless strong complexing anions are also present. However it is to be expected that UO_3 would be more basic than MoO_3 and WO_3 because of the greater ionic size. Therefore it is not possible to conclude that the difference in basicity does in fact arise from a change in the type of bonding.

Kraus and Dam[5] have pointed out that in the case of the oxides and ions of the +5 oxidation states an even greater difference in behavior is found. Niobium, tantalum and protactinium oxides are all chemically inert and only very slightly soluble in strongly acidic solutions which do not contain complexing anions. In contrast the ions UO_2^+, NpO_2^+ and PuO_2^+ are easily obtained in aqueous solution. They show very little tendency to hydrolyze; for example the equilibrium constant for the reaction

$$PuO_2^+ + H_2O = PuO_2OH + H^+$$

is 2×10^{-10} or smaller.[5] As far as coulombic effects are concerned, the +5 oxidation states of uranium, neptunium and plutonium should have hydrolytic properties between those of protactinium and tantalum since their radii lie between those of the latter two elements. Kraus and Dam concluded that there must be a difference in electronic structure responsible for this change and that these actinide elements are "characterized by greater

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, New York, March, 1952.

[2] E. Glueckauf and H. A. C. McKay, *Nature*, **165**, 594 (1950).

[3] L. I. Katzin, *ibid.*, **166**, 605 (1950).

[4] K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **72**, 2790 (1950); R. M. Diamond, U. S. Atomic Energy Commission Report, UCRL-1434, August 1951.

[5] K. A. Kraus and J. R. Dam, "The Transuranium Elements," National Nuclear Energy Series, Division IV, Volume 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 478.